Part II

PHOTOCHEMISTRY OF INORGANIC AND ORGANOMETALLIC COMPOUNDS

By J. M. KELLY

1 Photochemistry of Transition-metal Complexes

Several reviews [1-3] and the proceedings of a symposium [4] have dealt with general aspects of work in this area. A comprehensive survey of the radiation chemistry of metal ions in aqueous solution also contains much of interest for the inorganic photochemist.[5]

New theoretical alternatives to Adamson's rules for predicting the course of photosolvolysis reactions of octahedral metal complexes have been considered in two recent publications.[6, 7] Both groups of authors have used angular overlap methods to calculate from spectroscopic data the excited-state metal–ligand bond energies, taking account of both σ- and π-bonding. In the more detailed study,[6] excellent agreement with experiment is reported for the prediction of the labilized ligand of some 29 Cr[III] and Co[III] complexes {including $[Cr(en)_2F_2]^+$ and $[Cr(en)_2FCl]^+$, which are exceptions to Adamson's rule}. In the case of these Cr–F complexes an important feature appears to be that the Adamson rules are related to $(I^* - I)$ rather than to I^* (I^* and I being the bond energies in the excited state and ground state respectively). Thus, although calculations do indeed show that in the lowest excited state of $[Cr(en)_2FCl]^+$ more of the excitation energy is concentrated in the Cr—F bond than in the Cr—Cl bond, the greater strength of the Cr—F bond in the ground state remains dominant, causing $I^*(\text{Cr}-\text{F})$ to be greater than $I^*(\text{Cr}-\text{Cl})$ and therefore the Cr—F bond less prone to labilization.

As the vast majority of photosubstitution reactions of transition-metal complexes have been conducted in aqueous solution, little is known about the course of these transformations in organic media. Raising the bulk viscosity of the solvent might be expected to cause an increase in the rate of geminate recombination within the solvent cage of the fragments produced upon photodissociation of the metal–ligand bond. It had previously been supposed that this was the origin of the apparent decrease in the quantum yield for the photoaquation of $[Co(CN)_6]^{3-}$ in water–alcohol mixed solvents.[8] However, consideration of a larger number of mixed solvents leads to the conclusion that any correlation with viscosity is largely fortuitous.[9] {In some cases errors might have been introduced through neglecting the formation of $[Co(CN)_5(\text{solvent})]^{2-}$.} The same authors have determined the variation of the efficiency of CNS⁻ photosubstitution in *trans*-$[Cr(NH_3)_2(NCS)_4]^-$ (1) and in *trans*-$[Cr(en)_2(NCS)F]^+$ (2) in various mixed solvents.[9] They have found that although there is a marked effect with complex ion (1) (Figure 1), no similar dependence is observed for (2). This contrasting behaviour probably stems from the need for water molecules in the solvation shell of the negatively charged (1) to rotate into a favourable

[1] M. S. Wrighton, *Topics Current Chem.*, 1976, **65**, 37.
[2] H. B. Abrahamson, A. B. Ellis, D. S. Ginley, D. L. Morse, M. A. Schroeder, and M. S. Wrighton, *Mol. Photochem.*, 1976, **7**, 263.
[3] J. F. Endicott, *Survey Progr. Chem.*, 1976, **7**, 41.
[4] 'Inorganic Compounds with Unusual Properties', *Adv. Chem. Series* No. 150, ed. R. B. King, Amer. Chem. Soc., Washington, 1976.
[5] G. V. Buxton and R. M. Sellers, *Coordination Chem. Rev.*, 1977, **22**, 195.
[6] L. G. Vanquickenborne and A. Ceulemans, *J. Amer. Chem. Soc.*, 1977, **99**, 2208.
[7] J. K. Burdett, *Chem. Phys. Letters*, 1977, **47**, 43.
[8] F. Scandola, M. A. Scandola, and C. Bartocci, *J. Amer. Chem. Soc.*, 1975, **97**, 4757.
[9] C. F. C. Wong and A. D. Kirk, *Canad. J. Chem.*, 1976, **54**, 3794.

orientation for the substitution reaction, whereas with the cation (2) the nucleophilic oxygen atom of the water is already suitably positioned.

The importance of solvation in determining the properties of co-ordination compound excited states is further emphasized by Conti and Forster's study of $[Cr(CN)_6]^{3-}$ phosphorescence lifetime in both 80% glycerol–water and aqueous solutions.[10] In both solvents the lifetime of the ^2E state is found to depend on the wavelength of excitation, the effect being most pronounced near the long-wavelength edge of the $(^4T_2 \leftarrow {}^4A_2)$ absorption band. This phenomenon is
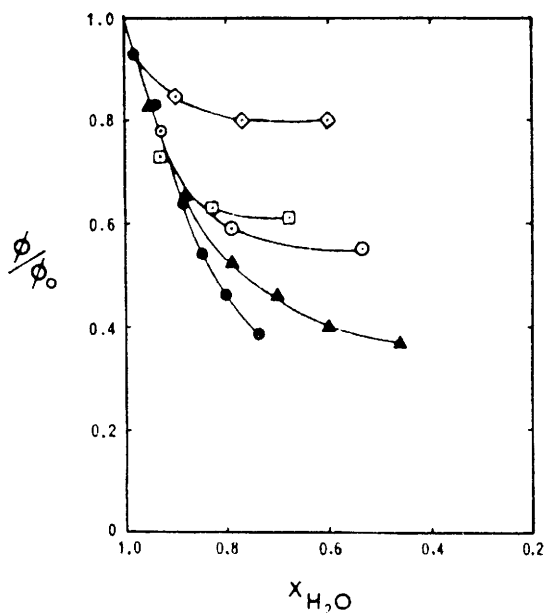
Figure 1 *Relative quantum yields for photosolvation of thiocyanate ion from* trans-$[Cr(NH_3)_2(NCS)_4]^-$ *as a function of aqueous mixed solvent composition.* $\diamondsuit$ *acetonitrile,* $\square$ *acetone,* $\bigcirc$ *ethanol,* $\blacktriangle$ *ethylene glycol, and* $\bullet$ *glycerol*

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attributed to the presence of various long-lived solvates. Clearly if such solvates are sufficiently long-lived to influence the photophysical properties of the ^2E state ($\tau > 0.1 \,\mu s$), they must also affect the behaviour of the very short-lived $^4T_2$ state of the Cr^{III} complex and, by extension, those of other complex ions.

The effect of viscosity on charge-transfer photoreactions has been the subject of several earlier investigations. Many of these studies have been carried out in mixed solvents, such as glycerol–water, where other effects such as change in polarity or preferential solvation may also be important.[11] Liu and Zink have

[10] C. Conti and L. S. Forster, *J. Amer. Chem. Soc.*, 1977, **99**, 613.
[11] J. F. Endicott in 'Concepts of Inorganic Photochemistry', ed. A. W. Adamson and P. D. Fleischauer, Wiley, New York and London, 1975, Chapter 3.

eliminated this problem by using tris(dibenzyldithiocarbamato)iron(III) as a probe for viscosity effects in mixtures of benzene and long-chain hydrocarbons.[12] Decomposition of the LMCT excited state in the presence of halogenated hydrocarbons ($CHCl_3$, CCl_4, or CBr_4) as scavengers proceeds as shown in equation (1).

$$[Fe(dtc)_3] \xrightarrow[RX]{h\nu} [Fe(dtc)_2X] + R-dtc \tag{1}$$
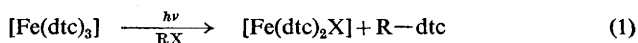
The dependence of the quantum yield of the reaction on the solvent viscosity has been analysed in terms of the Noyes treatment for radical pairs.

Quenching and sensitization of the excited states of transition-metal complexes may involve a number of physical and chemical processes, and the factors determining which is predominant have not yet been thoroughly elucidated.[13] The deactivation of the triplet states of several organic molecules in aqueous solution [E_T varying from 24 800 cm^{-1} (xanthone) to 12 900 cm^{-1} (protonated haematoporphyrin)] by $[PdCl_4]^{2-}$, $[PtCl_4]^{2-}$, and $[Ni(CN)_4]^{2-}$ proceeds by triplet–triplet energy transfer.[14] In cases where the energy transfer is exothermic, the quenching is more efficient than it normally is for octahedral complexes, indicating that the ease of orbital overlap with these square-planar complexes facilitates the exchange mechanism for energy transfer. An exchange mechanism also appears to operate for the quenching of the singlet states of quinine and other organic bases by metal aquo-ions, although with Ag^+ and Fe^{2+} some type of charge-transfer process is implicated.[15] However, a resonance-energy-transfer mechanism has been suggested for the quenching of anthracene and rhodamine B fluorescence by $[Cr(NCS)_6]^{3-}$ and $[Cr(NH_3)_2(NCS)_4]^{-}$.[16] Other related publications consider the quenching of eosine fluorescence [17] and duroquinone triplet state [18] by various metal aquo-ions and the effect of heavy-metal ions on the excited-state interaction of the boric acid–benzoylacetone complex.[19]

Except for transition-metal organometallics and low oxidation state compounds, which are considered in Section 2, the photochemistry of compounds of each transition element, including metalloporphyrins, will now be treated systematically.

Titanium.—Photo-oxidation of the solvent appears to be the primary process upon irradiation of $\alpha\beta$-unsaturated ketones [20] and nitriles [21] in methanolic solutions containing $TiCl_4$.

Hydrogen is evolved upon irradiation of acidic solutions of Ti^{3+} in the presence of catalytic amounts of Cu^I salts.[22] The reaction appears to involve initial photo-oxidation of Cu^I to Cu^{II} [equation (2)], no hydrogen being released in the absence of copper salts.

[12] P.-H. Liu and J. I. Zink, *J. Amer. Chem. Soc.*, 1977, **99**, 2155.
[13] V. Balzani, L. Moggi, F. Bolletta, and M. F. Manfrin, in ref. 4, p. 160.
[14] K. C. Marshall and F. Wilkinson, *Z. phys. Chem. (Frankfurt)*, 1976, **101**, 67.
[15] J. A. Kemlo and T. M. Shepherd, *Chem. Phys. Letters*, 1977, **47**, 158.
[16] E. B. Sveshnikova and S. P. Naumov, *Optika i Spektroskopiya*, 1976, **41**, 225.
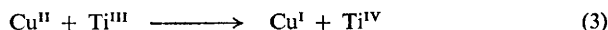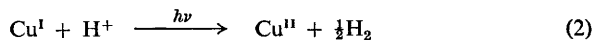[17] T. A. Sakhverdov and Z. H. Turaeva, *Optika i Spektroskopiya*, 1976, **41**, 1082.
[18] A. P. Darmanyan, I. V. Khudyakov, and V. A. Kuz'min, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1976, 1772.
[19] M. Marcantonatos, *Inorg. Chim. Acta*, 1976, **16**, 17; 1976, **19**, 109; 1977, **21**, 65, 75.
[20] T. Sato and S. Yoshiie, *Chem. Letters*, 1976, 415.
[21] T. Sato, G. Izumi, and T. Imamura, *J.C.S. Perkin I*, 1976, 788.
[22] K. L. Stevenson and D. D. Davis, *Inorg. Nuclear Chem. Letters*, 1976, **12**, 905.

$$Cu^{I} + H^{+} \xrightarrow{\ h\nu\ } Cu^{II} + \tfrac{1}{2}H_2 \qquad (2)$$

$$Cu^{II} + Ti^{III} \xrightarrow{\quad\quad} Cu^{I} + Ti^{IV} \qquad (3)$$

Vanadium.—Photoreduction of $VOCl_3$ in alcoholic solution proceeds in stages to give eventually V^{2+}.[23] In the case of reduction of V^{3+} to V^{2+}, acetaldehyde, the final oxidation product, is presumably formed by disproportionation of the ethoxy-radicals formed in the initial process (4).[24] The quantum yield for V^{2+} formation is 0.23 at 280 nm. Irradiation of the V^{2+} solution so formed causes evolution of hydrogen ($\Phi_{280} = 0.019$; $\Phi_{343} = 0.009$).

$$V^{3+}\cdot EtOH \xrightarrow{\ h\nu\ } V^{2+} + EtO\cdot + H^{+} \qquad (4)$$
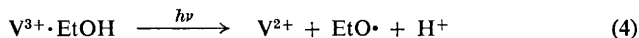
Irradiation of V^{V}-doped silica gel in the presence of methane and oxygen leads to the reduction of V^{V} to V^{IV} and the oxidation of methane.[25]

Aliwi and Bamford have studied the photolysis of 19 derivatives of type $[VOQ_2(OR)]$ (Q = 8-quinolyloxo-, R = alkyl) by a combination of spectroscopic, tracer, and spin-trapping experiments.[26] These investigations indicate that the sole photochemical process is (5). The quantum yields for the various

$$[VOQ_2(OR)] \xrightarrow{\ h\nu\ } VOQ_2 + \cdot OR \qquad (5)$$
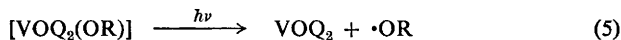
derivatives lie in the range 0.7×10^{-3}—9.2×10^{-3}, and increase with increasing electron-withdrawing power of the R-group. Photoactive polymers have been synthesized by attaching the VOQ_2 chromophore to copolymers of methyl methacrylate and 2-hydroxyethyl methacrylate or of styrene and p-vinylbenzyl alcohol.[27, 28] The radicals formed on photolysis of the first type of copolymer cause grafting and cross-linking of the polymer and consequent gelation.

The active initiator of the photoinduced polymerization of 2-methylprop-1-ene [29] or of butadiene [30] containing VCl_4 is the olefin radical-cation. This species is produced upon excitation of the corresponding olefin–VCl_4 charge-transfer complex.

$$\text{olefin—}VCl_4 \xrightarrow{\ h\nu\ } [VCl_4]^- + \text{olefin}^{\cdot+} \qquad (6)$$
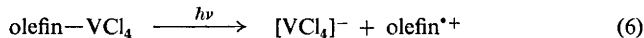
Chromium.—Kläning has carried out experiments on the photoinduced oxidation of propan-2-ol using flash photolysis, quantum yield measurements, e.s.r. at low temperatures, and spin-trapping.[31] These confirm earlier conclusions that the principal primary process is photolysis of the chromate ester [reaction (7)].

[23] A. I. Kryukov, S. Y. Kuchmii, I. S. Shchegoleva, and A. V. Korzhak, *Teor. i eksp. Khim.*, 1977, **13**, 135.
[24] B. V. Koryakin, T. S. Dzhabiev, and A. E. Shilov, *Doklady Akad. Nauk S.S.S.R.*, 1976, **229**, 128.
[25] S. A. Surin, A. D. Shuklov, B. N. Shelimov, and V. B. Kazanski, *Khim. vysok. Energii*, 1977, **11**, 147.
[26] S. M. Aliwi and C. H. Bamford, *J.C.S. Faraday I*, 1977, **73**, 776.
[27] S. M. Aliwi and C. H. Bamford, *Polymer*, 1977, **18**, 375, 381.
[28] C. H. Bamford, *Polymer*, 1976, **17**, 321.
[29] L. Toman and M. Marek, *Makromol. Chem.*, 1976, **177**, 3325.
[30] J. Pilar, L. Toman, and M. Marek, *J. Polymer Sci., Polymer Chem.*, 1976, **14**, 2399.
[31] U. K. Kläning, *J.C.S. Faraday I*, 1977, **73**, 434.

The Cr^{IV} species so formed normally disproportionates to Cr^{III} and Cr^V, or reacts with Cr^V to give Cr^{III} and Cr^{VI}. Related publications consider the photo-reduction of dichromate by diols,[32] by poly(vinyl alcohol),[33] and on sensitization by methylene blue.[34, 35]

$$[Me_2CHOCrO_3]^- \xrightarrow{\ h\nu\ } Me_2CO + Cr^{IV} + H^+ \qquad (7)$$

Irradiation of *trans*-[Cr(en)$_2$(NH$_3$)Cl]$^{2+}$ in its lowest quartet LF band (^4E_a) produces almost exclusively (100 ± 3%) *cis*-[Cr(en)$_2$(H$_2$O)Cl]$^{2+}$.[36] This pronounced stereochemical preference lends further support to the theory that Cr^{III} photosubstitutions proceed *via* a concentrated associative pathway in the quartet state. On excitation to higher LF states ($^4B_2$, ^4E_b) some equatorial labilization is also observed, indicating that under these conditions more than one reactive excited state is involved, probably the $^4B_2$ and ^4E_a thermally equilibrated (thexi) states.

The photoanation of [Cr(DMSO)$_6$]$^{3+}$ (DMSO = dimethyl sulphoxide) by N$_3^-$ in DMSO solution has a markedly higher quantum yield than that by SCN$^-$, suggesting that the photosubstitution reactions of this complex under these conditions take place by an associative mechanism.[37] This conclusion is further strengthened by the observation that the exchange of DMSO upon irradiation of the complex in deuteriated solvent is very inefficient.

Hydroxide ion has in the past been used in mechanistic studies as a quencher of the ^2E state of Cr^{III} complexes. An investigation of the quenching of both the phosphorescence and thiocyanate photosubstitution in [Cr(en)$_2$(NCS)$_2$]$^+$ reveals that OH$^-$ behaves differently from other quenchers, which act *via* energy transfer.[38] Thus whereas experiments with these other physical quenchers show that 20% of the yield of CNS$^-$ is 'unquenchable', results with OH$^-$ suggest a value of 55%. This larger amount of CNS$^-$ release must arise by OH$^-$ inducing CNS$^-$ formation from the doublet state of the complex, possibly *via* a seven-co-ordinate intermediate.

The photochemistry and photophysics of [Cr(bipy)$_3$]$^{3+}$ (bipy = 2,2′-bipyridyl) have been the subjects of several recent papers.[39-41] The metal-centred (^2E) state of the complex, formed on excitation with unit efficiency,[39] may be monitored in fluid solution either by its emission or by conventional flash photolysis. It has been demonstrated that this state is highly oxidizing, efficiently accepting an electron from [Ru(bipy)$_3$]$^{2+}$ or Fe^{2+}.[40] Quenching studies indicate that the photosubstitution reactions, to give [Cr(bipy)$_2$(H$_2$O)$_2$]$^{3+}$, [Cr(bipy)$_2$(OH)$_2$]$^+$, or [Cr(bipy)$_2$(OH)(H$_2$O)]$^{2+}$, depending on pH, proceed through the ^2E state, although whether directly from this state or by reaction of the $^4T_2$ species formed

[32] M. Miteva, P. Bonchev, and A. Malinovski, *Doklady bolgarsk. Akad. Nauk*, 1976, **29**, 81.
[33] V. Rek and M. Bravar, *Nafta* (*Zagreb*), 1976, **27**, 267.
[34] M. Sasaki, S. Kikuchi, and K. Honda, *Nippon Kagaku Kaishi*, 1976, 886 (*Chem. Abs.*, 1976, **85**, 70 636).
[35] M. Sasaki, N. Sakai, S. Kikuchi, and K. Honda, *Nippon Kagaku Kaishi*, 1976, 895 (*Chem. Abs.*, 1976, **85**, 70 637).
[36] C. F. C. Wong and A. D. Kirk, *Inorg. Chem.*, 1976, **15**, 1519.
[37] C. H. Langford and J. P. K. Tong, *J.C.S. Chem. Comm.*, 1977, 138.
[38] D. Sandrini, M. T. Gandolfi, A. Juris, and V. Balzani, *J. Amer. Chem. Soc.*, 1977, **99**, 4523.
[39] F. Bolletta, M. Maestri, and V. Balzani, *J. Phys. Chem.*, 1976, **80**, 2499.
[40] R. Ballardini, G. Varani, F. Scandola, and V. Balzani, *J. Amer. Chem. Soc.*, 1976, **98**, 7432.

by back ISC is not yet apparent.[41] The previously reported [42] luminescence of the $^4T_2$ state on CW laser excitation of DMSO solutions of $[Cr(bipy)_3]^{3+}$ has now been reassigned to some artefact, possibly some strongly emitting by-product.[41]

The redox decomposition of $[Cr(NH_3)_5Br]^{2+}$ induced by light with wavelengths shorter than 360 nm is one of the few examples of this type of reaction established for Cr^{III} complexes.[43] Evidence includes the scavenging of Cr^{2+} by $[Co(NH_3)_5F]^{2+}$ and the observation of $Br_2^{\cdot-}$ on flash photolysis in the presence of bromide ion. Although the observed quantum yields for Cr^{2+} are modest $(0.02 \leqslant \Phi_{254} \leqslant 0.04)$, the authors point out that recombination within the solvent cage may be very important, and that the primary redox yield may be an order of magnitude higher.

A re-examination of the photolysis of $[Cr(NH_3)_5(N_3)]^{2+}$ at 313 nm indicates that the primary photochemical reaction is formation of a chromium–nitrene complex [equation (8)] and not redox decomposition as previously supposed.[44]

$$[Cr(NH_3)_5(N_3)]^{2+} \xrightarrow{\;h\nu\;} [Cr(NH_3)_5N]^{2+} + N_2 \qquad (8)$$
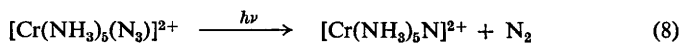
The reaction probably originates in a low-lying azide-centred excited state, as has previously been proposed for the analogous rhodium complex.

In a recent study with the optically active complex tris-[(+)-3-acetyl-camphorato]chromium(III) (3), it has been shown that the photoisomerization

(3)

(4) a; R = Me
b; R = Pr^i
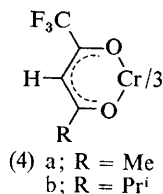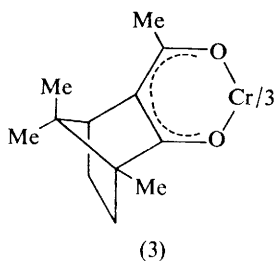
proceeds *via* a square-pyramidal intermediate formed upon cleavage of one of the Cr—O bonds.[45] With the tris-(β-diketonato)Cr^{III} complexes (4a) and (4b), the ratios $\Phi_{trans-cis}/\Phi_{cis-trans}$ are markedly different [0.20 for (4a); $\leqslant 0.05$ for (4b)].[46] This difference has been attributed to the influence of steric factors on the rate of formation of products from the five-co-ordinate species formed on photolysis. Irradiation of $[Cr(acac)_3]$ in the presence of (S)-alanine, (S)-valine, and (S)-phenylalanine is a convenient route to derivatives of the type $[Cr(acac)_2L]$.[47]

[41] M. Maestri, F. Bolletta, L. Moggi, V. Balzani, M. S. Henry, and M. Z. Hoffman, *J.C.S. Chem. Comm.*, 1977, 491.
[42] N. A. P. Kane-Maguire, J. Conway, and C. H. Langford, *J.C.S. Chem. Comm.*, 1974, 801.
[43] R. Sriram and J. F. Endicott, *J.C.S. Chem. Comm.*, 1976, 683.
[44] M. Katz and H. D. Gafney, *J. Amer. Chem. Soc.*, 1976, **98**, 7458.
[45] S. S. Minor and G. W. Everett, jun., *Inorg. Chem.*, 1976, **15**, 1526.
[46] S. S. Minor and G. W. Everett, jun., *Inorg. Chim. Acta*, 1976, **20**, L51.
[47] S. S. Minor, G. Witte, and G. W. Everett, jun., *Inorg. Chem.*, 1976, **15**, 2052.

Energy-transfer experiments using Cr^{III} complexes as both donors and acceptors have allowed the determination of their quantum yields for ISC in fluid solution at room temperature:[39] *trans*-$[Cr(en)_2(NCS)_2]^+$, 0.4; $[Cr(CN)_6]^{3-}$, 0.5; $[Cr(bipy)_3]^{3+}$, 1.0; $[Cr(phen)_3]^{3+}$, 0.2; $[Cr(en)_3]^{3+}$, 0.7. Measurements of the phosphorescence lifetimes of various Cr^{III} complexes, $[Cr(en)_3]^{3+}$, $[Cr(NH_3)_5$-$(NCS)]^{2+}$, *cis*- and *trans*-$[Cr(en)_2(NCS)_2]^+$, during quenching by $[Cr(CN)_6]^{3-}$ reveal that the intermolecular energy transfer is reversible.[48] For this reason the system is not governed by Stern–Volmer kinetics, and apparent Stern–Volmer constants are quite misleading.

Photophysical processes in Cr^{III} complexes have been discussed in a recent short review.[49] Studies of the rise-time of the phosphorescence of various Cr^{III} complexes confirm that the $({}^4T_2 \rightarrow {}^2E)$ ISC is a fast process $(k > 10^8 \text{ s}^{-1})$.[50, 51] Other reports have dealt with the luminescence of $[Cr(en)_3]^{3+}$,[52] $[Cr(NH_3)_5$-$(OH)]^{2+}$,[53] $[Cr(CN)_6]^{3-}$,[54] and *cis*-$[Cr(en)_2X_2]^+$ (X = F, Cl, or Br).[55]

Molybdenum and Tungsten.—Photolysis of the metal–metal-bonded species $[Mo_2(SO_4)_4]^{4-}$ in sulphuric acid solution leads to production of hydrogen $(\Phi_{254} = 0.17)$:[56]

$$2H^+ + 2[Mo_2(SO_4)_4]^{4-} \xrightarrow{h\nu} H_2 + 2[Mo_2(SO_4)_4]^{3-} \qquad (9)$$
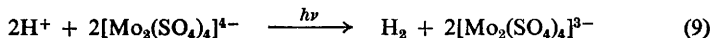
Recent experiments, including isolation of the salt $Ag_3[W(CN)_7(H_2O)]$, have confirmed that $[W(CN)_8]^{4-}$ undergoes efficient photoaquation in acid solution:[57]

$$[W(CN)_8]^{4-} + H_2O \xrightarrow{h\nu} [W(CN)_7(H_2O)]^{3-} + CN^- \qquad (10)$$
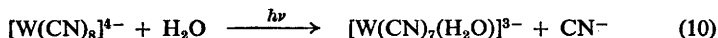
Although at low pH photoreduction of $[Mo(CN)_8]^{3-}$, to give $[Mo(CN)_8]^{4-}$, appears to proceed cleanly,[58] in alkaline solution secondary photochemical and thermal reactions cause complications.[59] These include the formation of Mo^{VI} by reaction of cyanide radical with the starting material.[59]

Other publications have considered the photochromism of alkylammonium molybdates[60] and the reduction of Mo^{VI} to Mo^V by laser radiation.[61]

Manganese.—Detailed knowledge of the excited-state interaction of chlorophyll and manganese complexes will be necessary for an understanding of the role of manganese in photosystem II of the chloroplast. In aqueous ethanol, both

[48] N. A. P. Kane-Maguire, C. G. Toney, B. Swiger, A. W. Adamson, and R. E. Wright, *Inorg. Chim. Acta*, 1977, **22**, L11.
[49] L. S. Forster, in ref. 4, p. 172.
[50] F. Castelli and L. S. Forster, *J. Phys. Chem.*, 1977, **81**, 403.
[51] D. C. Stuart and A. D. Kirk, *Rev. Sci. Instr.*, 1977, **48**, 186.
[52] G. L. Hilmes, H. G. Brittain, and F. S. Richardson, *Inorg. Chem.*, 1977, **16**, 528.
[53] S. Decurtins, H. U. Güdel, and K. Neuenschwander, *Inorg. Chem.*, 1977, **16**, 796.
[54] C. D. Flint and D. J. D. Palacio, *J.C.S. Faraday II*, 1977, **73**, 649.
[55] C. D. Flint, A. P. Matthews, and P. J. O'Grady, *J.C.S. Faraday II*, 1977, **73**, 655.
[56] D. K. Erwin, G. L. Geoffroy, H. B. Gray, G. S. Hammond, E. I. Solomon, W. C. Trogler, and A. A. Zagars, *J. Amer. Chem. Soc.*, 1977, **99**, 3620.
[57] H. Mohan, *J. Inorg. Nuclear Chem.*, 1976, **38**, 1303.
[58] R. P. Mitra, B. K. Sharma, S. K. Gupta, and H. Mohan, *Indian J. Chem., Sect. A*, 1976, **14**, 457.
[59] A. Marchaj, A. Plesinski, and Z. Stasicka, *Roczniki Chem.*, 1976, **50**, 1239.
[60] T. Yamase and T. Ikawa, *Bull. Chem. Soc. Japan*, 1977, **50**, 746.
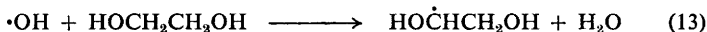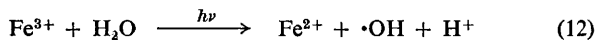[61] B. V. Sarkisov, N. N. Milyaeva, V. A. Shkoda-Ul'yanov, and B. V. Anikeev, *Ukrain. khim. Zhur.*, 1976, **42**, 936.

Photochemistry

excited singlet and triplet states of chlorophyll-*a* are quenched by manganese complexes, the efficiency decreasing in the order $Mn^{IV} > Mn^{III} > Mn^{II}$.[62] With Mn^{II} compounds, the quenching efficiency is dependent on the co-ordinated ligand {being most rapid with $[Mn(phen)_3]^{2+}$}, and it is proposed that the deactivation process proceeds by enhanced radiationless conversion following complex formation [equation (11)].

$$Chl^* + Q \;\; \underset{\longleftarrow}{\overset{\longrightarrow}{=\!=\!=}} \;\; (Chl^* \cdots Q) \; \longrightarrow \; Chl + Q \qquad (11)$$
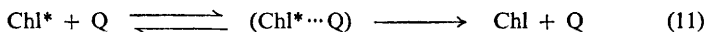
Irradiation ($300 < \lambda < 580$ nm) of aqueous solutions of manganese(IV) sulphate leads to the evolution of oxygen and reduction of the complex to Mn^{III}.[63] Other authors have investigated the photoreduction of Mn^{III} in $K_2[Mn\text{-}2\text{-}\alpha\text{-hydroxyethylisochlorin } e_4]$ acetate and have found, contrary to earlier work with related systems, that there is no evidence for concurrent hydroxyl radical formation.[64]

Other recent publications have considered the photodecomposition of Mn^{II} complexes of both amine *N*-oxides [65] and edta,[66] the Mn^{II}-catalysed photo-oxidation of sulphite ions in solution,[67] and the luminescence [68] and tribo-luminescence [69] of Mn^{II} complexes.

Iron.—As previously noted for other alcohols bearing on α-hydrogen, two distinct processes are observed on photolysis of Fe^{3+} in acidic aqueous ethylene glycol solution.[70] Thus hydroxyl radicals produced by reaction (12) react with the glycol to yield acetaldehyde, while oxidation by the CT state of the substrate in the second co-ordination sphere leads primarily to formaldehyde. With tertiary alcohols, where no α-hydrogen atom is present, direct reaction with the CT excited state does not occur.[71]

$$Fe^{3+} + H_2O \; \xrightarrow{\;h\nu\;} \; Fe^{2+} + \cdot OH + H^+ \qquad (12)$$

$$\cdot OH + HOCH_2CH_2OH \; \longrightarrow \; HO\overset{\cdot}{C}HCH_2OH + H_2O \qquad (13)$$

Methanol is oxidized to formaldehyde on aerobic irradiation of solutions of $[Fe(tim)(MeOH)(OMe)]^{2+}$ (tim = 2,3,9,10-tetramethyl-1,4,8,11-tetra-azacyclo-tetradeca-1,3,8,10-tetraene).[72] The primary process probably involves homolysis of the Fe—OMe bond. Other related studies include the use of benzene as a scavenger for $\cdot OH$ formed on irradiation of Fe^{3+},[73] and the photo-oxidation of alcohols,[74] trichloroethylene,[75] and poly(methyl methacrylate) [76] by $FeCl_3$.

[62] R. G. Brown, A. Harriman, and G. Porter, *J.C.S. Faraday II*, 1977, **73**, 113.
[63] T. S. Dzhabiev and V. Y. Shafirovich, *Reaction Kinetics and Catalysis Letters*, 1976, **4**, 419.
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[66] H. B. Lockhart and R. V. Blakeley, *Environ. Letters*, 1975, **9**, 19.
[67] S. Lunak and J. Vepřek-Šiška, *Reaction Kinetics and Catalysis Letters*, 1976, **5**, 157.
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[69] G. E. Hardy and J. I. Zink, *Inorg. Chem.*, 1976, **15**, 3061.
[70] J. H. Carey, E. G. Cosgrove, and B. G. Oliver, *Canad. J. Chem.*, 1977, **55**, 625.
[71] J. H. Carey, B. G. Oliver, and C. H. Langford, *Canad. J. Chem.*, 1977, **55**, 1207.
[72] D. W. Reichgott and N. J. Rose, *J. Amer. Chem. Soc.*, 1977, **99**, 1813.
[73] N. Jacob, I. Balakrishnan, and M. P. Reddy, *J. Phys. Chem.*, 1977, **81**, 17.
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[75] Z. A. Tkachenko, S. Y. Kuchmii, A. V. Korzhak, and A. I. Kryukov, *Ukrain. khim. Zhur.*, 1976, **42**, 539.
[76] N. I. Zaitseva, T. V. Pokholok, G. B. Pariiskii, and D. Y. Toptygin, *Doklady Akad. Nauk S.S.S.R.*, 1976, **229**, 906.

It has been found that the carbon dioxide evolved on photodecomposition of potassium ferrioxalate is isotopically enriched in ^{12}C, the extent of fractionation depending on wavelength [77] [$(^{12}C/^{13}C)_{sample}/(^{12}C/^{13}C)_{ref} = 1.050$ at 520 nm and 1.001 at 366 nm]. The results are interpreted in terms of two reactive intermediates. The photolysis of $(Hphen)_3[Fe(ox)_3]$,[78] difficulties with the ferrioxalate actinometer,[79] and the solid-state photolysis of $K_3[Fe(ox)_3],3H_2O$ [80] have been the subjects of recent reports.

Photolysis of the Fe^{III} complex of pyridine-2-carboxylic acid gives a surprisingly high yield of 2,2'-bipyridyl, possibly because the pyridine radical, formed after decarboxylation, remains co-ordinated to the iron atom.[81] The formation of their Fe^{III} complexes and subsequent photo-oxidation cause the aerobic decomposition of edta [66] and sodium sulphite.[82]

Excitation of the LMCT state of $Fe(S_2CNR_2)_3$ ($R = Et$ or CH_2Ph) causes homolytic cleavage of the Fe—S bond, with, in the presence of halogenated hydrocarbons, the resultant formation of $Fe(S_2CNR_2)_2X$.[12, 83, 84] The quantum yield for the overall reaction is dependent on the C—X bond strength of the halogenated hydrocarbon, being markedly larger for CBr_4 than for CH_2Br_2 and for $CHCl_3$ than for PhCl.

As noted in previous Reports, the nature of the primary photoprocesses of $[Fe(CN)_5NO]^{2-}$ is a matter of debate. Recent comparative e.s.r. and absorption spectroscopic investigations of its photolysis products in DMF, dimethylacetamide, or methanol solutions at both 77 K and room temperature demonstrate that the reaction course is also markedly medium-dependent.[85] Other workers have studied the flash photolysis of $[Fe(CN)_6]^{3-}$ in the presence of N_3^- and SCN^-.[86]

Intramolecular electron transfer from the iron to the cobalt centre in the pyrazine derivative (5a) is induced by excitation of the Fe–heterocycle MLCT band at 620 nm ($\Phi = 0.9$).[87] In the analogous complex (5b) the quantum yield is dramatically lower (0.02), probably owing to the lower oxidizing power of the

$$(NC)_5FeN\diagdown\diagup NCoL_2$$
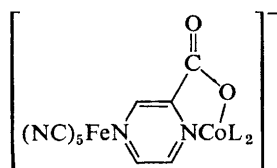
(5) a; $L = (NH_3)_2$
b; $L = en$

[77] R. H. Betts and W. D. Buchannon, *Canad. J. Chem.*, 1976, **54**, 2577.
[78] P. Thomas, M. Benedix, and H. Hennig, *Z. Chem.*, 1977, **17**, 114.
[79] W. D. Bowman and J. N. Demas, *J. Phys. Chem.*, 1976, **80**, 2434.
[80] E. L. Simmons, *J. Phys. Chem.*, 1976, **80**, 1592.
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[82] S. Lunak and J. Vepřek-Šiška, *Coll. Czech. Chem. Comm.*, 1976, **41**, 3495.
[83] D. P. Schwendiman and J. I. Zink, *J. Amer. Chem. Soc.*, 1976, **98**, 4439.
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[85] R. B. Zhutkovskii and K. I. Zamaraev, *Khim. vysok. Energii*, 1976, **10**, 150.
[86] D. J. Kenney and H. M. Lin, *Bull. Inst. Chem., Acad. Sinica*, 1976, **23**, 53.
[87] D. A. Piering and J. M. Malin, *J. Amer. Chem. Soc.*, 1976, **98**, 6045.

8

Photochemistry

Co(en)$_2$ moiety.[87] Intermolecular electron transfer from other pentacyanoferrate(II) complexes to the [Ru(bipy)$_3$]$^{2+}$ excited state is responsible for quenching of its emission.[88] Further studies have been carried out to assess the potential of thionine–Fe^{II} [89] and iodine–Fe^{II} systems as solar energy converters.[90]

The efficiency of photodissociation of the Fe—L bonds in carbonyl, nitrosyl, isocyanide, and oxygen complexes of haemoglobin and myoglobin upon excitation of the porphyrin may be rationalized in terms of a one-electron MO theory, when account is taken of the d_π(Fe)–π(L) character of the bond.[91] The rebinding of carbon monoxide following laser flash photolysis of carbonyl–haem protein complexes has been monitored at temperatures between 5 and 340 K. The results for carbonylmyoglobin reveal that in the recombination reaction it is necessary to surmount (or tunnel through) four separate activation barriers caused by the solvent, the globin, and the haem.[92, 93] Horse-radish peroxidase becomes photosensitive when it is converted from its high-spin paramagnetic form into a low-spin diamagnetic species on complexation with cyanide.[94]

Ruthenium.—The photosensitization and luminescence properties of [Ru(bipy)$_3$]$^{2+}$ have been the subject of many publications in the past few years. As in other areas of inorganic photochemistry, however, there is a dichotomy between luminescence studies at low temperature (77 K and below) and those on the photophysical and photochemical processes under ambient conditions. From low-temperature data it has been suggested that the luminescent MLCT (d–π^*) state of [Ru(bipy)$_3$]$^{2+}$ consists of a manifold of three states separated by *ca.* 60 cm^{-1}, and therefore thermally equilibrated except at extremely low temperatures.[95, 96] Two groups of authors have recently reported on the variation of the luminescence lifetime of the complex in a variety of solvents as a function of temperature (up to 373 K).[97, 98] In both studies non-Arrhenius behaviour was noted, indicating that at higher temperatures ($T > 320$ K) some non-luminescent state plays a major role in the radiationless deactivation of the emitting excited state. Raising the temperature also causes the disappearance of the solvent isotope effect on the emission lifetime (at 298 K, $\tau_{H_2O} = 0.58$ μs, $\tau_{D_2O} = 1.02$ μs; at 363 K, $\tau_{H_2O} = 0.10$ μs, $\tau_{D_2O} = 0.10$ μs). From these and other data, Van Houten and Watts argue that a LF excited state lying 3600 cm^{-1} above the emitting MLCT level is responsible for its efficient deactivation at those higher temperatures where its population is possible. Observation of photoinduced substitution of [Ru(bipy)$_3$]$^{2+}$ at 368 K corroborates this hypothesis.[97] Other authors have recorded the luminescence spectra of

[88] H. E. Toma and C. Creutz, *Ingor. Chem.*, 1977, **16**, 545.
[89] T. Sakata, Y. Suda, J. Tanaka, and H. Tsubomura, *J. Phys. Chem.*, 1977, **81**, 537.
[90] T. Ohta, S. Asakura, M. Yamaguchi, N. Kamiya, N. Gotoh, and T. Otagawa, *Internat. J. Hydrogen Energy*, 1976, **1**, 113.
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[93] L. Eisenstein, *Internat. J. Quantum Chem., Quantum Biol. Symp.*, 1976, **3**, 21.
[94] Y.-J. Kang and J. D. Spikes, *Biochem. Biophys. Res. Comm.*, 1977, **74**, 1160.
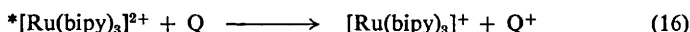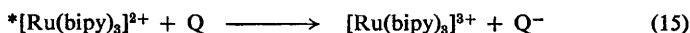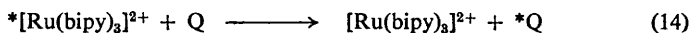[95] G. A. Crosby, in ref. 4, p. 149.
[96] K. W. Hipps and G. A. Crosby, *J. Amer. Chem. Soc.*, 1975, **97**, 7042.
[97] J. Van Houten and R. J. Watts, *J. Amer. Chem. Soc.*, 1976, **98**, 4853.
[98] S. R. Allsopp, A. Cox, S. H. Jenkins, T. J. Kemp, and S. M. Tunstall, *Chem. Phys. Letters*, 1976, **43**, 135.

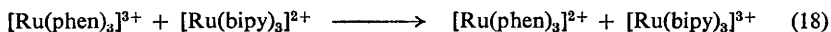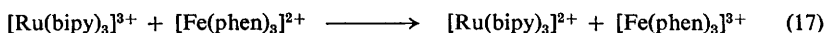[Ru(bipy)$_n$(phen)$_{3-n}$]$^{2+}$,[99] and of [RuL$_3$]$^{2+}$ [L = 2-(2'-pyridyl)quinoline or 2,2'-biquinoline].[100]

Previous work has shown that *[Ru(bipy)$_3$]$^{2+}$ may undergo intermolecular deactivation by energy transfer or by either oxidative or reductive electron transfer [equations (14)—(16)]. This is further illustrated in a recent study of the

$$*[Ru(bipy)_3]^{2+} + Q \longrightarrow [Ru(bipy)_3]^{2+} + *Q \qquad (14)$$

$$*[Ru(bipy)_3]^{2+} + Q \longrightarrow [Ru(bipy)_3]^{3+} + Q^- \qquad (15)$$

$$*[Ru(bipy)_3]^{2+} + Q \longrightarrow [Ru(bipy)_3]^{+} + Q^+ \qquad (16)$$

luminescence lifetime and intensity of [Ru(bipy)$_3$]$^{2+}$ and [Ru(phen)$_3$]$^{2+}$ during quenching by some 20 metal complexes.[101] Diffusional energy and electron transfer are the principal deactivation routes, although some static quenching due to ion-pairing occurs with anionic complexes. No evidence could be found for heavy-atom or paramagnetic quenching. The neutral complex [Ru(bipy)$_2$(CN)$_2$], being free of the problems of ion-pairing or electrostatic repulsion, offers some advantages over [Ru(bipy)$_3$]$^{2+}$ as a sensitizer.[102] Nevertheless, static quenching occurs with Cu^{2+}, Ni^{2+}, and Co^{2+}, where the co-ordinated cyanide acts as a bridging ligand.

Complexes of the type [RuL$_3$]$^{2+}$ with Me-, Ph-, Cl-, Br-, or NO$_2$-substituted phenanthrene or bipyridine ligands all possess lowest-lying MLCT states which may be quenched by Fe^{3+}, Eu^{3+}, or Cr^{3+}.[103] In the first two cases quenching is by oxidative electron transfer (15), whereas for Cr^{3+} energy transfer takes place. Other authors have used Cr^{III} complexes as energy-transfer acceptors to estimate the quantum yield for intersystem crossing in [Ru(bipy)$_2$(CN)$_2$] ($\Phi = 1.0$) and [Ru(phen)$_3$]$^{2+}$ ($\Phi = 0.65$).[39] For this purpose Φ_{ISC} for [Ru(bipy)$_3$]$^{2+}$ was taken to be 1.0, as is now generally accepted. Competitive electron- and energy-transfer processes are responsible for the quenching of *[Ru(bipy)$_3$]$^{2+}$ by various 1,2-dipyridylethylenes.[104] Thus with 1,2-bis-(3-pyridyl)ethylene the rate constant for energy transfer (14) is 6×10^6 dm^3 mol^{-1} s^{-1} while that for oxidative electron transfer (15) is 7×10^5 dm^3 mol^{-1} s^{-1}.

Flash photolysis is a useful tool for studying electron-transfer reactions not only of excited states but also of reactive ground-state compounds. Thus from the decay kinetics of the corresponding [RuL$_3$]$^{3+}$, formed from *[Ru(bipy)$_3$]$^{2+}$ or *[Ru(phen)$_3$]$^{2+}$ and Fe^{3+}, the rate constants for processes (17) and (18) have been deduced (1.8×10^9 and 1.2×10^9 dm^3 mol^{-1} s^{-1}).[105] A drop in the rate constant for electron transfer between *[Ru(bipy)$_3$]$^{2+}$ or *[Ru(4,4'-diMebipy)$_3$]$^{2+}$

$$[Ru(bipy)_3]^{3+} + [Fe(phen)_3]^{2+} \longrightarrow [Ru(bipy)_3]^{2+} + [Fe(phen)_3]^{3+} \qquad (17)$$

$$[Ru(phen)_3]^{3+} + [Ru(bipy)_3]^{2+} \longrightarrow [Ru(phen)_3]^{2+} + [Ru(bipy)_3]^{3+} \qquad (18)$$

[99] G. A. Crosby and W. H. Elfring, *J. Phys. Chem.*, 1976, **80**, 2206.
[100] D. M. Klassen, *Inorg. Chem.*, 1976, **15**, 3166.
[101] J. N. Demas and J. W. Addington, *J. Amer. Chem. Soc.*, 1976, **98**, 5800.
[102] J. N. Demas, J. W. Addington, S. H. Peterson, and E. W. Harris, *J. Phys. Chem.*, 1977, **81**, 1039.
[103] C. T. Lin, W. Boettcher, M. Chou, C. Creutz, and N. Sutin, *J. Amer. Chem. Soc.*, 1976, **98**, 6536.
[104] A. R. Gutierrez, T. J. Meyer, and D. G. Whitten, *Mol. Photochem.*, 1976, **7**, 349.
[105] R. C. Young, F. R. Keene, and T. J. Meyer, *J. Amer. Chem. Soc.*, 1977, **99**, 2468.

and other $[M(bipy)_3]^{2+}$ complexes on increasing the free energy for electron transfer may be confirmation of the 'inverted region' predicted by Marcus theory.[106]

Flash spectroscopy has provided direct evidence for the reductive quenching (16) of $*[Ru(bipy)_3]^{2+}$ by Eu^{2+}, $[Ru(NH_3)_6]^{2+}$, or $[Fe(CN)_6]^{4-}$,[107] or by various organic donor molecules, including phenothiazines.[108, 109] The efficiency of quenching of $[Ru(bipy)_3]^{2+}$ luminescence by $[Fe(CN)_5L]^{3-}$ complexes parallels their reduction potentials, again indicating a reductive mechanism.[88] All these quenching experiments confirm that the reduction potential for $*[Ru(bipy)_3]^{2+}/$ $[Ru(bipy)_3]^+$ is close to the thermodynamic limit of approximately 0.8 V. It has also been observed that the Ru^I complex reacts rapidly with oxygen to give the superoxide ion [equation (19)].[108, 109]

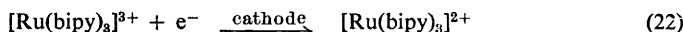$$[Ru(bipy)_3]^+ + O_2 \longrightarrow [Ru(bipy)_3]^{2+} + O_2^- \qquad (19)$$
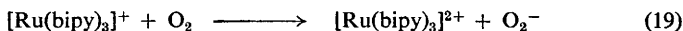
It has been known for some time that $[Ru(bipy)_3]^{2+}$ is an efficient ($\Phi = 0.85$) singlet oxygen sensitizer, and this property has now been utilized in the construction of a laser actinometer.[110] Similar activity is also reported for various substituted phenanthroline complexes of ruthenium(II) and osmium(II).[111] The precise nature of the complex $\{[Ru(bipy)_3] \cdots O_2\}^{2+}$ is not clear, some authors favouring an exciplex which may subsequently form singlet oxygen or undergo deactivation[111] whereas others prefer a species with a high degree of charge transfer $\{[Ru(bipy)_3]^{3+} \cdots O_2^-\}$.[112]

The small anodic photocurrent produced on irradiation of $[Ru(bipy)_3]^{2+}$ at a SnO_2 electrode has been attributed to direct electron transfer from the excited state to the conduction band of the semiconductor [equation (20)].[113] Much

$$*[Ru(bipy)_3]^{2+} \xrightarrow{\text{anode}} [Ru(bipy)_3]^{3+} + e^- \qquad (20)$$
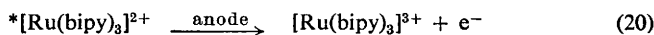
larger cathodic currents are observed on irradiation of acidic solutions of $[Ru(bipy)_3]^{2+}$ in the presence of mild oxidants (X) such as oxygen, methylviologen, or Fe^{3+}; the proposed mechanism is that shown by reactions (21) and (22).[114, 115] From the variation of the magnitude of the photocurrent with Fe^{3+}

$$*[Ru(bipy)_3]^{2+} + X \longrightarrow [Ru(bipy)_3]^{3+} + X^- \qquad (21)$$

$$[Ru(bipy)_3]^{3+} + e^- \xrightarrow{\text{cathode}} [Ru(bipy)_3]^{2+} \qquad (22)$$

concentration the lifetime of the excited Ru^{II} complex has been estimated and found to be in good agreement with that determined directly in luminescence studies.[115] Emission from $*[Ru(bipy)_3]^{2+}$ is induced during cathodic polarization of SiC or GaP electrodes in solutions of $[Ru(bipy)_3]^{3+}$, indicating that electron transfer from the semiconductor to the Ru^{III} complex occurs [*i.e.* the reverse of reaction (20)].[116]

[106] C. Creutz and N. Sutin, *J. Amer. Chem. Soc.*, 1977, **99**, 241.
[107] C. Creutz and N. Sutin, *J. Amer. Chem. Soc.*, 1976, **98**, 6384.
[108] M. Maestri and M. Grätzel, *Ber. Bunsengesellschaft phys. Chem.*, 1977, **81**, 504.
[109] C. P. Anderson, D. J. Salmon, T. J. Meyer, and R. C. Young, *J. Amer. Chem. Soc.*, 1977, **99**, 1980.
[110] J. N. Demas, R. P. McBride, and E. W. Harris, *J. Phys. Chem.*, 1976, **80**, 2248.
[111] J. N. Demas, E. W. Harris, and R. P. McBride, *J. Amer. Chem. Soc.*, 1977, **99**, 3547.
[112] J. S. Winterle, D. S. Kliger, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1976, **98**, 3719.
[113] M. Gleria and R. Memming, *Z. phys. Chem. (Frankfurt)*, 1975, **98**, 303.
[114] S. O. Kobayashi, N. Furuta, and O. Simamura, *Chem. Letters*, 1976, 503.
[115] J. Phillips, C. H. Langford, and J. A. Koningstein, *J.C.S. Chem. Comm.*, 1977, 425.
[116] M. Gleria and R. Memming, *Z. phys. Chem. (Frankfurt)*, 1976, **101**, 171.

The exciting observation by Whitten and co-workers [117] of oxygen and hydrogen evolution on irradiation of assemblies of monolayers of (6) has provided a

(6)
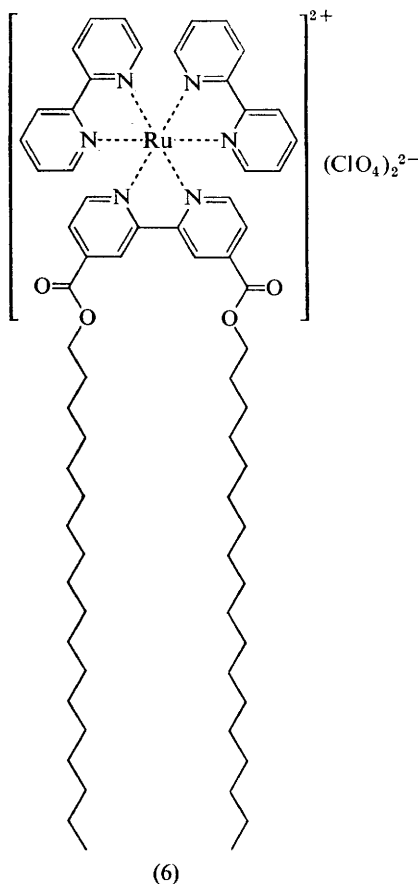
stimulus for many groups. However, it has now been demonstrated that the behaviour of such monolayers is dependent on the particular sample used and on its purity.[118, 119] Highly purified samples of (6) do not catalyse the photo-decomposition of water, but are themselves destroyed by undergoing ester hydrolysis. It is likely that the reactive species in the active monolayer assembly is some trap centre, possibly another Ru^{II} complex.

Derivatives of the type $[Ru^{II}(bipy)_2L_2]^{n+}$ have provided the first direct evidence for acid–base equilibria in the excited states of metal complexes.[120, 121] With

[117] G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch, and D. G. Whitten, *J. Amer. Chem. Soc.*, 1976, **98**, 2337.
[118] G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch, and D. G. Whitten, *J. Amer. Chem. Soc.*, 1977, **99**, 4947.
[119] S. J. Valenty and G. L. Gaines, *J. Amer. Chem. Soc.*, 1977, **99**, 1285.
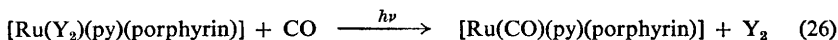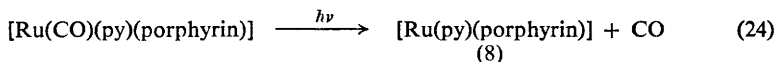[120] S. H. Peterson and J. N. Demas, *J. Amer. Chem. Soc.*, 1976, **98**, 7880.
[121] P. J. Giordano, C. R. Bock, M. S. Wrighton, L. V. Interrante, and R. F. X. Williams, *J. Amer. Chem. Soc.*, 1977, **99**, 3187.

Photochemistry

$[Ru(bipy)_2(CN)_2]$ (D) in strongly acid solution ($[H^+] = 2.5$ mol dm^{-3}) emission is only from *D even though the protonated forms DH$^+$ and DH$_2^{2+}$ predominate in the ground state (27% and 65% respectively).[120] These observations are consistent with rapid excited-state protonation–deprotonation equilibria involving *D, *DH$^+$, and *DH^{2+} in which *D is favoured. With complex (7) emission is observed from both the protonated and deprotonated forms [reaction (23)].[121]

$$(23)$$
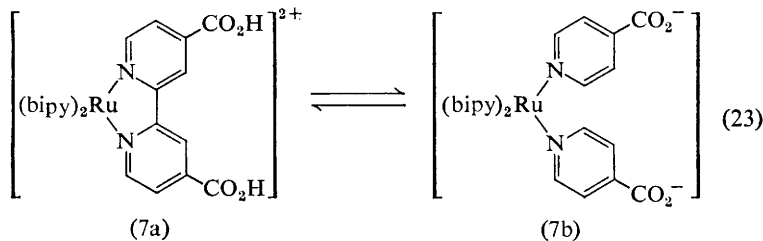
However, the ground-state and excited-state complexes have quite different pK_a values. From the pH dependence, the pK_a for the excited state was calculated to be 8.50, indicating that the excited state of (7) is a weaker acid than the ground state ($pK_a = 5.5$). Thus at pH = 3.5, on excitation of the deprotonated form (7b), emission originates mainly from the excited state of the protonated species (7a). This behaviour is in agreement with the expected increased negative charge on the ligand in the MLCT excited state.

Monolayers of the dioctadecyl ester of [Ru(CO)(py)(mesoporphyrin IX)] exhibit some remarkable properties.[122] Thus, in contrast to the behaviour of the parent complex [Ru(CO)(py)(mesoporphyrin IX)], the co-ordinatively un-saturated species (8) formed on photoinduced CO expulsion may be readily isolated and characterized [reaction (24)]. It reacts with oxygen or nitrogen to form stable derivatives, which on further irradiation in the presence of CO re-form the original carbonyl compound [reactions (25) and (26)].

$$[Ru(CO)(py)(porphyrin)] \xrightarrow{h\nu} [Ru(py)(porphyrin)] + CO \qquad (24)$$
$$(8)$$

$$[Ru(py)(porphyrin)] + Y_2 \longrightarrow [Ru(Y_2)(py)(porphyrin)] \qquad (25)$$

$$[Ru(Y_2)(py)(porphyrin)] + CO \xrightarrow{h\nu} [Ru(CO)(py)(porphyrin)] + Y_2 \qquad (26)$$

In $[Ru(NO)X_5]^{2-}$ (X = Cl, Br, or I)[123] and $[Ru(bipy)_2(NO)Cl]^{2+}$,[124] sub-stitution of NO by solvent is induced by light, although it is not clear at present whether the initial step is expulsion of NO or NO$^+$. The Ru^{IV} complex $[Ru(S_2CNEt_2)_3Cl]$ has been isolated after photolysis of $[Ru(S_2CNEt_2)_3]$ in chloroform or dichloromethane.[125]

Cobalt.—Excitation of ligand-field states of Co^{III} ammine complexes normally leads to low-efficiency photoaquation. The reactive species is probably a thermally equilibrated (thexi) singlet state.[126] The ligand labilized may be

[122] F. R. Hopf and D. G. Whitten, *J. Amer. Chem. Soc.*, 1976, **98**, 7422.
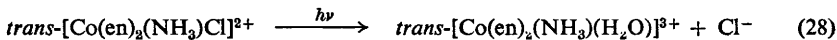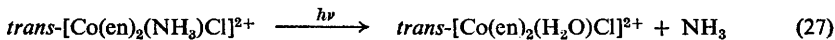[123] A. B. Nikol'skii, A. M. Popov, and I. V. Vasilevskii, *Koord. Khim.*, 1976, **2**, 671.
[124] R. W. Callahan and T. J. Meyer, *Inorg. Chem.*, 1977, **16**, 574.
[125] K. W. Given, B. M. Mattson, and L. H. Pignolet, *Inorg. Chem.*, 1976, **15**, 3152.
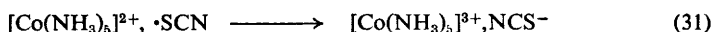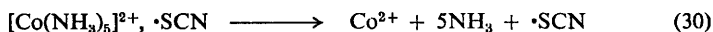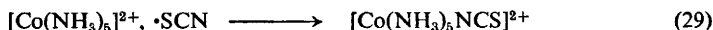[126] A. W. Adamson, in ref. 4, p. 129.

predicted by rules similar to those introduced by Adamson for Cr^{III} complexes. Thus with *trans*-$[Co(en)_2(NH_3)Cl]^{2+}$, ammonia aquation ($\Phi = 1.5 \times 10^{-3}$) is more important than chloride aquation ($\Phi = 3.0 \times 10^{-4}$), although unlike the corresponding Cr^{III} system the reaction proceeds with retention of stereo-chemistry [reactions (27) and (28)].[127] The low quantum yields are attributed

$$\text{*trans*-}[Co(en)_2(NH_3)Cl]^{2+} \xrightarrow{\quad h\nu \quad} \text{*trans*-}[Co(en)_2(H_2O)Cl]^{2+} + NH_3 \qquad (27)$$

$$\text{*trans*-}[Co(en)_2(NH_3)Cl]^{2+} \xrightarrow{\quad h\nu \quad} \text{*trans*-}[Co(en)_2(NH_3)(H_2O)]^{3+} + Cl^- \qquad (28)$$

to efficient radiationless deactivation. With *cis*-$[Co(en)_2(NH_3)Cl]^{2+}$ the overall reactions are low-efficiency chloride aquation ($\Phi = 3.1 \times 10^{-4}$) and ammonia aquation ($\Phi = 2.1 \times 10^{-4}$), although it is suggested that labilization of one of the ethylenediamine $Co-N$ bonds followed by either recombination or displacement of an adjacent ligand is an important reaction pathway.

Direct population of the triplet states of $[Co(NH_3)_6]^{3+}$ or of $[Co(NH_3)_5Cl]^{2+}$ by laser excitation (647 nm) causes photoaquation with lower quantum yields than those found for irradiation into the spin-allowed ligand-field bands (514 nm).[128] Interestingly the relative amounts of chloride *versus* ammonia aquation are inverted (1:3 at 514 nm, 1:0.11 at 647 nm). Thus, as in the thermal reactions, direct population of the triplet state induces mainly chloride replacement, whereas excitation of the singlet states produces predominantly the anti-thermal product. On the other hand, the bimolecular reaction of $[Co(en)_3]^{3+}$ with $[Fe(CN)_6]^{4-}$ is more efficient upon direct triplet excitation, and it has been proposed that this reaction proceeds from a ^5T state formed by intersystem crossing.[128]

In an analogous fashion to $[Co(NH_3)_5(NO_2)]^{2+}$, $[Co(NH_3)_5SCN]^{2+}$ undergoes both linkage isomerization and redox decomposition, the ratio of the two processes being essentially independent of wavelength.[129] (In contrast, $[Co(NH_3)_5NCS]^{2+}$ does not isomerize.) It is probable that the isomerization, redox decomposition, and (low-efficiency) photoaquation proceed through the secondary radical pair [equations (29)—(31)], whereas re-formation of the $[Co(NH_3)_5SCN]^{2+}$ takes place either by direct deactivation of the LMCT state or by collapse of the solvent-caged radical pair.

$$[Co(NH_3)_5]^{2+}, \cdot SCN \longrightarrow [Co(NH_3)_5NCS]^{2+} \qquad (29)$$

$$[Co(NH_3)_5]^{2+}, \cdot SCN \longrightarrow Co^{2+} + 5NH_3 + \cdot SCN \qquad (30)$$

$$[Co(NH_3)_5]^{2+}, \cdot SCN \longrightarrow [Co(NH_3)_5]^{3+}, NCS^- \qquad (31)$$

Two Russian groups [130, 131] have reported some observations on intermediates formed on u.v. photolysis of $[(NH_3)_5Co(O_2CR)]^{2+}$ (R = alkyl). In aerated solution, complexes of the type $[Co(NH_3)_5O_2Co(NH_3)_5]^{4+}$ could be identified,[130]

[127] R. A. Pribush, R. E. Wright, and A. W. Adamson, *J. Amer. Chem. Soc.*, 1977, **99**, 2495.
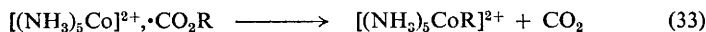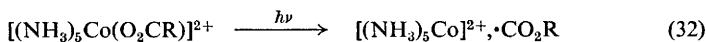[128] C. H. Langford and C. P. J. Vuik, *J. Amer. Chem. Soc.*, 1976, **98**, 5409.
[129] M. Orhanovic and N. Sutin, *Inorg. Chem.*, 1977, **16**, 550.
[130] L. N. Neokladnova, V. A. Repina, and N. I. Zotov, *Zhur. neorg. Khim.*, 1976, **21**, 149.
[131] A. L. Poznyak, V. V. Pansevich, and S. I. Arzhankov, *Koord. Khim.*, 1976, **2**, 472.

whereas species formed at 77 K were assigned to $[Co(NH_3)_5R]^{2+}$ on the basis of characteristic bands in the u.v. absorption spectrum.[131] These latter complexes are assumed to be formed by decomposition of the radical pair [equations (32) and (33)]. Other authors describe the photoaquation and photoredox reactions

$$[(NH_3)_5Co(O_2CR)]^{2+} \xrightarrow{h\nu} [(NH_3)_5Co]^{2+}, \cdot CO_2R \qquad (32)$$

$$[(NH_3)_5Co]^{2+}, \cdot CO_2R \xrightarrow{\hspace{2cm}} [(NH_3)_5CoR]^{2+} + CO_2 \qquad (33)$$

of $[Co(en)_2(S_2O_3)_2]^-$,[132] thermal gravimetric data for both anation and redox products after solid-state photolysis of $[Co(NH_3)_5(H_2O)]X_3$,[133] and the photo-polymerization of acrylamide by $[Co(NH_3)_6]^{3+}$–SCN^- mixtures.[134]

By use of electrochemical monitoring it has been confirmed that the benzophenone triplet state sensitizes the photoreduction of $[Co(NH_3)_6]^{3+}$ *via* energy transfer.[135] Pulse radiolysis studies with Co^{III} ammine and macrocyclic complexes provide useful information about the reactivity of the corresponding Co^{II} complexes in solution.[136-139]   For example, $[Co(NH_3)_5Cl]^+$ decomposes to $[Co(NH_3)_3]^{2+}$ within 2 μs, whereas the remaining ammonia ligands are lost in a stepwise fashion with half-lives of 10, 65, and 540 μs.[136] The reactivity of $[Co(acac)_2]$ produced photochemically has been compared with that formed from ^{60}Co recoil species in $[Co(acac)_3]$.[140]

Irradiation of $[Co(CN)_4(SO_3)_2]^{5-}$ in the presence of labelled cyanide ion produces a mixture of *cis*- and *trans*-$[Co(CN)_4(*CN)(SO_3)]^{4-}$, in contrast with the thermal reaction which proceeds stereospecifically to give the *trans*-isomer as the sole product.[141] This scrambling in the photochemical reaction is taken as evidence for the creation of an excited state of $[Co(CN)_4(SO_3)]^{3-}$ upon photo-dissociation of the starting material.

Phosphorescence spectra of $[Co(CN)_6]^{3-}$,[142] and of $[Co(CN)_5(SO_3)]^{4-}$ and $[Co(CN)_5(NO_2)]^{3-}$,[143] have been recorded at low temperatures.

Rhodium and Iridium.—Previous work has suggested that, in contrast with Cr^{III} complexes, the photoaquation of Rh^{III} compounds proceeds with retention of configuration. However, most experiments have been conducted either with *trans*-$[RhL_4X_2]^+$ complexes or with *cis*-complexes, such as $[Rh(cyclam)X_2]^+$ (cyclam = 1,4,8,11-tetra-azacyclotetradecane), which contain a ligand that resists isomerization. Strauss and Ford [144] have now shown that photoaquation of *cis*-$[Rh(NH_3)_4Cl_2]^+$ leads to the *trans*-product ($\Phi = 0.33$) [equation (34)].

[132] K. P. Balashev, I. P. Serova, and G. A. Shagisultanova, *Koord. Khim.*, 1977, **3**, 82.
[133] G. d'Ascenzo, U. B. Ceipidor, and A. Marino, *Thermochim. Acta*, 1976, **16**, 69.
[134] F. Takemura and K. Sakaguchi, *Nippon Kagaku Kaishi*, 1976, 1470 (*Chem. Abs.*, 1976, **85**, 160 653).
[135] B. S. Hall, K. F. Dahnke, S. S. Fratoni, and S. P. Perone, *J. Phys. Chem.*, 1977, **81**, 866.
[136] J. Lilie, N. Shinohara, and M. G. Simic, *J. Amer. Chem. Soc.*, 1976, **98**, 6516.
[137] M. G. Simic, M. Z. Hoffman, and N. V. Brezniak, *J. Amer. Chem. Soc.*, 1977, **99**, 2166.
[138] A. M. Tait, M. Z. Hoffman, and E. Hayon, *Internat. J. Radiation Phys. and Chem.*, 1976, **8**, 691.
[139] J. F. Endicott, J. Lilie, J. M. Kuszaj, B. S. Ramazwamy, W. G. Schmonsees, M. G. Simic, M. D. Glick, and D. P. Rillema, *J. Amer. Chem. Soc.*, 1977, **99**, 429.
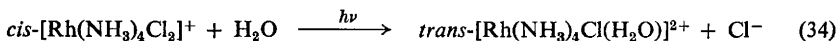[140] Y. Nishi and T. Tominaga, *Radiochem. Radioanalyt. Letters*, 1976, **24**, 249.
[141] K. F. Miller and R. A. D. Wentworth, *Inorg. Chem.*, 1976, **15**, 1467.
[142] K. W. Hipps, G. A. Merrell, and G. A. Crosby, *J. Phys. Chem.*, 1976, **80**, 2232.
[143] B. Loeb and F. Zuloaga, *J. Phys. Chem.*, 1977, **81**, 59.
[144] D. Strauss and P. C. Ford, *J.C.S. Chem. Comm.*, 1977, 194.

$$cis\text{-}[Rh(NH_3)_4Cl_2]^+ + H_2O \xrightarrow{h\nu} trans\text{-}[Rh(NH_3)_4Cl(H_2O)]^{2+} + Cl^- \quad (34)$$
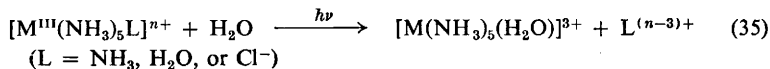
This important result, coupled with those of earlier studies, is most readily rationalized by assuming that the light-induced cleavage of the Rh—Cl bond is followed by isomerization of the five-co-ordinate fragment, so that identical products are formed from both *cis*- and *trans*-complexes. Other authors have made further observations on the photoaquation of $[Rh(NH_3)_5X]^{2+}$ (X = Cl, Br, I, or OH).[145]

Excitation of the ligand-field states of Ir^{III} ammine complexes induces photo-aquation [equation (35)] with quantum yields which are very similar to those found previously for the analogous Rh^{III} complexes (Table 1).[146] This quantitative
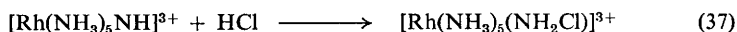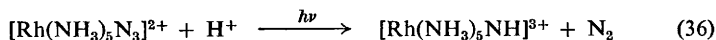
Table 1 *Comparison of quantum yields for photosubstitution reactions (35) upon ligand-field excitation of* Rh^{III} *and* Ir^{III} *complexes* [146]

| | Rh^{III} | | Ir^{III} | |
| | Excitation | | Excitation | |
Complex	wavelength/nm	Φ	wavelength/nm	Φ
$[M(NH_3)_6]^{3+}$	313	0.09	313	0.075
	254	0.082	254	0.07
$[M(NH_3)_5(H_2O)]^{3+}$	313	0.42	313	0.43
$[M(NH_3)_5Cl]^{2+}$	313	0.13	280—380	0.12—0.16

similarity, although possibly fortuitous, is quite surprising, as the ligand-field excited-state lifetimes are much shorter for iridium compounds than for the analogous rhodium species, and further the thermal substitution rates are smaller for the heavier element. These moderately efficient photoaquation reactions contrast with those observed for Co^{III} complexes (Φ for $[Co(NH_3)_6]^{3+}$ = 2×10^{-4}).

$$[M^{III}(NH_3)_5L]^{n+} + H_2O \xrightarrow{h\nu} [M(NH_3)_5(H_2O)]^{3+} + L^{(n-3)+} \quad (35)$$
$$(L = NH_3, H_2O, or Cl^-)$$

The production of metal nitrene complexes on irradiation ($\lambda > 214$ nm) of $[Rh(NH_3)_5N_3]^{2+}$ in acidic solution has been reinvestigated.[147] When account is taken of the photolysis of $[Rh(NH_3)_5(NH_2Cl)]^{3+}$ it can be demonstrated that process (36) is the only significant mode of reaction; no evidence was found for

$$[Rh(NH_3)_5N_3]^{2+} + H^+ \xrightarrow{h\nu} [Rh(NH_3)_5NH]^{3+} + N_2 \quad (36)$$
$$[Rh(NH_3)_5NH]^{3+} + HCl \longrightarrow [Rh(NH_3)_5(NH_2Cl)]^{3+} \quad (37)$$

redox decomposition such as is observed for $[Co(NH_3)_5(N_3)]^{2+}$. A qualitative treatment of the energetics of the system indicates that decomposition to the nitrene complex should be energetically favourable for both the cobalt and rhodium compounds, and it is suggested that $d_\pi\text{-}p_\pi$ bonding in the excited state of the azide complex promotes production of nitrene products by inducing mixing of the LMCT and ligand-centred excited states. The nature of the state responsible for metal nitrene production, however, is put in doubt by recent experiments

[145] G. A. Shagisultanova and V. V. Yasinetskii, *Zhur. fiz. Khim.*, 1976, **50**, 91.
[146] A. W. Zanella, M. Talebinasab-Sarvari, and P. C. Ford, *Inorg. Chem.*, 1976, **15**, 1980.
[147] T. Inoue, J. F. Endicott, and G. J. Ferraudi, *Inorg. Chem.*, 1976, **15**, 3098.

with $[M(CN)_5N_3]^{3-}$ (M = Rh or Ir).[148] Irradiation (λ = 313 nm) in absorption bands assigned to azide ligand-centred excited states led not to nitrene formation but to azide aquation (38) (Φ = 0.42 for Rh, 0.60 for Ir). Although this effect

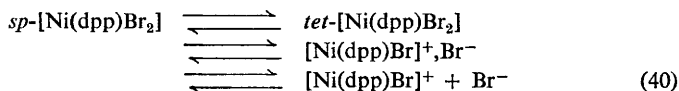$$[M(CN)_5N_3]^{3-} + H_2O \xrightarrow{h\nu} [M(CN)_5(H_2O)]^{2-} + N_3^- \qquad (38)$$
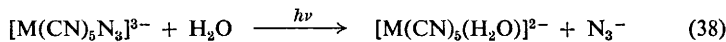
may be due to weaker back-bonding in the nitrene due to the π-interaction of the cyanide ligands, the contrast with the reactions of the penta-ammine complexes is nevertheless surprising.

A Rh^{III} superoxo-complex is formed upon irradiation as shown in equation (39).[149]

$$[Rh(en)_2(NO_2)_2]^+ + O_2 \xrightarrow{h\nu} [Rh(en)_2(NO_2)(O_2)]^+ + NO_2 \qquad (39)$$
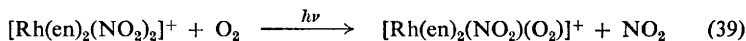
Recent publications have considered the luminescence of bis-chelated derivatives of Ir^{III}, including $[Ir(bipy)_2(H_2O)(bipy)]^{3+}$,[150, 151] and of *trans*-$[RhBr_2(4-Mepy)_4]^+$ and *trans*-$[RhX_2(py)_4]^+$ (X = Cl or Br).[142]

Nickel.—Pulse laser irradiation of $[Ni(dpp)Br_2]$ [dpp = 1,3-bis(diphenyl-phosphino)propane] in dichloromethane perturbs the equilibrium between its square-planar and tetrahedral forms.[152] In acetonitrile, monitoring of the absorbance and conductivity following the pulse reveals that ionization is also occurring in this more polar solvent [equation (40)].

$$sp\text{-}[Ni(dpp)Br_2] \rightleftharpoons tet\text{-}[Ni(dpp)Br_2]$$
$$\rightleftharpoons [Ni(dpp)Br]^+,Br^-$$
$$\rightleftharpoons [Ni(dpp)Br]^+ + Br^- \qquad (40)$$

Other publications have considered the photoreduction of Ni^{2+} in methanol solutions,[153] the photoisomerization of the azo-substituent of a Ni^{II} Schiff-base complex,[154] and the quenching of organic singlet and triplet states by $[Ni(4\text{-}Mepy)_4Cl_2]$ and $[Ni(4\text{-}Mepy)_4(NCS)_2]$.[155]

Platinum.—Transient Pt^{III} complexes have been formed both by the reaction of pulse-radiolytically generated hydroxyl radicals with Pt^{II} complexes and by flash photolysis of Pt^{IV} species.[156] It is proposed that the first transient observed on photolysis of $[Pt(en)_2Cl_2]^{2+}$ is the distorted octahedral *trans*-$[Pt(en)_2Cl(H_2O)]^{2+}$. Photoredox decomposition of $[PtN_4X_2]^{2+}$ (N$_4$ = 4NH$_3$, 4MeNH$_2$, 4EtNH$_2$, 2en, or 2 × 1,3-diaminopropane; X = Cl, Br, or I) has been reported.[157]

Photosolvation (Φ = 0.1) of *cis*-$[Pt(1\text{-naphthylamine})_2Cl_2]$ in aqueous DMF solution occurs upon irradiation into the intra-ligand band (λ_{max} = 293 nm) [reaction (41)].[158] No reaction is found after direct excitation of the LF states.

[148] V. M. Miskowski, G. L. Nobinger, and G. S. Hammond, *Inorg. Chem.*, 1976, **15**, 2904.
[149] R. D. Gillard, J. D. Pedrosa de Jesus, and L. R. H. Tipping, *J.C.S. Chem. Comm.*, 1977, 58.
[150] R. J. Watts, B. Griffith, and J. S. Harrington, in ref. 4, p. 201.
[151] R. J. Watts, J. S. Harrington, and J. Van Houten, *J. Amer. Chem. Soc.*, 1977, **99**, 2179.
[152] L. Campbell and J. J. McGarvey, *J.C.S. Chem. Comm.*, 1976, 749.
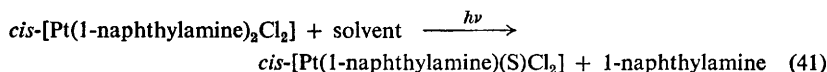[153] E. F. Abdrashitov and L. A. Tikhomirov, *Khim. vysok. Energii*, 1976, **10**, 401.
[154] D. P. Fisher, V. Piermattie, and J. C. Dabrowiak, *J. Amer. Chem. Soc.*, 1977, **99**, 2811.
[155] A. Guarino, G. Occhiucci, E. Possagno, and R. Bassanelli, *J. Photochem.*, 1976, **5**, 415.
[156] J. C. Brodovitch, D. K. Storer, W. L. Waltz, and R. L. Eager, *Internat. J. Radiation Phys. and Chem.*, 1976, **8**, 465.
[157] A. V. Loginov and G. A. Shagisultanova, *Zhur. priklad. Spektroskopii*, 1976, **49**, 2353.
[158] A. Vogler and A. Kern, *Angew. Chem.*, 1976, **88**, 686; *Angew. Chem. Internat. Edn.*, 1976, **15**, 625.

cis-[Pt(1-naphthylamine)$_2$Cl$_2$] + solvent $\xrightarrow{h\nu}$

$$\text{cis-[Pt(1-naphthylamine)(S)Cl}_2] + \text{1-naphthylamine} \quad (41)$$

This labilization effect is attributed to the reduced basicity of the amine in the excited state.

The photoisomerization of [Pt(PEt$_3$)$_2$Cl$_2$] has been re-examined in greater detail.[159] In degassed solution the quantum yields ($\Phi_{trans-cis} = 1.0$, $\Phi_{cis-trans} = 0.09$) are essentially independent of wavelength. The *trans–cis* interconversion is partially quenched by oxygen or piperylene; however, 13% remains unquenchable even at higher quencher concentrations.

Intense emission from [Pt{OP(OH)$_2$}$_2${P(OH)$_3$}$_2$] in aqueous solution at room temperature[160] and activation-energy barriers for intersystem crossing in platinum phthalocyanine[161] have been the subjects of recent articles.

Copper.—Suspensions of cuprous chloride in water are photochromic, turning green in the presence of u.v. light.[162, 163] This is due to the formation of fine particles of copper of grain size 3 nm [equation (42)].

$$2\text{CuCl} \xrightarrow{h\nu} \text{Cu}^0 + \text{Cu}^{2+} + 2\text{Cl}^- \quad (42)$$
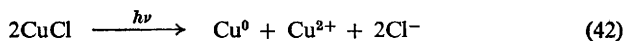
Excitation of the MLCT band of [Cu(2,9-diMephen)$_2$]$^+$ in the presence of Co^{III} complexes leads to oxidation of the copper complex and production of Co^{2+}, probably by electron transfer from the CT excited state to the acceptor complex.[164]

Other recent papers have considered the photoredox reactions of Cu^{II} carboxylates at 77 K,[165] the photopolymerization of acrylamide by bis(glutamato)-copper(II),[166] the use of [Cu(acac)$_2$] as a light stabilizer for polyamides,[167] the use of Cu^{2+} and benzophenone as a catalyst system for the photodehydrogenation of cyclohexane,[168] and the photochemistry of $\alpha\beta$-unsaturated ketones[169] and isoxazoles[170] in the presence of Cu^{2+}.

Silver and Gold.—Photoreduction of Ag$^+$ has been monitored in aqueous solution and in alcohols.[171] As has previously been observed for photoreactions of the CT state of Fe^{3+}, this reaction is most efficient with alcohols having an α-hydrogen, such as ethanol or propan-2-ol, but inefficient for t-butyl alcohol. Photoreduction of silver ions in zeolites (ZO$^-$ is the zeolite lattice) gives concomitant oxygen evolution [equation (43)].[172] On heating to 873 K, hydrogen is released.

[159] S. H. Goh and C. Y. Mok, *J. Inorg. Nuclear Chem.*, 1977, **39**, 531.
[160] R. P. Sperline, M. K. Dickson, and D. M. Roundhill, *J.C.S. Chem. Comm.*, 1977, 62.
[161] T.-H. Huang, K. E. Rieckhoff, and E. M. Voigt, *Canad. J. Phys.*, 1976, **54**, 633.
[162] B. Carlsson and G. Wettermark, *J. Photochem.*, 1976, **5**, 321, 421.
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[164] D. R. McMillin, M. T. Buckner, and B. T. Ahn, *Inorg. Chem.*, 1977, **16**, 943.
[165] V. K. Rumas and A. L. Poznyak, *Doklady Akad. Nauk Belarus. S.S.R.*, 1976, **20**, 1106.
[166] P. Natarajan, K. Chandrasekaran, and M. Santappa, *J. Polymer Sci., Polymer Letters*, 1976, **14**, 455.
[167] A. L. Margolin, I. A. Kabanova, L. M. Postnikov, and V. Y. Shlyapintok, *Vysokomol. Soedineniya, Ser. B*, 1976, **18**, 378.
[168] G. H. Jones, D. W. Edwards, and D. Parr, *J.C.S. Chem. Comm.*, 1976, 969.
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[171] H. Hada, Y. Yonezawa, A. Yoshida, and A. Kurakake, *J. Phys. Chem.*, 1976, **80**, 2728.
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$$2Ag^+ + 2ZO^- + H_2O \xrightarrow{h\nu} 2Ag^0 + 2ZOH\cdot + \tfrac{1}{2}O_2 \qquad (43)$$
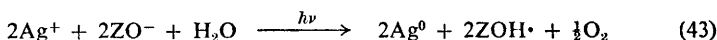
Formation of a thin layer of colloidal silver is the first stage in the light-induced decomposition of silver azide.[173]

The photochemical redox reactions of $[AuCl_4]^-$ and carboxylic acids have been investigated.[174]

Zinc.—A pronounced enhancement of the phosphorescence intensity and diminution of the fluorescence of bis-(N-salicylidenealkylamine)zinc(II) complexes compared with the monosubstituted derivatives is attributed to enhanced ISC through interaction of the two ligands with each other.[175] NN'-(4,4'-Sulphonyldiphenylene)dimaleimide photopolymerizes in the presence of $ZnBr_2$.[176]

Mercury.—The observation that photolysis of various amino-acids in the presence of $HgCl_2$ gives methylmercury derivatives may be environmentally important.[177]

Lanthanides.—The general interest in photochemical decomposition of water has prompted several groups of workers to examine the photolysis of Eu^{2+} in acid solution in more detail.[178-180] The quantum yield for hydrogen evolution in perchloric acid solutions (8.7×10^{-3}–3.74 mol dm^{-3}) varies with the square root of the hydrogen-ion concentration.[178] This dependence is that predicted by the Noyes theory for reaction of H^+ with the geminate radical pair $[EuOH,H]^{2+}$ formed from the excited state.

$$2Eu^{2+} + 2H^+ \xrightarrow{h\nu} 2Eu^{3+} + H_2 \qquad (44)$$

In another recent study it has been demonstrated that in strong solutions the perchlorate ion may not always be inert.[179] Thus at 77 K in perchloric acid (9 mol dm^{-3}) glasses, photolysis of Eu^{2+} produces ClO_3, which was identified by its u.v.–visible absorption spectrum [reaction (45)]. No reaction was observed at perchloric acid concentrations of 0.2 mol dm^{-3}.

$$Eu^{2+} + HClO_4 \xrightarrow{h\nu} Eu^{3+} + ClO_3 + OH^- \qquad (45)$$
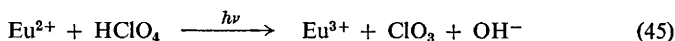
An absorption band observed in the u.v. spectrum ($\lambda_{max} = 225$ nm) after photolysis of Eu^{2+} in 8 mol dm^{-3} hydrochloric acid glasses at 77 K has been assigned to hydrated hydrogen atoms,[180] although it is markedly different from that previously reported, but similar to that of the $HO_2\cdot$ radical ($\lambda_{max} = 225$ nm, $\varepsilon_{max} = 1200$).[181]

Investigation of the influence of thiocyanate ion on the intensity and lifetime of the emission from both the $^5D_1$ and $^5D_0$ levels of $[Eu(CF_3COCHCOCF_3)_3]$ shows that the quenching occurs by interaction with the metal-centred state and

[173] A. V. Dubovitskii, E. V. Prokhorin, and G. B. Manelis, *Khim. vysok. Energii*, 1976, **10**, 59.
[174] B. S. Maritz and R. Van Eldik, *J. Inorg. Nuclear Chem.*, 1976, **38**, 2124.
[175] T. Ohno, S. Kato, A. Takeuchi, and S. Yamada, *Bull. Chem. Soc. Japan*, 1977, **50**, 6.
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[181] P. Pagsberg, H. Christensen, J. Rabani, G. Nilsson, J. Fenger, and S. O. Nielsen, *J. Phys. Chem.*, 1969, **73**, 1029.

not with the $^1(n-\pi^*)$ ligand state as previously postulated.[182] Other authors have also observed quenching of the $^5D_0$ level of Eu^{3+} by CNS^- caused by complex formation in water, methanol, or acetone solution.[183]

Energy transfer between [Tb(thd)₃] and [Eu(thd)₃] (thd = $Bu^tCOCHCOBu^t$) has been monitored in a variety of solvents.[184] Lifetime and intensity data indicate that there is no significant contribution from static quenching due to formation of [Tb(thd)₃]–[Eu(thd)₃] dimers. Other authors have reviewed work on energy transfer between cationic donors and rare-earth ions [185] and discussed the sensitization of Eu^{3+} luminescence in AMP or ATP complexes (ATP = adenosine 5′-triphosphate) at room temperature.[186]

The circularly polarized emission (CPE) from Eu^{3+} and Tb^{3+} in L-malic acid complexes has been examined in D_2O and H_2O solutions as a function of pH.[187] Other systems for which CPE data have recently been published are tris-(3-trifluoro-*d*-camphorato)europium(III),[188] tris-(β-diketonato)europium(III) complexes in optically active solvents,[189] and Tb^{III} in substituted bovine cardiac troponin C.[190]

The observed pressure-induced variation of the quantum yield of luminescence from [Eu(PhCOCHCOMe)₄]⁻[Hpip]⁺ is attributed to a lowering of the triplet energy level (by *ca.* 1500 cm⁻¹ at 55 kbar).[191] Luminescence from filter-paper adsorbates of lanthanide–β-diketone complexes has been described.[192]

The effect of solvent deuteration on the rate of radiationless decay has been examined for Sm^{3+} in water, DMSO, and acetonitrile,[193] and for Dy^{3+} in DMSO, acetone, and acetonitrile.[194] The lower rate in deuteriated solvents is predicted by the modified energy-gap theory of radiationless transitions,[193] but the role of anharmonicity is invoked to explain the effect for deuteriated acetonitrile.[194] Luminescence data, particularly lifetime determinations, have been used to establish the nature of the primary solvation shell for lanthanides in aqueous propan-1-ol solutions,[195] as probes for the metal environment in lanthanide edta and enzyme complexes,[196] and in polymers.[197, 198] Other publications describe the emission characteristics of rare-earth complexes of 1,8-naph-

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[184] H. G. Brittain and F. S. Richardson, *J.C.S. Faraday II*, 1977, **73**, 545.

[185] R. Reisfeld, *Structure and Bonding*, 1976, **30**, 65.

[186] R. Reisfeld, S. Nathanson, and E. Greenberg, *J. Phys. Chem.*, 1976, **80**, 2538.

[187] H. G. Brittain and F. S. Richardson, *Inorg. Chem.*, 1976, **15**, 1507.

[188] H. G. Brittain and F. S. Richardson, *J. Amer. Chem. Soc.*, 1976, **98**, 5858.

[189] H. G. Brittain and F. S. Richardson, *J. Amer. Chem. Soc.*, 1977, **99**, 65.

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[198] V. F. Zolin, L. G. Koreneva, V. A. Barabanov, and S. L. Davydova, *Koord. Khim.*, 1976, **2**, 695.

thyridines [199] and the luminescence properties of lanthanide ions in $POCl_3$–MCl_4 mixtures.[200, 201]

The luminescence properties of a large number of rare-earth porphyrin complexes have been investigated.[202] The emission characteristics of these compounds are governed by the relative energies of the porphyrin singlet and triplet excited states and those of the metal. Thus when the S_1 and T_1 levels of the porphyrin are below those of the metal, fluorescence and phosphorescence are normally observed, although the fluorescence is weak because of enhanced ISC due to spin–orbit coupling and/or the paramagnetism of the metal. However, with Nd and Yb complexes, where the metal-centred excited states are below the porphyrin S_1 and T_1 levels, no porphyrin emission, only that characteristic of the metal, is observed. Intermolecular transfer of energy to ytterbium-aetioporphyrin from porphyrins having their triplet levels lower in energy than that of the acceptor has been monitored by flash photolysis and emission spectroscopy.[203] In this case energy transfer, presumably *via* an exchange mechanism, directly populates the emitting $^2F_{5/2}$ level of the ytterbium. Complexes of Y^{III}, Lu^{III}, and Th^{IV} of *meso*-tetraphenylporphyrin are noteworthy in exhibiting fluorescence from the second excited singlet state.[204] In the case of the Th^{IV} compound this emission is actually more intense than that from the lowest singlet state.

Actinides.—The tunnel-effect theory of radiationless transitions has been applied to hydrogen-abstraction processes by the excited state of the uranyl ion $*[UO_2]^{2+}$.[205] Good agreement between the theoretical and experimental values was found for the rate constants of quenching of $*[UO_2]^{2+}$ by various alcohols and ethers. It has also been predicted that reversible hydrogen abstraction is the principal route for the deactivation of $*[UO_2]^{2+}$ in aqueous solution at room temperature.

Chibisov and co-workers have published a full account of their flash photolysis studies of the photochemical reactions of $[UO_2]^{2+}$.[206] The recording of the absorption spectra of the transient $*[UO_2]^{2+}$ and U^V species has allowed them to obtain quantitative data on the physical (46) and chemical (47) deactivation routes for the excited states in the presence of quenchers such as alcohols, amines, and organic acids.

$$*U^{VI} + Q \longrightarrow U^{VI} + *Q \qquad (46)$$

$$*U^{VI} + Q \longrightarrow U^V + Q^{\cdot+} \qquad (47)$$
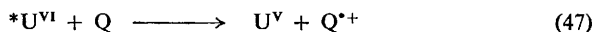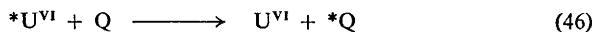
Electron transfer (47) is responsible for the quenching of uranyl ion luminescence by halide ions.[207, 208] Thus, on flash photolysis of UO_2^{2+} in the

[199] M. Ngsee, H. W. Latz, and D. G. Hendricker, in ref. 4, p. 214.

[200] J. Chrysochoos and P. Tokousbalides, *J. Luminescence*, 1976, **14**, 325.

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[207] H. D. Burrows and J. D. Pedrosa de Jesus, *J. Photochem.*, 1976, **5**, 265.

[208] Y. Yokoyama, M. Moriyasu, and S. Ikeda, *J. Inorg. Nuclear Chem.*, 1976, **38**, 1329.

presence of I^-, CNS^-, or Br^-, the species $I_2^{\cdot-}$, $(CNS)_2^{\cdot-}$, and $Br_2^{\cdot-}$ have been detected.[207] The light-induced exchange reaction between labelled U^{VI} and U^{IV} species in 8 mol dm^{-3} hydrochloric acid proceeds *via* initial production of U^V as shown in equation (48).[209]

$$*U^{VI} + U^{IV} \longrightarrow 2U^V \qquad (48)$$

Although uranium(v) complexes normally disproportionate in aqueous solutions, photolysis of $[UO_2Cl_2(py)_2]$ in dry ethanol provides a convenient route to $UOCl_3$.[210] More extended irradiation gives $[U(OEt)_5]$. It is postulated that the first stage in the reaction is photochemical production of UO_2Cl.

A detailed study of the photolysis of uranyl oxalate has been presented.[211] The photoactive species has been identified as $[UO_2(oxH)_2]$. Related topics recently reported are the decomposition of uranyl formate in the solid state [212] and the photoreduction of $[UO_2]^{2+}$ by citrate ions [213] and by tri-n-butyl phosphate.[214] Other publications discuss the possible application of $[UO_2]^{2+}$ in solar energy conversion,[215] the use of uranyl nitrate as a sensitizer for preparation of cellulose–styrene graft copolymers,[216] and the photochemical formation of furan derivatives by irradiation of $\alpha\beta$-unsaturated ketones in methanol containing UO_2Cl_2.[217]

The luminescence intensity of $[UO_2]^{2+}$ increases with H^+ concentration.[218] The effect is attributed to changes in the co-ordination sphere of the ion which lead to reduced efficiency of deactivation. Other recent papers have described the polarized luminescence of uranyl compounds.[219, 220]

U.v. irradiation increases the extent of disproportionation of plutonium(IV) in acidic solution.[221]

$$3Pu^{4+} + 2H_2O \rightleftharpoons 2Pu^{3+} + [PuO_2]^{2+} + 4H^+ \qquad (49)$$
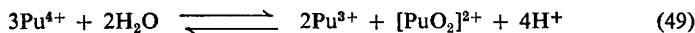
2 Transition-metal Organometallics and Low-oxidation-state Compounds

Recent reviews have considered the photochemistry of transition-metal organometallics and its biological implications,[222] possible applications of organo-

[209] Y. Kato and H. Fukutomi, *J. Inorg. Nuclear Chem.*, 1976, **38**, 1323.
[210] S. Sostero, O. Traverso, C. Bartocci, P. di Bernardo, L. Magon, and V. Carassiti, *Inorg. Chim. Acta*, 1976, **19**, 229.
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[212] B. Claudel and J. P. Puaux, *Compt. rend.*, 1976, **282**, C, 571.
[213] A. Ohyoshi, *Asahi Garasu Kogyo Gijutsu Shoreikai Kenkyu Hokoku*, 1975, **26**, 57 (*Chem. Abs.*, 1976, **85**, 134 106).
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[218] V. P. Kazakov, R. G. Bulgakov, Y. E. Nikitin, and G. L. Sharunov, *Optika i Spektroskopiya*, 1976, **41**, 1091.
[219] V. E. Karasev, in 'Inorganic and Nuclear Chemistry – Herbert H. Hyman Memorial Volume', ed. J. J. Katz, Pergamon, Oxford, 1976, p. 199.
[220] L. V. Volod'ko, A. I. Komyak, M. R. Posledovich, and S. E. Sleptsov, *Izvest. Akad. Nauk S.S.S.R., Ser. fiz.*, 1975, **39**, 2235.
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[222] E. A. Koerner von Gustorf, L. H. G. Leenders, I. Fischler, and R. N. Perutz, *Adv. Inorg. Chem. Radiochem.*, 1976, **19**, 65.

metallics to photo-imaging systems,[223] co-ordination compounds as photo-catalysts,[224] and photoactivated catalytic hydrogenation with transition-metal complexes.[225]

As in previous Reports, a selection of recent examples of photochemical substitution reactions of metal carbonyls is presented in Table 3 (p. 237).

Titanium and Zirconium.—Earlier work has shown that photolysis of $[Cp_2TiMe_2]$ ($Cp = \eta^5$-cyclopentadienyl) in the presence of diphenylacetylene yields the metallocycle (9). It has now been demonstrated that under similar conditions

(9)
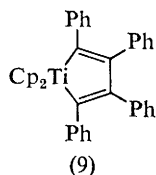
the mono-insertion product $[Cp_2TiMe(CPh=CPhMe)]$ is also produced (in 18% yield).[226] With $C_6F_5C\equiv CC_6F_5$ no metallocyclic species is formed, and the mono-insertion product $[Cp_2TiMe\{C(C_6F_5)=C(C_6F_5)Me\}]$ is the only organometallic product.

Irradiation of $[Cp_2ZrMe_2]$, $[Cp_2ZrPh_2]$,[227] or $[Cp_2Zr(CPh=CMe_2)_2]$ [228] in solutions of chlorinated hydrocarbons induces cleavage of the Zr—C bond, and leads eventually to $[Cp_2ZrCl_2]$. Similarly, dissociation of the Ti—Ge is the primary photochemical process upon irradiation of $[Cp_2Ti(GePh_3)_2]$ and related compounds.[229]

The methylation of co-ordinated carbon monoxide [reaction (50)] presumably proceeds by reaction of photochemically produced $[(\eta^5-C_5Me_5)_2Zr(CO)]$ with hydrogen.[230]

$$[(\eta^5-C_5Me_5)_2Zr(CO)_2] + 2H_2 \xrightarrow{h\nu} [(\eta^5-C_5Me_5)Zr(OMe)H] + CO \quad (50)$$
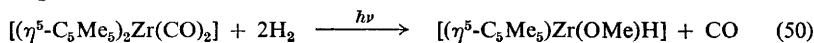
Chromium, Molybdenum, and Tungsten.—Our knowledge of the properties of co-ordinatively unsaturated compounds formed on photolysis of metal carbonyls owes much to matrix-isolation studies with the Group VI metal hexacarbonyls at low temperatures. Absolute quantum yields for such reactions are difficult to determine under these conditions, but in a recent paper the relative quantum efficiencies for reactions (51) have been reported.[231] It was found that Φ_{436}/Φ_{300}

$$[Mo(CO)_6] \underset{h\nu \, (436 \text{ nm})}{\overset{h\nu \, (300 \text{ nm})}{\rightleftharpoons}} [Mo(CO)_5] + CO \quad (51)$$
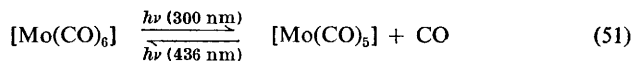
[223] D. M. Allen, *J. Photogr. Sci.*, 1976, **24**, 61.
[224] H. Hennig, P. Thomas, R. Wagner, D. Rehorek, and K. Jurdeczka, *Z. Chem.*, 1977, **17**, 241.
[225] W. Strohmeier, *Chem. Tech. (Heidelberg)*, 1975, **4**, 433.
[226] W. H. Boon and M. D. Rausch, *J.C.S. Chem. Comm.*, 1977, 397.
[227] G. A. Razuvaev, V. N. Latyaeva, L. I. Vyshinskaya, G. A. Vasil'eva, V. I. Khruleva, and L. I. Smirnova, *Doklady Akad. Nauk S.S.S.R.*, 1976, **231**, 114.
[228] C. J. Cardin, D. J. Cardin, J. M. Kelly, R. J. Norton, and A. Roy, *J. Organometallic Chem.*, 1977, **132**, C23.
[229] L. I. Vyshinskaya, G. A. Vasil'eva, and N. V. Klimova, *Trudy Khim. i khim. Tekhnol.*, 1975, 79.
[230] J. M. Manriquez, D. R. McAlister, R. D. Sanner, and J. E. Bercaw, *J. Amer. Chem. Soc.*, 1976, **98**, 6733.
[231] M. Poliakoff, *J.C.S. Faraday II*, 1977, **73**, 569.

was much greater for argon matrices (0.25) than for methane matrices (0.04), indicating that the methane markedly reduces the efficiency of the light-induced recombination reaction.

Poliakoff has recently carried out some matrix-isolation experiments with $[M(CO)_5(CS)]$ (M = Cr or W) which illustrate the power of this technique in the study of the isomerization of molecules that are fluxional under ambient conditions.[232, 233] After photolysis (λ = 297 nm), two species, (10) and (11), resulting from CO elimination, are produced. However, CS formation is insignificant. As (10) and (11) have quite distinct absorption spectra, their

$$\text{(52)}$$
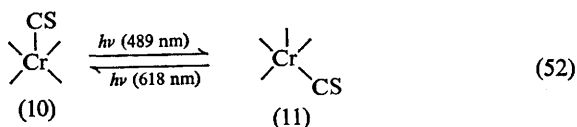
photoinduced interconversion (52) is possible by suitable choice of excitation wavelength.[232] Using stereospecifically labelled *trans*-$[W(CO)_4(^{13}CO)(CS)]$, it has been demonstrated that labilization of the axial and equatorial CO ligands is equally probable.[233] However, the five-co-ordinate species so formed undergoes isomerization in either a vibrationally or electronically excited state, so that the distribution of products (10) and (11) is non-statistical.

Two types of primary process have been postulated for $[(nbd)Cr(CO)_4]$ (12), namely axial CO dissociation or cleavage of one of the metal–olefin bonds (Scheme 1).[234, 235] The evidence of photoexchange with ^{13}CO, which yields
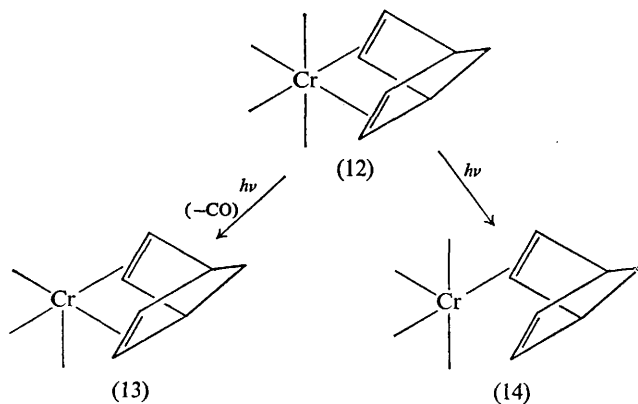
Scheme 1

firstly the monosubstituted axial product and, on more extended irradiation, the diaxially substituted $[(nbd)Cr(^{13}CO)_2(CO)_2]$, supports CO expulsion as the initial reaction step.[234] However, phosphine substitution, even at low temperatures, gives equatorially substituted $[(nbd)Cr(CO)_3(PPh_3)]$, and this has been

[232] M. Poliakoff, *Inorg. Chem.*, 1976, **15**, 2022.
[233] M. Poliakoff, *Inorg. Chem.*, 1976, **15**, 2892.
[234] D. J. Darensbourg, H. H. Nelson, and M. A. Murphy, *J. Amer. Chem. Soc.*, 1977, **99**, 896.

rationalized in terms of phosphine reaction with (14).[235] For hydrogenation reactions catalysed by such [(diene)Cr(CO)$_4$] complexes there is agreement that cleavage of the metal–olefin bond plays some role in the activating step.[234–236] Once again it is apparent that more information on the reactivity of the five-co-ordinate intermediates will be required before definitive mechanisms can be established.

Photodissociation of carbon monoxide is the principal reaction mode of [(C$_6$H$_6$)Cr(CO)$_3$], and studies with C$_6$D$_6$ and [13]CO have revealed that even the photoexchange of benzene [reaction (53)] proceeds *via* [(η^6-C$_6$H$_6$)Cr(CO)$_2$]

$$C_6D_6 + [(C_6H_6)Cr(CO)_3] \xrightarrow{h\nu} C_6H_6 + [(C_6D_6)Cr(CO)_3] \quad (53)$$
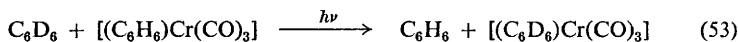
rather than [(η^4-C$_6$H$_6$)Cr(CO)$_3$].[237] The ease of benzene exchange in the tricarbonyl complex contrasts with the extreme photostability of [(C$_6$H$_6$)$_2$Cr]. As no transients could be detected by flash photolysis, and as no isomerization of [(*p*-xylene)$_2$Cr] was observed, it appears that, as with ferrocene and ruthenocene, the excited states of [(C$_6$H$_6$)$_2$Cr] and its derivatives undergo very rapid radiationless deactivation.[237] Other authors have described the photodecomposition reactions of [(*p*-XC$_6$H$_4$)Cr(CO)$_2$L] (L = CO or PPh$_3$, X = H, Me, OMe, COMe, or CO$_2$Me)[238] and the photochemical synthesis of various (1,3,5-cycloheptatriene)Cr(CO)$_2$(phosphine) complexes.[239]

The spectroscopic and photochemical properties of a series of complexes of type [W(CO)$_5$L] have been examined (Table 2).[240] All the complexes are luminescent in EPA glasses at 77 K. As shown in Table 2, emission originates

Table 2 *Emission and photochemical data for* [W(CO)$_5$L] [240]

| Ligand L | Emission [a] | | Quantum yields for reaction (54) | | Lowest excited state |
	λ_{max}/nm	τ/µs	436 nm	514 nm	
3,4-Dimethylpyridine	508	0.96	0.53	—	LF
4-Methylpyridine	510	1.07	0.55	—	LF
Pyridine	524	0.86	0.62	—	LF
3-Bromopyridine	529	1.00	0.66	—	LF
3-Acetylpyridine	535	1.17	0.75	—	LF
3-Benzoylpyridine	540	1.25	0.73	—	LF
3,5-Dibromopyridine	552	1.25	0.82	—	LF
4-Cyanopyridine	602	33.0	0.12	0.02	W → LCT
4-Acetylpyridine	588	38.3	0.15	0.02	W → LCT
4-Benzoylpyridine	595	29.5	0.12	0.02	W → LCT
4-Formylpyridine	658	15.0	0.05	0.002	W → LCT
Piperidine	546	0.82	0.58	—	LF

[a] In EPA at 77 K.

[235] D. Rietvelde and L. Wilputte-Steinert, *J. Organometallic Chem.*, 1976, **118**, 191.

[236] G. Platbrood and L. Wilputte-Steinert, *J. Mol. Catalysis*, 1976, **1**, 265.

[237] A. Gilbert, J. M. Kelly, M. Budzwait, and E. A. Koerner von Gustorf, *Z. Naturforsch.*, 1976, **31b**, 1091.

[238] V. N. Trembovler, N. K. Baranetskaya, N. V. Fok, G. B. Zaslavskaya, B. M. Yavorskii, and V. N. Setkina, *J. Organometallic Chem.*, 1976, **117**, 339.

[239] M. Djazayeri, C. G. Kreiter, H. M. Kurz, M. Lang, and S. Oezkar, *Z. Naturforsch.*, 1976, **31b**, 1238.

[240] M. S. Wrighton, H. B. Abrahamson, and D. L. Morse, *J. Amer. Chem. Soc.*, 1976, **98**, 4105.
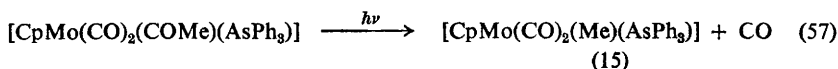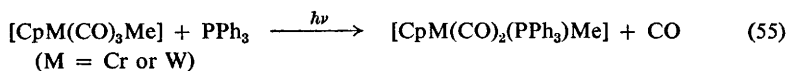
either from an LF state or from a W → LCT state, the latter being the luminescent species for complexes with strongly electron-withdrawing substituents. The photosubstitution reaction (54) is the sole photochemical process observed for

$$[W(CO)_5L] + \text{pent-1-ene} \xrightarrow{h\nu} [W(CO)_5(\text{pent-1-ene})] + L \qquad (54)$$
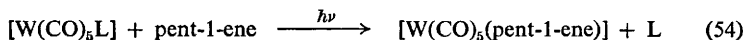
all complexes, the quantum yield being high (0.5—0.8) when the lowest excited state has LF character but small when the CT state is lowest. This strongly suggests that in this case, as in that of $[Ru(NH_3)_5L]^{2+}$, the MLCT state is inactive towards photosubstitution. Further, in this type of excited state the depopulation of the $d\pi$-orbitals involved in back-bonding does not appear to cause sufficient destabilization to induce dissociation of the W—CO bond.

The lack of photosubstitution reactivity in MLCT states of this type of complex is confirmed by the photostability of $[W(CO)_4(trans\text{-}4\text{-styrylpyridine})_2]$ on long-wavelength excitation.[241] Also, in contrast with the behaviour of other styryl-pyridine complexes, population of the MLCT state does not cause the *trans* to *cis* isomerization of the co-ordinated ligand ($\Phi_{436} < 0.001$). Moderately efficient ligand isomerization can, however, be induced by direct excitation of the ligand-localized excited state ($\Phi_{313} = 0.10$) or by biacetyl sensitization ($\Phi = 0.04$).

Photolysis of $[CpCr(CO)_3Me]$ in pentane solution gives both $[CpCr(CO)_3]_2$ and $[CpCr(CO)_2]_2$, whereas in the presence of triphenylphosphine, substitution reactions (55) and (56) take place.[242] The arsine-substituted methyl complex (15) is conveniently synthesized by photolytic decarbonylation [reaction (57)].[243]

$$[CpM(CO)_3Me] + PPh_3 \xrightarrow{h\nu} [CpM(CO)_2(PPh_3)Me] + CO \qquad (55)$$
$$(M = Cr \text{ or } W)$$

$$[CpM(CO)_3Me] + PPh_3 \xrightarrow{h\nu} [CpM(CO)_2(PPh_3)(COMe)] \qquad (56)$$

$$[CpMo(CO)_2(COMe)(AsPh_3)] \xrightarrow{h\nu} [CpMo(CO)_2(Me)(AsPh_3)] + CO \qquad (57)$$
$$(15)$$

In solutions containing acetylenes, photolysis of $[CpW(CO)_3Me]$ yields both the '16-electron' compound $[CpW(CO)(RC{\equiv}CR)Me]$[244, 245] and also an insertion product of type (16).[244, 246, 247] With $CF_3C{\equiv}CCF_3$ and $[CpMo(CO)_3(CH_2CH{=}CH_2)]$, the double-insertion product (17) and a dinuclear complex $[Cp_2Mo_2(CO)_4(CF_3C{\equiv}CCF_3)]$, probably (18), are formed.[248] A better synthetic route to (18) is by irradiation of $[CpMo(CO)_3]_2$ in the presence of the acetylene.

The photogeneration of the triple-bonded dinuclear species $[CpM(CO)_2]_2$ (M = Cr, Mo, or W) from $[CpM(CO)_3]_2$ has been examined in more detail.[249]

[241] L. Pdungsap and M. S. Wrighton, *J. Organometallic Chem.*, 1977, **127**, 337.
[242] H. G. Alt, *J. Organometallic Chem.*, 1977, **124**, 167.
[243] A. C. Gingell, A. Harris, A. J. Rest, and R. N. Turner, *J. Organometallic Chem.*, 1976, **121**, 205.
[244] H. G. Alt, *J. Organometallic Chem.*, 1977, **127**, 349.
[245] H. G. Alt and W. Stadler, *Z. Naturforsch.*, 1977, **32b**, 144.
[246] H. G. Alt, *Angew. Chem.*, 1976, **88**, 800; *Angew. Chem. Internat. Edn.*, 1976, **15**, 759.
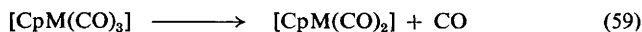[247] J. L. Davidson, M. Green, J. Z. Nyathi, C. Scott, F. G. A. Stone, A. J. Welch, and P. Woodward, *J.C.S. Chem. Comm.*, 1976, 714.
[248] J. L. Davidson, M. Green, F. G. A. Stone, and A. J. Welch, *J.C.S. Dalton*, 1976, 2044.
[249] D. S. Ginley, C. R. Bock, and M. S. Wrighton, *Inorg. Chim. Acta*, 1977, **23**, 85.

CpW(CO)$_2$

O
‖
Me — C

R

R

(16)

(17)

(18)
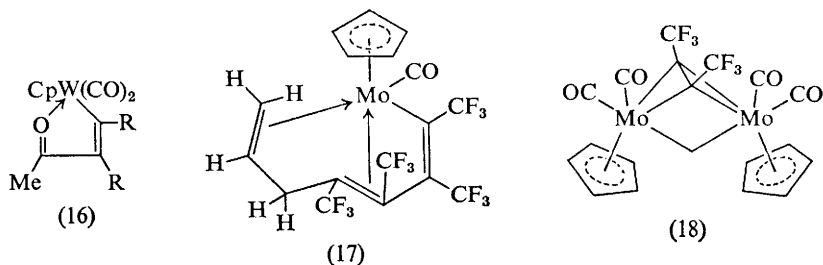
It is proposed that the reaction proceeds by initial cleavage of the M—M bond with production of the '17-electron' complex [CpM(CO)$_3$]. As in the analogous case of [Mn(CO)$_5$], this species is probably labile, losing carbon monoxide to give a '15-electron' complex which dimerizes to give the dinuclear product [reactions (58)—(60)].

$$[CpM(CO)_3]_2 \xrightarrow{h\nu} 2[CpM(CO)_3] \qquad (58)$$

$$[CpM(CO)_3] \longrightarrow [CpM(CO)_2] + CO \qquad (59)$$

$$2[CpM(CO)_2] \longrightarrow [CpM(CO)_2]_2 \qquad (60)$$

Radicals CpW(CO)$_3$ generated by process (58) show considerable selectivity in their reactions (61) with chlorinated hydrocarbons, the rates of reaction

$$[CpW(CO)_3] + RCl \longrightarrow [CpW(CO)_3Cl] + R\cdot \qquad (61)$$
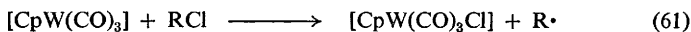
decreasing in the order CCl$_4$ $\gg$ CHCl$_3$ > PhCH$_2$Cl $\gg$ CH$_2$Cl$_2$.[250] From changes in the i.r. spectra it has been deduced that photolysis of [CpM(CO)$_3$]$_2$ (M = Mo or W) in methyltetrahydrofuran glasses at 30 or 80 K also leads to rupture of the metal–metal bond.[251]

The isocyanide complexes [M(CNR)$_6$] [M = Cr, Mo, or W, R = Ph or iPh (2,6-di-isopropylphenyl)] are formal analogues of the hexacarbonyls, and like them undergo photosubstitution in the presence of pyridine, albeit with lower quantum yields [reaction (62)].[252] However, the sensitivity of the quantum yields for the substitution of the molybdenum and tungsten compounds to the bulk of the ligand (for [W(CNPh)$_6$] Φ = 0.011; for [W{CN(iPh)}$_6$] Φ = 0.0003) suggests to the authors that the reaction has associative character. Another interesting feature of these complexes is that they are all strongly luminescent at 77 K, and the molybdenum and tungsten species also emit at room temperature in fluid solution. These observations are consistent with the lowest excited state being MLCT in character. Further evidence for the dipolar nature of this state is the efficient oxidation of the complexes in chloroform solution [reactions (63) and (64)]. In both cases the initial process is probably electron transfer (65).

[250] R. M. Laine and P. C. Ford, *Inorg. Chem.*, 1977, **16**, 388.
[251] D. M. Allen, A. Cox, T. J. Kemp, and Q. Sultana, *Inorg. Chim. Acta*, 1977, **21**, 191.
[252] K. R. Mann, H. B. Gray, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1977, **99**, 306.

$$[M(CNR)_6] + py \xrightarrow{h\nu} [M(CNR)_5py] + CNR \quad (62)$$

$$[M\{CN(iPh)\}_6] \xrightarrow[CHCl_3]{h\nu} [M\{CN(iPh)\}_6]^+ \quad (63)$$

$$[M(CNPh)_6] \xrightarrow[CHCl_3]{h\nu} [M(CNPh)_6Cl]^+ \quad (64)$$

$$[M(CNR)_6] + CHCl_3 \xrightarrow{h\nu} [\{M(CNR)_6\}^+ \cdots CHCl_3^{\cdot-}] \quad (65)$$
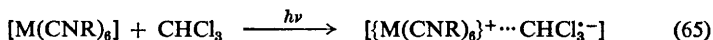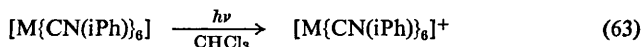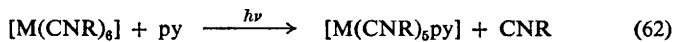
Photolysis of the metallocyclobutane derivative (19) yields ethylene as the principal product, in contrast with the thermal decomposition.[253] It is postulated that the primary photochemical process is production of the η^3-cyclopentadienyl derivative (20), which appears to be in equilibrium with the olefin–carbene complex (21) (Scheme 2). This latter reaction is similar to the essential step previously proposed in catalytic olefin dismutation.
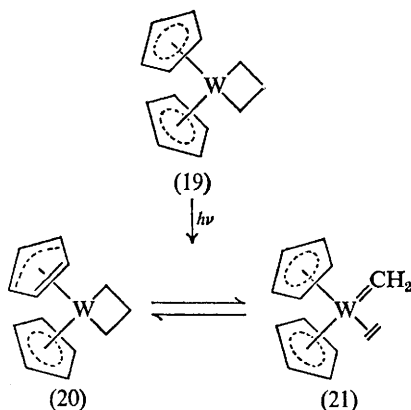
Scheme 2

Other authors have described the *cis* to *trans* isomerization of $[M(CO)_4\text{-}(carbene)_2]$ complexes,[254–256] the preparation of an active catalyst for olefin dismutation by photolysis of a mixture of $[W(CO)_5\{C(OEt)Ph\}]$ and $TiCl_4$,[257] the polymerization of phenylacetylene induced by photodecomposition of $[(mesitylene)Mo(CO)_3]$,[258] and the production of a photocatalyst by irradiation of $[Mo(CO)_6]$ and amberlite.[259]

Mechanistic studies confirm that the light-induced interaction of $[Mo(N_2)_2\text{-}(dppe)_2]$ [dppe = 1,2-bis(diphenylphosphino)ethane] is initiated by photo-expulsion of dinitrogen from the complex.[260, 261]

[253] M. Ephritikhine and M. L. H. Green, *J.C.S. Chem. Comm.*, 1977, 926.
[254] K. Oefele, E. Roos, and M. Herberhold, *Z. Naturforsch.*, 1976, 31b, 1070.
[255] M. F. Lappert, P. L. Pye, and G. M. McLaughlin, *J.C.S. Dalton*, 1977, 1272.
[256] M. F. Lappert and P. L. Pye, *J.C.S. Dalton*, 1977, 1283.
[257] Y. Chauvin, D. Commereuc, and D. Cruypelinck, *Makromol. Chem.*, 1976, 177, 2637.
[258] L. M. Svanidze, E. A. Mushina, A. M. Sladkov, N. I. Sirotkin, A. K. Artemov, I. R. Gol'ding, T. G. Samedova, G. N. Bondarenko, and B. E. Davydov, *Vysokomol. Soedineniya, Ser. B*, 1977, 19, 51.
[259] S. Ivanov, R. Boeva, and S. Tanielyan, *Reaction Kinetics and Catalysis Letters*, 1976, 5, 297.
[260] J. Chatt, A. A. Diamantis, G. A. Heath, N. E. Hooper, and G. J. Leigh, *J.C.S. Dalton*, 1977, 688.
[261] J. Chatt, R. A. Head, G. J. Leigh, and C. J. Pickett, *J.C.S. Chem. Comm.*, 1977, 299.

Manganese and Rhenium.—There is now general agreement that the dominant decomposition process for photoexcited $[Mn_2(CO)_{10}]$ is cleavage of the metal-metal bond [reaction (66)], and this is confirmed by recent reports.[262–264] The recombination process (67), monitored by flash photolysis, is rapid in both

$$[Mn_2(CO)_{10}] \xrightarrow{h\nu} 2Mn(CO)_5 \qquad (66)$$

$$2Mn(CO)_5 \longrightarrow [Mn_2(CO)_{10}] \qquad (67)$$
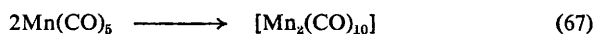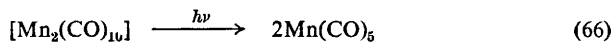
cyclohexane $(k = 4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1})$ and THF $(k = 2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1})$.[262] However, small amounts of a long-lived photoproduct are also formed, and it is suggested that it is secondary photolysis of these species which leads to the permanent photodecomposition previously observed. The radical $Mn(CO)_5$ may be scavenged by the spin-trapping agents nitrosodurene[263] or 2,4,6-tri-t-butylnitrosobenzene,[264] and the product $[Mn(CO)_5\{\dot{N}(O)Ar\}]$ has been identified by e.s.r. Other spin-trapped paramagnetic species are produced under different experimental conditions. For example, if the concentration of spin-trap is deficient, a signal attributed to $[\{Ar(O)\dot{N}\}(OC)_4MnMn(CO)_5]^+$ is observed, this possibly indicating a reaction of type (68).[263] E.s.r. investigations confirm that

$$Mn(CO)_5 + [Mn_2(CO)_{10}] \longrightarrow [Mn(CO)_5]^- + [Mn_2(CO)_{10}]^+ \qquad (68)$$

in basic solvents the disproportionation of the $Mn(CO)_5$ radical produces Mn^{II} compounds.[264] $[Mn_2(CO)_{10}]^-$ has been identified by e.s.r. following ^{60}Co γ-ray irradiation of $[Mn_2(CO)_{10}]$ at 77 K.[265]

Photoreaction of $[Mn_2(CO)_{10}]$ and hydrogen gives $[HMn(CO)_5]$, whereas with $[Re_2(CO)_{10}]$, depending on the excitation wavelength, $[HRe(CO)_5]$, $[H_2Re_2(CO)_8]$, or $[H_3Re_3(CO)_{14}]$ is produced.[266] These and other substitution experiments substantiate previous proposals about the lability of the Group VII metal penta-carbonyls. A detailed kinetic study of the polymerization of tetrafluoroethylene photoinitiated by $[Mn_2(CO)_{10}]$ reveals that the propagating species is $Mn(CO)_5$-$CF_2CF_2\cdot$.[28, 267] Irradiation of mixtures of $[Mn_2(CO)_{10}]$ with cyclohexadienes or butadiene yields small amounts of substitution products.[268, 269]

I.r. analytical data on the products of photolysis of $[M(CO)_5X]$ (M = Mn or Re, X = Cl or Br) in methyltetrahydrofuran glasses at 77 K demonstrate that CO is expelled from the manganese complexes but not from their rhenium analogues.[251]

The results of a thorough investigation of the photosubstitution reactions of $[CpM(CO)_2L]$ (M = Mn or Re, L = amine) have been communicated.[270] The study shows that the only reaction observed is amine substitution (69). This

[262] J. L. Hughey, C. P. Anderson, and T. J. Meyer, *J. Organometallic Chem.*, 1977, **125**, C49.
[263] A. Hudson, M. F. Lappert, and B. K. Nicholson, *J.C.S. Dalton*, 1977, 551.
[264] A. S. Huffadine, B. M. Peake, B. H. Robinson, J. Simpson, and P. A. Dawson, *J. Organometallic Chem.*, 1976, **121**, 391.
[265] S. W. Bratt and M. C. R. Symons, *J.C.S. Dalton*, 1977, 1314.
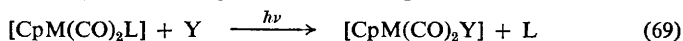[266] B. H. Byers and T. L. Brown, *J. Amer. Chem. Soc.*, 1977, **99**, 2527.
[267] C. H. Bamford and S. U. Mullik, *Polymer*, 1976, **17**, 225.
[268] M. Zoeller, H. E. Sasse, and M. L. Ziegler, *Z. anorg. Chem.*, 1976, **425**, 257.
[269] M. Zoeller and M. L. Ziegler, *Z. anorg. Chem.*, 1976, **425**, 265.
[270] P. J. Giordano and M. S. Wrighton, *Inorg. Chem.*, 1977, **16**, 160.

$$[CpM(CO)_2L] + Y \xrightarrow{h\nu} [CpM(CO)_2Y] + L \qquad (69)$$

behaviour is consistent with the observation that trisubstituted products [Cp$_2$MnL$_3$] are only formed when the entering ligand has π-bonding characteristics similar to those of carbon monoxide. The quantum yields for reaction (69) are dependent on the nature of the metal and the ligand L but independent of both the nature and concentration of the reactant Y, as expected for a photodissociative mechanism. Although the quantum yield for substitution of [CpMn(CO)$_2$L] is high (0.14—0.40) for all derivatives, those for [CpRe(CO)$_2$L] complexes depend markedly on the electron-accepting ability of the ligand (*e.g.* for L = 4-methylpyridine, $\Phi = 0.29$; for L = 4-acetylpyridine, $\Phi < 10^{-4}$). This variation with the nature of L is attributed to the presence of a low-lying MLCT excited state. As in the analogous case of [W(CO)$_5$L],[240] these MLCT excited states appear to be substitutionally unreactive. The species responsible for reaction (69) is probably a triplet LF state, even though the MLCT band is lowest in the absorption spectra for most of the derivatives considered. In the
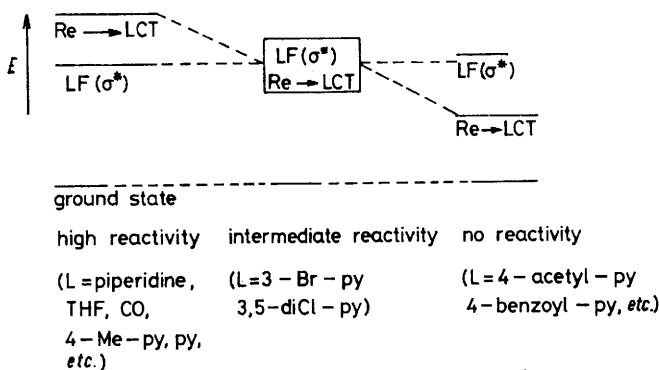
Figure 2 *Relaxed excited-state energies and photoreactivities of* [CpRe(CO)$_2$L] *derivatives*

(Adapted by permission from *Inorg. Chem.*, 1977, **16**, 160)

case of the rhenium derivatives the marked dependence of quantum yield on L is presumably indicative of a changeover in the nature of the lowest-lying thermally equilibrated excited state (Figure 2).

Photochemical synthesis of optical isomers of [{Me(CO$_2$Me)Cp}Mn(CO)(PPh$_3$){P(OMe)$_3$}] [271] and the preparation of bridged complex of the type [Cp(CO)$_2$Mn—AsMe$_2$—M] [M = Mn(CO)$_4$, Re(CO)$_4$, or Co(CO)$_3$] [272] have been reported.

Iron and Ruthenium.—The absence of solvated electrons following flash photolysis of either acetylferrocene (22a) [273] or benzoylferrocene (22b) [274] in aqueous or

[271] F. Le Moigne, R. Dabard, and M. Le Plouzennec, *J. Organometallic Chem.*, 1976, **122**, 365.
[272] U. Richter and H. Vahrenkamp, *J. Chem. Res. (S)*, 1977, 156.
[273] E. K. Heaney and S. R. Logan, *Inorg. Chim. Acta*, 1977, **22**, L3.
[274] E. K. Heaney, S. R. Logan, and J. A. Powell, *J.C.S. Faraday I*, 1977, **73**, 699.

(22) a; R = Me
     b; R = Ph
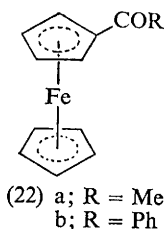
alcoholic solutions demonstrates that, contrary to what had been previously proposed,[275] photoionization is not an important reaction for these compounds [reaction (70)]. It is suggested that the photoprocess leading to decomposition involves intramolecular charge transfer.

$$[CpFe(CpCOR)] \xrightarrow{\quad h\nu \atop \times\quad} [CpFe(CpCOR)]^+ + e^- \qquad (70)$$

Other reports on the photochemistry of ferrocene and derivatives describe the quenching of the singlet states of naphthalene, phenanthrene, triphenylene, and tetracene by ferrocene,[276] the polymerization of epichlorohydrin initiated by photolysis of ferrocene–$TiCl_4$ mixtures,[277] and the ferrocene-catalysed photo-condensation of cyclohexyl isocyanate and butan-1-ol.[278]

At present, little is known about the photochemistry of metal cluster compounds. Therefore the appearance of a recent report on $[CpFe(CO)]_4$ is of special interest.[279] It has been shown that the compound is inert towards photo-substitution but that in the presence of halogenocarbons efficient photo-oxidation occurs [reaction (71)]. As in the analogous reaction with ferrocene, charge transfer to the halocarbon in a CTTS excited state appears to be responsible for transformation (71).

$$[CpFe(CO)]_4 + RX \xrightarrow{\quad h\nu \quad} [CpFe(CO)]_4{}^+ + X^- + R\cdot \qquad (71)$$
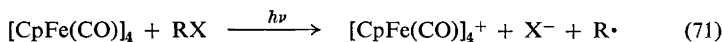
Irradiation of $[Fe(CO)_5]$ in carbon monoxide matrices at 20 K with plane-polarized light induces partial orientation of the sample.[280] Thus excitation in the $(^1A'_1 - {}^1E')$ band of the $[Fe(CO)_5]$, with consequent dissociation and recombination (72), results in movements of the molecules so that they are less

$$[Fe(CO)_5] \xrightarrow{\quad h\nu \quad} [Fe(CO)_4] + CO \xrightarrow{\qquad\qquad} [Fe(CO)_5] \qquad (72)$$
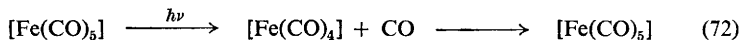
likely to absorb light of the particular polarization used. In another study, photochemical reactions of ^{13}CO-enriched $[Fe(CO)_4]$ in methane matrices have been initiated by i.r. radiation.[281] Excitation with a CO laser, tunable in the region 1900—2000 cm^{-1}, causes production of the methane complex [reaction (73)]. Interestingly, the laser radiation not only causes selective excitation of

[275] O. Traverso, R. Rossi, S. Sostero, and V. Carassiti, *Mol. Photochem.*, 1973, **5**, 457.
[276] E. Penigault, A. M. Braun, and J. Faure, *Compt. rend.*, 1976, **283**, *C*, 655.
[277] K. Kaeriyama, *J. Polymer Sci.*, *Polymer Chem.*, 1976, **14**, 1547.
[278] S. P. McManus, H. S. Bruner, H. D. Coble, and M. Ortiz, *J. Org. Chem.*, 1977, **42**, 1428.
[279] C. R. Bock and M. S. Wrighton, *Inorg. Chem.*, 1977, **16**, 1309.
[280] J. K. Burdett, J. M. Grzybowski, M. Poliakoff, and J. J. Turner, *J. Amer. Chem. Soc.*, 1976, **98**, 5728.
[281] A. McNeish, M. Poliakoff, K. P. Smith, and J. J. Turner, *J.C.S. Chem. Comm.*, 1976, 859.

$$[Fe(CO)_4] + CH_4 \xrightarrow{\ h\nu\ (i.\,r.)\ } [Fe(CO)_4(CH_4)] \tag{73}$$

molecules with differing degrees of isotopic substitution but also of molecules with an identical degree of substitution but differing stereochemistry. A recent publication on the photolysis of matrix-isolated $[Fe(CO)_2(NO)_2]$ at 20 K reports that photoexpulsion of CO to give the planar $[Fe(CO)(NO)_2]$ is the predominant process.[282] Photolysis of $[CpFe(CO)_2X]$ (X = Cl, Br, or I) in methyltetra-hydrofuran matrices at 77—80 K also causes CO dissociation.[251]

Whereas the photochemical synthesis of $[Fe_2(CO)_9]$ from $[Fe(CO)_5]$ is well established and may be conducted at room temperature, the analogous routes to $[Os_2(CO)_9]$ and $[Ru_2(CO)_9]$ require irradiation at low temperatures (233 K) in heptane solution.[283]

$[Fe(CO)_5]$ photocatalyses the reaction of trialkylsilanes with olefins under mild conditions.[284] It is proposed that the active catalytic species is $[(olefin)\text{-}Fe(H)(SiR_3)(CO)_3]$.

Photolysis of $[Fe(CO)_5]$, methyl acrylate, and 2,3-dimethylbutadiene yields compound (23).[285] In further experiments it could be shown that the reaction proceeds *via* the photoexcitation of either $[(\eta^2\text{-}CH_2{=}CHCO_2Me)Fe(CO)_4]$ or

(23)

(24) R = H or Me

(25)

(26)
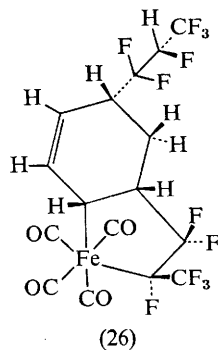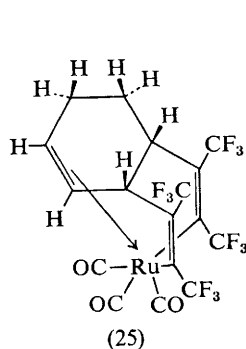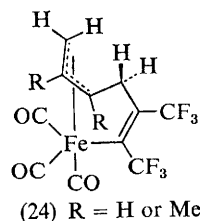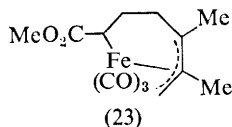
the $[(\eta^4\text{-diene})Fe(CO)_3]$ complex, leading to $[(\eta^2\text{-}CH_2{=}CHCO_2Me)(\eta^2\text{-diene})\text{-}Fe(CO)_3]$ as a common intermediate. 1 : 1 Adducts of type (24) are formed upon photolysis of various $[(1,3\text{-diene})Fe(CO)_3]$ complexes with hexafluorobut-2-yne, whereas the 1 : 2 derivative (25) is produced from $[(1,3\text{-cyclohexadiene})\text{-}$

[282] O. Crichton and A. J. Rest, *J.C.S. Dalton*, 1977, 656.
[283] J. R. Moss and W. A. G. Graham, *J.C.S. Dalton*, 1977, 95.
[284] M. A. Schroeder and M. S. Wrighton, *J. Organometallic Chem.*, 1977, **128**, 345.
[285] F. W. Grevels, U. Feldhoff, J. Leitich, and C. Krueger, *J. Organometallic Chem.*, 1976, **118**, 79.

Ru(CO)$_3$].[286] No clear distinction could be made between photoinduced CO expulsion and alternative photoformation of the [(η^2-diene)M(CO)$_3$] complexes as the initial step in these reactions. A related publication gives details of the structure determination of a photoproduct (26) formed from [(1,3-cyclo-hexadiene)Fe(CO)$_3$] and hexafluoropropene.[287]

Other authors have presented a full paper on the formation of (27) from dimethyldiacetylene and [Fe(CO)$_5$],[288] described the photoinduced reactions of

(27)
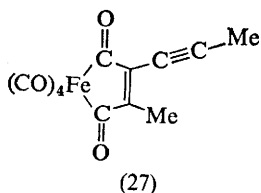
[Fe(CO)$_5$] with dicyclopropylacetylene,[289] and reviewed the [Fe(CO)$_5$]-catalysed formation of cyclic ketones.[290]

U.v. irradiation of [CpFe(CO)$_2$]$_2$ with hexafluorobut-2-yne gives a ferrocyclo-hexadienone complex (28), the first example of such a system to be structurally characterized.[248] By contrast [CpRu(CO)$_2$]$_2$ reacts with the same acetylene to give the mononuclear complexes (29) and (30).[248]

(28)   (29)   (30)
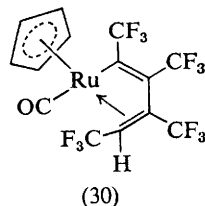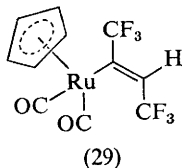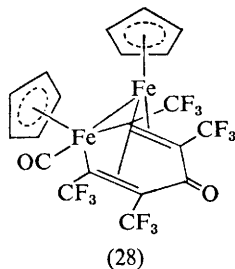
Photolysis of ether solutions of [CpFe(CO)$_2$(B$_{10}$H$_{13}$)], a compound where the borane fragment is bonded to the metal by an Fe—B single bond, yields the icosahedral metallocarborane [CpFe(η^5-B$_{10}$H$_{10}$COEt$_2$)], apparently by CO insertion into the boron cage.[291]

Substitution of [Fe(CO)$_5$] by triferrocenylphosphine only occurs if the mixture is irradiated under reflux.[292] Other novel substitution reactions of [Fe(CO)$_5$] are considered in Table 3 (see p. 237).

[286] M. Bottrill, R. Davies, R. Goddard, M. Green, R. P. Hughes, B. Lewis, and P. Woodward, *J.C.S. Dalton*, 1977, 1252.
[287] R. Goddard and P. Woodward, *J.C.S. Dalton*, 1977, 1181.
[288] F. R. Young, D. H. O'Brien, R. C. Pettersen, R. A. Levenson, and D. L. Von Minden, *J. Organometallic Chem.*, 1976, **114**, 157.
[289] R. Victor, V. Usieli, and S. Sarel, *J. Organometallic Chem.*, 1977, **129**, 387.
[290] E. Weissberger and P. Laszlo, *Accounts Chem. Res.*, 1976, **9**, 209.
[291] R. V. Schultz, F. Sato, and L. J. Todd, *J. Organometallic Chem.*, 1977, **125**, 115.
[292] G. P. Sollott, D. L. Daughdrill, and W. R. Peterson, *J. Organometallic Chem.*, 1977, **133**, 347.

Recent communications give further details on the photoproduction of (31) from (32),[293] describe the photoreaction of the cationic complex [{CpFe(CO)$_2$}$_2$-(H$_2$C=C=C=CH$_2$)]$^{2+}$,[294] and report on the lack of isotope effects in the photo-chemical formation of [(butadiene)Fe(CO)$_3$].[295]


(31)   (32)

A recent example of photochemical orthometallation is the solid-state reaction (74).[296]

$$[FeH_2(dppe)_2],C_6H_6 \xrightarrow{h\nu} [FeH_3(C_6H_4PPhCH_2CH_2PPh_2)(dppe)],C_6H_6 \quad (74)$$
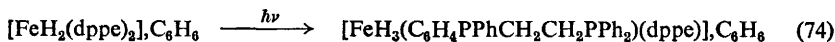
Photoisomerization of [Ru(CO)Cl$_2$(PMe$_2$Ph)$_2$Y] [equation (75); L = PMe$_2$Ph, Y = P(OMe)$_3$ or PPh(OMe)$_2$] is probably initiated by dissociation of either a

(33)   (34)
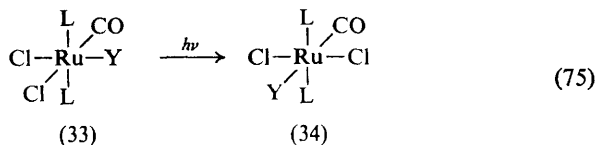
phosphine or carbon monoxide.[297] However, a quite different type of mechanism has been proposed for the isomerization of several analogous trimethylphosphine–iron derivatives such as (35).[298] In solution, this rearrangement is accelerated by excess carbon monoxide but retarded by iodine. These observations may be rationalized by the mechanism given in Scheme 3, which is supported by isolation

(37)
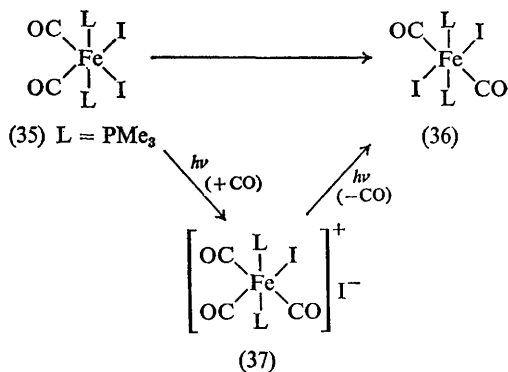
Scheme 3

[293] A. N. Nesmeyanov, N. E. Kolobova, I. B. Zlotina, B. V. Lokshin, I. F. Leshcheva, G. K. Znobina, and K. N. Anisimov, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1976, 1124.
[294] T. E. Bauch, H. Konowitz, and W. P. Giering, *J. Organometallic Chem.*, 1976, **114**, C15.
[295] R. Noyori and K. Yokoyama, *Bull. Chem. Soc. Japan*, 1976, **49**, 1723.
[296] T. Ikariya and A. Yamamoto, *J. Organometallic Chem.*, 1976, **118**, 65.
[297] C. F. J. Barnard, J. A. Daniels, J. Jeffrey, and R. J. Mawby, *J.C.S. Dalton*, 1976, 1861.
[298] M. Pankowski and M. Bigorgne, *J. Organometallic Chem.*, 1977, **125**, 231.

of (37) from the solid-state photolysis of (35). Photoisomerization of [RuClH-$(CO)_2(PPh_3)_2$] has also been described.[199]

Irradiation of [RuClH(CO)(PPh$_3$)$_3$] leads to CO release and formation of the active hydrogenation catalyst [RuClH(PPh$_3$)$_3$];[299] the usefulness of this method is restricted by the thermal reaction (76). This latter reaction is not reversed on

$$[RuClH(CO)(PPh_3)_3] + CO \longrightarrow [RuClH(CO)_2(PPh_3)_2] + PPh_3 \quad (76)$$
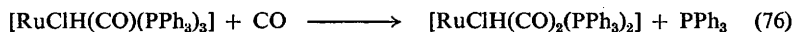
irradiation, isomerization of the dicarbonyl complex being the only process observed. Hydrogen is evolved upon excitation of the dihydride complex [RuH$_2$(CO)(PPh$_3$)$_3$].

Cobalt, Rhodium, and Iridium.—The only photochemical reaction observed on irradiation of [Co([14]aneN$_4$)(OH$_2$)Me]$^{2+}$ {[14]aneN$_4$ = formula (38)}
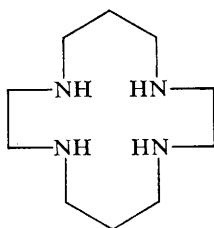
(38)

is homolytic cleavage of the Co—C(methyl) bond [reaction (77)].[300] The quantum yield for the reaction (0.30) is essentially independent of wavelength (250 $\leqslant \lambda \leqslant$ 540 nm), the threshold energy therefore being less than 18 000 cm^{-1}

$$[Co([14]ane\ N_4)(OH_2)Me]^{2+} \xrightarrow{h\nu} [Co([14]ane\ N_4)]^{2+} + Me\cdot + H_2O \quad (77)$$
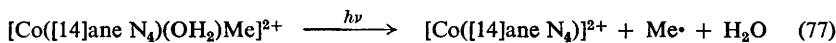
(217 kJ mol^{-1}). The reaction is induced upon irradiation into absorption bands much lower in energy than any associated with charge transfer. This behaviour is in marked contrast with the redox reactions of other Co^{III} complexes such as acidopenta-ammines, where redox decomposition is principally associated with LMCT bands and where the quantum yield is often wavelength dependent. The dependence of the homolysis energy (ΔH_B) on the covalency of the Co—C(methyl) bond has been attributed to the lower difference in ligand-field stabilization energy (ΔLFSE) compared with that of other Co—X complexes (see Scheme 4).[300, 301]

It has long been suspected that the initial step on photolysis of methyl-cobalamin (39; R^1 = Me) is also homolytic cleavage of the Co—C(methyl) bond (78), and this has now been verified by flash photolysis.[302] In the presence of oxygen, the Co^{II}-cobalamin (B$_{12r}$) so formed decays, following second-order kinetics, presumably due to process (80).
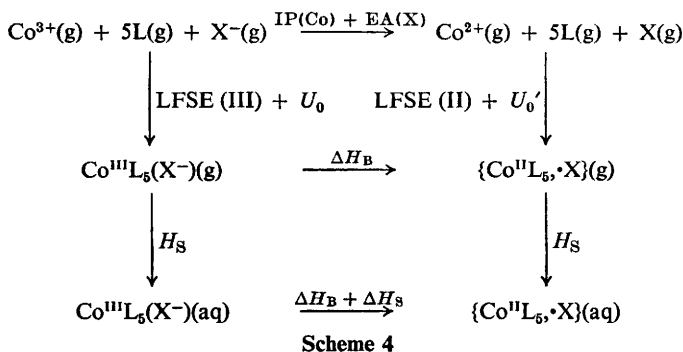
[299] G. L. Geoffroy and M. G. Bradley, *Inorg. Chem.*, 1977, **16**, 744.
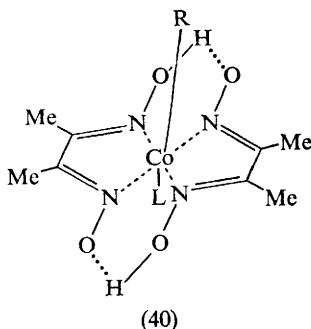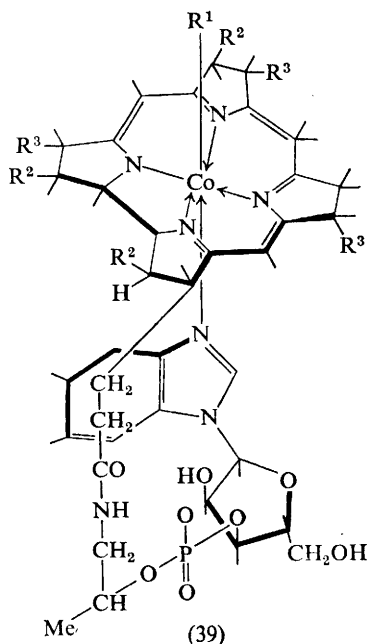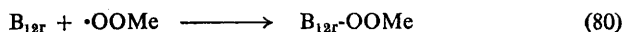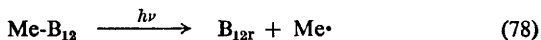[300] C. Y. Mok and J. F. Endicott, *J. Amer. Chem. Soc.*, 1977, **99**, 1276.
[301] J. F. Endicott, *Inorg. Chem.*, 1977, **16**, 494.
[302] J. F. Endicott and G. J. Ferraudi, *J. Amer. Chem. Soc.*, 1977, **99**, 243.

$$Co^{3+}(g) + 5L(g) + X^-(g) \xrightarrow{IP(Co) + EA(X)} Co^{2+}(g) + 5L(g) + X(g)$$

$$\downarrow LFSE\,(III) + U_0 \qquad LFSE\,(II) + U_0' \downarrow$$

$$Co^{III}L_5(X^-)(g) \xrightarrow{\Delta H_B} \{Co^{II}L_5, \cdot X\}(g)$$

$$\downarrow H_S \qquad\qquad\qquad\qquad H_S \downarrow$$

$$Co^{III}L_5(X^-)(aq) \xrightarrow{\Delta H_B + \Delta H_S} \{Co^{II}L_5, \cdot X\}(aq)$$

Scheme 4

A review of recent developments in B_{12} chemistry contains some discussion on photochemical reactions.[303] Other publications have considered the photo-decomposition reactions of phenacylcobalamin,[304] and of some sixteen analogues of coenzyme B_{12} (39) with the ligand R composed of various base and sugar moieties closely related to those of the natural 5'-deoxyadenosyl.[305]

$$Me\text{-}B_{12} \xrightarrow{h\nu} B_{12r} + Me\cdot \qquad (78)$$

$$Me + O_2 \longrightarrow MeOO\cdot \qquad (79)$$

$$B_{12r} + \cdot OOMe \longrightarrow B_{12r}\text{-}OOMe \qquad (80)$$

(39)

(40)

[303] G. N. Schrauzer, *Angew. Chem.*, 1976, **88**, 465; *Angew. Chem. Internat. Edn.*, 1976, **15**, 417.
[304] K. L. Brown, M. M. L. Chu, and L. L. Ingraham, *Biochemistry*, 1976, **15**, 1402.
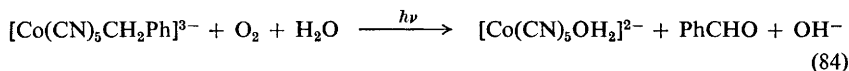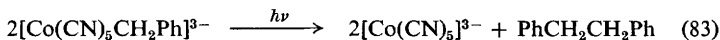[305] T. Toraya, K. Ushio, S. Fukui, and H. P. C. Hogenkamp, *J. Biol. Chem.*, 1977, **252**, 963.

It has been found that acidic solutions of alkylaquocobaloximes (40) [$R = Pr^n$, Pr^i, n-hexyl, or $Ph(CH_2)_3$; $L = H_2O$] are much more susceptible to photodecomposition than are neutral solutions.[306] Further, at pH = 7, the alkyl group is transformed into the corresponding 1-alkene, whereas in acidic solutions the products are those derived from free radicals. This pH dependence of the reactions has been attributed to protonation of a reactive LMCT state in acidic solution [reactions (81) and (82)]. The photoreactions of dihydroxy-

$$
\begin{bmatrix}
CH_2CH_2R^1 \\
| \\
Co(dmg)_2 \\
| \\
H_2O
\end{bmatrix}^*
\longrightarrow
\begin{matrix}
H \quad CH_2{=}CHR^1 \\
| \\
Co(dmg)_2 \\
| \\
H_2O
\end{matrix}
\tag{81}
$$

$$
\begin{bmatrix}
CH_2CH_2R^1 \\
| \\
Co(dmg)_2 \\
| \\
H_3O^+
\end{bmatrix}^*
\longrightarrow
\begin{matrix}
\cdot CH_2CH_2R^1 \\
| \\
{}^{II}Co(dmg)_2 \\
| \\
H_3O^+
\end{matrix}
\tag{82}
$$
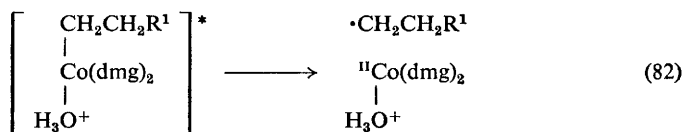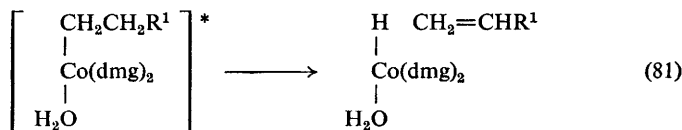
alkylcobaloximes have been studied as model systems for the diol dehydration reactions catalysed *in vivo* by coenzyme B_{12}.[307]

The homolysis of the Co—C bond in $[Co(CN)_5CH_2Ph]^{3-}$ after excitation to the LMCT state leads to overall reaction (83) in degassed solution ($\Phi_{313} = 0.13$), or to reaction (84) in aerated solution.[308] In the latter case, the intermediacy of a peroxy-complex $[Co(CN)_5O_2CH_2Ph]^{3-}$ is probable.

$$
2[Co(CN)_5CH_2Ph]^{3-} \xrightarrow{h\nu} 2[Co(CN)_5]^{3-} + PhCH_2CH_2Ph \tag{83}
$$

$$
[Co(CN)_5CH_2Ph]^{3-} + O_2 + H_2O \xrightarrow{h\nu} [Co(CN)_5OH_2]^{2-} + PhCHO + OH^- \tag{84}
$$

Controversy still surrounds the photoinsertion reactions of oxygen into the Co—C bonds of alkylcobaloximes (85). A comparison with the thermally induced insertion reaction has led Bied-Charreton and Gaudemer to propose

$$
[(dmg)_2CoLR] + O_2 \xrightarrow{h\nu} [(dmg)_2Co(L)(OOR)] \tag{85}
$$
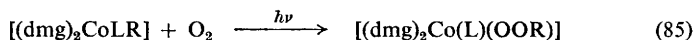
that the primary photoprocess is not rupture of the Co—C bond but rather a direct bimolecular reaction of oxygen with the activated cobaloxime.[309] In another study it has been shown that the quantum yield for decomposition of $[(dmg)_2Co(py)Me]$ and related complexes is greater in aerated than degassed solutions.[310] Oxygen insertion into the Co—C bonds of alkyl cobalt porphyrins has also been reported.[311]

[306] B. T. Golding, T. J. Kemp, P. J. Sellars, and E. Nocchi, *J.C.S. Dalton*, 1977, 1266.
[307] B. T. Golding, C. S. Sell, and P. J. Sellars, *J.C.S. Chem. Comm.*, 1976, 773.
[308] A. Vogler and R. Hirschmann, *Z. Naturforsch.*, 1976, **31b**, 1082.
[309] C. Bied-Charreton and A. Gaudemer, *J. Organometallic Chem.*, 1977, **124**, 299.
[310] G. Roewer, C. Kraetzschmar, and G. Kempe, *Z. Chem.*, 1976, **16**, 67.
[311] M. Perree-Fauvet, A. Gaudemer, P. Boucly, and J. Devynck, *J. Organometallic Chem.*, 1976, **120**, 439.

By studying the i.r. spectra of $[Co_2(CO)_8]$ before and after photolysis, it has been demonstrated that $[Co_2(CO)_8]$ exists in three isomeric forms in low-temperature argon and hexane matrices.[312] The only photoproduct observed is $[Co_2(CO)_7]$.[313] Upon irradiation into bands associated with a non-bridged isomer of $[Co_2(CO)_8]$, where cleavage of the Co—Co bond might be expected, no evidence could be obtained for $Co(CO)_4$ fragments. This may indicate that recombination is very efficient.

Carbon monoxide expulsion is the primary process upon photolysis of $[Co(CO)_3(NO)]$ in argon or methane matrices at 20 K.[314] Photosubstitution occurs in nitrogen matrices, yielding $[Co(CO)_2(NO)(N_2)]$ and probably $[Co(CO)(NO)(N_2)_2]$.

The limiting value of the quantum yield for photochemical insertion of $SnCl_2$ into the Co—Co bond of $[(Bu^n_3)PCo(CO)_3]_2$ is 1.0 for 365 nm radiation and *ca.* 6.0 for 546 nm radiation.[315] This surprising observation is attributed to the initiation of a chain reaction at 546 nm, with $[Co(CO)_3(PBu^n_3)]$ as the chain carrier, but a stoicheiometric reaction at 365 nm. This is the more remarkable as excitation at 365 nm is in a band assigned to a σ–σ^* transition of the Co—Co bond.

Substitution of CO in $[Cl_3SnCo(CO)_4]$ by PBu^n_3, PPh_3, or $AsPh_3$ is catalysed by light.[316] The initial step appears to be homolytic cleavage of the Co—Sn bond in $[Cl_3SnCo(CO)_4]$ or its base complex.

The co-ordinatively unsaturated species $[CpCo(CO)]$ has been identified upon low-temperature (195 K) photolysis of $[CpCo(CO)_2]$.[317] This species may then dimerize to form $[Cp_2Co_2(CO)_2]$ or react with the starting material to give $[Cp_2Co_2(CO)_3]$. In the presence of substituted acetylenes at 195 K, irradiation of $[CpCo(CO)_2]$ yields $[CpCo(CO)(RC\equiv CR)]$ (R = Ph or Me).[318] On warming the mixture with diphenylacetylene, $[Cp_2Co_2(CO)(PhC\equiv CPh)]$, $[Cp_3Co_3(CO)(PhC\equiv CPh)]$, and (41) are formed.

(41)
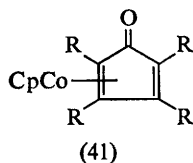
Molecular hydrogen is released when $[IrClH_2(PPh_3)_3]$ and *mer-* or *fac-* $[IrH_3(PPh)_3]$ are irradiated with u.v. or visible light [*e.g.* reaction (86)].[319] The elimination of hydrogen proceeds in a concerted fashion. Thus when a mixture of $[IrClH_2(PPh_3)_3]$ and $[IrClD_2(PPh_3)_3]$ was photolysed, no HD was produced.

$$[IrClH_2(PPh_3)_3] \xrightarrow{h\nu} [IrCl(PPh_3)_3] + H_2 \qquad (86)$$

[312] R. L. Sweany and T. L. Brown, *Inorg. Chem.*, 1977, **16**, 415.
[313] R. L. Sweany and T. L. Brown, *Inorg. Chem.*, 1977, **16**, 421.
[314] O. Crichton and A. J. Rest, *J.C.S. Dalton*, 1977, 536.
[315] P. F. Barrett, A. Fox, and R. E. March, *Canad. J. Chem.*, 1977, **55**, 2279.
[316] M. Absi-Halabi and T. L. Brown, *J. Amer. Chem. Soc.*, 1977, **99**, 2982.
[317] W.-S. Lee and H. H. Brintzinger, *J. Organometallic Chem.*, 1977, **127**, 87.
[318] W.-S. Lee and H. H. Brintzinger, *J. Organometallic Chem.*, 1977, **127**, 93.
[319] G. L. Geoffroy and R. Pierantozzi, *J. Amer. Chem. Soc.*, 1976, **98**, 8054.

Photochemistry

On the basis of simple MO theory (Figure 3), it appears that population of a $\sigma_{x^2-y^2}$ orbital is responsible for the labilization of hydrogen.

Strohmeier and co-workers have shown that the activity of $[IrCl(CO)(PPh_3)_2]$ and related complexes as catalysts for homogeneous hydrogenation is enhanced by u.v. radiation.[225, 320-324] The effectiveness of different catalysts of type $[IrCl(CO)(PR_3)_2]$ (R = Ph, Pr^i, OPh, or cyclohexyl) for the photoactivated hydrogenation of various activated olefins has been studied.[320-322] The activity
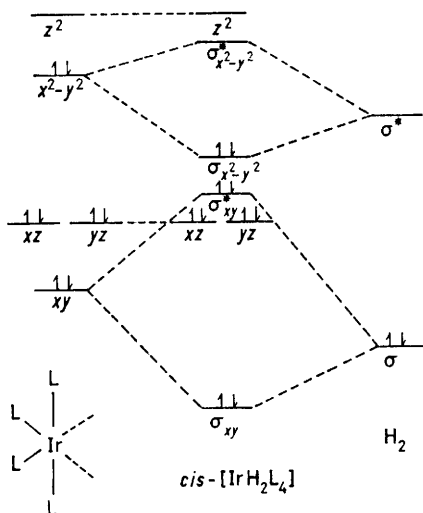
Figure 3 *Molecular orbital energy level diagram for six-co-ordinate dihydride complexes of iridium*
(Reproduced by permission from *J. Amer. Chem. Soc.*, 1976, **98**, 8054)

is dependent on the nature of both the substrate and the phosphine ligand. With ethyl acrylate, for example, the most active catalyst is $[IrCl(CO)(PPr^i_3)_2]$.[321] With certain substrates, *e.g.* cyclohexa-1,3-diene, the hydrogenation is truly photocatalytic, the reaction proceeding at the same rate after the light source is switched off, and a study of the dependence of the reaction rate on the light intensity has been carried out.[323] With $[IrCl(CO)(PPh_3)_2]$ in the absence of solvent this photocatalytic hydrogenation is exceptionally efficient, possessing a turn-over number of about 100 000.[324]

Photolysis of $[RhCl(CO)(PPh_3)_2]$ in aerated solution leads to oxidation of its ligands to carbon dioxide and triphenylphosphine oxide.[325] The reaction is inhibited by excess phosphine present in solution, supporting the assignment of phosphine dissociation (87) as the primary process.

[320] W. Strohmeier and L. Weigelt, *J. Organometallic Chem.*, 1977, **129**, C47.
[321] W. Strohmeier and L. Weigelt, *J. Organometallic Chem.*, 1977, **125**, C40.
[322] W. Strohmeier and L. Weigelt, *J. Organometallic Chem.*, 1977, **133**, C43.
[323] W. Strohmeier, H. Steigerwald, and L. Weigelt, *J. Organometallic Chem.*, 1977, **129**, 243.
[324] W. Strohmeier and H. Steigerwald, *J. Organometallic Chem.*, 1977, **125**, C37.
[325] G. L. Geoffroy, D. A. Denton, M. E. Keeney, and R. R. Bucks, *Inorg. Chem.*, 1976, **15**, 2382.

$$[RhCl(CO)(PPh_3)_2] \xrightarrow{h\nu} [RhCl(CO)(PPh_3)] + PPh_3 \qquad (87)$$

Nickel.—A full paper on the matrix photolysis of CpNi(NO) has been published.[326] In carbon monoxide matrices, short periods of irradiation lead to substitution of NO, yielding [CpNi(CO)] and [CpNi(CO)$_2$], whereas Ni(CO)$_4$ is formed on longer exposure. In non-reactive matrices (argon, methane, or nitrogen), photolysis produces an isomeric species, possibly [CpNi]$^+$NO$^-$ or more probably one of the type [CpNi(NO*)], in which the nitrosyl group behaves as a one- or two-electron ligand.

The Ni^0 complex [Ni(NO)Cl(dppe)], upon irradiation, reacts with oxygen to form the Ni^{II} species [Ni(NO$_2$)Cl(dppe)].[327] The initial step appears to be an attack of oxygen on an (MLCT ?) excited state of the starting material to give a peroxynitrate complex [Ni(NO$_3$)Cl(dppe)]. This latter species reacts with [Ni(NO)Cl(dppe)] to yield (42), which has been characterized by e.s.r., and which decomposes to the final product.

$$(dppe)ClNi-N \underset{O-O}{\overset{O \quad O}{\diagup\diagdown}} N-NiCl(dppe)$$

(42)
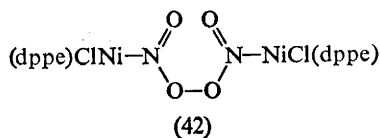
Copper.—In the presence of copper(I) chloride, norbornadiene effectively isomerizes to quadricyclene ($\Phi_{313} = 0.3$—0.4 in CHCl$_3$).[328] The photoactive species is a 1 : 1 norbornadiene–CuCl complex. It is also noteworthy that no dimeric species are formed in this case, in contrast with what is found with other organometallic catalysts such as [Cr(CO)$_6$]. If analogous systems can be developed in which visible light is active in inducing isomerization, these might have potential for solar energy storage.

$$\xrightarrow[CuCl]{h\nu} \qquad (88)$$

Photolysis of 7-methylenenorcarane (43) in the presence of Cu^I salts leads to both fragmentation (giving cyclohexene and acetylene) and to rearrangement [the main products being (44) and (45)].[329] The most probable mechanism is one in which photoexcitation causes rearrangement of a Cu^I–olefin π-complex to σ-complexes of types (46) and (47): complex (46) then fragments to give acetylene and cyclohexene, whereas (47) forms (44), (45), and other minor products.

The photodecomposition of the copper cluster compound [Cu(CH$_2$SiMe$_3$)]$_4$ has been described.[330]

[326] O. Crichton and A. J. Rest, *J.C.S. Dalton*, 1977, 986.
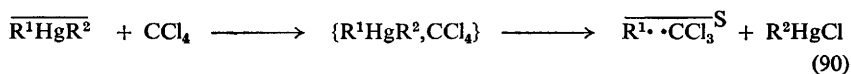[327] R. Ugo, S. Bhaduri, B. F. G. Johnson, A. Khair, A. Pickard, and Y. Benn-Taarit, *J.C.S. Chem. Comm.*, 1976, 694.
[328] D. P. Schwendiman and C. Kutal, *Inorg. Chem.*, 1977, **16**, 719.
[329] R. G. Salomon and M. F. Salomon, *J. Amer. Chem. Soc.*, 1976, **98**, 7454.
[330] J. A. J. Jarvis, R. Pearce, and M. F. Lappert, *J.C.S. Dalton*, 1977, 999.

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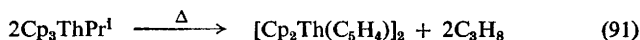(43)   (44)   (45)

(46)   (47)
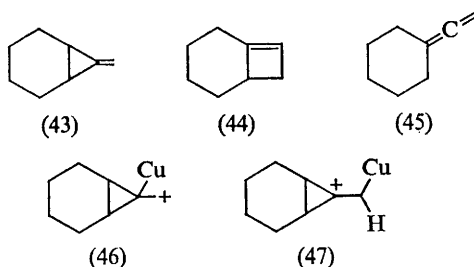
Mercury.—The results of CIDNP investigations on the photodecomposition of dialkylmercury (R^1HgR^2) compounds have been communicated.[331, 332] In deuteriated benzene or toluene, decomposition to give R^1R^2, R^1H, R^2H, or olefins proceeds through a triplet precursor, either directly [equation (89)] or perhaps by initial formation of a radical pair ($R^1Hg\cdot,R^2\cdot$) followed by rapid decomposition of the RHg· species. In chlorinated solvents, reaction involves both triplet (89) and singlet processes [*e.g.* reaction (90)].[331]

$$R^1HgR^2 \xrightarrow{h\nu} \overline{R^1\cdot\cdot R^2}^T + Hg \qquad (89)$$

$$\overline{R^1HgR^2} + CCl_4 \longrightarrow \{R^1HgR^2,CCl_4\} \longrightarrow \overline{R^1\cdot\cdot CCl_3}^S + R^2HgCl \qquad (90)$$

Other papers dealing with reactions of related mercury derivatives describe the photodecomposition of $Bu^tCH_2HgBu^i$,[333] of $(SiMe_2Ph)_2Hg$,[334] and of $[(Bu^tCH_2)_3Sn]_2Hg$,[335] and the polymerization of styrene induced by $SiMe_3$ radicals formed on photodissociation of $(SiMe_3)_2Hg$.[336]

Thorium.—On photolysis Cp_3ThPr^i forms Cp_3Th and [approximately equal quantities of propane and propene.[337] This behaviour contrasts with thermal decomposition, where intramolecular hydrogen abstraction occurs [reaction (91)]. Evidence has been presented to show that the photochemical reaction does not proceed by homolytic cleavage of the Th—C bond, but rather by β-elimination of the olefin [reaction (92)].

$$2Cp_3ThPr^i \xrightarrow{\Delta} [Cp_2Th(C_5H_4)]_2 + 2C_3H_8 \qquad (91)$$

$$Cp_3Th-CHMe_2 \xrightarrow{h\nu} Cp_3ThH + H_2C=CHMe \qquad (92)$$

[331] F. J. J. de Kanter, *Org. Magn. Resonance*, 1976, **8**, 129.
[332] R. Benn, *Chem. Phys.*, 1976, **15**, 369.
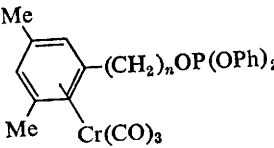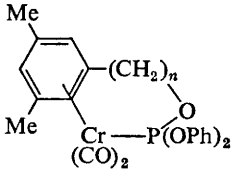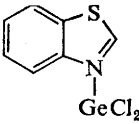[333] W. A. Nugent and J. K. Kochi, *J. Organometallic Chem.*, 1977, **124**, 327.
[334] E. N. Gladyshev, L. O. Yuntila, G. A. Razuvaev, N. S. Vyazankin, and V. S. Sokolov, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1976, 204.
[335] O. A. Kruglaya, B. V. Fedot'ev, I. B. Fedot'eva, and N. S. Vyazankin, *Zhur. obshchei Khim.*, 1976, **46**, 1517.
[336] H. Ikeda, Y. Miura, and M. Kinoshita, *Makromol. Chem.*, 1976, **177**, 2647.
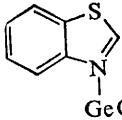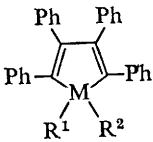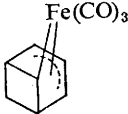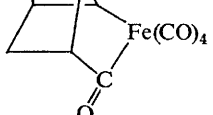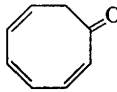[337] D. G. Kauna, T. J. Marks, and W. A. Wachter, *J. Amer. Chem. Soc.*, 1977, **99**, 3877.

Table 3 *Photochemical substitution reactions of metal carbonyl compounds*

Substrate	Reactant L	Products	Ref.
$[V(CO)_6]^-$	$Ph_2P(CH_2)_nPPh_2$ $n = 2, 3,$ or 4	cis-$[V(CO)_4L]^-$	338
	$[Ph_2P(CH_2)_2PPhCH_2]_2$	$[V(CO)_3L]^-$ and polymeric $[\{V(CO)_4\}_2L]^{2-}$	338
$[CpV(CO)_4]$	$Ph_2P(CH_2)_nPPh_2$ $n = 1, 2,$ or 4	cis-$[CpV(CO)_2L]$	338
$[V(CO)_4Y]^-$ $Y = (CO)_2$ or dppe	C_3H_4RX $R = H, Me,$ or $Ph,$ $X = Cl$ or Br	$[(\eta^3$-$C_3H_4R)V(CO)_3Y]$	339, 340
$[CpV(CO)_4]$	$MeN(PF_2)_2$	$CpVL_2$	341
$[M(CO)_6]$ $M = Cr, Mo,$ or W	$MeN(PF_2)_2$	ML_3	342
	$Me_2S(O)=CH_2$	$[M(CO)_4L_2]$	343
$[Cr(CO)_6]$	$[Co(NO)_2X]_2$ $X = Cl, Br,$ or I	$[Cr(NO)X_2(THF)_n]$	344
$[M(CO)_5X]^-$ $M = W$ or $Mo,$ $X = Cl$ or Br	PR_3	$[M(CO)_4XL]^-$	345
$[(C_6H_6)Cr(CO)_2(CS)]$	PPh_3	$[(C_6H_6)Cr(CO)(CS)L]$	346
$[CpMo(CO)_3]_2$	$MeSSMe +$ $F_3CC{\equiv}CCF_3$	$[CpMo(CO)_3C(CF_3)=$ $C(CF_3)SMe]$	347
$[CpMo(CO)_3]_2$	NO	$[CpMo(CO)_2L]$	348
$[CpM(CO)_3Cl]$ $M = Mo$ or W	$MeN(PF_2)_2$	$[CpML_2Cl]$	349

350

| $[(C_6R^1_3R^2_3)Cr(CO)_3]$ $R^1 = R^2 = H,$ $R^1 = R^2 = Me,$ or $R^1 = H, R^2 = Me$ | | $[(C_6R^1_3R^2_3)Cr(CO)_2L]$ | 351 |

[338] D. Rehder, L. Dahlenburg, and I. Müller, *J. Organometallic Chem.*, 1976, **122**, 53.
[339] M. Schneider and E. Weiss, *J. Organometallic Chem.*, 1976, **121**, 345.
[340] U. Franke and E. Weiss, *J. Organometallic Chem.*, 1976, **121**, 355.
[341] R. B. King and K.-N. Chen, *Inorg. Chim. Acta*, 1977, **23**, L19.
[342] R. B. King and J. Gimeno, *J.C.S. Chem. Comm.*, 1977, 142.
[343] L. Weber, *Z. Naturforsch.*, 1976, **31b**, 780.
[344] J. Schmidt and D. Rehder, *Chem. Letters*, 1976, **9**, 933.
[345] W. A. Schenk, *J. Organometallic Chem.*, 1976, **117**, C97.
[346] I. S. Butler, N. J. Coville, and D. Cozak, *J. Organometallic Chem.*, 1977, **133**, 59.
[347] F. Y. Petillon and D. W. A. Sharp, *J. Fluorine Chem.*, 1976, **8**, 323.
[348] A. M. Rosan and J. W. Faller, *Synth. React. Inorg. Metal-org. Chem.*, 1976, **6**, 357.
[349] R. B. King, M. G. Newton, J. Gimeno, and M. Chang, *Inorg. Chim. Acta*, 1977, **23**, L35.
[350] A. N. Nesmeyanov, V. V. Krivykh, P. V. Petrovskii, and M. I. Rybinskaya, *Doklady Akad. Nauk S.S.S.R.*, 1976, **231**, 110.
[351] P. Jutzi and W. Steiner, *Chem. Ber.*, 1976, **109**, 3473.

Table 3   *(cont.)*

Substrate	Reactant L	Products	Ref.
[CpMn(CO)$_3$]		[CpMn(CO)$_2$L]	351
[CpMn(CO)$_3$]	RNC R = Ph, C$_6$H$_4$Cl, C$_6$Cl$_5$, or Me	[CpMnL$_3$]	352
[Mn$_2$(CO)$_{10}$]	N(SCF$_3$)$_3$	[Mn(CO)$_4$(SCF$_3$)]$_2$	353
	[Se(CF$_3$)]$_2$	[Mn(CO)$_4$(SeCF$_3$)]$_2$	353
[CpRe(CO)$_2$(CS)]	PPh$_3$	[CpRe(CO)(CS)L]	346
[Fe(CO)$_5$]	 M = Si or Ge, R^1, R^2 = Me, CH$_2$Ph, CH$_2$Cl, or Cl	[Fe(CO)$_3$L]	354
	N(SCF$_3$)$_3$	[Fe(CO)$_3$(SCF$_3$)]$_2$	352
	[SeCF$_3$]$_2$	[Fe(CO)$_3$(SeCF$_3$)]$_2$	352
		[Fe(CO)$_4$]L and 	355
	 X = or (CH$_2$)$_2$		356
		[Fe(CO)$_3$L]	357
	MeN(PF$_2$)$_2$	[Fe$_2$(CO)$_5$L$_2$]	358

[352] P. M. Treichel and H. J. Mueh, *Inorg. Chim. Acta*, 1977, **22**, 265.
[353] M. K. Chaudhuri, A. Haas, and A. Wensky, *J. Organometallic Chem.*, 1976, **116**, 323.
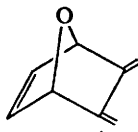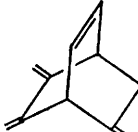[354] P. Jutzi and A. Karl, *J. Organometallic Chem.*, 1977, **128**, 57.
[355] R. Aumann, H. Woermann, and C. Krueger, *Angew. Chem.*, 1976, **88**, 640; *Angew. Chem. Internat. Edn.*, 1976, **15**, 609.
[356] R. Aumann and H. Averbeck, *Angew. Chem.*, 1976, **88**, 641; *Angew. Chem. Internat. Edn.*, 1976, **15**, 610.
[357] M. S. Brookhart, G. W. Koszalka, G. O. Nelson, G. Scholes, and R. A. Watson, *J. Amer. Chem. Soc.*, 1976, **98**, 8155.
[358] M. G. Newton, R. B. King, M. Chang, and J. Gimeno, *J. Amer. Chem. Soc.*, 1977, **99**, 2802.

Table 3   (*cont.*)

Substrate	Reactant L	Products	Ref.
	(epoxynorbornene structure)	[Fe(CO)$_4$L] and [Fe(CO)$_3$L]	359
[Fe(CO)$_5$]	(diene-bicyclic structure)	[Fe(CO)$_3$L]	360
[Fe$_3$(CO)$_{12}$]	SbPh$_3$	[Fe(CO)$_4$L], [Fe(CO)$_3$L$_2$], and Ph(L)(CO)$_3$FeSb(Ph)$_2$ | Fe(CO)$_4$	361
[Os$_3$(CO)$_{12}$]	Cyclohexa-1,3-diene	[Os(CO)$_3$L]	362

3 Main-group Elements

Reports on the photochemistry of anions in solution are dealt with in the next section: those on other compounds are considered under the particular element concerned.

Anions.—It is well established that the photolysis of inorganic anions, such as iodide, causes ionization [reaction (93)]. However, it has previously been

$$I^- \xrightarrow{\ h\nu\ } I\cdot + e_{aq}^- \tag{93}$$

observed in scavenging experiments that the decay profile of the solvated electrons so produced differs markedly from that of those formed upon radiolysis of water. Recently the reactions of the solvated electron have been monitored in the sub-microsecond region following 265 nm laser photolysis of iodide, [Fe(CN)$_6$]$^-$, tryptophan, or tyrosine.[363] Either recombination of the electron with its radical co-product or bimolecular reactions of the electron with a scavenger may account for its decay. The experimentally determined decay profiles have been shown to correlate well with those determined theoretically, although the recombination lifetime (*ca.* 10^{-6} s) is about 10^4 times longer than that predicted by the Noyes theory. This behaviour is apparently caused both by the large initial displacement ($\sim$ 1 nm) of the electron from its radical co-product after photodissociation and by the energy barrier created by the hydration of the electron. The effect of temperature on the CTTS transition of iodide ion in supercooled water or glass-forming aqueous solutions[364] and correlation of ν_{max} for the CTTS transition in

[359] T. Boschi, P. Vogel, and R. Roulet, *J. Organometallic Chem.*, 1977, **133**, C36.
[360] T. Boschi, P. Narbel, P. Vogel, and R. Roulet, *J. Organometallic Chem.*, 1977, **133**, C39.
[361] D. J. Cane, E. J. Forbes, and T. A. Hamor, *J. Organometallic Chem.*, 1976, **117**, C101.
[362] E. G. Bryan, A. L. Burrows, B. F. G. Johnson, J. Lewis, and G. M. Schiavon, *J. Organometallic Chem.*, 1977, **129**, C19.
[363] L. I. Grossweiner and J. F. Baugher, *J. Phys. Chem.*, 1977, **81**, 93.
[364] A. Barkatt and C. A. Angell, *J. Phys. Chem.*, 1977, **81**, 114.

chloride, bromide, and iodide ions with that of the solvated electron in some 43 solvents, including acetone, ethers, and alcohols,[365] have been reported.

Bromide and iodide ions enhance the photoisomerization yields for protonated *trans*-4'-methoxy-3-styrylpyridine and diprotonated *trans*-1,2-bis-(3-pyridyl)-ethylene, while quenching their fluorescence.[366] The effect is attributed to complex formation with consequent heavy-atom induction of ISC to the reactive triplet states of the olefin derivatives. Examples of iodide quenching of fluorescence of aliphatic ketones,[367] of pyrene in aqueous micelles,[368] and of flavins in aqueous solution [369] have been described. The decay of the triplet state of triphenylene in ethanol solutions at 77 K is accelerated by potassium iodide, the effect on the radiative transition being greater than that on the radiationless deactivation.[370]

Photo-oxidation of cyanide to cyanate at titanium dioxide surfaces has been observed.[371] The redox reaction appears to involve oxidation of cyanide ions by valence-band holes of the semiconductor [reaction (94)].

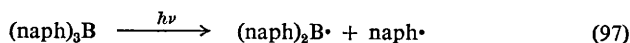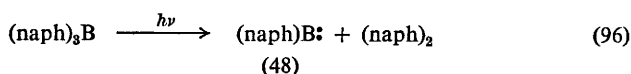$$CN^- + 2OH^- + 2p^+ \longrightarrow CNO^- + H_2O \qquad (94)$$
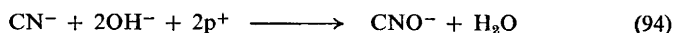
Oxidation of carbonate ions by the triplet state of duroquinone in micellar solutions has been monitored by laser photolysis.[372] It has been demonstrated that singlet oxygen is involved in the photo-oxidation of iodide ion by various anthracene sulphonate derivatives.[373, 374] Hydrogen abstraction from the hydrocarbon by an excited state of the ion appears to be responsible for the photo-reduction of nitrite ions in the presence of alkanes.[375]

The luminescence of nitrite [376, 377] and of selenite [378] ions has been studied in aqueous glassy media at temperatures from 4.2 to 200 K.

Barium.—Flash photolysis of the barium salt of triphenylethylene causes electron ejection, allowing the study of the kinetics of the equilibrium shown in reaction (95).[379]

$$TPE + Ba^{2+} TPE^{2-} \underset{\longleftarrow}{\overset{\longrightarrow}{\rule{2cm}{0pt}}} Ba^{2+} TPE^{\cdot-} + TPE^{\cdot-} \qquad (95)$$

Boron.—Photodecomposition of tri-1-naphthylboron in non-polar solvents appears to proceed *via* two quite distinct pathways [reactions (96) and (97)].[380]

$$(naph)_3B \xrightarrow{h\nu} (naph)B\colon + (naph)_2 \qquad (96)$$
$$(48)$$

$$(naph)_3B \xrightarrow{h\nu} (naph)_2B\cdot + naph\cdot \qquad (97)$$

[365] M. F. Fox and E. Hayon, *J.C.S. Faraday I*, 1976, **72**, 1990.
[366] G. Bartocci, U. Mazzucato, and P. Bortolus, *J. Photochem.*, 1977, **6**, 309.
[367] I. V. Sokolova amd L. V. Orlovskaya, *Zhur. priklad. Spektroskopii*, 1977, **26**, 167.
[368] M. A. J. Rogers and M. E. Da Silva e Wheeler, *Chem. Phys. Letters*, 1976, **43**, 587.
[369] S. Bergstrom and B. Holmstrom, *Chem. Scripta*, 1976, **9**, 193.
[370] J. Najbar and A. Chodkowska, *J. Luminescence*, 1976, **11**, 215.
[371] S. N. Frank and A. J. Bard, *J. Amer. Chem. Soc.*, 1977, **99**, 303.
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[374] K. K. Rohatgi-Mukherjee and A. K. Gupta, *Chem. Phys. Letters*, 1977, **46**, 368.
[375] G. L. Petriconi and H. M. Papee, *Water, Air, Soil Pollution*, 1976, **5**, 403.
[376] M. U. Belyi, Y. T. Kononenko, and I. Y. Kushnirenko, *Ukrain. fiz. Zhur.*, 1977, **22**, 306.
[377] Y. T. Kononenko and I. Y. Kushnirenko, *Ukrain. fiz. Zhur.*, 1976, **21**, 1599.
[378] I. Y. Kushnirenko and S. G. Nedel'ko, *Zhur. priklad. Spektroskopii*, 1976, **25**, 812.
[379] B. De Groof, G. Levin, and M. Szwarc, *J. Amer. Chem. Soc.*, 1977, **99**, 474.
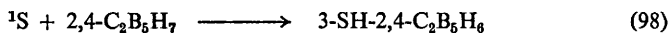[380] B. G. Ramsey and D. M. Anjo, *J. Amer. Chem. Soc.*, 1977, **99**, 3182.

The boryne species (48) has been trapped by cyclohexene, giving (49). In protic solvents irradiation of tribenzylboron, or its ammonia complex, induces heterolytic cleavage of a B—C bond.[381] The resulting benzyl anion protonates to give the major product, toluene.

(49)
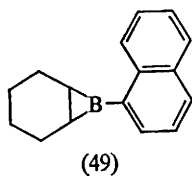
Mercury-photosensitized reactions of *N*-mono-, -di-, or -tri-methylborazine in the presence of hydrogen give exclusively C—C-bonded diborazinyl derivatives. The products arise by coupling of radicals formed upon hydrogen atom abstraction from the methyl group of the borazine derivatives.[382]

Photodecomposition of carbonyl sulphide in *closo*-carbaboranes provides a convenient synthetic route to boron-substituted mercaptocarbaboranes.[383] The reaction involves initial generation of sulphur atoms in their ^1D excited state and subsequent insertion into a B—H bond [*e.g.* reaction (98)]. On further irradiation these mercaptans may dehydrodimerize to form boron-bridged disulphides [reaction (99)].

$$^1S + 2,4\text{-}C_2B_5H_7 \longrightarrow 3\text{-}SH\text{-}2,4\text{-}C_2B_5H_6 \tag{98}$$

$$2C_2B_5H_6SH \xrightarrow{h\nu} (C_2B_5H_6S)_2 + H_2 \tag{99}$$

The study of specific reactions induced by i.r. radiation from carbon dioxide lasers continues to be a rapidly developing area, and is the subject of a recent review article.[384] Excitation of diborane by CO_2 laser radiation in a vibrational mode associated with a rocking vibration of a terminal BH_2 group causes reactions quite different from those observed on thermolysis. Thus, in the presence of hydrogen sulphide, $HB(SH)_2$ and HSB_2H_5 are formed,[385] and with isobutylene alkylated diboranes are the products.[386] Upon similar i.r. excitation, boron trichloride sensitizes the 'trimerization' of tetrachloroethylene to hexachlorobenzene in *ca.* 88% yield.[387] The CO_2-laser-induced disproportionation of boron trichloride and trimethylboron [388] and the laser-augmented decomposition (100) [389] have been examined in greater detail.

$$2H_3B\text{-}PF_3 \xrightarrow{h\nu \text{ (i.r.)}} B_2H_6 + 2PF_3 \tag{100}$$
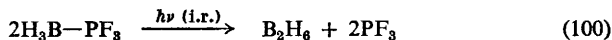
[381] Vo Van Chung, K. Inagaki, M. Tokuda, and M. Itoh, *Chem. Letters*, 1976, 209.
[382] G. A. Kline and R. F. Porter, *Inorg. Chem.*, 1977, **16**, 11.
[383] J. S. Plotkin and L. G. Sneddon, *J. Amer. Chem. Soc.*, 1977, **99**, 3011.
[384] R. V. Ambartzumian and V. S. Letokhov, *Accounts Chem. Res.*, 1977, **10**, 61.
[385] H. R. Bachmann, F. Bachmann, K. L. Kompa, H. Nöth, and R. Rinck, *Chem. Ber.*, 1976, **109**, 3331.
[386] Y. A. Adamova, A. A. Bukharov, A. V. Pankratov, and A. N. Skachkov, *Zhur. neorg. Khim.*, 1976, **21**, 938.
[387] H. R. Bachmann, R. Rinck, N. Nöth, and K. L. Kompa, *Chem. Phys. Letters*, 1977, **45**, 169.
[388] F. Bachmann, H. Nöth, R. Rinck, W. Fuss, and K. L. Kompa, *Ber. Bungengesellschaft phys. Chem.*, 1977, **81**, 313.
[389] K. R. Chien and S. H. Bauer, *J. Phys. Chem.*, 1976, **80**, 1405.

Silicon.—The organic photochemistry of silicon derivatives is considered in Part III, Chapter 6.

Previous studies have provided much indirect evidence for the participation of compounds containing silicon–carbon double bonds as reactive intermediates. By use of matrix-isolation techniques, two groups of workers have now spectroscopically characterized such a species.[390, 391] Photolysis of trimethylsilyldiazomethane (50) in argon matrices produced a photostationary mixture containing trimethylsilyldiazirine (51) (Scheme 5). On extended irradiation
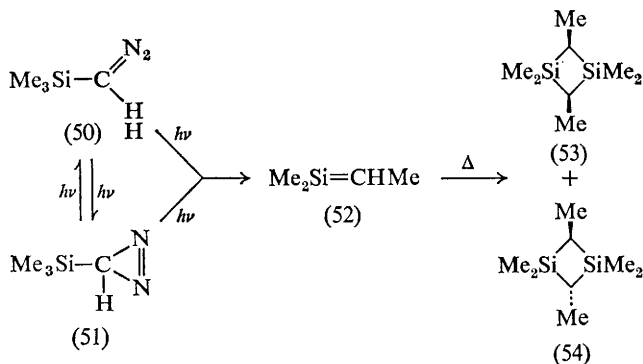
Scheme 5

($\lambda > 300$ nm), the silaethylene (52) was produced. On warming to room temperature, this unsaturated species dimerized, giving (53) and (54). Longer-wavelength irradiation ($\lambda > 360$ nm) of the diazirine–diazomethane mixture yielded the carbene $Me_3Si\dot{C}H$, which could be characterized by e.s.r. as a linear ground-state triplet. At the low temperatures used in these experiments this carbene species did not appear to isomerize thermally to the silaethylene (52), although such a rearrangement probably takes place at room temperature.[392]

Photolysis of the silacyclopropene (55) in the presence of $[PdCl_2(PEt_3)_2]$ gives (56).[393]

(55)   (56)
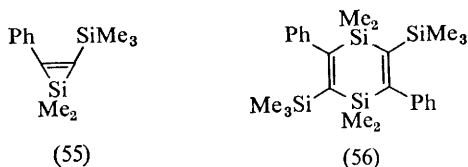
Germanium and Tin.—A full report on the synthesis of stable germanium- and tin-centred radicals of type $\cdot M[CH(SiMe_3)_2]_3$, $\cdot M[N(SiMe_3)_2]_3$, and $\cdot M[N(SiMe_3)Bu^t]_3$ (M = Ge or Sn), formed by photolysis of the bivalent

[390] O. L. Chapman, C. C. Chang, J. Kolc, M. E. Jung, J. A. Lowe, T. J. Barton, and M. L. Tumey, *J. Amer. Chem. Soc.*, 1976, **98**, 7844.
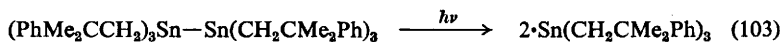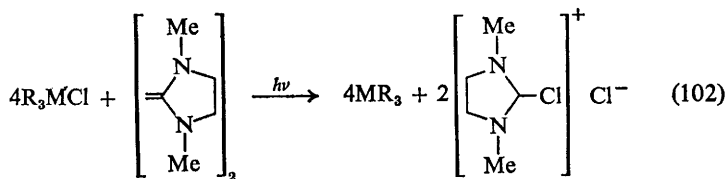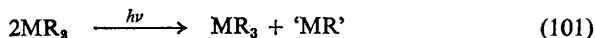
[391] M. R. Chedekel, M. Skoglund, R. L. Kreeger, and H. Shechter, *J. Amer. Chem. Soc.*, 1976, **98**, 7846.

[392] W. Ando, A. Sekiguchi, and T. Migita, *Chem. Letters*, 1976, 779.

[393] M. Ishikawa, T. Fuchikami, and M. Kumada, *J.C.S. Chem. Comm.*, 1977, 352.

alkyls or amides [reaction (101)], has been published.[394] An alternative route to the tervalent alkyl complexes $M[CH(SiMe_3)_2]_3$ is shown in equation (102).[395]

The metal-centred radical $\cdot Sn(CH_2CMe_2Ph)_3$, which is sufficiently stable to be observed by e.s.r. in solution at room temperature, has been prepared *inter alia* by reaction (103).[396]

$$2MR_2 \xrightarrow{h\nu} MR_3 + \text{'MR'} \qquad (101)$$

$$(PhMe_2CCH_2)_3Sn-Sn(CH_2CMe_2Ph)_3 \xrightarrow{h\nu} 2\cdot Sn(CH_2CMe_2Ph)_3 \quad (103)$$

Production of $\cdot SnBu^n_3$ by photochemical cleavage of the Sn—Sn bond in $(Bu^n_3Sn)_2$ has allowed the determination of the rate of reaction of this tin-centred radical with dialkyl-selenium or -tellurium compounds.[397] Photo-desulphurization of (57) by $(Bu^n_3Sn)_2$ is a useful method for preparing tetra-thiafulvalenes (58).[398]

(57)   (58)
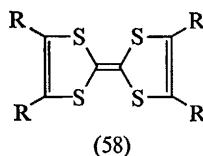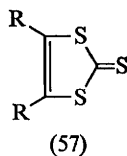
Dibutylstannylene, formed by photodissociation of polymeric dibutyltin, inserts into the carbon–halogen bond of alkyl halides [*e.g.* reaction (104)].[399]

$$Bu_2Sn + EtBr \longrightarrow Bu_2EtSnBr \qquad (104)$$

The light-induced addition of $GeMe_3H$ to fluoroethylenes,[400] the photo-initiated polymerization of methyl methacrylate in the presence of organotin compounds,[401] the photodecomposition of dibutyltin dilaurate and other PVC stabilizers,[402] and the u.v. decomposition of $(Bu_2Sn)_2O$ [403] have all been described recently.

[394] A. Hudson, M. F. Lappert, and P. W. Lednor, *J.C.S. Dalton*, 1976, 2369.
[395] M. J. S. Gynane and M. F. Lappert, *J. Organometallic Chem.*, 1976, **114**, C4.
[396] H. U. Buschhaus, M. Lehnig, and W. P. Neumann, *J.C.S. Chem. Comm.*, 1977, 129.
[397] J. C. Scaiano, P. Schmid, and K. U. Ingold, *J. Organometallic Chem.*, 1976, **121**, C4.
[398] Y. Ueno, A. Nakayama, and M. Okawara, *J. Amer. Chem. Soc.*, 1976, **98**, 7440.
[399] S. Kozima, K. Kobayashi, and M. Kawanisi, *Bull. Chem. Soc. Japan*, 1976, **49**, 2837.
[400] K. D. R. Winton and J. M. Tedder, in ref. 219, p. 29.
[401] S. F. Zhil'tsov, V. N. Kashaeva, G. I. Anikanova, Y. A. Kaplin, and L. F. Kudryavtsev, *Izvest. Vyssh. Uchebn. Zaved. Khim. i khim. Tekhnol.*, 1976, **19**, 633.
[402] Y. Oki, F. Mori, and M. Koyama, *Kobunshi Ronbunshu*, 1977, **34**, 43 (*Chem. Abs.*, 1977, **86**, 122 184).
[403] D. Kloetzer and U. Thust, *Chem. Tech. (Leipzig)*, 1976, **28**, 614.

The photoreduction of $K_2Sn_2(ox)_7$ in aqueous solution to give Sn^{2+} has been monitored both spectrophotometrically and by radiochemical determination of $^{14}CO_2$.[404]

Nitrogen, Phosphorus, Arsenic, Antimony, and Bismuth.—A comparison of the photodissociation reactions of MPh_3 (M = N, P, As, Sb, or Bi) has been made at both 77 K and 300 K, using e.s.r. and spectrophotometric methods.[405] With the aid of the spin-trap reagent $PhCH=N(O)Bu^t$, quantum yields for the production of phenyl radicals from the arsenic (0.05), antimony (0.1), and bismuth (0.15) derivatives could be estimated, whereas with triphenylamine and triphenylphosphine the radical concentration was too low to be detected. Quenching of the fluorescence of aromatic compounds by MPh_3 (M = N, P, Sb, or As) involves a deactivation of the excited state by both charge-transfer and heavy-atom induced ISC processes.[406]

Tertiary phosphines are readily photo-oxidized to the corresponding phosphine oxide [reaction (105)].[407] For PPh_3, $PEtPh_2$, PEt_2Ph, PMe_2Ph, and $PMePh_2$ the quantum yields (at 254 nm) range from 3.3 to 5.4, indicating that a chain reaction mechanism is operative.

$$2PR_3 + O_2 \xrightarrow{h\nu} 2R_3PO \tag{105}$$
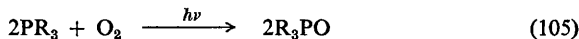
Persistent radicals of the type PR_2 have been prepared by irradiation of $[(Me_3Si)_2CH]_2MCl$ or $[(Me_3Si)_2N]_2MCl$ (M = P or As) in the presence of electron-rich olefins such as (59).[408]
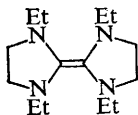
(59)

Photolysis of the ylide $Me_3\overset{+}{N}-\overset{-}{N}P(O)Ph_2$ gives singlet phosphinylnitrene.[409] Attack of triplet benzophenone upon tetraphenyl- or tetraethyl-diphosphine causes cleavage of the P—P bond as indicated in equation (106).[410]

$$Ph_2CO^T + R_2PPR_2 \longrightarrow Ph_2\overset{\cdot}{C}OPR_2 + \cdot PR_2 \tag{106}$$
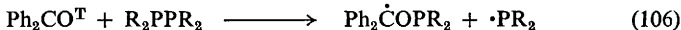
Oxygen and Sulphur.—Autoradioluminescence of solutions of uranyl ion in 57% aqueous perchloric acid under intrinsic ^{238}U α-radiation has been assigned to emission from the $^3B_1$ state of water.[411] A report on the thermoluminescence of polycrystalline ice after u.v. irradiation has been published.[412]

[404] E. L. J. Breet and R. Van Eldik, *Inorg. Chim. Acta*, 1977, **21**, 89, 95.
[405] S. G. Smirnov, A. N. Rodionov, K. L. Rogozhin, O. P. Syutkina, E. M. Panov, D. N. Shi-gorin, and K. A. Kocheshkov, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1976, 335.
[406] H. D. Burrows, S. J. Formosinho, A. M. Da Silva, and S. E. Carlin, *J. Photochem.*, 1977, **6**, 317.
[407] G. L. Geoffroy, D. A. Denton, and C. W. Eigenbrot, *Inorg. Chem.*, 1976, **15**, 2310.
[408] M. J. S. Gynane, A. Hudson, M. F. Lappert, P. P. Power, and H. Goldwhite, *J.C.S. Chem. Comm.*, 1976, 623.
[409] E. Kameyama, S. Inokuma, and T. Kuwamura, *Bull. Chem. Soc. Japan*, 1976, **49**, 1439.
[410] R. Okazaki, K. Tamura, Y. Hirabayashi, and N. Inamoto, *J.C.S. Perkin I*, 1976, 1924.
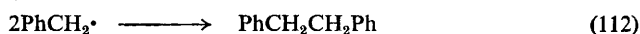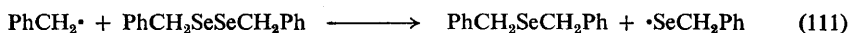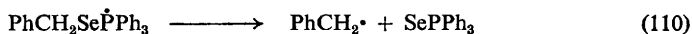[411] G. L. Sharipov, V. P. Kazakov, and R. G. Bulgakov, *Zhur. priklad. Spektroskopii*, 1977, **26** 289.
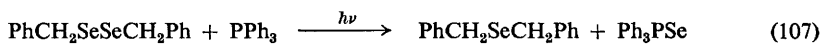[412] J. R. Pettit and P. Duval, *Solid State Comm.*, 1976, **19**, 475.

Recent publications have considered the photolysis of hydrogen peroxide in methanol, using e.s.r.-monitored flash photolysis [413] and the photo-oxidation of sulphur by hydrogen peroxide.[414]

A mixture of addition products is formed following the photodissociation of OF_2 in the presence of $FCONSF_2$.[415]

Multiphoton dissociation of SF_6 by carbon dioxide laser radiation has been investigated by a number of research groups.[384, 416-421]

Selenium and Tellurium.—Two groups have presented their results on the photo-deselenation (107) of benzyl diselenides in the presence of tertiary phosphines.[422, 423] The primary process appears to be cleavage of the Se—Se bond, followed by a chain reaction [steps (108)—(112)], and this is confirmed by

$$PhCH_2SeSeCH_2Ph + PPh_3 \xrightarrow{h\nu} PhCH_2SeCH_2Ph + Ph_3PSe \qquad (107)$$

$$PhCH_2SeSeCH_2Ph \xrightarrow{h\nu} 2PhCH_2Se\cdot \qquad (108)$$

$$PhCH_2Se\cdot + PPh_3 \longrightarrow PhCH_2Se\overset{\cdot}{P}Ph_3 \qquad (109)$$

$$PhCH_2Se\overset{\cdot}{P}Ph_3 \longrightarrow PhCH_2\cdot + SePPh_3 \qquad (110)$$

$$PhCH_2\cdot + PhCH_2SeSeCH_2Ph \longrightarrow PhCH_2SeCH_2Ph + \cdot SeCH_2Ph \qquad (111)$$

$$2PhCH_2\cdot \longrightarrow PhCH_2CH_2Ph \qquad (112)$$

the observation of quantum yields greater than unity at phosphine concentrations greater than 0.05 mol dm^{-3}.[422] Photolysis of diethyl and dibenzyl ditellurides also results in demetallation [reaction (113)].[424] However, in this case the reaction appears to involve rupture of the Te—C bond rather than the Te—Te linkage.

$$RTeTeR \xrightarrow{h\nu} RTeR + Te \qquad (113)$$
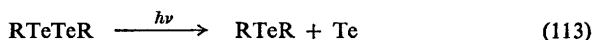
The photochemical and photophysical properties of bis(benzoylmethyl)-tellurium dichloride have been studied.[425] At 77 K, emission is observed from the lowest-lying triplet state, which appears to be a $\pi-\pi^*$ species, although with appreciable $n-\pi^*$ character. At room temperature, this excited state reacts either by a process similar to the Norrish Type II reaction [equation (114);

[413] J. Hellebrand and P. Wuensche, *Faserforsch. Textiltech.*, 1976, **27**, 589.
[414] I. N. Barshchevskii, *Zhur. fiz. Khim.*, 1976, **50**, 1176.
[415] I. Stahl, R. Mews, and O. Glemser, *Chem. Ber.*, 1977, **110**, 2398.
[416] J. Dupre, P. Pinson, J. Dupre-Maquaire, C. Meyer, and P. Barchewitz, *Compt. rend.*, 1976, **283**, C, 311.
[417] B. J. Orr and M. V. Keentok, *Chem. Phys. Letters*, 1976, **41**, 68.
[418] H. N. Rutt, *J. Phys. (D)*, 1977, **10**, 869.
[419] V. D. Klimov, V. A. Kuz'menko, and V. A. Legasov, *Zhur. neorg. Khim.*, 1976, **21**, 2100.
[420] A. K. Petrov, Y. N. Samsonov, A. V. Baklanov, V. V. Vizhin, and A. Orishich, *Izvest. Akad. Nauk S.S.S.R. Ser. khim.*, 1976, 2148.
[421] P. Kolodner, C. Winterfeld, and E. Yablonovitch, *Opt. Comm.*, 1977, **20**, 119.
[422] J. Y. C. Chu and D. G. Marsh, *J. Org. Chem.*, 1976, **41**, 3204.
[423] D. H. Brown, R. J. Cross, and D. Millington, *J.C.S. Dalton*, 1977, 159.
[424] D. H. Brown, R. J. Cross, and D. Millington, *J. Organometallic Chem.*, 1977, **125**, 219.
[425] D. G. Marsh, J. Y. C. Chu, J. W. Lewicki, and J. L. Weaver, *J. Amer. Chem. Soc.*, 1976, **98**, 8432.

Photochemistry

the ylide could not be isolated] or by cleavage of the Te—C bond [equation (115)].

$$(\text{PhCOCH}_2)_2\text{TeCl}_2 \xrightarrow{h\nu} \text{PHCOCH}_3 + \text{PhC(O)}\bar{\text{C}}\text{H}\overset{+}{\text{T}}\text{eCl}_2 \quad (114)$$

$$(\text{PhCOCH}_2)_2\text{TeCl}_2 \xrightarrow{h\nu} \text{PhCO}\dot{\text{C}}\text{H}_2 + \text{PhCOCH}_2\dot{\text{T}}\text{eCl}_2 \quad (115)$$

Upon photolysis in an argon or nitrogen matrix at 8 K, the selenadiazole (60) decomposes to yield ethynylselenol, selenoketen, and acetylene.[426] On further irradiation, the selenoketen partially isomerizes to ethynylselenol.

Photolysis of (61) provides a convenient route to the novel heterocyclic compound (62).[427] In the presence of oxygen, irradiation of (63) gives (64).[428]

(60)

(61)   (62)

(63)   (64)
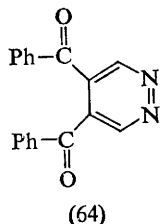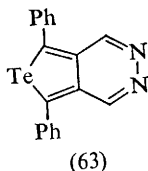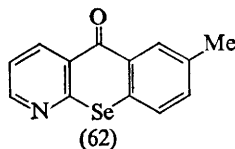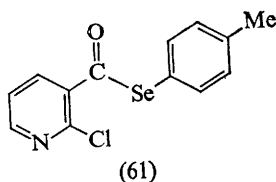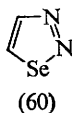
Halogens and the Noble Gases.—Chlorine difluoride has been identified by i.r. and Raman spectroscopy, following its preparation by irradiation of chlorine mono-fluoride and fluorine in low-temperature nitrogen matrices.[429] The results of a detailed investigation of the emission from chlorine in noble-gas matrices have been communicated.[430]

The photochemical synthesis of krypton difluoride from its elements has been examined quantitatively.[431-433] The highest quantum yield (0.013) was recorded

[426] J. Laureni, A. Krantz, and R. A. Hajdu, *J. Amer. Chem. Soc.*, 1976, **98**, 7872.
[427] B. Pakzad, K. Praefcke, and H. Simon, *Angew. Chem.*, 1977, **89**, 329; *Angew. Chem. Internat. Edn.*, 1977, **16**, 319.
[428] E. Luppold, W. Winter, and E. Mueller, *Chem. Ber.*, 1976, **109**, 3886.
[429] E. S. Prochaska and L. Andrews, *Inorg. Chem.*, 1977, **16**, 339.
[430] V. E. Bondybey and C. Fletcher, *J. Chem. Phys.*, 1976, **64**, 3615.
[431] A. A. Artyukhov, V. A. Legasov, G. N. Makeev, B. M. Smirnov, and B. B. Chaivanov, *Khim. vysok. Energii*, 1976, **10**, 512.
[432] A. A. Artyukhov, V. A. Legasov, G. N. Makeev, L. A. Palkina, B. M. Smirnov, and B. B. Chaivanov, *Khim. vysok. Energii*, 1977, **11**, 88.
[433] A. A. Artyukhov, V. A. Legasov, G. N. Makeev, and B. B. Chaivanov, *Khim. vysok. Energii*, 1977, **11**, 89.

for 313 nm irradiation of solid krypton in liquid fluorine at 77 K.[433] Mono-halides of the noble gases (KrF, XeF, XeCl, and XeBr) have been prepared by photolysis of the elements at 20 K, and their emission spectra have been recorded.[434, 435] Photolysis of argon–xenon–ozone mixed matrices at 22 K yields xenon monoxide, which was identified by its u.v. absorption spectrum.[436]

[434] B. S. Ault and L. Andrews, *J. Chem. Phys.*, 1976, **65**, 4192.
[435] B. S. Ault, L. Andrews, D. W. Green, and G. T. Reedy, *J. Chem. Phys.*, 1977, **66**, 2786.
[436] B. S. Ault and L. Andrews, *Chem. Phys. Letters*, 1976, **43**, 350.