

Part II

PHOTOCHEMISTRY OF INORGANIC AND ORGANOMETALLIC COMPOUNDS

By J. M. KELLY

1 Photochemistry of Metal Ions and Co-ordination Compounds

Two recent reviews consider quenching and sensitization processes involving co-ordination compounds¹ and energy transfer between organic molecules and transition-metal ions.² The photochemistry of hexaco-ordinate compounds of second- and third-row transition metals (principally Rh^{III}, Ir^{III}, Pt^{IV}, and Ru^{II}) has been reviewed.³ Briefer surveys of transition-metal complex photochemistry^{4, 5} and of flash photolysis of co-ordination compounds⁶ have been published. Other authors have discussed relaxation processes for excited states of transition-metal compounds,⁷ vibronic spectra of co-ordination compounds,⁸ and the use of two-dimensional potential energy surface cross-sections in analysing such spectra.⁹ A collection of Russian publications on the photochemistry of co-ordination compounds has appeared.¹⁰

Zink, who has previously developed a ligand field theory to explain the pattern of the photochemical reactions of d^3 and d^6 compounds,¹¹ has now presented an MO approach to the problem.¹² In particular he has calculated the increase in antibonding character along the labilized axis for the vertical ligand field excited state. This was performed first for a linear model system and then for Cr^{III} and Co^{III} ammine complexes. These calculations showed that labilization is greater the larger the metal–ligand overlap and the smaller the ligand orbital ionization energy. MO theory has also been used to explain the reactions of co-ordinated azide complexes.¹³

Incorvia and Zink¹⁴ have used ligand field theory to interpret the photosolvation quantum yields for d^6 complexes of C_{4v} and D_{4h} symmetry. The theory

¹ V. Balzani, L. Moggi, M. F. Manfrin, F. Bolletta, and G. S. Laurence, *Coordination Chem. Rev.*, 1975, **15**, 321.

² V. L. Ermolaev, E. B. Sveshnikova, and T. A. Shakhverdov, *Uspekhi Khim.*, 1975, **44**, 75.

³ P. C. Ford, J. D. Petersen, and R. E. Hintze, *Coordination Chem. Rev.*, 1974, **14**, 67.

⁴ V. Balzani, *Gazzetta*, 1974, **104**, 55.

⁵ T. Yoshida and S. Otsuka, *Kagaku*, 1974, **29**, 445.

⁶ G. Semerano, *Coordination Chem. Rev.*, 1974, **16**, 185.

⁷ M. K. DeArmond, *Accounts Chem. Res.*, 1974, **7**, 309.

⁸ C. D. Flint, *Coordination Chem. Rev.*, 1974, **14**, 47.

⁹ P. E. Hoggard and H. H. Schmidtke, *Chem. Phys. Letters*, 1974, **25**, 274.

¹⁰ 'Prevrashch. Kompleks. Soedin Deistviem Sveta, Radiats. Temp.', ed. G. A. Lazerko, Izd. Beloruss. Gos. Univ., 1973.

¹¹ J. I. Zink, *J. Amer. Chem. Soc.*, 1972, **94**, 8039; *Mol. Photochem.*, 1973, **5**, 151.

¹² J. I. Zink, *J. Amer. Chem. Soc.*, 1974, **96**, 4464.

¹³ J. I. Zink, *Inorg. Chem.*, 1975, **14**, 446.

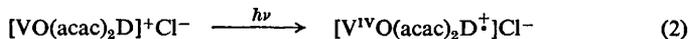
¹⁴ M. J. Incorvia and J. I. Zink, *Inorg. Chem.*, 1974, **13**, 2489.

assumes that a greater concentration of excitation energy along a particular axis will lead to a higher quantum yield for loss of the ligands along that axis, and this has been calculated using crystal field parameters. Certain aspects of this theory have been criticized by Ford.¹⁵

Models for photoredox reactions of transition-metal ammine complexes have been critically examined.¹⁶ The role of the solvent is stressed; in particular it will participate in the processes involved in the relaxation of the Franck–Condon excited state to the primary radical pair products.

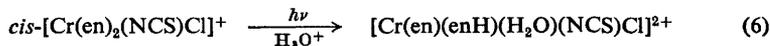
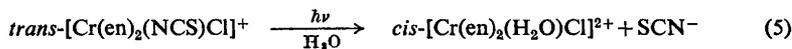
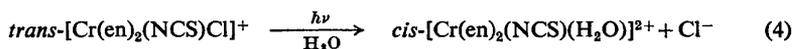
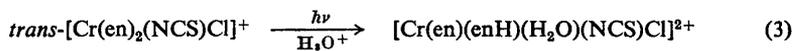
As in last year's Report, the photochemistry of each transition metal is treated systematically. Transition-metal organometallics, low oxidation-state compounds, and porphyrins are considered in later sections.

Vanadium.—VO(acac)₂Cl (acac = acetylacetonate) is a photo-initiator for methyl-methacrylate polymerization both in the absence^{17a} and in the presence^{17b} of electron donors D, such as dimethyl sulphoxide or pyridine. Reactions (1) and (2) have been proposed as the initial photochemical steps.



Photolysis of V^V in perchloric acid solution leads to V^{IV} and oxygen.¹⁸ Photo-reduction of VOCl₃ proceeds efficiently in ethanol solutions.¹⁹

Chromium.—The photochemical behaviour of *trans*- and *cis*-[Cr(en)₂(NCS)Cl]⁺ has been studied.^{20, 21} The reactions observed for the *trans*-complex²⁰ are (3)—(5), while for the *cis*-complex²¹ the principal reaction is (6), but NCS[−] and Cl[−]



aquation also occur. The spectra and quantum yields for the reactions are shown in Figure 1. For the *trans*-complex, SCN[−] and Cl[−] release originates from the lowest ⁴E state, while the ⁴B₂ state is responsible for reaction (3). For the *cis*-complex reaction (6) also occurs from the ⁴T_{2g} state (splitting into the ⁴B₂ and ⁴E components is not observed in this case), but in contrast to the *trans*-complex, SCN[−] and Cl[−] aquation appear to originate from a charge-transfer excited state.

¹⁵ P. C. Ford, *Inorg. Chem.*, 1975, **14**, 1440.

¹⁶ J. F. Endicott, G. J. Ferraudi, and J. R. Barber, *J. Phys. Chem.*, **79**, 630.

¹⁷ (a) S. M. Aliwi and C. H. Bamford, *J. C. S. Faraday I*, 1974, **70**, 2092; (b) S. M. Aliwi and C. H. Bamford, *ibid.*, 1975, **71**, 52.

¹⁸ B. G. Jeliaskowa, S. Nakamura, and H. Fukutomi, *Bull. Chem. Soc. Japan*, 1975, **48**, 347.

¹⁹ A. I. Kryukov, Z. A. Trachenko, and S. Y. Kuchmii, *Doklady Akad. Nauk S.S.S.R.*, 1974, **216**, 592.

²⁰ M. T. Gandolfi, M. F. Manfrin, A. Juris, L. Moggi, and V. Balzani, *Inorg. Chem.*, 1974, **13**, 1342.

²¹ M. F. Manfrin, M. T. Gandolfi, L. Moggi, and V. Balzani, *Gazzetta*, 1973, **103**, 1189.

Photochemistry of Inorganic and Organometallic Compounds

$[\text{Cr}(\text{en})_2(\text{NH}_3)\text{NCS}]^{2+}$ provides another exception to Adamson's empirical rules.²² These predict that excitation of the ligand field states of the complex should lead mainly to NH_3 separation, whereas NH_3 made up only 40% of the base released on photolysis, just double that which would be predicted on a purely statistical basis.

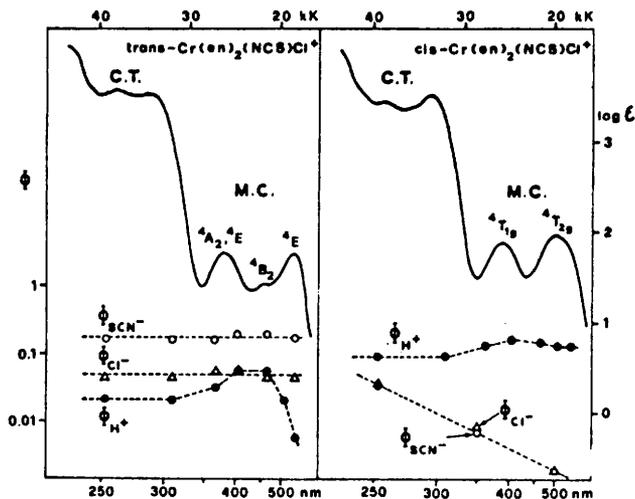
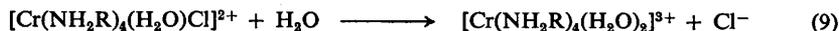
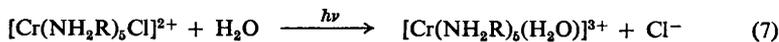


Figure 1 Electronic absorption spectra of *trans*- and *cis*- $[\text{Cr}(\text{en})_2(\text{NCS})\text{Cl}]^+$ and quantum yields for the observed photoreactions (Reproduced by permission from *Inorg. Chem.*, 1974, 13, 1342)

The photosolvation reactions of $[\text{Cr}(\text{NH}_2\text{R})_6\text{Cl}]^{2+}$ ($\text{R} = \text{H}, \text{Me}, \text{Et}, \text{Pr}^n$, or Bu^n) in acidic media have been examined for both aqueous solution and water-acetone mixtures.²³ Estimation of the relative efficiencies of the processes (7) and (8) is hampered by the occurrence of thermal processes corresponding to (8) and (9). When these complications were minimized, however, the quantum yield (at



565 nm) for Cl^- formation from $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$ in water was found to be <0.001 , an order of magnitude smaller than that reported previously. While reaction (8) is unaffected by change of the solvent from water to 33% acetone, Cl^- photosubstitution (7) increases substantially. From this and other observations, the authors conclude that the excited state causing reaction (8) is a quartet ligand field state and that responsible for reaction (7) has some charge-transfer character.

²² A. D. Kirk and T. L. Kelly, *Inorg. Chem.*, 1974, 13, 1613.

²³ (a) C. F. C. Wong and A. D. Kirk, *Canad. J. Chem.*, 1974, 52, 3384; (b) C. F. C. Wong and A. D. Kirk, *ibid.*, 1975, 53, 419.

The photoaquation quantum yield for $[\text{Cr}(\text{CN})(\text{H}_2\text{O})_5]^{3+}$ increases with wavelength in the range 500–650 nm.²⁴ By assuming no conversion between the states, the authors deduce that the quantum yields for aquation of the 4E and 4B_2 states are 0.20 and 0.55 respectively.

Possible mechanisms normally considered for isomerization of tris-chelate complexes require either intramolecular twisting or bond rupture. Irradiation of $\text{Cr}(\text{tfa})_3$ (tfa = 1,1,1-trifluoropentane-2,4-dionate) with circularly polarized light shows that both pathways are involved.²⁵ Although in solution $[\text{Cr}(\text{ox})_3]^{3-}$ (ox = oxalate) also undergoes isomerization, irradiation ($\lambda > 250$ nm) of $[\text{Cr}(\text{ox})_3]^{3-}$ in $\text{K}_3\text{Al}(\text{ox})_3 \cdot 3\text{H}_2\text{O}$ crystals at 100 and 250 K produced no detectable photoreactions.²⁶

Energy transfer from $[\text{Cr}(\text{en})_3]^{3+}$ to $[\text{Cr}(\text{CN})_6]^{3-}$ in $[\text{Cr}(\text{en})_3][\text{Cr}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ has been observed by monitoring the rise time (6.2 ns) of the $[\text{Cr}(\text{CN})_6]^{3-}$ emission.^{27a} The same authors have reported evidence for energy transfer from $[\text{Co}(\text{CN})_6]^{3-}$ to $[\text{Cr}(\text{CN})_6]^{3-}$ in their non-stoichiometric mixed crystals.^{27b} The quenching of the fluorescence of 10-methylacridinium chloride by Cr^{III} complexes in aqueous solution proceeds with rate constants in the range $1.3 \times 10^9 \rightarrow 7.7 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.²⁸

Emissions from $[\text{Cr}(\text{MIDA})_2]^-$ and $[\text{Cr}(\text{IDA})_2]^-$ [$(\text{M})\text{IDA} = (\text{methyl})\text{imino-diacetate}$] have been reported²⁹ to exhibit pronounced 'pseudo Stokes shifts', attributed to a displacement of the potential energy surface of the 2E_g state relative to the ground state. A reassignment of the spectra indicates that this is incorrect.³⁰

The emission spectra of $[\text{Cr}(\text{phen})_3]^{3+}$ and $[\text{Cr}(\text{bipy})_3]^{3+}$ in aqueous solution at room temperature contain not only ${}^2E \rightarrow {}^4A_2$ emission bands but also others assigned to ${}^2T_1 \rightarrow {}^4A_2$.³¹ As the 2T_1 emission becomes stronger at higher temperatures, it is suggested that the 2T_1 emission takes place after repopulation from the 2E state. On addition of dimethyl sulphoxide to the $[\text{Cr}(\text{bipy})_3]^{3+}$ solution, emission assigned to the ${}^4T_2 \rightarrow {}^4A_2$ transition was recorded – apparently the first report of emission from the quartet state in fluid solution at room temperature.

Other reports consider the luminescence properties of $[\text{Cr}(\text{py})_4\text{F}_2]^+$,^{32a} $[\text{Cr}(\text{NCS})_6]^{3-}$,^{32b} $[\text{Cr}(\text{en})_2\text{F}_2]^+$,^{32c} $[\text{Cr}(\text{CN})_6]^{3-}$,³³ oxygen-co-ordinated Cr^{III} complexes at 5 K,³⁴ $\text{Cr}(\text{CH}_2\text{NH}_2\text{CO}_2)_3 \cdot \text{H}_2\text{O}$ and $\text{Cr}_2(\text{OH})_2(\text{CH}_2\text{NH}_2\text{CO}_2)_4$,³⁵ and Cr^{III} ions in MgO ³⁶ and $\text{Al}(\text{urea})_6\text{I}_3$.³⁷

²⁴ W. Coleman and W. Schaap, *J.C.S. Chem. Comm.*, 1975, 225.

²⁵ K. L. Stevenson and T. P. van den Driesche, *J. Amer. Chem. Soc.*, 1974, **96**, 7964.

²⁶ D. C. Doetschman, *J. Chem. Phys.*, 1974, **60**, 2647.

²⁷ (a) F. Castelli and L. S. Forster, *Chem. Phys. Letters*, 1975, **30**, 465; (b) F. Castelli and L. S. Forster, *J. Phys. Chem.*, 1974, **78**, 2122.

²⁸ K. K. Chatterjee and S. Chatterjee, *Z. phys. Chem. (Frankfurt)*, 1975, **94**, 107.

²⁹ P. E. Hoggard and H. H. Schmidtke, *Ber. Bunsengesellschaft phys. Chem.*, 1972, **76**, 1013.

³⁰ C. D. Flint and A. P. Matthews, *J.C.S. Faraday II*, 1975, **71**, 379.

³¹ N. A. P. Kane-Maguire, J. Conway, and C. H. Langford, *J.C.S. Chem. Comm.*, 1975, 801.

³² (a) C. D. Flint and A. P. Matthews, *Inorg. Chem.*, 1975, **14**, 1008; (b) C. D. Flint and A. P. Matthews, *J.C.S. Faraday II*, 1974, **70**, 1301; (c) C. D. Flint and A. P. Matthews, *ibid.*, p. 1307.

³³ C. D. Flint and P. Greenhough, *J.C.S. Faraday II*, 1974, **70**, 815.

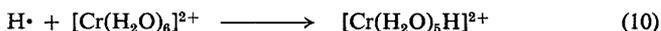
³⁴ H. Otto, H. Yersin, and G. Gliemann, *Z. phys. Chem. (Frankfurt)*, 1974, **92**, 193.

³⁵ A. Ranade, E. Koglin, and W. Krasser, *Z. analyt. Chem.*, 1975, **273**, 463.

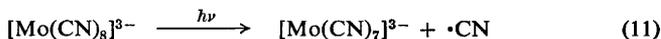
³⁶ F. Castelli and L. S. Forster, *Phys. Rev. (B)*, 1975, **11**, 920.

³⁷ E. Koglin, W. Krasser, G. Wolff, and H. W. Nuernberg, *Z. Naturforsch.*, 1974, **29a**, 211.

Quantum yields for production of D_2 on photolysis of Cr^{2+} in D_2O solution are lower than those for H_2 liberation from H_2O .³⁸ From pulse radiolysis experiments Cohen and Meyerstein³⁹ have determined the rate constant for reaction (10) ($1.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) and they have compared their results with those obtained in earlier photochemical studies of Cr^{2+} .



Molybdenum and Tungsten.—Flash photolysis and e.s.r. studies⁴⁰ have been carried out on $[Mo(CN)_8]^{3-}$ in solutions of varying pH, concentration, and solvent. The results are consistent with (11) as the primary reaction following excitation of the complex to an LMCT state.



Aspects of the photochemistry of $[M(CN)_8]^{4-}$ ($M = Mo$ or W) recently reported include an e.s.r. study of irradiated crystalline $M_2[M(CN)_8]_2 \cdot xH_2O$ and $[M^1(en)_2]_2[M(CN)_8]$ ($M^1 = Cu$ or Zn),⁴¹ photolysis of $[Mo(CN)_8]^{4-}$ in liquid ammonia,⁴² the photosubstitution of $[Mo(CN)_8]^{4-}$ in alkaline solution,⁴³ a modified preparation of the blue $K_3[MoO(OH)(CN)_4] \cdot 2H_2O$,⁴⁴ and the photo-aquation chemistry of $[Mo(CN)_8]^{4-}$.⁴⁵

Efficient photoreduction of nitrate to nitrite by riboflavin can be effected using molybdate in glacial acetic acid.⁴⁶

From a study of a large number of amine molybdates it has been shown that only secondary amines and tri- or di-molybdates give strongly photochromic compounds.⁴⁷ Reaction (12) is proposed as the initial photoprocess followed by reduction of the molybdate.^{47b}



Manganese.—The quantum yield for photochemical decomposition of $K_3[Mn(ox)_3] \cdot 3H_2O$ has been determined for reactions both in thin powdered layers⁴⁸ and bulk powder.⁴⁹ The photochemical redox reaction of $K_3Mn(edta)$ in the solid state has been investigated.⁵⁰

Rhenium.—The photochemical cleavage of the Re—Re quadruple bond in $[Re_2Cl_8]^{2-}$ has been reported.⁵¹ After irradiation in acetonitrile solution, (2) and

³⁸ M. W. Rophael and M. A. Malati, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1326.

³⁹ H. Cohen and D. Meyerstein, *J.C.S. Dalton*, 1974, 2559.

⁴⁰ Z. Stasicka and H. Bulska, *Roczniki Chem.*, 1974, **48**, 389.

⁴¹ E. Nagorsnik, D. Rehorek, and P. Thomas, *Z. Chem.*, 1974, **14**, 366.

⁴² R. D. Archer and D. A. Drum, *J. Inorg. Nuclear Chem.*, 1974, **36**, 1979.

⁴³ E. Nagorsnik, P. Thomas, and E. Hoyer, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 353.

⁴⁴ R. L. Marks and S. E. Popielski, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 885.

⁴⁵ R. P. Mitra and H. Mohan, *J. Inorg. Nuclear Chem.*, 1974, **36**, 3739.

⁴⁶ P. W. Moors, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1089.

⁴⁷ (a) F. Arnaud-Neu and J. Schwing-Weill, *J. Less Common Metals*, 1974, **36**, 71; (b) F. Arnaud-Neu and J. Schwing-Weill, 'Chemistry and Uses of Molybdenum', ed. P. C. H. Mitchell, Climax Molybdenum Co. Ltd., London, 1974, p. 35; (c) T. Yamase, H. Hayashi, and T. Ikawa, *Chem. Letters*, 1974, 1055.

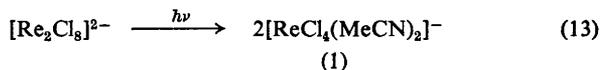
⁴⁸ E. L. Simmons, *J. Phys. Chem.*, 1974, **78**, 1265.

⁴⁹ E. L. Simmons and W. W. Wendlandt, *J. Phys. Chem.*, 1975, **79**, 1158.

⁵⁰ T. Takeuchi and A. Ouchi, *Nippon Kagaku Kaishi*, 1974, 1486.

⁵¹ G. L. Geoffroy, H. B. Gray, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1974, **96**, 5565.

a small amount of (1) were isolated. A two-step mechanism was proposed for



radiation between 300 and 366 nm. Excitation at longer wavelengths corresponding to the δ - δ^* band did not produce any photoreaction. Nevertheless the facile photochemical cleavage is not consistent with previous estimates for the Re—Re bond strength of 1200—1700 kJ mol⁻¹. The electronic structure of $[\text{Re}_2\text{Cl}_8]^{2-}$ has recently been discussed.⁵²

Iron.—E.s.r. spectra taken after u.v. irradiation of $[\text{Fe}(\text{CN})_6]^{3-}$ in aqueous methanol at 77 K indicated the presence of $\cdot\text{CH}_2\text{OH}$, $\text{H}\dot{\text{C}}\text{O}$, and an Fe^{III} species assigned to $[\text{Fe}(\text{CN})_5(\text{MeOH})]^{2-}$.⁵³ It is postulated that the reactions proceed *via* an LMCT process followed by extraction of an electron from the solvent by the electron-deficient ligand, as in reaction (15).



Previous workers^{54, 55} have suggested that the primary step on photolysis of $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$ is (16) and this mechanism has been favoured by Stoeri and



West from studies of the reaction of the photoproducts with SCN⁻^{56a} and thiourea.^{56b} Wolfe and Swinehart⁵⁷ have proposed, however, that the principal reaction after irradiation at 366 nm ($\Phi = 0.35$) and 436 nm ($\Phi = 0.18$) is (17), and that previously reported effects on varying the pH and oxygen concentration may be rationalized by secondary reactions of NO.



The OH \cdot radical formed on photolysis of Fe³⁺ may be effectively scavenged by low concentrations of alcohols.⁵⁸ At higher concentrations (0.1—5 mol l⁻¹) an additional quenching effect for methanol and propan-2-ol, but not for *t*-butyl alcohol, was observed. This was attributed to reaction of the alcohol either with a vibrationally equilibrated charge-transfer state of Fe³⁺ or with the geminate pair $[\text{Fe}^{\text{II}}, \cdot\text{OH}]$.

⁵² A. P. Mortola, J. W. Moskowitz, N. Roesch, C. D. Cowman, and H. B. Gray, *Chem. Phys. Letters*, 1975, **32**, 283.

⁵³ M. C. R. Symons, D. X. West, and J. G. Wilkinson, *J. Phys. Chem.*, 1974, **78**, 1335.

⁵⁴ R. P. Mitra, B. K. Sharma, and S. P. Mittal, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3919.

⁵⁵ A. Lodzinska and R. Gogolin, *Roczniki Chem.*, 1973, **47**, 497, 881, 1101.

⁵⁶ (a) P. A. Stoeri and D. X. West, *J. Inorg. Nuclear Chem.*, 1974, **36**, 2347; (b) P. A. Stoeri and D. X. West, *ibid.*, p. 3883.

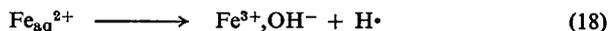
⁵⁷ S. K. Wolfe and J. H. Swinehart, *Inorg. Chem.*, 1975, **14**, 1049.

⁵⁸ J. H. Carey and C. H. Langford, *Inorg. Nuclear Chem. Letters*, 1974, **20**, 591.

Photochemical decomposition of $[\text{Fe}(\text{ox})_3]^{3-}$ may be induced by a Q -switched ruby laser pulse ($\lambda = 694.3 \text{ nm}$).⁵⁹ Intensity studies showed that a two-photon absorption process was involved. The photochemical decomposition of $\text{K}_3\text{Fe}(\text{ox})_3 \cdot 3\text{H}_2\text{O}$ has been discussed in a series of publications.^{60–63}

Other reports consider the light-induced decomposition of Fe^{III} (dibenzoyl-methanate)₃ in the presence of O_2 ,⁶⁴ the photoreactions of FeCl_3 with toluene and substituted toluenes,⁶⁵ the photoredox reactions of Fe^{III} (tartrate)⁶⁶ and Fe^{III} -(citrate)⁶⁷ complex ions, the $[\text{Fe}(\text{CN})_6]^{3-}$ and UO_2^{2+} sensitized photochemical cleavage of pyrimidine dimers,⁶⁸ and e.s.r. studies of the photo-oxidation of amino-acids and dipeptides⁶⁹ and of wool⁷⁰ in the presence of Fe^{III} .

Photo-oxidation of Fe^{2+} in H_2SO_4 and HClO_4 glasses at 77 K has been investigated:⁷¹ the primary process appears to be (18) rather than (19).



Ruthenium and Osmium.—The quenching of the luminescent excited state of $[\text{Ru}(\text{bipy})_3]^{2+}$ has continued to receive attention.^{72–76} As discussed in last year's Report, controversy exists as to whether this process for Co^{III} complexes proceeds *via* electron-transfer (20) or energy-transfer (21). Navon and Sutin⁷² have obtained



the Stern–Volmer constants for quenching of $[\text{Ru}(\text{bipy})_3]^{2+}$ phosphorescence by $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}]^{3+}$ ($\text{X} = \text{NH}_3, \text{H}_2\text{O}, \text{Br}^-, \text{or Cl}^-$) and also by $[\text{Ru}^{\text{III}}(\text{NH}_3)_6\text{X}]^{3+}$ ($\text{X} = \text{Cl}^- \text{ or } \text{NH}_3$). From consideration of the Co^{III} excited state which would be formed and of the effect of propan-2-ol on the Stern–Volmer constant, it was concluded that an electron-transfer mechanism is operative for the Co^{III}

⁵⁹ H. Zipin and S. Speiser, *Chem. Phys. Letters*, 1975, **31**, 102.

⁶⁰ G. G. Savelev, A. A. Medvinskii, V. L. Shcherinskii, L. P. Gevlich, N. I. Gavryusheva, Y. T. Pavlyukhin, and L. I. Stepanova, *J. Solid State Chem.*, 1975, **12**, 92.

⁶¹ G. G. Savelev, A. A. Medvinskii, V. L. Shcherinskii, L. P. Gevlich, N. I. Gavryusheva and Y. V. Mitrenin, *Khim. vysok. Energii*, 1974, **8**, 458.

⁶² G. N. Belozerskii, O. I. Bogdanov, A. N. Murin, Y. T. Pavlyukhin, and V. V. Sviridov, *Zhur. fiz. Khim.*, 1974, **48**, 2785.

⁶³ A. A. Medvinskii, G. N. Belozerskii, Y. T. Pavlyukhin, V. N. Stolpovskaya, V. V. Sviridov, A. N. Murin, and V. V. Boldyrev, *Teor i eksp. Khim.*, 1974, **10**, 411.

⁶⁴ C. Parkanyi and J. H. Richards, *J. Coordination Chem.*, 1974, **4**, 41.

⁶⁵ H. Inoue, M. Izumi, and E. Imoto, *Bull. Chem. Soc. Japan*, 1974, **47**, 1712.

⁶⁶ N. A. Kostromina, N. V. Beloshitskii, and V. F. Romanov, *Doklady Akad. Nauk S.S.S.R.*, 1974, **215**, 373.

⁶⁷ S. I. Arzhankov and A. L. Poznyak, *Zhur. priklad. Spektroskopii*, 1974, **21**, 745.

⁶⁸ I. Rosenthal, M. M. Rao, and J. Salomon, *Biochim. Biophys. Acta*, 1975, **378**, 165.

⁶⁹ A. L. Poznyak, S. I. Arzhankov, and G. A. Shagisultanova, *Biofizika*, 1974, **19**, 233.

⁷⁰ G. J. Smith, *New Zealand J. Sci.*, 1974, **17**, 349.

⁷¹ V. V. Korolev and N. M. Bazhin, *Khim. vysok. Energii*, 1974, **8**, 506.

⁷² G. Navon and N. Sutin, *Inorg. Chem.*, 1974, **13**, 2159.

⁷³ C. R. Bock, T. J. Meyer, and D. G. Whitten, *J. Amer. Chem. Soc.*, 1974, **96**, 4710.

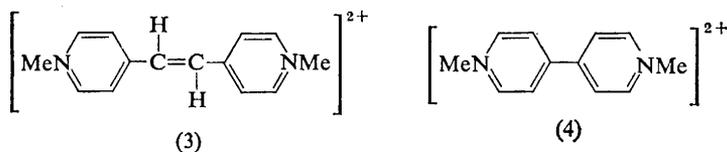
⁷⁴ C. R. Bock, T. J. Meyer, and D. G. Whitten, *J. Amer. Chem. Soc.*, 1975, **97**, 2909.

⁷⁵ G. S. Laurence and V. Balzani, *Inorg. Chem.*, 1974, **13**, 2976.

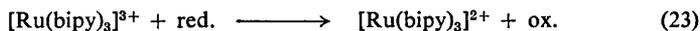
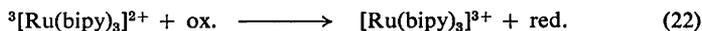
⁷⁶ C. Lin and N. Sutin, *J. Amer. Chem. Soc.*, 1975, **97**, 3543.

complexes. For Ru^{III} quenchers, which in general react more efficiently than the Co^{III} complexes, the electron-transfer pathway is also favoured.

Other workers⁷³ have unambiguously shown by luminescence quenching and flash photolysis studies that for the weak organic oxidants (3) and (4) and for



[Fe(H₂O)₆]³⁺ and [Ru(NH₃)₆]³⁺ the initial step is electron transfer (22), followed by a thermal recombination (23). For example, energy transfer to (3) would



produce its triplet state which would then undergo *trans-cis* isomerization; however, the yield of this reaction was small indicating that energy transfer is responsible for <1% of the quenching. In another study⁷⁴ substituted nitrobenzenes were used as quenchers. The quenching rate constants (k_q) were calculated and values are given in Table 1. From these results a value for

Table 1 Comparison of the quenching rate constants for ${}^3[\text{Ru}(\text{bipy})_3]^{2+}$ by substituted nitrobenzenes with their reduction potentials⁷⁴

Quencher	$-E_4$	$k_q/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
<i>p</i> -Nitronitrosobenzene	0.525	9.18×10^9
<i>p</i> -Dinitrobenzene	0.69	6.56×10^9
<i>o</i> -Dinitrobenzene	0.81	3.10×10^9
<i>p</i> -Nitrobenzaldehyde	0.863	1.96×10^9
<i>m</i> -Dinitrobenzene	0.898	1.56×10^9
Methyl-4-nitrobenzoate	0.947	6.56×10^8
<i>cis</i> -4,4'-Dinitrostilbene	1.00	1.83×10^8
4,4'-Dinitrobiphenyl	1.004	1.18×10^8
3-Nitrobenzaldehyde	1.016	4.89×10^7
Methyl-3-nitrobenzoate	1.044	1.66×10^7
4-Chloronitrobenzene	1.063	8.04×10^6
4-Fluoronitrobenzene	1.128	8.32×10^5
Nitrobenzene	1.147	$< 2 \times 10^5$
4-Methylnitrobenzene	1.203	$< 3 \times 10^5$

$E_4([\text{Ru}(\text{bipy})_3]^{3+}/{}^3[\text{Ru}(\text{bipy})_3]^{2+})$ of $-0.81 \pm 0.02 \text{ V}$ was obtained. Electron transfer from ${}^3[\text{Ru}(\text{bipy})_3]^{2+}$ to Ti^{3+} ,⁷⁵ and to $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ⁷⁶ has been demonstrated.

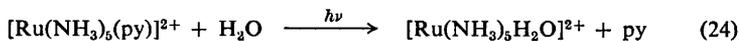
Two reports of a static contribution to the quenching of emission from Ru^{III} complexes have been published. Measurement of both phosphorescence lifetimes and intensities allowed Bolletta *et al.*,⁷⁷ to observe static quenching (through ion-pair formation) of ${}^3[\text{Ru}(\text{bipy})_3]^{2+}$ by $[\text{Mo}(\text{CN})_6]^{4-}$ and $[\text{PtCl}_4]^{2-}$ in DMF. For $[\text{IrCl}_6]^{3-}$ only dynamic quenching was found. Demas and Addington⁷⁸

⁷⁷ F. Bolletta, M. Maestri, L. Moggi, and V. Balzani, *J. Phys. Chem.*, 1974, **78**, 1374.

⁷⁸ J. N. Demas and J. W. Addington, *J. Amer. Chem. Soc.*, 1974, **96**, 3663.

found that Cu^{2+} caused static quenching of $[\text{Ru}(\text{phen})_2(\text{CN})_2]$ emission. In this case ground-state association of the Cu^{2+} , probably through the CN group, is postulated.

Deuteriation of the ligand in $[\text{Ru}(\text{bipy})_3]^{2+}$ causes only a 20% increase in the lifetime of the emitting state, whereas change of the solvent from H_2O to D_2O produces a doubling of the lifetime.⁷⁹ This is surprising in view of the usual assignment of the excited state as MLCT, and the authors suggest that some CTTS character must be present. Other reports on $[\text{Ru}(\text{bipy})_3]^{2+}$ include a review (in Japanese) of energy transfer⁸⁰ and a report on the effect of magnetic field on the low-temperature emission spectrum.⁸¹



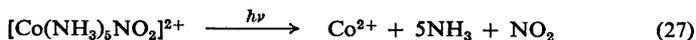
The quantum yield for pyridine photo-aquation (24) from $[\text{Ru}(\text{NH}_3)_5(\text{py})]^{2+}$ varies only slightly with wavelength in the range 436–254 nm, and photo-oxidation to give Ru^{III} is only important at $\lambda < 334$ nm.^{82a} Similarly, only photo-aquation of $[\text{Ru}(\text{NH}_3)_5(\text{MeCN})]^{2+}$ is found on irradiation at 366 nm while photoredox reactions are very important at shorter wavelengths ($\Phi = 0.51$ at 214 nm).^{82b} For both complexes a CTTS state is implicated in the photoredox reactions. As H_2 is a significant product for $[\text{Ru}(\text{NH}_3)_5(\text{MeCN})]^{2+}$ photolysis at 254 nm, particularly in the presence of propan-2-ol, steps (25) and (26) are probably important.



In contrast to results obtained at $\lambda > 200$ nm, irradiation at 185 nm of $[\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{X}]^{3+}$ ($\text{X} = \text{H}_2\text{O}$, NH_3 , or Cl^-), in the presence of propan-2-ol, leads to photoreduction.⁸³ *cis*- $[\text{Ru}(\text{NH}_3)_4\text{X}_2]^+$ ($\text{X} = \text{Br}$ or I) undergo photo-aquation of X^- in acidic solution.⁸⁴

Several luminescent Os^{II} and Ir^{III} complexes, including $[\text{Os}(\text{bipy})_3]^{2+}$, have been used as singlet oxygen sensitizers.⁸⁵

Cobalt.—It has previously been suggested⁸⁶ that only solvent viscosity is responsible for the change in the relative yields of the photoreactions (27) and (28) on



⁷⁹ J. Van Houten and R. J. Watts, *J. Amer. Chem. Soc.*, 1975, **97**, 3843.

⁸⁰ Y. Kaizu and H. Kobayashi, *Kagaku*, 1975, **30**, 67.

⁸¹ D. C. Baker and G. A. Crosby, *Chem. Phys.*, 1974, **4**, 428.

⁸² (a) R. E. Hintze and P. C. Ford, *Inorg. Chem.*, 1975, **14**, 1211; (b) R. E. Hintze and P. C. Ford, *J. Amer. Chem. Soc.*, 1975, **97**, 2664.

⁸³ J. Siegel and J. N. Armor, *J. Amer. Chem. Soc.*, 1974, **96**, 4102.

⁸⁴ A. Ohyoshi, N. Takebayashi, Y. Hiroshima, K. Yoshikuni, and K. Tsuji, *Bull. Chem. Soc. Japan*, 1974, **47**, 1414.

⁸⁵ J. N. Demas, E. W. Harris, C. M. Flynn, and D. Diemente, *J. Amer. Chem. Soc.*, 1975, **97**, 3838.

⁸⁶ F. Scandola, C. Bartocci, and M. A. Scandola, *J. Amer. Chem. Soc.*, 1973, **95**, 7898.

will have important consequences for sensitization reactions of Co^{III} complexes. The nature of the solvent environment of the complex will be strongly affected by the energy donor, particularly if it is ionic, and thus the authors see 'no clear way to relate intermolecular energy transfer studies to intrinsic processes within "molecular" CT states of co-ordination complexes'.

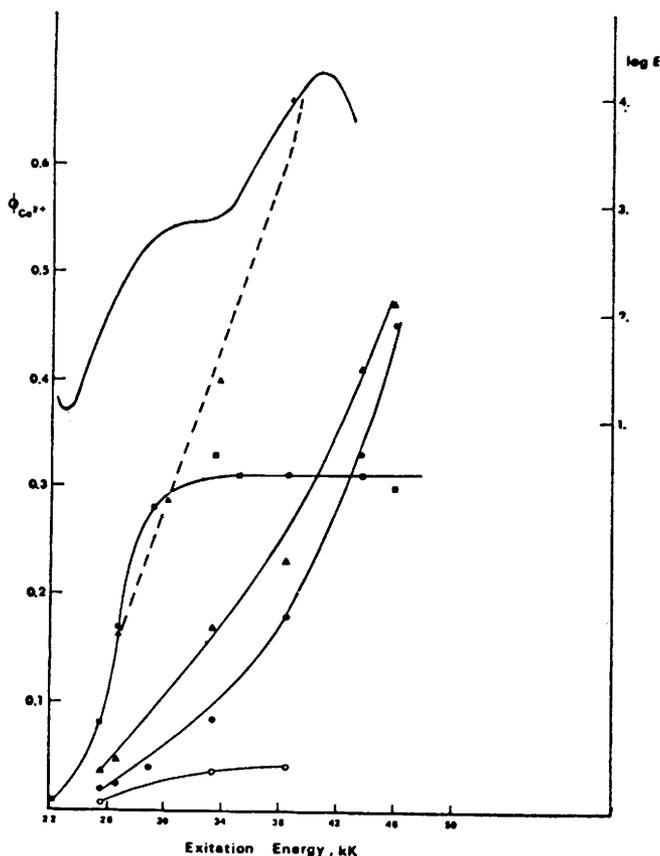


Figure 2 Absorption spectrum in water (upper curve) and variations in quantum yields of Co^{2+} (lower curves) with excitation energy and solvent medium on irradiation of $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$. Aqueous solvent media employed: H_2O , ■; 80% MeCN, △; 50% glycerol, ▲; 75% glycerol, ●; 87% H_2PO_4 , ○ (Reproduced by permission from *J. Amer. Chem. Soc.*, 1975, 97, 219)

Consideration of the nature of the LMCT transitions, redox energetics, and photoredox behaviour of transition-metal ammine complexes has allowed Endicott and co-workers¹⁶ to propose new models for the potential energy surfaces describing their photoredox reactions. These models have been used to discuss the differences in photoreactivity of $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$ and $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$.⁹¹ These differences are ascribed to (i) more Co-radical bonding in the

LMCT excited state of the bromo-complex and to (ii) the vibrational relaxation being faster than solvent dielectric relaxation for $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$ but proceeding with similar rates for $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$.

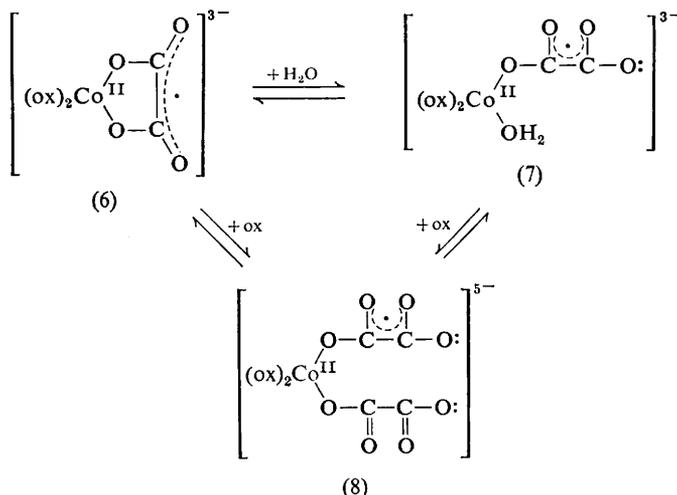
Using MO calculations of the type outlined earlier,¹² Zink has predicted the expected reaction modes of the various types of excited state of $[\text{M}(\text{NH}_3)_5\text{N}_3]^{2+}$ ($\text{M} = \text{Co}, \text{Rh}, \text{or Ir}$) (Table 2).¹³ Generally good agreement with experiment⁹² is observed.

Table 2 Predictions of the photoreactivity of $[\text{M}(\text{NH}_3)_5\text{N}_3]^{2+}$ ($\text{M} = \text{Co}, \text{Rh}, \text{or Ir}$)¹³

Excited state ^a	Trend in bonding state	
	Cobalt	to Iridium
LMCT	no N—N labilization	weakly labilize N'—N" form IrN + N ₂
MLCT	all N—N labilized CoN ₂ + N more probable	strongly labilize N"—N" form IrN ₂ + N
LL	all N—N labilized CoN ₂ + N more probable	strongly labilize N'—N" form IrN + N ₂ only

^a LL = ligand localized; M—N'—N"—N'''.

Two reports on the flash photolysis of $[\text{Co}(\text{ox})_3]^{3-}$ in aqueous solution have been published.^{93, 94} Hoffman and co-workers⁹³ assigned the intermediate species observed in solution at pH = 6.0 to (6) in equilibrium with small amounts of (7) (Scheme 1). In the presence of excess oxalate, another species (8) could be detected. For $[\text{Cr}(\text{ox})_3]^{3-}$ in the presence of $3 \times 10^{-3}\text{M}$ oxalic acid, Cordemans



Scheme 1

⁹² J. L. Reed, H. D. Gafney, and F. Basolo, *J. Amer. Chem. Soc.*, 1974, **96**, 1363.

⁹³ N. S. Rowan, M. Z. Hoffman, and R. M. Milburn, *J. Amer. Chem. Soc.*, 1974, **96**, 6060.

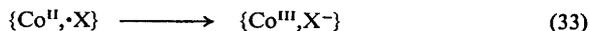
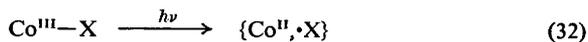
⁹⁴ L. Cordemans, J. D'Olieslager, J. Hendrix, and S. De Jaegere, *J. Phys. Chem.*, 1974, **78**, 1361.

*et al.*⁹⁴ also recorded a transient absorption spectrum similar to that reported for (8). At high flash intensities this species further photolysed to yield another transient species ascribed to $[\text{Co}(\text{ox})(\text{C}_2\text{O}_4^-)_2]^{2-}$.

Photolysis of $[\text{Co}(\text{NH}_3)_5\text{O}_2\text{CR}]^{2+}$ (R = Me or Et) in the presence of $\text{Co}^{\text{II}}(\text{N}_4)$ complexes (N_4 = cyclic tetra-amine or cyclic di-imine-diamine) provides the first preparative route to Co^{III} -alkyl compounds with a saturated equatorial ligand system.⁹⁵ The reactivity of CO_3^- , generated by photolysis of $[\text{Co}(\text{NH}_3)_4-\text{CO}_3]^+$, towards tryptophan and derivatives has been investigated.⁹⁶ Free radicals formed by photolysis of various Co^{III} complexes in NaClO_4 and H_2SO_4 glasses at low temperatures have been studied by e.s.r.⁹⁷ Sensitization of $[\text{Co}(\text{NH}_3)_6\text{Br}]^{2+}$ by the excited singlet state of acridinium or quinolinium ions can be most readily explained in terms of electron transfer.⁹⁸

Sheridan and Adamson⁹⁹ have reported the photochemistry of ligand-field band excitation of *cis*- α - $[\text{Co}^{\text{III}}(\text{tren})\text{ClX}]^{2+}$, *cis*- β - $[\text{Co}^{\text{III}}(\text{tren})\text{ClX}]^{2+}$, and $[\text{Co}^{\text{III}}(\text{tren})\text{ClX}]^{2+}$ (X = Cl^- or H_2O) [tren = $(\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2)_3$; tren = $(\text{NH}_2\text{CH}_2\text{CH}_2)_3\text{N}$]. In no case was photoredox behaviour observed ($\Phi < 10^{-6}$). Further, the photochemical reactions are very different from those induced thermally; for example, no light-induced Cl^- exchange was observed for the aquo-chloro-complexes although they readily undergo aquation in the dark. A striking difference was observed between the geometric isomers *cis*- α - and *cis*- β - $[\text{Co}(\text{tren})\text{Cl}_2]^+$. The *cis*- α -compound (9) is photostable, whereas the *cis*- β -compound (10) reacts to form *trans*- $[\text{Co}(\text{tren})\text{Cl}(\text{H}_2\text{O})]^{2+}$ (11) ($\Phi_{488} = 0.011$; $\Phi_{514} = 0.0080$). $[\text{Co}(\text{tren})\text{Cl}_2]^{2+}$ also photoaquates ($\Phi_{514} = 0.015$). These and other observations with Co^{III} complexes of uni-, bi-, and quadri-dentate ligands can be rationalized using rules similar to those applied to Cr^{III} complexes: (i) octahedral axis having average weakest crystal field will be labilized; (ii) on the labilized axis, the ligand with greatest ligand field is activated; (iii) for Co^{III} complexes heterolytic bond cleavage, possibly solvent assisted, is stereoretentive. Scheme 2 shows how this applies for various ammine complexes (labilized ligand marked with an asterisk).

Co^{III} derivatives of the type (13) undergo predominantly photo-aquation of the ligand X, even after irradiation in charge-transfer bands of the complex, a quite different photochemistry from that of Co^{III} ammine complexes.¹⁰⁰ It is proposed, however, that at shorter wavelengths, homolysis (32) does occur, but that a reverse



electron transfer takes place within the solvent cage (33) and that the Co^{III} species then rapidly aquates.

Photoredox reactions following irradiation in LF bands of Co^{III} complexes are unusual. Recently reported examples are those due to $[\text{Co}(\text{phen})_2\text{ox}]^+$ and

⁹⁵ T. S. Roche and J. F. Endicott, *Inorg. Chem.*, 1974, 13, 1575.

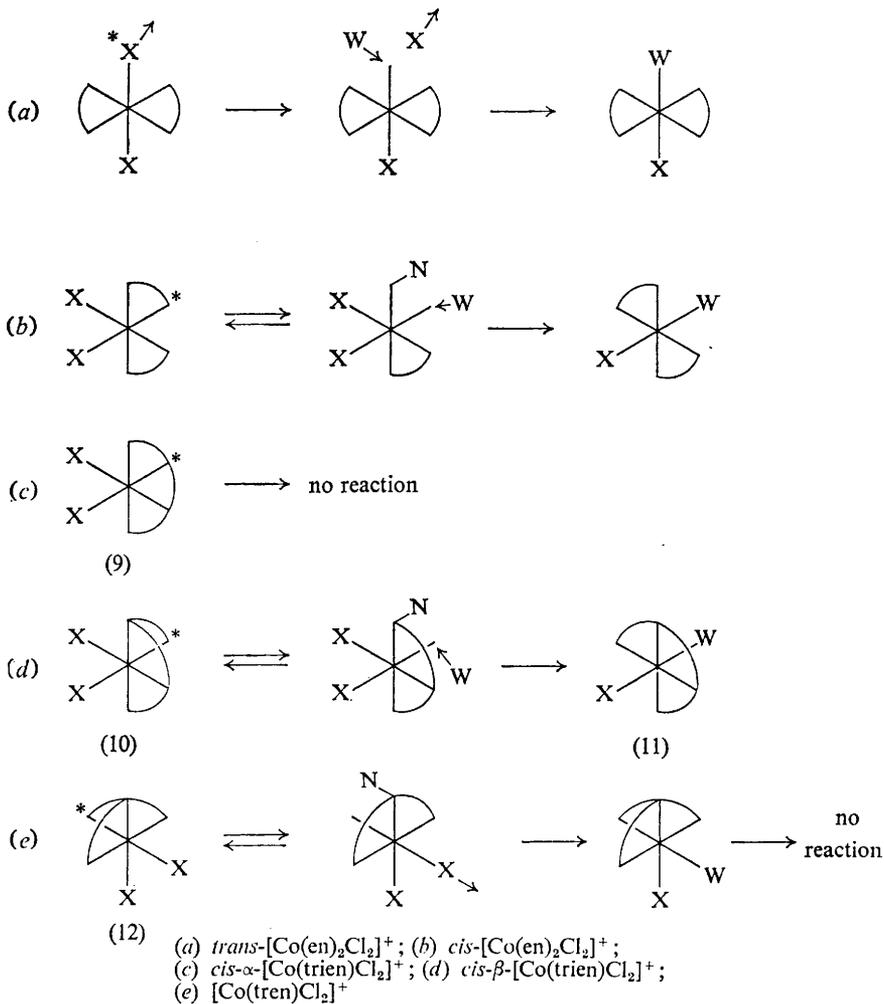
⁹⁶ S. N. Chen and M. Z. Hoffman, *J. Phys. Chem.*, 1974, 78, 2099.

⁹⁷ A. L. Poznyak and S. I. Arzhankov, *Doklady Akad. Beloruss. S.S.R.*, 1974, 18, 523.

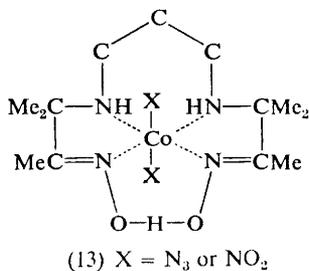
⁹⁸ H. Gafney and A. W. Adamson, *Coordination Chem. Rev.*, 1975, 16, 171.

⁹⁹ P. S. Sheridan and A. W. Adamson, *Inorg. Chem.*, 1974, 13, 2482.

¹⁰⁰ F. Diomedi-Camassei, E. Nocchi, G. Sartori, and A. W. Adamson, *Inorg. Chem.*, 1975, 14, 25.

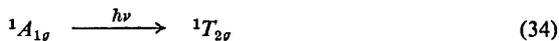


Scheme 2



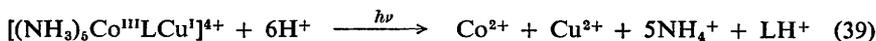
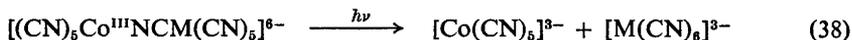
[Co(bipy)₂ox]⁺. [Co(phen)₃]³⁺ also undergoes photoreduction in the presence of oxalate, illustrating that the oxalate may function as either an inner- or an outer-sphere reducing agent.¹⁰¹

Irradiation of [Co(NH₃)₆]³⁺ in its LF ¹A_{1g} → ¹T_{2g} band with light (λ = 337 nm) from a pulsed nitrogen laser causes photoreduction of the complex.¹⁰² A two-photon mechanism is presented in which a ligand field state *LF absorbs a further photon to give the reactive CT state (steps 34—37).



A detailed analysis of the spectrum and temperature dependent lifetime of the emission of crystalline K₃Co(CN)₆ and comparison with a computer-generated fit have given information about the geometry and energy of the E(³T₁) state.¹⁰³ The effect of the counter-ions K⁺, Cd²⁺, and Ir³⁺ on the low-temperature emission of M(CN)₆³⁻ (M = Co, Rh, or Ir) has been discussed.¹⁰⁴

Two groups have reported photoreactions of cobalt-containing bridged dinuclear ions. Vogler and Kunkely¹⁰⁵ have studied the ions [(CN)₅Co^{III}NCM^{II}(CN)₅]⁶⁻ (M = Ru or Fe). These compounds exhibit an absorption band assigned to an M → Co intervalence CT band. Irradiation in this band causes reaction (38). In the case of M = Fe, in the absence of oxygen, the reaction is thermally reversible. Other workers¹⁰⁶ have investigated reaction (39), where L = O₂C(CH₂)_nCH=CHR or NH₂(CH₂)_nCH=CHR. Irradiation in the



Cu(*d*)-olefin(π*) band causes efficient reaction (Φ = 0.34—0.65), but the process is also observed following population of the Co^{III} ligand-field bands.

The photoreactions of alkyl-cobaloximes are discussed in the Organometallic Compounds section.

Rhodium and Iridium.—Ford¹⁵ has discussed the deficiencies of the ligand-field model for *d*⁶ systems¹⁴ when applied to Rh^{III} photochemistry. In particular he criticizes (i) the neglect of possible variations in the efficiency of radiationless processes in estimating the relative quantum yields for the reactions of the photoexcited states and (ii) the use of crystal-field parameters derived from the ground-state configuration.

¹⁰¹ C. H. Langford, C. P. J. Vuik, and N. A. P. Kane-Maguire, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 377.

¹⁰² K. M. Cunningham and J. F. Endicott, *J.C.S. Chem. Comm.*, 1974, 1024.

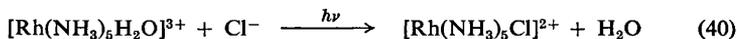
¹⁰³ K. W. Hipps and G. A. Crosby, *Inorg. Chem.*, 1974, **13**, 1543.

¹⁰⁴ A. Woelpl and D. Oelkrug, *Ber. Bunsengesellschaft phys. Chem.*, 1975, **79**, 394.

¹⁰⁵ A. Vogler and H. Kunkely, *Ber. Bunsengesellschaft phys. Chem.*, 1975, **79**, 83, 301.

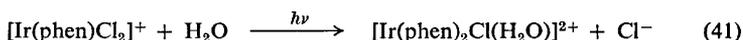
¹⁰⁶ J. K. Farr, L. G. Hulett, R. H. Lane, and J. K. Hurst, *J. Amer. Chem. Soc.*, 1975, **97**, 2654.

Photo-exchange of water from $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ in oxygen-18 enriched water proceeds efficiently on ligand-field excitation of the complex.¹⁰⁷ In the presence of Cl^- photo-anation (40) takes place.



The first report of luminescence from a transition-metal exciplex has been published.¹⁰⁸ In DMF solution the emission of $\text{cis-}[\text{Ir}(\text{phen})_2\text{Cl}_2]^+$ is quenched by naphthalene and replaced by a new structureless emission band at longer wavelengths.

In aqueous solution $\text{cis-}[\text{Ir}(\text{phen})_2\text{Cl}_2]^+$ undergoes Cl^- aquation (reaction 41) with a quantum yield of 0.05 independent of λ in the range 250–404 nm.¹⁰⁹ On flash photolysis a transient species, which is not an intermediate in reaction (41),



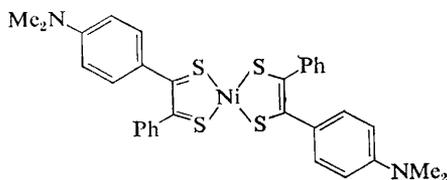
was observed. This was assigned to a species of the type $[\text{Cl}_2(\text{phen})\text{Ir}^{\text{IV}}(\text{phen}^-)]^+$ arising from the MLCT excited state.

$\text{mer-}[\text{Rh}^{\text{III}}(\text{py})_3(\text{ox})\text{Cl}]$ produces $\text{Rh}^{\text{I}}(\text{py})_3\text{Cl}$ on photolysis.¹¹⁰

Investigation by e.s.r. reveals that Rh^{3+} acts as an efficient electron-trapping centre when present in irradiated AgBr single crystals.¹¹¹

The emission of the complex $[\text{IrCl}_2(\text{phen})(5,6\text{-Me}_2\text{phen})]^+\text{Cl}^-$ in ethanol-methanol glasses at 77 K originates from at least two non-thermally equilibrated states.¹¹² The longer-lived component is assigned to a $\pi\text{-}\pi^*$ transition localized on the 5,6- Me_2phen ligand, while the other is ascribed to a $d\text{-}\pi^*$ transition involving the metal and the phen ligand. The emission spectra of substituted 1,10-phenanthroline complexes of Rh^{III} and Ir^{III} ,¹¹³ and of phosphine complexes of Rh^{I} and Ir^{I} ,¹¹⁴ have been discussed.

Nickel.—Studies of the time-resolved absorption spectra of (14) following mode-locked laser photolysis have been reported.¹¹⁵ Spectra could be recorded down



(14)

¹⁰⁷ P. C. Ford and J. D. Petersen, *Inorg. Chem.*, 1975, 14, 1404.

¹⁰⁸ R. Ballardini, G. Varani, L. Moggi, and V. Balzani, *J. Amer. Chem. Soc.*, 1974, 96, 7123.

¹⁰⁹ R. Ballardini, G. Varani, L. Moggi, V. Balzani, K. R. Olson, F. Scandola, and M. Z. Hoffman, *J. Amer. Chem. Soc.*, 1975, 97, 728.

¹¹⁰ A. W. Addison, R. D. Gillard, P. S. Sheridan, and L. R. H. Tipping, *J.C.S. Dalton*, 1974, 709.

¹¹¹ R. S. Eachus and R. E. Graves, *J. Chem. Phys.*, 1974, 61, 2860.

¹¹² R. J. Watts, *J. Amer. Chem. Soc.*, 1974, 96, 6186.

¹¹³ R. J. Watts and J. Van Houten, *J. Amer. Chem. Soc.*, 1974, 96, 4334.

¹¹⁴ G. L. Geoffroy, M. S. Wrighton, G. S. Hammond, and H. B. Gray, *J. Amer. Chem. Soc.*, 1974, 96, 3105.

¹¹⁵ D. Magde, B. A. Bushaw, and M. W. Windsor, *Chem. Phys. Letters*, 1974, 28, 263.

[Pt(dien)(H₂O)]²⁺ is the intermediate. The different behaviour of the two complexes is attributed to greater residual electrostatic attraction within the geminate pair of the iodo-complex.

Calculations have been carried out on the electronic structures of [Pt(CN)₄]²⁻,¹²⁵ [PtCl₄]²⁻ and [PdCl₄]²⁻,¹²⁶ and [Pt(C₂H₄)Cl₂]⁻.¹²⁷ The allowed u.v. transitions of [PtCl₄]²⁻ and [PdCl₄]²⁻ have been assigned.¹²⁸

Copper.—The labile complexes [Cu(mal)₂]²⁻ and Cu(mal) (mal = malonate) undergo photolysis in solution to give acetate and carbon dioxide but Cu^{II} is not permanently reduced.¹²⁹ On flash photolysis, however, transient species assigned to Cu^I compounds were observed. Cu^{II} derivatives of carboxylic acids have been used in the preparation of photosensitive plates.¹³⁰

Light has been found to inhibit the oxidation of peptides by molecular oxygen in Cu^{II} peptide complexes.¹³¹ A possible explanation is that light causes the decomposition of the Cu^{II}-peptide-O₂ complex required for the dark reaction.

Other reports consider the fluorescence thermochromism of Cu^I-base complexes,¹³² the fluorescence of Cu^I complexes of pyridine carboxylic acids,¹³³ the light-induced darkening of CuCl crystals,¹³⁴ and the quenching of flavosemiquinone radicals by Cu²⁺ and Ni²⁺.¹³⁵

Silver.—In a 1 : 1 complex, Ag⁺ quenches the fluorescence of tryptophan and induces a three-fold increase in the phosphorescence quantum yield.¹³⁶ This observation is attributed to an intramolecular heavy-atom effect in the complex.

Zinc.—Changes in the fluorescence and phosphorescence yields of β-diketone chelates of Zn²⁺, Be²⁺, and Al³⁺ have been attributed to interligand interactions.¹³⁷ Other authors have studied the luminescence properties of salicylalaniline chelates of Zn²⁺, Hg²⁺, Cd²⁺, and Be²⁺,¹³⁸ and of a dinuclear complex of ZnCl₂ with zinc salicylidene-toluidinate.¹³⁹

The photolysis of Zn(N₃)₂ in the solid state has been reported.¹⁴⁰

Mercury.—Two mechanisms are possible to explain the formation of I₂⁻ following flash photolysis of HgI₂. Following laser flash photolysis, it was possible both to observe HgI and to follow the formation of I₂⁻ (reaction 46).¹⁴¹ This shows that

¹²⁵ L. V. Interrante and R. P. Messmer, *Chem. Phys. Letters*, 1974, **26**, 225.

¹²⁶ R. P. Messmer, L. V. Interrante, and K. H. Johnson, *J. Amer. Chem. Soc.*, 1974, **96**, 3847.

¹²⁷ N. Roesch, R. P. Messmer, and K. H. Johnson, *J. Amer. Chem. Soc.*, 1974, **96**, 3855.

¹²⁸ B. G. Anex and N. Takeuchi, *J. Amer. Chem. Soc.*, 1974, **96**, 4411.

¹²⁹ J. Y. Morimoto and B. A. Degraff, *J. Phys. Chem.*, 1975, **79**, 326.

¹³⁰ K. Sugita, H. Ide, K. Tamura, and S. Suzuki, *Bull. Soc. Photogr. Sci. Technol. Japan*, 1973/4, **6**.

¹³¹ G. L. Burke, E. B. Paniago, and D. W. Margerum, *J.C.S. Chem. Comm.*, 1975, 261.

¹³² H. D. Hardt, *Naturwiss.*, 1974, **61**, 107.

¹³³ M. A. S. Goher and M. Dratovsky, *Naturwiss.*, 1975, **62**, 96.

¹³⁴ Y. V. Karyakin and A. V. Zaval'skaya, *Zhur. fiz. Khim.*, 1974, **48**, 346.

¹³⁵ I. V. Khudiyakov, A. V. Popkov, and V. A. Kuzmin, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1974, 2208.

¹³⁶ R. F. Chen, *Arch. Biochem. Biophys.*, 1975, **166**, 584.

¹³⁷ T. Ohno and S. Kato, *Bull. Chem. Soc. Japan*, 1974, **47**, 1901.

¹³⁸ M. I. Knyazhanskii, P. V. Gilyanovskii, O. A. Shchipakina, O. A. Osipov, V. V. Litvinov, and V. A. Kogan, *Zhur. priklad. Spektroskopii*, 1974, **21**, 183.

¹³⁹ V. V. Litvinov, M. I. Knyazhanskii, O. A. Osipov, V. A. Kogan, A. S. Rakov, P. V. Gilyanovskii, O. T. Asmaev, and A. S. Burlov, *Zhur. priklad. Spektroskopii*, 1974, **20**, 426.

¹⁴⁰ S. R. Yoganasarimhan and R. K. Sood, *J. Solid State Chem.*, 1974, **10**, 323.

¹⁴¹ P. Fournier de Violet, R. Bonneau, and S. R. Logan, *J. Phys. Chem.*, 1975, **78**, 1698.

process (47) cannot be operative and the mechanism is presumed to involve steps (45) and (46).



Akagi *et al.*¹⁴² have considered the effect of sulphur and mercuric sulphide on the photolysis of $\text{Hg}(\text{OAc})_2$ to give methylmercury compounds.

Lanthanides.—The quenching of Ce^{III} fluorescence in aqueous solution by $[\text{S}_2\text{O}_8]^{2-}$ involves irreversible electron transfer and results in overall photo-oxidation (48).¹⁴³ It was also shown that quenching of $\text{Ce}^{\text{III}*}$ by H_3O^+ does not result in the production of hydrogen atoms.



Energy transfer between an exciplex and a Eu^{III} chelate has been observed.¹⁴⁴ The exciplex was generated by the reaction of tri-*p*-tolylamine radical cation (D^\dagger) and the radical anion (A^\cdot) of either dibenzoylmethane or benzophenone. In the presence of Eu^{III} , quenching of the exciplex luminescence and appearance of Eu^{III} emission was detected.



Quenching of the singlet state of indole and its derivatives appears to proceed *via* electron transfer from the indole to the lanthanide ion, as the order of quenching efficiency ($\text{Eu}^{\text{III}} > \text{Yb}^{\text{III}} > \text{Sm}^{\text{III}} > \text{Tb}^{\text{III}} > \text{Gd}^{\text{III}} > \text{Ho}^{\text{III}} \sim \text{Dy}^{\text{III}}$) parallels the reduction potential.¹⁴⁵

Study of energy transfer from *o*-benzoylacetate to Eu^{III} in aqueous ethanol solutions shows that this occurs only when the species are complexed.¹⁴⁶ Assuming this, the stability constant for the complex was calculated, and good agreement found with the value determined potentiometrically. Although in crystalline $[\text{Eu}^{\text{III}}(\text{CF}_3\text{COCHCOCF}_3)_4] \cdot [\text{Bu}^\dagger\text{NH}_3]^+$ energy transfer from the β -diketone ligand to the Eu^{III} occurs *via* the triplet state,^{147a} in $[\text{Eu}^{\text{III}}(\text{PhCOCHCOCF}_3)_4] \cdot [\text{pipH}]^+$ (pip = piperidine) direct ligand singlet to Eu^{III} transfer takes place.^{147b} Other authors have reported on the luminescence properties of Eu^{III} complexes of β -diketones^{148–151} and Schiff bases,¹⁵² and on the quenching of $\text{Eu}(\text{R}\text{COCH}$ -

¹⁴² H. Akagi, Y. Fujita, and E. Takabatake, *Chem. Letters*, 1975, 171; *Nippon Kagaku Kaishi*, 1974, 1180; H. Akagi, E. Takabatake, and Y. Fujita, *Chem. Letters*, 1974, 761.

¹⁴³ R. W. Matthews and T. J. Sworski, *J. Phys. Chem.*, 1975, 79, 681.

¹⁴⁴ R. E. Hemingway, S.-M. Park, and A. J. Bard, *J. Amer. Chem. Soc.*, 1975, 97, 200.

¹⁴⁵ R. W. Ricci and K. B. Kilichowski, *J. Phys. Chem.*, 1974, 78, 1953.

¹⁴⁶ S. P. Tanner and D. L. Thomas, *J. Amer. Chem. Soc.*, 1974, 96, 706.

¹⁴⁷ (a) C. R. S. Dean and T. M. Shepherd, *J.C.S. Faraday II*, 1975, 71, 146; (b) C. R. S. Dean and T. M. Shepherd, *Chem. Phys. Letters*, 1975, 32, 480.

¹⁴⁸ G. D. R. Napier, J. D. Neilson, and T. M. Shepherd, *Chem. Phys. Letters*, 1975, 31, 328.

¹⁴⁹ B. A. Knyazev and E. P. Fokin, *Zhur. priklad. Spektroskopii*, 1974, 20, 818.

¹⁵⁰ G. A. Cotton, F. A. Hart, and G. P. Moss, *J.C.S. Dalton*, 1975, 221.

¹⁵¹ R. A. Puko, N. N. Mitkina, V. V. Kuznetsova, V. N. Kotlo, and V. S. Khomenko, *Zhur. priklad. Spektroskopii*, 1974, 21, 736.

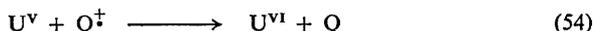
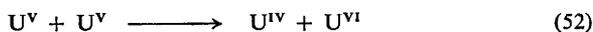
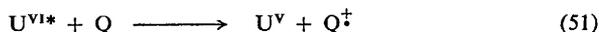
¹⁵² V. F. Zolin, V. A. Kudryashova, V. V. Kuznetsova, and T. I. Razvina, *Zhur. priklad. Spektroskopii*, 1974, 21, 831.

COR)₃ (R = Me or Ph) phosphorescence by anthracene and α -naphthylamine.¹⁵³

The rate constant for Tb³⁺ (⁵D₄) to Nd³⁺ energy transfer is dependent on the extent of complexation of the ions, increasing markedly with the number of anion (AcO⁻) groups present between donor and acceptor.¹⁵⁴ By determining the rate of transfer as a function of [OAc⁻] it was possible to estimate the stability constants for the various complex ions present.

Stein and Wuerzberg^{155a} have reported results on the fluorescence yields and lifetimes for Tb³⁺, Dy³⁺, Sm³⁺, Pr³⁺, and Tm³⁺ in H₂O and D₂O solutions. From consideration of these and earlier results, it was shown that solvent isotope effects on the rates of radiationless decay are expected to be high when $(E/\hbar\omega) = 2-5$ (E is the energy gap between the emitting excited state and the ground state and $\hbar\omega$ the vibrational quantum energy of the O—H or O—D bond). Within this range the energy-gap law applies, whereas for larger energy gaps other deactivating pathways are more efficient. The same authors^{155b} have shown that the quantum yield for Eu³⁺ emission is dependent on the excitation wavelength and they discuss critically the methods to be used in measuring emission quantum yields for rare earth ions. Other authors have discussed the fluorescence of Tb³⁺¹⁵⁶ and Nd³⁺^{157, 158} in POCl₃, SnCl₄.

Uranium.—The mechanism for photoreduction of UO₂²⁺ (U^{VI}) by many organic compounds (Q) may be represented by reactions (51)—(55). Chibisov and co-workers¹⁵⁹ have followed the decay of the U^V species formed after flash photolysis



of UO₂²⁺ in the presence of ethanol, ascorbic acid, and hydroquinone. For hydroquinone (54) is the only process involved in consumption of U^V, whereas for ethanol, at these flash intensities, step (52) is most important.

Quantum yields for the photoreduction of UO₂²⁺ by ethanol using light from an argon ion laser ($\lambda = 476$ and 514 nm) and a neon laser (633 nm) have been reported.^{160a} At 633 nm, the authors assume that the light is absorbed by water bonded to the UO₂²⁺. The variation of quantum yield with temperature in the

¹⁵³ B. D. Joshi, A. G. Page, and B. M. Patel, *Z. phys. Chem. (Leipzig)*, 1974, **255**, 103.

¹⁵⁴ V. P. Gruzdev and V. L. Ermolaev, *Optika i Spektroskopiya*, 1974, **37**, 1097.

¹⁵⁵ (a) G. Stein and E. Wuerzberg, *J. Chem. Phys.*, 1975, **62**, 208; (b) G. Stein and E. Wuerzberg, *Chem. Phys. Letters*, 1974, **29**, 21.

¹⁵⁶ P. Tokousbalides and J. Chrysochoos, *Chem. Phys. Letters*, 1974, **29**, 226.

¹⁵⁷ T. K. Andreeva, M. E. Zhabotinskii, L. V. Levkin, and V. I. Ralchenko, *Optika i Spektroskopiya*, 1974, **37**, 927.

¹⁵⁸ O. V. Yanush, G. O. Karapetyan, V. I. Mosichev, and S. V. Chinyakov, *Zhur. priklad. Spektroskopii*, 1974, **20**, 431.

¹⁵⁹ G. I. Sergeeva, A. K. Chibisov, L. V. Levshin, A. V. Karyakin, B. F. Myasoedov, and A. A. Nemodruk, *Khim. vysok. Energii*, 1974, **8**, 358.

¹⁶⁰ (a) J. T. Bell and S. R. Buxton, *J. Inorg. Nuclear Chem.*, 1974, **36**, 1575; (b) J. T. Bell and S. R. Buxton, *ibid.*, 1975, **37**, 1469.

range 25–87 °C has also been studied.^{160b} The photoreduction of UO_2^{2+} by citric acid gives U^{IV} , acetone, and carbon dioxide as products.¹⁶¹ Quantum yields are pH dependent, and it is proposed that intramolecular decomposition of UO_2^{2+} -citrate complexes is involved.

On irradiation into a band corresponding to co-ordinated pyridine, $\text{UO}_2(\text{py})_2(\text{NO}_3)_2$ undergoes photosolvation [reaction (56)].¹⁶² Pyridine photoproducts are



also formed but it was shown that these arise as a result of a secondary photo-reaction of the liberated pyridine. Irradiation of $\text{UO}_2(\text{py})_2\text{Cl}_2$ in dry ethanol gave $(\text{pyH})_2\text{U}^{\text{V}}\text{OCl}_5$ and $\text{U}(\text{OEt})_6$.¹⁶³ The photochemical processes following excitation of $[\text{U}^{\text{IV}}\text{Cl}_6]^{2-}$ and $[\text{U}^{\text{VI}}\text{O}_2\text{Cl}_4]^{2-}$ in their (Cl^- to metal) CT bands have been discussed.¹⁶⁴

Quenching of UO_2^{2+} emission by inorganic ions has been investigated.¹⁶⁵ For anions, the order of quenching ($\text{I}^- > \text{SCN}^- > \text{Br}^- > \text{Cl}^- > \text{F}^- > \text{CN}^-$) suggests strongly that an electron transfer mechanism is operative. For metal aquo-ions no single correlation was possible, probably indicating that several types of deactivating process are involved. The authors also showed that energy transfer from UO_2^{2+} results in sensitization of Eu^{III} emission and in the sensitized photo-aquation of $[\text{Co}(\text{CN})_6]^{3-}$ and $[\text{Cr}(\text{en})_3]^{3+}$. Other authors¹⁶⁶ have reported the quenching by Tl^+ of UO_2^{2+} emission and of its photoreduction by lactic acid ($k_q = 5.2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 22 °C).

The spectrum of the triboluminescence (*i.e.* emission caused by mechanical stress) of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is similar to that for photo-induced luminescence.¹⁶⁷ Possible causes for this effect are electrical excitation (*i.e.* pressure-induced electrochemiluminescence), intermolecular interactions, and intramolecular deformations. Arguments are presented to show that the third mechanism is not important in this case. Other relevant publications are concerned with electrochemiluminescence of UO_2^{2+} in perchloric acid,¹⁶⁸ absorption and luminescence spectra of UO_2^{2+} in solution,¹⁶⁹ and detailed analyses of the emission spectrum of crystalline UO_2^{2+} salts at low temperatures.^{170–174}

¹⁶¹ A. Ohyoshi and K. Uneo, *J. Inorg. Nuclear Chem.*, 1974, **36**, 379.

¹⁶² O. Traverso, V. Carassiti, R. Portanova, and P. A. Vigato, *Inorg. Chim. Acta*, 1974, **9**, 227.

¹⁶³ O. Traverso, R. Portanova, and V. Carassiti, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 771.

¹⁶⁴ G. Condorelli, L. L. Costanzo, S. Pistara, and E. Tondello, *Inorg. Chim. Acta*, 1974, **10**, 115.

¹⁶⁵ R. Matsushima, H. Fujimori, and S. Sakuraba, *J.C.S. Faraday I*, 1974, **70**, 1702.

¹⁶⁶ Y. Yokoyama, M. Moriyasu, and S. Ikeda, *J. Inorg. Nuclear Chem.*, 1974, **36**, 385.

¹⁶⁷ J. I. Zink, *Inorg. Chem.*, 1975, **14**, 555.

¹⁶⁸ R. G. Bulgakov, V. P. Kazakov, G. S. Parshin, and G. L. Sharipov, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1974, 1916.

¹⁶⁹ D. D. Pant and H. B. Tripathi, *J. Luminescence*, 1974, **8**, 492.

¹⁷⁰ L. V. Volod'ko, A. I. Komyak, G. P. Vitkovskii, and S. E. Slepstov, *Zhur. priklad. Spektroskopii*, 1974, **20**, 634.

¹⁷¹ V. I. Belomestnykh, V. I. Burkov, V. A. Kizel, Y. I. Krasilov, V. A. Madii, and R. N. Shchelokov, *Zhur. priklad. Spektroskopii*, 1974, **20**, 814.

¹⁷² L. V. Volod'ko, A. N. Sevchenko, A. I. Komyak, and D. S. Umreiko, *Doklady Akad. Nauk Beloruss. S.S.R.*, 1974, **18**, 601.

¹⁷³ A. P. Abramov and N. A. Tolstoi, *Optika i Spektroskopiya*, 1974, **37**, 360.

¹⁷⁴ A. P. Abramov and I. K. Razumova, *Optika i Spektroskopiya*, 1975, **38**, 565.

2 Transition-metal Organometallics and Low-oxidation-state Compounds

The photochemistry of metal carbonyl compounds has been reviewed.¹⁷⁵

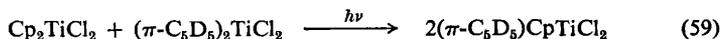
The relationship between photochemistry in low-temperature matrices and atom synthesis methods has been discussed with special reference to metal carbonyls.¹⁷⁶ Both of these types of study have been useful in allowing the determination of spectroscopic properties, and hence of the structures, of species such as $\text{Cr}(\text{CO})_6$ and $\text{Fe}(\text{CO})_4$, which at room temperature are highly reactive. One particular problem has been whether the structures observed for these compounds in rare-gas matrices might differ from those in the gas phase because of constraints in the matrices. Recent articles by Burdett have described MO calculations of the structures of $\text{M}(\text{CO})_x$ and $\text{M}(\text{N}_2)_x$ species ($x = 2-6$)^{177a} and a method for predicting the geometry of these and other binary transition-metal complexes.^{177b} The results of these calculations are in good agreement with the observed structures of $\text{Fe}(\text{CO})_4$ ¹⁷⁸ and $\text{Cr}(\text{CO})_6$ ¹⁷⁹ in rare-gas matrices.

Recent examples of preparative applications of photosubstitution reactions of metal carbonyls are collected in Table 5 (see p. 193). Others, less suited to tabular presentation, are discussed below in the section dealing with the particular element. In general, synthetic methods involving initial photochemical formation of the metal carbonyl-THF complex, followed by thermal reaction of this complex with an added substituent, have not been included.

Titanium, Zirconium, and Hafnium.—Several reports on the photochemistry of titanocene derivatives have appeared this year. Harrigan *et al.*¹⁸⁰ observed that the photolysis ($\lambda > 480$ nm) of Cp_2TiCl_2 in chlorinated hydrocarbons gave CpTiCl_3 , and they proposed that light-induced cleavage of the Ti-Cp bond occurs, as in reactions (57) and (58). In support of this mechanism, photo-



decomposition in neat benzene is inefficient, leading to CpTiCl_2 in low yield. Similarly no evidence for Ti-Br bond rupture was found on photolysis ($\lambda > 580$ nm) of Cp_2TiBr_2 in chloroform. [With Cp_2TiMe_2 ($\lambda > 300$ nm), however, cleavage of the Ti-Me bond was observed.] Under somewhat different irradiation conditions ($\lambda = 313$ nm), Vitz and Brubaker¹⁸¹ observed the exchange reaction (59), while in the presence of methanol $\text{Cp}(\text{OMe})\text{TiCl}_2$ was formed.



These findings are consistent with a recent report of the photoelectron spectra of Cp_2MCl_2 (M = Ti, Zr, or Hf), which shows that transitions involving electron

¹⁷⁵ M. Wrighton, *Chem. Rev.*, 1974, **74**, 401.

¹⁷⁶ J. J. Turner, *Angew. Chem.*, 1975, **87**, 326; *Angew. Chem. Internat. Edn.*, 1975, **14**, 304.

¹⁷⁷ (a) J. K. Burdett, *J.C.S. Faraday II*, 1974, **70**, 1599; (b) J. K. Burdett, *Inorg. Chem.*, 1975, **14**, 375.

¹⁷⁸ M. Poliakoff and J. J. Turner, *J.C.S. Dalton*, 1974, 2276.

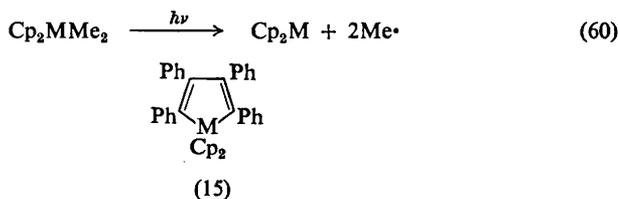
¹⁷⁹ R. N. Perutz and J. J. Turner, *Inorg. Chem.*, 1975, **14**, 262.

¹⁸⁰ R. W. Harrigan, G. S. Hammond, and H. B. Gray, *J. Organometallic Chem.*, 1974, **81**, 79.

¹⁸¹ E. Vitz and C. H. Brubaker, *J. Organometallic Chem.*, 1974, **82**, C16.

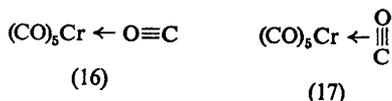
transfer from the cyclopentadienyl ring to the empty *d*-orbitals of the metal occur at lower energy than those arising from the Cl ligands.¹⁸²

Photolysis of Cp_2MMe_2 ($\text{M} = \text{Ti}, \text{Zr}, \text{or Hf}$) leads to the corresponding metallocenes, which may be isolated if the solvent is inert.¹⁸³ Irradiation in the presence of diphenylacetylene yields the metallocycle (15).

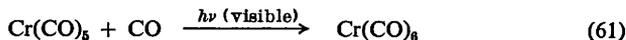


Niobium.—The reactions of Cp_2NbH_2 , generated photolytically from *t*-butylperoxide and Cp_2NbH_3 , have been studied by e.s.r.^{184, 185}

Chromium, Molybdenum, and Tungsten.—The debate about the structure of $\text{Cr}(\text{CO})_5$ has continued this year. Perutz and Turner¹⁷⁹ have analysed the i.r. spectra of $\text{M}(\text{CO})_5$ ($\text{M} = \text{Cr}, \text{Mo}, \text{or W}$) formed by photolysis of ^{13}CO -enriched $\text{M}(\text{CO})_6$ in argon or methane matrices at 20 K. In all cases the spectrum of the isotopically substituted $\text{M}(\text{CO})_5$ agrees with that calculated for a square-pyramidal (C_{4v}) structure and is inconsistent with that for the trigonal-bipyramidal (D_{3h}) isomer. Evidence is also presented that the matrix material is weakly co-ordinated to the complex. On the other hand, Kuendig and Ozin¹⁸⁶ have interpreted spectra recorded on condensing Cr atoms in CO matrices at 10 K as indicating that $\text{Cr}(\text{CO})_5$ exists as the D_{3h} form. They have also suggested that the species produced by photolysis of $\text{Cr}(\text{CO})_6$ is an isomeric compound (16)



or (17). However, both Turner¹⁷⁹ and Braterman¹⁸⁷ have convincingly argued that both these proposals are incorrect. In a later publication Ozin *et al.*¹⁸⁸ agree that the species formed photochemically is the C_{4v} isomer and report that the fragment they assign to the D_{3h} is converted into the C_{4v} structure on annealing the matrix at 40–45 K.



It has previously been shown that recombination of the fragments formed on photolysis of $\text{Cr}(\text{CO})_6$ in methane matrices may be induced by irradiation in the

¹⁸³ G. Condorelli, I. Fragala, A. Centineo, and E. Tondello, *J. Organometallic Chem.*, 1975, **87**, 311.

¹⁸⁸ H. Alt and M. D. Rausch, *J. Amer. Chem. Soc.*, 1974, **96**, 5936.

¹⁸⁴ I. H. Elson, J. K. Kochi, U. Klabunde, L. E. Manzer, G. W. Parshall, and F. N. Tebbe, *J. Amer. Chem. Soc.*, 1974, **96**, 7374.

¹⁸⁵ I. H. Elson and J. K. Kochi, *J. Amer. Chem. Soc.*, 1975, **97**, 1263.

¹⁸⁶ E. P. Kuendig and G. A. Ozin, *J. Amer. Chem. Soc.*, 1974, **96**, 3820.

¹⁸⁷ J. D. Black and P. S. Braterman, *J. Amer. Chem. Soc.*, 1975, **97**, 2908.

¹⁸⁸ H. Huber, E. P. Kuendig, G. A. Ozin, and A. J. Poe, *J. Amer. Chem. Soc.*, 1975, **97**, 308.

absorption band ($\lambda_{\text{max}} = 489 \text{ nm}$) of $\text{Cr}(\text{CO})_6$. This reaction has now been stimulated using plane-polarized light.¹⁸⁹ Figure 3 illustrates the polarized i.r. and visible spectra of $\text{Cr}(\text{CO})_6$ after 15 min of such irradiation. Two effects may be observed. Firstly, as the absorption band corresponds to a ${}^1A_1 \rightarrow {}^1E$ transition

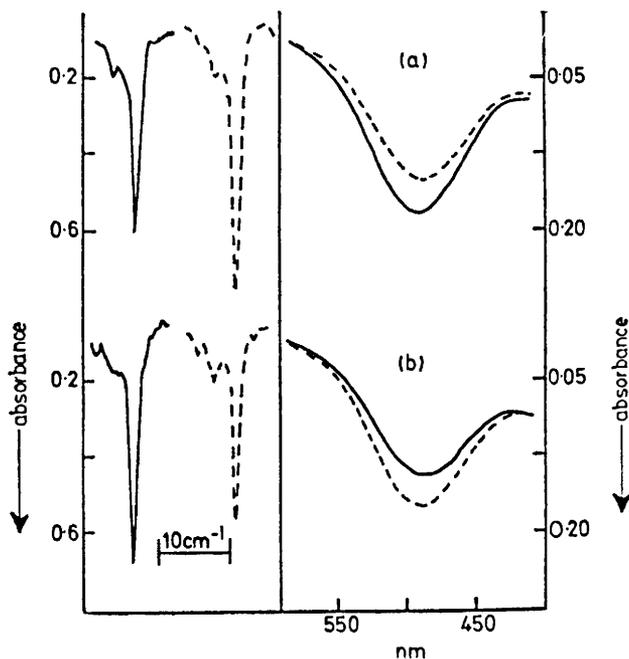


Figure 3 Polarized absorption spectra of $\text{Cr}(\text{CO})_6$. A_1 C—O stretching vibration (i.r. = 1932 cm^{-1}) and electronic transition ($\lambda_{\text{max}} = 489 \text{ nm}$). —, polarizer \parallel ; - - - - -, polarizer \perp . Spectra taken after (a) 15 min \perp ; (b) 15 min \parallel photolysis with $\lambda > 375 \text{ nm}$
(Reproduced from *J.C.S. Chem. Comm.*, 1975, 157)

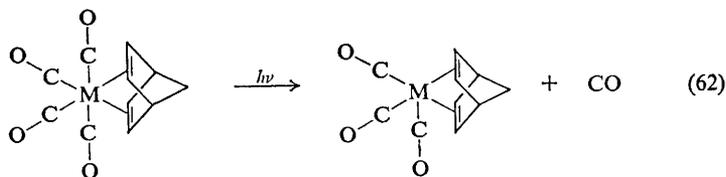
of $\text{Cr}(\text{CO})_6$, only correctly oriented $\text{Cr}(\text{CO})_6$ molecules may be excited. Secondly, as the intensities of the absorption bands of the other orientation actually increase, photo-orientation of the $\text{Cr}(\text{CO})_6$ must be taking place. It is suggested that this may involve an excited state of $\text{Cr}(\text{CO})_6$ having D_{3h} symmetry, as has been predicted by recent MO calculations.^{177a}

Flash photolysis of $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, $\text{W}(\text{CO})_6$, or $\text{Fe}(\text{CO})_5$ in the gas phase produced the respective metal atoms and also species assigned as Cr_2 and MoO_2 .¹⁹⁰ In the presence of O_2 the corresponding monoxides were detected, and CrH and CrD were formed on photolysis of $\text{Cr}(\text{CO})_6$ in a hydrogen or deuterium atmosphere.

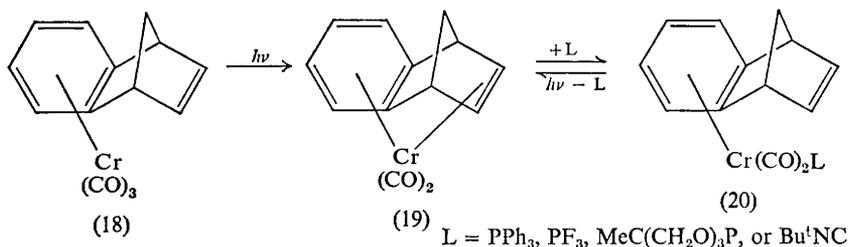
¹⁸⁹ J. K. Burdett, R. N. Perutz, M. Poliakoff, and J. J. Turner, *J.C.S. Chem. Comm.*, 1975, 157.

¹⁹⁰ A. N. Samoilova, Y. M. Efremov, D. A. Zhuravlev, and L. V. Gurvich, *Khim. vysok. Energii*, 1974, 8, 229.

In a study of the light-induced exchange of CO from (norbornadiene)M(CO)₄ (M = Cr, Mo, or W) using ¹³CO, it was found that the axial ligand is preferentially displaced (equation 62).¹⁹¹ Secondary reactions then cause scrambling



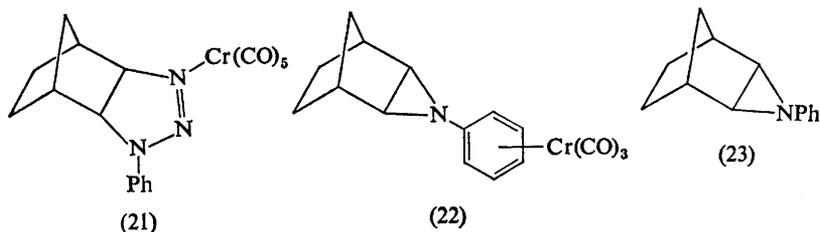
of the CO ligands. The authors suggest that a mechanism involving initial photodissociation of one of the metal–olefin bonds would be inconsistent with the experimental observations. In contrast to the thermal reaction, where the norbornadiene is readily displaced, photochemical reaction of (norbornadiene)Cr(CO)₄ with PPh₃ gives (norbornadiene)Cr(CO)₃(PPh₃).¹⁹² Photo-induced transformations of (benzonorbornadiene)Cr(CO)₃ derivatives are shown in Scheme 3.¹⁹³



Scheme 3

On photolysis (21), which is itself prepared photochemically, forms (22) and (23).¹⁹⁴

Recent publications dealing with (arene)chromium compounds include an investigation of the photodecomposition of (benzene)Cr(CO)₃ in cyclohexane



¹⁹¹ D. J. Darensbourg and H. H. Nelson, *J. Amer. Chem. Soc.*, 1974, **96**, 6511.

¹⁹² G. Platbrood and L. Wilputte-Steinert, *J. Organometallic Chem.*, 1975, **85**, 199.

¹⁹³ B. A. Howell and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, 1975, **97**, 2136.

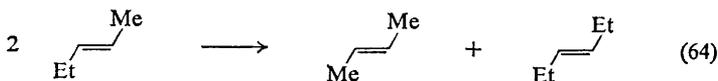
¹⁹⁴ M. Herberhold and W. Golla, *Chem. Ber.*, 1974, **107**, 3199.

solution,¹⁹⁵ the photochemical preparation of compounds of the type (arene)Cr(CO)LL', in which the Cr atom is asymmetric,^{196–198} a report on the photostability of (benzene)₂Cr in cyclohexane solution,¹⁹⁹ and two studies of the photoelectron spectra of various (arene)chromium compounds.^{200, 201}

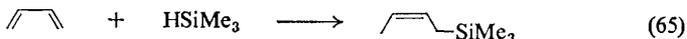
Photochemical substitution of a homoleptic isocyanide complex has been reported [equation (63); R = Ph or MePh; L = dimethylfumarate or fumaronitrile].²⁰²



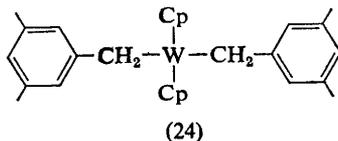
Previously reported photo-induced M(CO)₆-catalysed reactions of olefins and dienes include isomerizations, hydrogenations, and polymerizations. Recently two groups have reported that irradiation of W(CO)₆ in CCl₄ causes the metathesis of olefins, e.g. of pent-2-ene (reaction 64).^{203, 204}



Another novel photo-initiated reaction is the Cr(CO)₆-catalysed addition of silanes to 1,3-dienes (e.g. reaction 65).²⁰⁵ The reactions of photochemically generated Mo(CO)₆(mma) (mma = methylmethacrylate) with chlorinated hydrocarbons have been studied.²⁰⁶



Photolysis of Cp₂WH₂ in methanol produces the insertion products Cp₂W(OH)(OMe) and Cp₂W(Me)(OMe).²⁰⁷ In mesitylene solution compound (24) is formed.²⁰⁸ As in the analogous insertion into benzene,²⁰⁹ it is proposed that tungstenocene WCP₂ is the reactive intermediate. This species can also be



¹⁹⁵ V. N. Trembovler, B. M. Yavorskii, V. N. Setkina, N. V. Fok, N. K. Baranetskaya, and G. B. Zaslavskaya, *Doklady Akad. Nauk S.S.S.R.*, 1974, **218**, 1153.

¹⁹⁶ G. Jaouen and R. Dabard, *J. Organometallic Chem.*, 1974, **72**, 377.

¹⁹⁷ J. Nasielski and O. Denisoff, *J. Organometallic Chem.*, 1974, **81**, 385.

¹⁹⁸ G. Simmoneau, A. Meyer, and G. Jaouen, *J.C.S. Chem. Comm.*, 1975, 69.

¹⁹⁹ P. Borrell and E. Henderson, *Inorg. Chim. Acta*, 1975, **12**, 215.

²⁰⁰ J. A. Connor, L. M. R. Derrick, and I. H. Hillier, *J.C.S. Faraday II*, 1974, **70**, 941.

²⁰¹ M. F. Guest, I. H. Hillier, B. R. Higginson, and D. R. Lloyd, *Mol. Phys.*, 1975, **29**, 113.

²⁰² K. Iuchi, S. Asada, and A. Sugimori, *Chem. Letters*, 1974, 801.

²⁰³ P. Krausz, F. Garnier, and J. E. Dubois, *J. Amer. Chem. Soc.*, 1975, **97**, 437.

²⁰⁴ A. Agapiou and E. McNelis, *J.C.S. Chem. Comm.*, 1975, 187.

²⁰⁵ M. S. Wrighton and M. A. Schroeder, *J. Amer. Chem. Soc.*, 1974, **96**, 6235.

²⁰⁶ C. H. Bamford and I. Sakamoto, *J.C.S. Faraday I*, 1974, **70**, 344.

²⁰⁷ L. Farrugia and M. L. H. Green, *J.C.S. Chem. Comm.*, 1975, 416.

²⁰⁸ K. Elmitt, M. L. H. Green, R. A. Forder, I. Jefferson, and K. Prout, *J.C.S. Chem. Comm.*, 1974, 747.

²⁰⁹ C. Giannotti and M. L. H. Green, *J.C.S. Chem. Comm.*, 1972, 1114.

Photochemistry of Inorganic and Organometallic Compounds

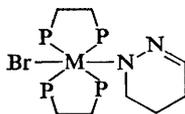
generated efficiently by photo-decarbonylation of $\text{Cp}_2\text{W}(\text{CO})$ and this method has been employed as a route to various alkyne and alkene derivatives.²¹⁰

Attempts to develop the photochemically induced and thermally reversible reaction (66) as a photochromic system have been unsuccessful.²¹¹ Photolysis of



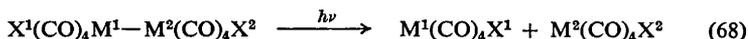
$[(\text{Me}_5\text{Cp})\text{Mo}(\text{CO})_3]_2$ gives $[(\text{Me}_5\text{Cp})\text{Mo}(\text{CO})_2]_2$ probably *via* cleavage of the Mo—Mo bond.²¹²

Some remarkable reactions of $\text{M}(\text{N}_2)_2(\text{dpe})_2$ [$\text{M} = \text{W}$ or Mo ; $\text{dpe} = 1,2$ -bis(diphenylphosphino)ethane] have been reported. Addition of an alkyl group to the dinitrogen ligand takes place during photolysis in the presence of RBr in benzene solution (reaction 67) ($\text{R} = \text{Me}$, Et , or Bu^t).²¹³ In THF solution compounds of type (25), in which the ligating N_2 has apparently displaced the oxygen from THF, are also formed.²¹⁴

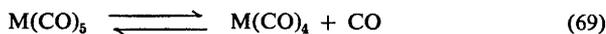


(25)

Manganese and Rhenium.—Wrighton and Ginley²¹⁵ have shown that photolysis of compounds $\text{X}^1(\text{CO})_4\text{M}^1-\text{M}^2(\text{CO})_4\text{X}^2$ [*i.e.* $\text{Mn}_2(\text{CO})_{10}$, $\text{Re}_2(\text{CO})_{10}$, $\text{MnRe}(\text{CO})_{10}$, $\text{Mn}_2(\text{CO})_9(\text{PPh}_3)$, and $\text{Mn}_2(\text{CO})_8(\text{PPh}_3)_2$] causes homolysis of the metal-metal bonds with high quantum efficiency (equation 68). The fragments have been



trapped with CCl_4 , PhCH_2Cl , Ph_3CCl , and I_2 . It is also suggested these species are thermally labile undergoing either dissociation (69) or association with a ligand present in solution (70).



Byers and Brown²¹⁶ have also presented evidence for the lability of $\text{Re}(\text{CO})_5$, although they propose that a dissociative process (69) is most important. They have also demonstrated that on photolysis $\text{Re}_2(\text{CO})_{10}$ activates molecular hydrogen, the important step being (71).^{216a} On irradiation, $\text{Re}_2(\text{CO})_{10}$ acts as a

²¹⁰ K. L. T. Wong, J. L. Thomas, and H. H. Britzinger, *J. Amer. Chem. Soc.*, 1974, **96**, 3694.

²¹¹ J. L. Hughey and T. J. Meyer, *Inorg. Chem.*, 1975, **14**, 946.

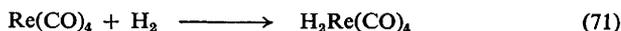
²¹² D. S. Ginley and M. S. Wrighton, *J. Amer. Chem. Soc.*, 1975, **97**, 3534.

²¹³ A. A. Diamantis, J. Chatt, G. J. Leigh, and G. A. Heath, *J. Organometallic Chem.*, 1975, **84**, C11.

²¹⁴ A. A. Diamantis, J. Chatt, G. A. Heath, and G. J. Leigh, *J.C.S. Chem. Comm.*, 1975, 27.

²¹⁵ M. S. Wrighton and D. S. Ginley, *J. Amer. Chem. Soc.*, 1975, **97**, 2065.

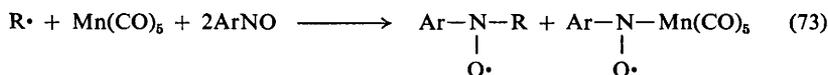
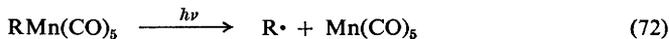
²¹⁶ (a) B. H. Byers and T. L. Brown, *J. Amer. Chem. Soc.*, 1975, **97**, 3260; (b) B. H. Byers and T. L. Brown, *ibid.*, p. 947.



catalyst for substitution reactions of $\text{HRe}(\text{CO})_5$ by phosphines.^{216b} Further details of the free-radical polymerization of methyl methacrylate on irradiation of $\text{Re}_2(\text{CO})_{10}$ have been published.²¹⁷

I.r. spectral data have been recorded for $\text{Re}(\text{CO})_5$ ²¹⁸ and for $\text{Mn}(\text{CO})_5$ ¹⁸⁸ prepared by metal atom reactions in CO matrices at 10 K. Symons and co-workers²¹⁹ have demonstrated that a species previously assigned²²⁰ to $\text{Re}(\text{CO})_5$ is in fact $\text{Re}(\text{CO})_5\text{O}_2$.

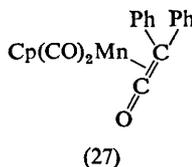
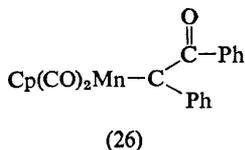
Evidence for the homolysis of the metal-carbon bond in $\text{R-Mn}(\text{CO})_5$ ($\text{R} = \text{Me}$ or PhCH_2) on irradiation has been provided by spin-trapping the radical species with nitrosodurene.²²¹ Similar results were obtained on irradiating the acyl compounds $\text{R}^1\text{COMn}(\text{CO})_5$ when the radical R^1 but not R^1CO was trapped. On photolysis of $\text{Mn}_2(\text{CO})_{10}$ in low concentration $\text{Mn}(\text{CO})_5$ was trapped, but at higher concentrations other unidentified species were also observed.



Photolysis of $\text{XRe}(\text{CO})_3\text{L}_2$ ($\text{X} = \text{Cl}$ or Br ; $\text{L} = \textit{trans}$ -3- or \textit{trans} -4-styrylpyridine) causes $\textit{trans} \rightarrow \textit{cis}$ isomerization of co-ordinated L with quantum yields and resulting photostationary states similar to those of the free ligand (Table 3).²²² As the lowest excited state is assigned to an intra-ligand excited state localized on the styrylpyridine, these results suggest that the perturbing effect upon co-ordination is small.

The photochemical disproportionation of $\text{Ti}[\text{Mn}(\text{CO})_5]_3$ to give $\text{TiMn}(\text{CO})_5$ and $\text{Mn}_2(\text{CO})_{10}$ has been described.²²³

The photoconversion of the carbene complex (26) to the keten complex (27) proceeds only in low yield because of the light-sensitive nature of the product.²²⁴



Photodecarbonylation of $\text{Mn}(\text{CO})_4(\text{B}_3\text{H}_8)$ leads to $\text{Mn}(\text{CO})_3(\text{B}_3\text{H}_8)$ in which the $[\text{B}_3\text{H}_8]^-$ acts as a terdentate ligand.²²⁵

²¹⁷ C. H. Bamford and S. U. Mullik, *J.C.S. Faraday I*, 1975, **71**, 625.

²¹⁸ H. Huber, E. P. Kuendig, and G. A. Ozin, *J. Amer. Chem. Soc.*, 1974, **96**, 5585.

²¹⁹ S. A. Fieldhouse, B. W. Fullam, G. W. Neilson, and M. C. R. Symons, *J.C.S. Dalton*, 1974, 567.

²²⁰ E. O. Fischer, E. Offhaus, J. Muller, and D. Nothe, *Chem. Ber.*, 1972, **105**, 1027.

²²¹ A. Hudson, M. F. Lappert, P. W. Lednor, and B. K. Nicholson, *J.C.S. Chem. Comm.*, 1974, 966.

²²² M. S. Wrighton, D. L. Morse, and L. Pdungsap, *J. Amer. Chem. Soc.*, 1975, **97**, 2073.

²²³ J. M. Burlitch and T. W. Theyson, *J.C.S. Dalton*, 1974, 828.

²²⁴ W. A. Herrmann, *Chem. Ber.*, 1975, **108**, 486.

²²⁵ D. F. Gaines and S. J. Hildebrandt, *J. Amer. Chem. Soc.*, 1974, **96**, 5574.

Table 3 Photoisomerization of co-ordinated styrylpyridines²²²

Compound	(t-c) (313 nm)	(t-c) (366 nm)	% cis at photostationary state			
			313 nm	366 nm	436 nm	
<i>trans</i> -3-Styrylpyridine	0.48	—	90	—	—	
<i>trans</i> -4-Styrylpyridine	0.38	—	88	—	—	
ClRe(CO) ₃ (<i>trans</i> -4-styrylpyridine) ₂	0.49	0.54	84	90	99	
BrRe(CO) ₃ (<i>trans</i> -4-styrylpyridine) ₂	0.64	0.51	99	98	> 99	
ClRe(CO) ₃ (<i>trans</i> -3-styrylpyridine) ₂	0.60	0.51	93	90	99	

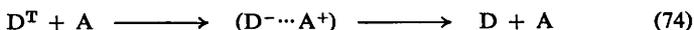
Iron, Ruthenium, and Osmium.—Although ferrocene has been extensively used as a quencher for triplet states of organic molecules, the mechanism for the quenching processes is by no means clear. Thus the observation²²⁶ that anthracene triplet ($E_T = 176 \text{ kJ mol}^{-1}$, $14\,700 \text{ cm}^{-1}$) is efficiently quenched by ferrocene ($E_T = 223 \text{ kJ mol}^{-1}$, $18\,600 \text{ cm}^{-1}$ from visible spectroscopy assignment²²⁷) appears to be incompatible with an energy-transfer mechanism. A flash photolysis study by Kikuchi *et al.* of the quenching of the triplet states of several organic molecules by ferrocene has led these authors to propose that E_T for ferrocene is *ca.* $15\,000 \text{ cm}^{-1}$. As shown in Table 4, triplet states having E_T lower

Table 4 Rate constants for the quenching of triplet states by ferrocene in ethanol solution²²⁸

Compound	E_T/cm^{-1}	Quenching rate constant/ $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
Triphenylene	23 800	6.5×10^9
Naphthalene	21 300	7.0×10^9
β -Acetonaphthone	20 700	6.0×10^9
1,2,5,6-Dibenzanthracene	18 300	5.0×10^9
Pyrene	16 800	6.0×10^9
Phenazine	15 250	4.6×10^9
Eosin	14 800	3.5×10^9
Anthracene	14 700	3.5×10^9
Perylene	12 600	1.3×10^9
Tetracene	10 250	4.6×10^7
Pentacene ^a	8000	$\leq 10^7$

^a In benzene solution.

than this value are still quenched but with reduced efficiency, and in these cases quenching *via* charge transfer is suggested.²²⁸ However, even in acetonitrile no ionic species were detected. The possibility that charge-transfer processes (74)



might be responsible for the quenching reactions of dibenzenechromium, ferrocene, and other iron organometallic compounds has been investigated and discounted at least for fluorenone and anthracene triplet states.²²⁹ In these cases an energy-transfer mechanism is preferred. Rate constants for quenching of benzil and $[\text{Ru}(\text{bipy})_3]^{2+}$ emission by ferrocene, ruthenocene, and various substituted metallocenes have been determined.²³⁰ The quenching efficiencies observed again suggest that neither charge transfer nor heavy-atom quenching pathways are important, and the results are consistent with energy transfer. The quenching of biacetyl phosphorescence by ferrocene in cyclohexane, chloroform, and carbon tetrachloride is diffusion controlled and therefore independent of the complexation of the ferrocene to the chlorinated solvent.²³¹

²²⁶ A. S. Fry, R. S. H. Liu, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1966, **88**, 4781.

²²⁷ Y. S. Sohn, D. N. Hendrickson, and H. B. Gray, *J. Amer. Chem. Soc.*, 1971, **93**, 3603.

²²⁸ M. Kikuchi, K. Kikuchi, and H. Kokubun, *Bull. Chem. Soc. Japan*, 1974, **47**, 1331.

²²⁹ A. Gilbert, J. M. Kelly, and E. Koerner von Gustorf, *Mol. Photochem.*, 1974, **6**, 225.

²³⁰ M. S. Wrighton, L. Páungsap, and D. L. Morse, *J. Phys. Chem.*, 1975, **79**, 66.

²³¹ F. Scandola, *Ann. Univ. Ferrara, Sez. 5*, 1974, **3**, 135.

All these quenching studies are therefore best explained by energy transfer to the triplet state of ferrocene. While no reproducible emission from ferrocene has been reported, luminescence from ruthenocene^{230, 232} and from 1,1'-diacetylruthenocene²³⁰ has recently been observed. The lifetime and quantum yield for emission of ruthenocene is markedly temperature dependent and this is attributed to thermal equilibration of the levels arising from spin-orbit coupling within the ³E₁ state.²³² A large Stokes' shift is observed indicating that the excited state of ruthenocene is substantially and symmetrically expanded. This distortion is certain to have important consequences on the quenching efficiencies of the metallocenes. Other reports deal with the electronic absorption spectra of ferrocene at 77 K,²³³ and *ab initio* calculations on excited states of ferrocene.²³⁴

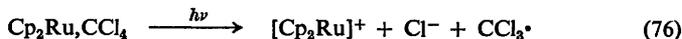
Quantum yields for photochemical decomposition of Cp₂M (M = Fe, Ru, Ni, or Co), (benzene)₂Cr, and their cations have been measured.¹⁹⁹ The 18-electron compounds were found to be photostable.

Electron transfer between ferrocene and nitrous oxide (reaction 75) takes place after excitation of a CT state of ferrocene (λ = 254 nm). No reaction is observed



for longer wavelength irradiation.²³⁵ Traverso *et al.* have reported on the photosensitivity of ferrocene-LiCl adducts,²³⁶ and improved methods for the photochemical preparation of [Cp₂Fe]⁺ from Cp₂Fe and CCl₄.^{237, 238}

In a similar fashion to Cp₂Fe, Cp₂Ru forms complexes with CCl₄ and other halogenocarbons. On irradiation of this complex [Cp₂Ru]⁺ is formed.^{239–241} With light corresponding to the maximum of the CTTS band of the complex (λ = 280 nm), the reaction is reported to proceed with Φ = 1.²⁴⁰ Other studies of the direct photolysis (λ = 313 or 365 nm), the naphthalene-sensitized reaction, and the quenching of the process by SmCl₃ or oxygen suggest that both singlet and triplet states of the complex are involved in reaction (76).²³⁹



Benzophenone-photosensitized hydrolysis of CpFe(Cp-CR¹=NR²) leads to the corresponding ketone or aldehyde CpFe(Cp-COR¹).²⁴² Photodecomposition of ferrocenyl ethers,²⁴³ and photochemical oxidation of ferrocene carboxylic acids on 254 nm irradiation have been discussed.²⁴⁴

²³² G. A. Crosby, G. D. Hager, K. W. Hipps, and M. L. Stone, *Chem. Phys. Letters*, 1974, 28, 497.

²³³ A. N. Nesmeyanov, B. M. Yavorskii, N. S. Kochetkova, E. I. Afrina, and N. S. Voroshilova, *Doklady Akad. Nauk S.S.S.R.*, 1974, 219, 123.

²³⁴ R. M. Rohmer, A. Veillard, and M. H. Wood, *Chem. Phys. Letters*, 1974, 29, 466.

²³⁵ J. A. Powell and S. R. Logan, *J. Photochem.*, 1974, 3, 189.

²³⁶ E. Horvath, S. Sostero, O. Traverso, and V. Carassiti, *Gazzetta*, 1974, 104, 1003.

²³⁷ O. Traverso, R. Rossi, and V. Carassiti, *Synth. React. Inorg. Metal-Org. Chem.*, 1974, 4, 309.

²³⁸ S. Sostero, O. Traverso, and R. Rossii, *Ann. Univ. Ferrara, Sez. 5*, 1974, 3, 183.

²³⁹ P. Borrell and E. Henderson, *J.C.S. Dalton*, 1975, 432.

²⁴⁰ O. Traverso, S. Sostero, and G. A. Mazzocchin, *Inorg. Chim. Acta*, 1974, 11, 237.

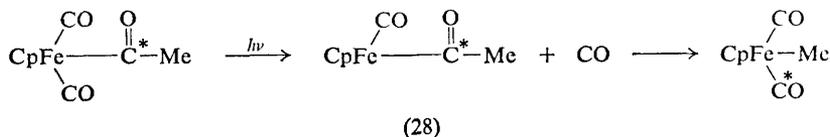
²⁴¹ O. Traverso and S. Sostero, *Ann. Univ. Ferrara, Sez. 5*, 1974, 3, 91.

²⁴² J. H. J. Peet and B. W. Rockett, *J. Organometallic Chem.*, 1975, 88, C1.

²⁴³ C. Baker and W. M. Horspool, *Tetrahedron Letters*, 1974, 3533.

²⁴⁴ O. Traverso, R. Rossi, and V. Carassiti, *Ann. Univ. Ferrara, Sez. 5*, 1974, 3, 103.

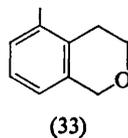
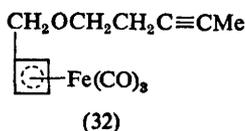
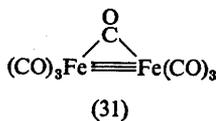
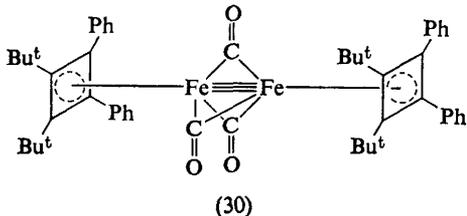
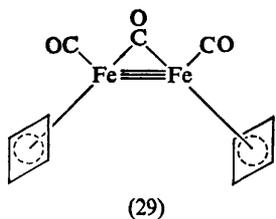
studies, Alexander²⁴⁸ has shown that for $\text{CpFe}(\text{CO})_2\text{COMe}$ the reaction proceeds by loss of a terminal CO group (Scheme 5). Species (28) may be trapped by PPh_3 , suggesting that the methyl migration is not synchronous with terminal-CO



Scheme 5

expulsion. The photodecarbonylation of each pair of enantiomers of $\text{CpFe}(\text{CO})_2(\text{PPh}_3)\{\text{C}(\text{O})\text{CH}_2\text{CHMePh}\}$ proceeds with high stereospecificity at both the Fe and C asymmetric centres.²⁴⁹ It is not clear however whether the reaction proceeds with retention or inversion of configuration at the Fe atom. Similar high stereospecificity has been obtained for the decarbonylation reaction of (1-Me-3-Ph-cyclopentadienyl) $\text{Fe}(\text{CO})(\text{PPh}_3)(\text{COMe})$,²⁵⁰ and of $\text{CpFe}(\text{CO})(\text{PPh}_3)(\text{COEt})$.²⁵¹ However, decarbonylation of $\text{CpFe}(\text{CO})(\text{PPh}_3)(\text{COMe})$ leads only to low optical activity in the product.²⁵²

Photolyses of (cyclobutadiene) $\text{Fe}(\text{CO})_3$ ²⁵³ and (1,2-diphenyl-3,4-di-*t*-butylcyclobutadiene) $\text{Fe}(\text{CO})_3$ ²⁵⁴ yield the products (29) and (30), respectively. By



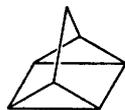
analogy with compound (29) it is suggested that (31) may be an important intermediate in reactions of $\text{Fe}(\text{CO})_4$ in solution.²⁵³ Irradiation of (32) and subsequent reaction with Ce^{IV} gives (33).²⁵⁵

The photo-induced reactions of $\text{Fe}(\text{CO})_5$ with strained hydrocarbons lead to a series of interesting compounds. Quadricyclane (34) reacts to give (35a), (36), and

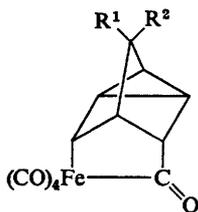
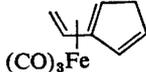
²⁵³ I. Fischler, K. Hildenbrand, and E. Koerner von Gustorf, *Angew. Chem.*, 1975, **87**, 35; *Angew. Chem. Internat. Edn.*, 1975, **14**, 54.

²⁵⁴ S. I. Murahashi, T. Mizoguchi, T. Hosokawa, I. Moritani, Y. Kai, M. Kohara, N. Yasuoka, and N. Kasai, *J.C.S. Chem. Comm.*, 1974, 563.

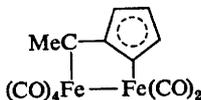
²⁵⁵ R. H. Grubbs, T. A. Pancoast, and R. A. Grey, *Tetrahedron Letters*, 1974, 2425.



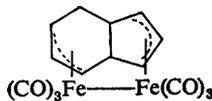
(34)

(35) a; R¹ = R² = H
b; R¹, R² = O

(36)

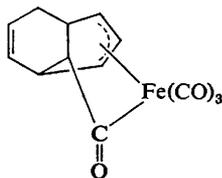


(37)

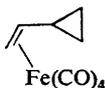


(38)

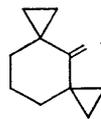
(37).^{256a} With quadricyclanone the major product is (35b). Reaction of homosemibullvalene gives (38) and (39) as well as the simple Fe(CO)₄ complex.^{256b} The Fe(CO)₄ complex (40) was isolated after photolysis of mixtures of Fe(CO)₅



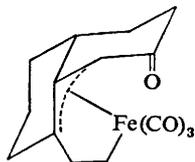
(39)



(40)



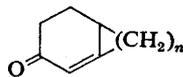
(41)



(42)



(43) n = 3 or 4



(44)

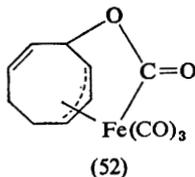
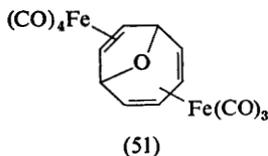
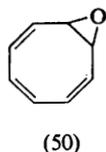
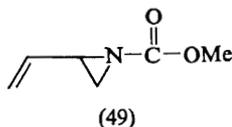
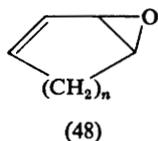
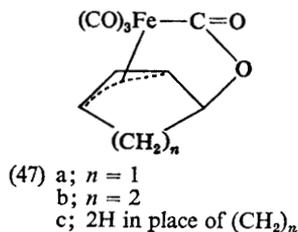
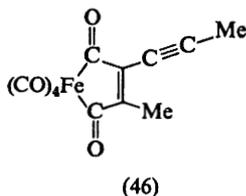
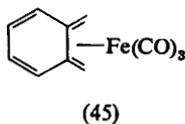
and vinylcyclopropane at $-50\text{ }^{\circ}\text{C}$.^{256c} While the dispirane compound (41) gives (42) as the main product on irradiation with Fe(CO)₅, the monospiranes (43) form the conjugated enones (44).²⁵⁷ The photoreaction of (45) and Fe(CO)₅ leads to a number of isomeric Fe₂(CO)₈(C₈H₈) complexes.²⁵⁸ Light-induced reaction of dimethyldiacetylene with Fe(CO)₅ yields (46).²⁵⁹

²⁵⁶ (a) R. Aumann, *J. Organometallic Chem.*, 1974, 76, C32; (b) R. Aumann, *ibid.*, 1974, 77, C33; (c) R. Aumann, *J. Amer. Chem. Soc.*, 1974, 96, 2631.

²⁵⁷ S. Sarel, A. Felzenstein, R. Victor, and J. Yovell, *J.C.S. Chem. Comm.*, 1974, 1025.

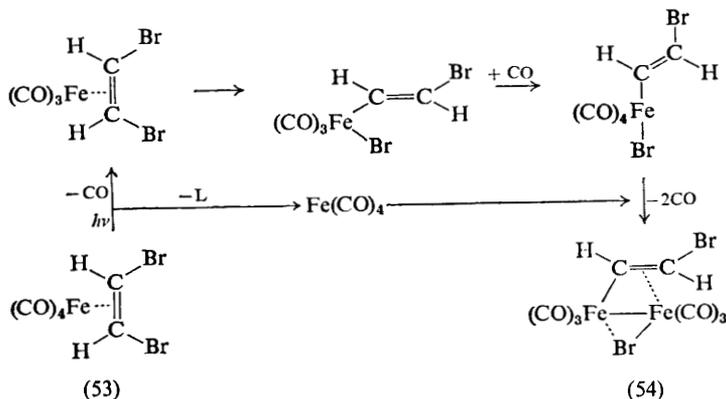
²⁵⁸ R. Victor and R. Ben-Shoshan, *J. Organometallic Chem.*, 1974, 80, C1.

²⁵⁹ R. C. Pettersen, J. L. Cihonski, F. R. Young, and R. A. Levenson, *J.C.S. Chem. Comm.*, 1975, 370.



Lactone derivatives (47) are the product of photochemical addition of $Fe(CO)_5$ to (48).²⁶⁰ Under similar conditions, (49) gives the analogous lactam compounds. Irradiation of (50) with $Fe(CO)_5$ produces (51) *via* (52), which may be isolated at low temperatures.²⁶¹

Excitation of $LFe(CO)_4$ ($L = cis$ - or $trans$ -dihalogenoethylene) causes both CO and L dissociation.²⁶² Typically irradiation of complex (53) leads to (54) (Scheme 6).



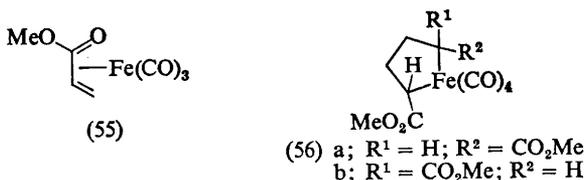
Scheme 6

²⁶⁰ R. Aumann, K. Froehlich, and H. Ring, *Angew. Chem.*, 1974, **86**, 309; *Angew. Chem. Internat. Edn.*, 1974, **13**, 275.

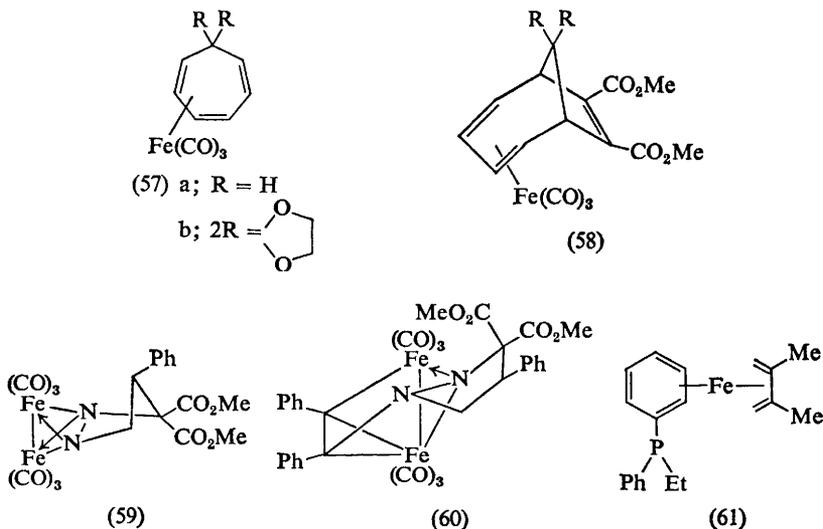
²⁶¹ R. Aumann and H. Averbek, *J. Organometallic Chem.*, 1975, **85**, C4.

²⁶² F. W. Grevels and E. Koerner von Gustorf, *Annalen*, 1975, 547.

Low-temperature ($-30\text{ }^{\circ}\text{C}$) photolysis of $\text{LFe}(\text{CO})_4$ ($\text{L} = \text{CH}_2=\text{CHCO}_2\text{Me}$) in the presence of L yields $\text{L}_2\text{Fe}(\text{CO})_3$ in two isomeric forms, in both of which L is co-ordinated to the metal by the olefinic double bond.²⁶³ On warming the solution to $0\text{ }^{\circ}\text{C}$ the ligand L is expelled and (55) is formed. At room temperature, however, the isomeric metallocycles (56a) and (56b) are the principal products from the photolysis reaction of $\text{LFe}(\text{CO})_4$ and L.



The cycloaddition of $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ to (57)⁻ giving (58) has been discussed in terms of the Woodward–Hoffmann Rules,²⁶⁴ although these Rules may not be strictly applicable to polyenes bearing transition-metal ligands. The light-induced addition of $\text{PhC}\equiv\text{CPh}$ to (59) gives (60).²⁶⁵



$\text{CpFe}(\text{CO})_2(\text{CH}_2\text{SiMe}_2\text{SiMe}_3)$ photoisomerizes to $\text{CpFe}(\text{CO})_2(\text{SiMe}_2\text{CH}_2\text{-SiMe}_3)$.²⁶⁶ The isocyanate complex $\text{CpFe}(\text{CO})_2(\text{NCO})$ is formed in low yield by photolysis of $\text{CpFe}(\text{CO})_2(\text{N}_3)$.²⁶⁷ Photochemical syntheses of $\text{LFe}(\text{CO})_3$ ($\text{L} =$

²⁶³ F. W. Grevels, D. Schulz, and E. Koerner von Gustorf, *Angew. Chem.*, 1974, **86**, 558; *Angew. Chem. Internat. Edn.*, 1974, **13**, 534.

²⁶⁴ R. E. Davis, T. A. Dodds, T. H. Hseu, J. C. Wagon, T. Devon, J. Tandredre, J. S. McKennis, and R. Pettit, *J. Amer. Chem. Soc.*, 1974, **96**, 7562.

²⁶⁵ C. Krueger and H. Kisch, *J.C.S. Chem. Comm.*, 1975, 65.

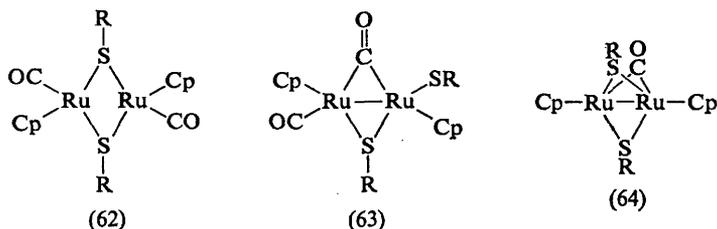
²⁶⁶ K. H. Pannell and J. R. Rice, *J. Organometallic Chem.*, 1974, **78**, C35.

²⁶⁷ A. Rosan and M. Rosenblum, *J. Organometallic Chem.*, 1974, **80**, 103.

1,2-dimethyl-1,2-dihydropyridazine-3,6-dione),²⁶⁸ and $[\text{Fe}(\text{CO})(\text{dienyl})(\text{diene})]^+$ ²⁶⁹ have been described.

Photo-induced replacement of the aromatic ligand in (61) by dimethylbutadiene,²⁷⁰ and of the arene in $(\text{arene})\text{RuCl}_2(\text{PR}_3)_3$ by other arenes²⁷¹ has been observed.

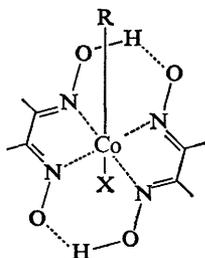
$\text{CpRu}(\text{CO})_2\text{SR}$ ($\text{R} = \text{C}_6\text{F}_5$) is more photoreactive than its iron analogue and, on photolysis, compounds (62)—(64) are produced.²⁷² The rearrangement of (62)



to (63), which is light-induced, is of a type not previously observed in the chemistry of organometallic compounds.

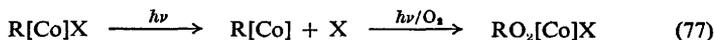
Cobalt, Rhodium, and Iridium.—Irradiation of vitamin B_{12} coenzyme or ethylcobalamin in the presence of a spin-trap (Bu^tNO or nitrosodurene) has allowed the trapping of the radicals formed by cleavage of the $\text{Co}-\text{C}$ bond.²⁷³

Alkylcobaloximes (65) are of interest as models for vitamin B_{12} . Giannotti and co-workers have previously shown that insertion of oxygen into the $\text{Co}-\text{C}$



- (65) a; $\text{R} = \text{Me}$
 b; $\text{R} = \text{Pr}^i$
 c; $\text{R} = \text{Bu}^t$
 d; $\text{R} = n\text{-pentyl}$
 e; $\text{R} = \text{cyclohexyl}$
 f; $\text{R} = \text{benzyl}$

bond, forming alkylperoxycobaloximes takes place, when alkylcobaloximes are photolysed in the presence of O_2 . It has been proposed in a recent publication that the initial step is photolysis of the $\text{Co}-\text{X}$ bond, followed by photocatalysed insertion of oxygen and recombination of the base X .²⁷⁴ However, e.s.r. spectra



²⁶⁸ A. N. Nesmeyanov, M. I. Rybinskaya, L. V. Rybin, A. V. Arutyunyan, L. G. Kuzmina, and Y. T. Struchkov, *J. Organometallic Chem.*, 1974, **73**, 365.

²⁶⁹ J. Ashley-Smith, D. V. Howe, B. F. G. Johnson, J. Lewis, and I. E. Ryder, *J. Organometallic Chem.*, 1974, **82**, 257.

²⁷⁰ I. Fischler and E. Koerner von Gustorf, *Z. Naturforsch.*, 1975, **30b**, 291.

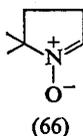
²⁷¹ M. A. Bennett and A. K. Smith, *J.C.S. Dalton*, 1974, 233.

²⁷² G. R. Knox and A. Pryde, *J. Organometallic Chem.*, 1974, **74**, 105.

²⁷³ K. N. Joblin, A. W. Johnson, M. F. Lappert, and B. K. Nicholson, *J.C.S. Chem. Comm.*, 1975, 441.

²⁷⁴ C. Giannotti, C. Fontaine, and B. Septe, *J. Organometallic Chem.*, 1974, **71**, 107.

taken during low-temperature (113–273 K) photolysis of (65a–f) ($X = py$) show that for all compounds except (65a) and (65f), fragments due to the radical $R\cdot$ and a Co^{II} complex are formed.²⁷⁵ This suggests that for these compounds, homolysis of the $Co-C$ bond is an important reaction, and it was further found that this is often followed by rupture of the $Co-X$ bond. The results for (65a) and (65f) are quite different: the e.s.r. spectra indicate that a Co^{II} species with intact $Co-C$ bond is generated on irradiation. In these cases it is proposed that electron transfer from the solvent or the dimethylglyoxime ligand is occurring. Further evidence for electron transfer from the equatorial ligand has been provided by irradiation of (65a) in the presence of spin-trap (66).²⁷⁶ This experi-



ment showed that hydrogen atoms are ejected from the photo-excited complex, and selective deuteration of the ligands and of the solvent indicated that these atoms originate from the dimethylglyoxime ligands. Further investigation of the primary processes of the photochemistry of these compounds should prove especially interesting in the light of recent work on macrocyclic ligand complexes of Co^{III} , *e.g.* ref. 100.

Another paper on the insertion of oxygen into the $Co-R$ bond of alkylcobaloximes confirms that this reaction proceeds non-stereospecifically.²⁷⁷ Other reports contain brief discussions of $Co-C$ bond homolysis in cobaloximes²⁷⁸ and related compounds.²⁷⁹

Strohmeier has reported on the effect of u.v. irradiation on catalytic hydrogenation by Co^I , Rh^I , and Ir^I compounds.^{280–283} It has been shown, for example, that the activity of $IrCl(CO)(PPh_3)_2$ as a catalyst for the hydrogenation of dimethylmaleate is increased by up to 40 times on irradiation.^{280b} This is attributed to the reaction (78) which produces the catalytically reactive species $IrCl(CO)(PPh_3)$.



Light-induced CO dissociation from $CpCo(CO)_2$ in solution at 5 °C leads to (67), which on standing is converted partially into (68).²⁸⁴

²⁷⁵ C. Giannotti and J. R. Bolton, *J. Organometallic Chem.*, 1974, **80**, 379.

²⁷⁶ C. Giannotti, G. Merle, C. Fontaine, and J. R. Bolton, *J. Organometallic Chem.*, 1975, **91**, 357.

²⁷⁷ H. Shinozaki and M. Tada, *Chem. and Ind.*, 1975, 178.

²⁷⁸ K. L. Brown and L. L. Ingraham, *J. Amer. Chem. Soc.*, 1974, **96**, 7681.

²⁷⁹ R. M. McAllister and J. H. Weber, *J. Organometallic Chem.*, 1974, **77**, 91.

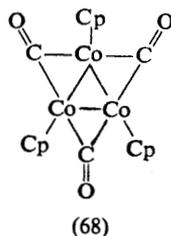
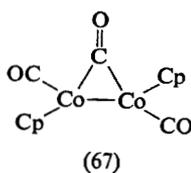
²⁸⁰ (a) W. Strohmeier and G. Csontos, *J. Organometallic Chem.*, 1974, **67**, C27; (b) W. Strohmeier and G. Csontos, *ibid.*, 1974, **72**, 277.

²⁸¹ W. Strohmeier and K. Gruenter, *J. Organometallic Chem.*, 1975, **90**, C48.

²⁸² W. Strohmeier and L. Weigelt, *J. Organometallic Chem.*, 1974, **82**, 417.

²⁸³ W. Strohmeier and E. Hitzel, *J. Organometallic Chem.*, 1975, **87**, 353.

²⁸⁴ K. P. C. Vollhardt, J. E. Bercaw, and R. G. Bergman, *J. Amer. Chem. Soc.*, 1974, **96**, 4998.

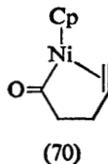
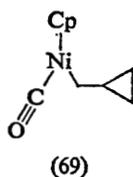


Compounds of the type $[\text{Rh}(\text{phen})(\text{CO})_2]^+\text{X}^-$ ($\text{X} = \text{Cl}$ or ClO_4) are phototropic.²⁸⁵

Nickel.—On irradiation in chlorocarbon solvents, nickelocene undergoes reaction (79).²⁸⁶ The photodecomposition of $[\text{Ni}(\text{allyl})\text{Cl}]_2$ compounds has been dis-



ussed.²⁸⁷ During the photo-induced transformation of (69) into (70) the carbonyl insertion into the cyclopropane and co-ordination of the incipient double bond appear to take place synchronously.²⁸⁸



Copper, Silver, and Gold.—The photoisomerization reaction (80) is catalysed by $\text{Cu}(\text{OAc})_2$, $\text{Cu}(\text{acac})_2$, or CuCl_2 .²⁸⁹ $\text{Cu}(\text{ClO}_4)_2$ promotes the photocyclodimerization of *N*-vinylcarbazole (VCZ).²⁹⁰ The process involves initial electron-transfer from the singlet or triplet state of VCZ to Cu^{II} , giving VCZ^+ and Cu^{I} . In contrast to its thermal decomposition, irradiation of $\text{Ag}(\text{Bu}^{\text{n}})(\text{PBU}^{\text{n}})_3$ causes cleavage of the $\text{Ag}-\text{C}$ bond and the liberation of butyl radicals.²⁹¹



Zinc and Mercury.—Photolysis of diphenylzinc in either CHCl_3 or CCl_4 produces PhZnCl .²⁹²

Homolysis of one of the $\text{Hg}-\text{C}$ bonds is the primary process on irradiation of

²⁸⁵ R. D. Gillard, K. Harrison, and I. H. Mather, *J.C.S. Dalton*, 1975, 133.

²⁸⁶ O. Traverso and R. Rossi, *Ann. Univ. Ferrara, Sez. 5*, 1974, 3, 167.

²⁸⁷ V. A. Kormer, L. F. Shelokhneva, and N. A. Kartsivadze, *Zhur. obshchei Khim.*, 1974, 44, 710.

²⁸⁸ J. M. Brown, J. A. Conneely, and K. Mertis, *J.C.S. Perkin II*, 1974, 905.

²⁸⁹ W. Strohmeier, *Z. Naturforsch.*, 1974, 29b, 282.

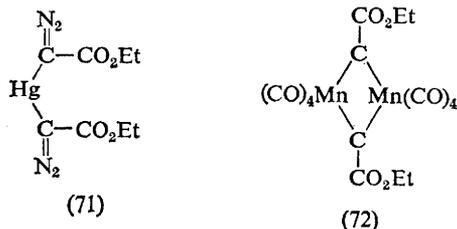
²⁹⁰ M. Asai, H. Matsui, and S. Tazuke, *Bull. Chem. Soc. Japan*, 1974, 47, 864.

²⁹¹ G. M. Whitesides, D. E. Bergbreiter, and P. E. Kendall, *J. Amer. Chem. Soc.*, 1974, 96, 2806.

²⁹² R. F. Galullina, G. G. Petukhov, V. I. Khruleva, and Y. N. Krasnov, *Zhur. obshchei Khim.*, 1974, 44, 1978.

$\text{Hg}(\text{CCl}_3)_2$ in the solid,²⁹³ solution, or gas phase.²⁹⁴ Similarly, $\text{Hg}(\text{OAc})\{\text{CH}(\text{COBu}^t)_2\}$ undergoes photolysis of the $\text{Hg}-\text{C}$ bond.²⁹⁵

CO_2R radicals formed from PhHgCO_2Me , $\text{Hg}(\text{CO}_2\text{Me})_2$, and PhHgCO_2Et have been trapped by nitrones and 2,4,6-tri-*t*-butylnitrosobenzene.²⁹⁶ The carbyne species formed on irradiation of (71) reacts with $\text{Mn}(\text{CO})_5\text{Br}$ to give (72).²⁹⁷

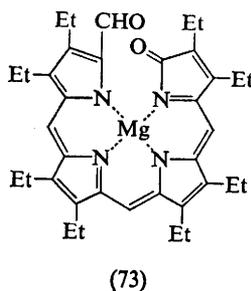


A study of $\text{R}^1_3\text{CHgMR}^2_3$ ($\text{M} = \text{Si}$ or Sn) showed that on irradiation, preferential cleavage of the $\text{Hg}-\text{C}$ bond occurs.²⁹⁸ *p*- $\text{Hg}(\text{OAc})(N$ -nitroso-*N*-methylaniline) undergoes light-induced intramolecular rearrangement to *N*-methyl-*p*-nitrosoaniline.²⁹⁹ The quenching of anthracene fluorescence by HgPh_2 is a consequence of increased intersystem crossing.³⁰⁰

3 Porphyrins and Related Molecules of Biological Importance

As in previous years this section consists of a short account of recent developments in metalloporphyrin photochemistry and photophysics and a selective survey of the *in vitro* photochemistry of chlorophyll and haem.

Metalloporphyrins.—Photolysis in pyridine converts $(\text{OEP})\text{M}(\text{CO})(\text{py})$ into $(\text{OEP})\text{M}(\text{py})_2$ ($\text{OEP} = \text{octaethylporphyrin}$) both for $\text{M} = \text{Ru}$ ³²⁵ and for $\text{M} = \text{Os}$.³²⁶ Photo-oxygenation of $(\text{OEP})\text{Mg}$ gives (73).³²⁷ The analogous



²⁹³ A. K. Mal'tsev, N. D. Kagramanov, and O. M. Nefedov, *Izvest. Akad. Nauk S.S.S.R.*, 1974, 1993.

²⁹⁴ N. D. Kagramanov, A. K. Mal'tsev, and O. M. Nefedov, *Izvest. Akad. Nauk S.S.S.R.*, 1974, 2146.

²⁹⁵ R. H. Fish, R. E. Lundin, and C. G. Salentine, *J. Organometallic Chem.*, 1975, **84**, 281.

²⁹⁶ A. L. Bluhm and J. Weinstein, *Spectroscopy Letters*, 1975, **8**, 43.

²⁹⁷ W. A. Herrmann, *Angew. Chem.*, 1974, **86**, 895; *Angew. Chem. Internat. Edn.*, 1974, **13**, 812.

²⁹⁸ T. N. Mitchell, *J. Organometallic Chem.*, 1974, **71**, 27.

²⁹⁹ E. Y. Belyaev, N. I. Rtischchev, S. V. Demko, B. B. Kochetkov, and A. V. El'tsov, *Zhur. org. Khim.*, 1974, **10**, 887.

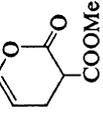
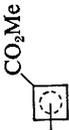
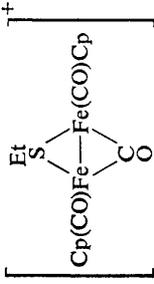
³⁰⁰ E. Vander Donckt, M. Lootens, D. Swinnen, and C. Haquin, *Bull. Soc. chim. belges*, 1975, **84**, 77.

Table 5 Photochemical substitution reactions of metal carbonyl compounds

Substrate	Reactant L	Products	Ref.
CpV(CO) ₄	SnCl ₃ ⁻	[CpV(CO) ₂ L ₂] ²⁻	301
V(CO) ₆ ⁻	PF ₃	[VL ₄] ⁻	302
V(CO) ₆ ⁻	CH ₂ =CH-CH ₂ Cl	(7-C ₃ H ₅)V(CO) ₅	303
HV(CO) ₆	CH ₂ =CH-CR=CH ₂	(7-C ₃ H ₅ RMe)V(CO) ₅	303
M(CO) ₆	2,2-paracyclophane	M(CO) ₅ L	304
M = Cr, Mo, or W	[SnBr _{3-n} Cl _n] ⁻	[M(CO) ₅ L] ⁻	305
M = Cr, Mo, or W	Ph ₂ M'(CH ₂) _n M'Ph ₂	M(CO) ₄ L	306
M = Cr, Mo, or W	(n = 2 or 4; M' = P or As)	M(CO) ₅ L	307
M = Cr or W	(PhCOCHCOMe) ₂ Sn	Cr(CO) ₅ L	307
M = Cr	Cp ₂ Sn	cis-Mo(CO) ₂ L ₂	308
M = Mo	Me ₂ PCH ₂ CH ₂ PMe ₂		309
M = Mo	SI ₄		
M = W	I ₂		
ArCr(CO) ₃			
Ar = subst. benzene			310

301 T. Kruck and H. Breuer, *Chem. Ber.*, 1974, **107**, 263.302 T. Kruck and H. U. Hempel, *Angew. Chem.*, 1974, **86**, 233; *Angew. Chem. Internat. Edn.*, 1974, **13**, 201.303 M. Schneider and E. Weiss, *J. Organometallic Chem.*, 1974, **73**, C7.304 F. Cristiani, D. De Filippo, P. Deplano, F. Devillanova, A. Diaz, E. F. Trogu, and G. Verani, *Inorg. Chim. Acta*, 1975, **12**, 119.305 T. Kruck, F. J. Becker, H. Breuer, K. Ehlert, and W. Rother, *Z. anorg. Chem.*, 1974, **405**, 95.306 S. S. Sandhu and A. K. Mehta, *J. Organometallic Chem.*, 1974, **77**, 45.307 A. B. Cornwell, P. G. Harrison, and J. A. Richards, *J. Organometallic Chem.*, 1974, **76**, C26.308 J. A. Connor, G. K. McEwen, and C. J. Rix, *J. Less-common Metals*, 1974, **36**, 207.309 G. Schmid, R. Boese, and E. Welz, *Chem. Ber.*, 1975, **108**, 260.310 M. Herberhold, K. Leonhard, and C. G. Kreiter, *Chem. Ber.*, 1974, **107**, 3222.

Table 5 (cont.)

Substrate	Reactant L	Products	Ref.
CpMn(CO) ₃ or (MeCp)Mn(CO) ₃	H ₂ C=CH-COMe, PhC=CH-COMe, or 2-cyclohexenone	CpMn(CO) ₂ L or (MeCp)Mn(CO) ₂ L	311
(MeCp)Mn(CO) ₃	CN ⁻	[MeCp)MnL ₃] ³⁻	312
CpMn(CO) ₃	(Ph) ₂ PCH ₂ CH ₂) ₂ PPh	CpMn(CO)L	313
CpMn(CO) ₂ (CS)	(Ph) ₂ PCH ₂ CH ₂) ₂ PPh	CpMn(CS)L	313
Mn(CO) ₄ (NO)	CH ₂ =CH-CH=CH ₂	Mn(CO) ₂ (NO)L and Mn(CO)L ₂	314
Cp(CO) ₂ MnAsMe ₂ Mn(CO) ₅ Fe(CO) ₅	R ¹ N=CR ² -CR ³ =NR ¹	Cp(CO) ₂ MnAsMe ₂ Mn(CO) ₄ Fe(CO) ₃ L	315 316
Fe(CO) ₅			317
Fe(CO) ₅ Fe(CO) ₅	HMe ₂ SiCH ₂ CH ₂ SiMe ₂ H Hg(SiMe ₃) ₂	(CO) ₄ FeSiMe ₂ CH ₂ CH ₂ SiMe ₂ <i>cis</i> -Fe(CO) ₄ (SiMe ₃) ₂ and Hg[Fe(CO) ₄ SiMe ₃] ₂	318 319
CpFe(CO) ₂ C=CPhC(CF ₃) ₂ OCH ₃ Fe(NO) ₂ (CO) ₃	PPh ₃ SnCl ₃ ⁻	CpFe(CO)(L)C=CPhC(CF ₃) ₂ OCH ₃ [Fe(NO) ₂ L ₂] ²⁻	320 321
[Cp(CO) ₂ FeS(Et)Fe(CO) ₂ Cp] ⁺	—		322

CpFe(CO) ₂ [Si(Ph)(Me)(1-Np)]	PPh ₃	323
Ru ₃ (CO) ₁₂	cycloheptatriene	324
Co(NO)(CO) ₃	SnCl ₃ ⁻	321

- 311 M. Gifford and P. Dixneuf, *J. Organometallic Chem.*, 1975, **85**, C26.
 312 J. A. Dineen and P. L. Pauson, *J. Organometallic Chem.*, 1974, **71**, 91.
 313 I. S. Butler and N. J. Coville, *J. Organometallic Chem.*, 1974, **80**, 235.
 314 M. Herberhold and A. Razavi, *Angew. Chem.*, 1975, **87**, 351; *Angew. Chem. Internat. Edn.*, 1975, **14**, 351.
 315 H. Vahrenkamp, *Chem. Ber.*, 1974, **107**, 3867.
 316 H. tom Dieck and A. Orlopp, *Angew. Chem.*, 1975, **87**, 246; *Angew. Chem. Internat. Edn.*, 1975, **14**, 251.
 317 J. Agar, F. Kaplan, and B. W. Roberts, *J. Org. Chem.*, 1974, **39**, 3451.
 318 L. Vancea and W. A. G. Graham, *Inorg. Chem.*, 1974, **13**, 511.
 319 W. Jetz and W. A. G. Graham, *J. Organometallic Chem.*, 1974, **69**, 383.
 320 D. W. Lichtenberg and A. Wojcicki, *Inorg. Chem.*, 1975, **14**, 1295.
 321 T. Kruck and W. Molls, *Z. anorg. Chem.*, 1975, **411**, 54.
 322 R. B. English, R. J. Haines, and C. R. Nolte, *J.C.S. Dalton*, 1975, 1030.
 323 G. Cerveau, E. Colomer, R. Corriu, and W. E. Douglas, *J.C.S. Chem. Comm.*, 1975, 410.
 324 J. C. Burt, S. A. R. Knox, and F. G. A. Stone, *J.C.S. Dalton*, 1975, 731.

reaction is not observed for (OEP)Zn, probably because of its higher oxidation potential; however, (octaethylchlorin)Zn is oxidized. Photo-oxygenation of other porphyrins has been reported.³²⁸

Whitten *et al.* have made a flash photolysis study of the quenching of the triplet states of (aetio I)Zn, (OEP)Zn, and (aetio I)Mg (aetio I = aetioporphyrin I) by aromatic nitro-compounds and by organic chloro-compounds in benzene.³²⁹ At low concentrations of Q (10^{-5} to 5×10^{-4} mol l⁻¹) only quenching of the triplet states was observed, but at higher concentrations the absorption spectra of new species were recorded. These species, which may be quenched by other substances having very low-lying triplet states, have been ascribed to exciplexes Por.Q and Por.Q₂. Ternary exciplexes also appear to be involved in the amine-stimulated reversible photoreduction of TPPH₂ and (TPP)Zn by quinones and nitro-compounds.³³⁰ Other authors have used e.s.r. techniques to study the photo-oxidation of Mg- and Zn-porphyrins,³³¹ and the electron-transfer reactions of aetioporphyrin II and benzoquinone.³³²

It has been found that OEP derivatives of Sc^{III}, Ti^{IV}, Zr^{IV}, Hf^{IV}, Nb^V, and Ta^V emit both fluorescence and phosphorescence – a behaviour which parallels that normally observed with other closed-shell metalloporphyrins.³³³ Values of Φ_f , Φ_p , and τ_p indicate greater spin-orbit coupling for the heavier elements, *i.e.* Zr, Hf, Nb, and Ta, although the extent of this effect is lessened if the metal atom is out of the porphyrin plane. The Mg and Al derivatives of aetioporphyrin I also emit both fluorescence and phosphorescence.³³⁴ The absorption spectra of the paramagnetic complexes, (TPP)Cr^{III}Cl and phenol-phenoxo-(TPP)Cr^{III}, show bands additional to the Soret and red bands of the porphyrin.³³⁵ The long-wavelength bands may be attributed to transitions to porphyrin triquartet states (*i.e.* states formed by coupling of the porphyrin triplet to the Cr^{III} d^3 system). Emission from these compounds is markedly temperature dependent, displaying two bands at low temperatures (at 811 nm and 847 nm; at 4 K, $I_{811}/I_{847} = 0.12$) but only one band (at 815 nm) at $T > 160$ K. These bands are assigned to ${}^4T_1 \rightarrow {}^4S_0$ and ${}^6T_1 \rightarrow {}^4S_0$ transitions, where the 4T_1 and 6T_1 states arise by the coupling mentioned earlier. For Yb^{III}-TBP complexes (TBP = tetra-benzoporphyrin) emission occurs from the Yb centre following transfer of energy from the porphyrin.³³⁶ It has been shown that an impurity was responsible for

³²⁶ F. R. Hopf, T. P. O'Brien, W. R. Scheidt, and D. G. Whitten, *J. Amer. Chem. Soc.*, 1975, **97**, 277.

³²⁸ J. W. Buchler and P. D. Smith, *Angew. Chem.*, 1974, **86**, 378; *Angew. Chem. Internat. Edn.*, 1974, **13**, 341.

³²⁷ J. H. Fuhrhop, P. K. W. Wasser, J. Subramanian, and U. Schrader, *Annalen*, 1974, 1450.

³²⁸ I. M. Byteva, G. P. Gurinovich, and O. M. Petsol'd, *Biofizika*, 1975, **20**, 51.

³²⁹ J. K. Roy, F. A. Carroll, and D. G. Whitten, *J. Amer. Chem. Soc.*, 1974, **96**, 6349.

³³⁰ I. N. Ivnitskaya and I. I. Dilung, *Biofizika*, 1974, **19**, 636.

³³¹ V. A. Umrikhin and Z. P. Gribova, *Biofizika*, 1974, **19**, 640.

³³² Y. V. Glazkov and N. I. Zotov, *Zhur. priklad. Spektroskopii*, 1974, **20**, 921.

³³³ M. Gouterman, L. K. Hanson, G. E. Khalil, J. W. Buchler, K. Rohbock, and D. Dolphin, *J. Amer. Chem. Soc.*, 1975, **97**, 3142.

³³⁴ M. P. Tsvirko, K. N. Solovev, A. T. Gradyushko, and S. S. Dvornikov, *Zhur. priklad. Spektroskopii*, 1974, **20**, 528.

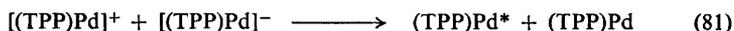
³³⁵ M. Gouterman, L. K. Hanson, G. E. Khalil, W. R. Leenstra, and J. W. Buchler, *J. Chem. Phys.*, **62**, 2343.

³³⁶ T. F. Kachura, A. N. Sevchenko, K. N. Solovev, and M. P. Tsvirko, *Doklady Akad. Nauk S.S.S.R.*, 1974, **217**, 1121.

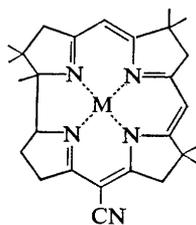
the previously reported³³⁷ anomalous phosphorescence of (TPP)SnCl₂.³³⁸ Studies on the polarization of fluorescence from upper excited states of TBPPh₂ and (TBP)Zn have been carried out.³³⁹

The effect of heavy atoms on the relative yields of fluorescence and phosphorescence has been investigated both by inserting Br and I substituents in the ring of deuterioporphyrin IX and its Zn derivative,³⁴⁰ and by adding ethyl iodide to the solution of a number of free base porphyrins.³⁴¹ Other authors discuss the luminescence of protoporphyrin IX dimethylester after pulse radiolysis in benzene,³⁴² and from monomeric and dimeric ethylenediamine-substituted protoporphyrin IX and some metal derivatives.³⁴³ Several reports consider the emission from porphyrins in Shpolskii matrices and other crystalline organic hosts.^{344–346}

Electrochemiluminescence of (TPP)Pd and (TPP)Pt originates from their triplet states formed after recombination of the cation and anion.³⁴⁷



Gardiner and Thomson have published an interesting paper on the luminescence properties of metallocorrins (74).³⁴⁸ Many parallels exist with the



(74)

analogous porphyrins. Thus fluorescence is observed for the free corrin and for its Li^I, Be^{II}, Mg^{II}, Zn^{II}, and Cd^{II} derivatives, phosphorescence (perturbed by the ion present) for the Pt^{II}, Pd^{II}, and Rh^{III} complexes, and no emission at all for the Co^{III}, Cu^{II}, and Ni^{II} compounds. The absence of luminescence from these latter species is consistent with their lack of reactivity in the photoisomerization of A/D secocorrin to corrin.

³³⁷ M. Gouterman, F. P. Schwarz, P. D. Smith, and D. Dolphin, *J. Chem. Phys.*, 1973, **59**, 676.

³³⁸ M. Gouterman and H. B. Howell, *J. Chem. Phys.*, 1974, **61**, 3491.

³³⁹ I. E. Zaleskii, V. N. Kotlo, A. N. Sevchenko, K. N. Solovev, and S. F. Shkirman, *Doklady Akad. Nauk S.S.S.R.*, 1974, **218**, 324.

³⁴⁰ A. T. Gradyushko, D. T. Kozhich, K. N. Solovev, and M. P. Tsvirko, *Optika i Spektroskopiya*, 1974, **37**, 892.

³⁴¹ M. Gouterman and G. E. Khalil, *J. Mol. Spectroscopy*, 1974, **53**, 88.

³⁴² S. J. Chantrell, C. A. McAuliffe, R. W. Munn, A. C. Pratt, and E. J. Land, *J.C.S. Chem. Comm.*, 1975, 470.

³⁴³ R. R. Das, *J. Inorg. Nuclear Chem.*, 1975, **37**, 153.

³⁴⁴ A. T. Gradyushko, K. N. Solovev, and S. G. Khokhlova, *Zhur. priklad. Spektroskopii*, 1974, **21**, 252.

³⁴⁵ V. N. Kotlo, K. N. Solovev, S. F. Shkirman, and I. E. Zaleskii, *Vestsi Akad. Navuk Belarus. S.S.R., Ser. fiz.-mat. Navuk*, 1974, 99.

³⁴⁶ B. F. Kim, J. Bohandy, and C. K. Jen, *Spectrochim. Acta*, 1974, **30A**, 2031.

³⁴⁷ N. E. Tokel-Takvoryan and A. J. Bard, *Chem. Phys. Letters*, 1975, **25**, 235.

³⁴⁸ M. Gardiner and A. J. Thomson, *J.C.S. Dalton*, 1974, 820.

It is clear from the first report of the application of picosecond flash photolysis to the study of porphyrin photophysics that this technique will become increasingly important.³⁴⁹ Thus it has been found possible to record the absorption spectra of both the singlet state ($\tau \approx 500$ ps) and triplet states of (OEP)SnCl₂. Further, Φ_{ISC} could be measured, and the value differed from that found by previous workers. For (OEP)Pd both singlet and triplet states could be observed, whereas only one species was found for the paramagnetic (OEP)Cu and (TPP)Cu complexes. Nanosecond laser flash photolysis has been used in the study of the transients formed from Cu^{II} and Pb^{II} porphyrins.³⁵⁰ No observable intermediates were detected for the Ag^{II}, Ni^{II}, and Co^{III} derivatives. Triplet-triplet absorption spectra of a series of porphyrins and their Zn complexes have been recorded.³⁵¹

The rate constants for radiationless decay of the triplet state of mesoporphyrin IX dimethyl ester at 77 K are 26 s⁻¹ in EtOD and 57 s⁻¹ in EtOH.³⁵² The most probable cause is a decrease in the rate of tautomerism in the porphyrin due to deuteration of the N-H hydrogen. However, for TPPH₂ triplet state in n-octane matrices³⁵³ such tautomerism does not appear to be an important mechanism for radiationless deactivation. Several recent reports deal with the low-temperature e.s.r. spectra of triplet states of porphyrins.³⁵⁴⁻³⁵⁸ The zero field splittings and depopulation rates of the various spin sub-levels of the triplet state of Zn-chlorophyll-a have been determined by an optically detected magnetic resonance method.³⁵⁹

Subjects of recent publications on the spectroscopic properties and electronic structure of porphyrins include the photochemically induced dichroism of [(aetio)Zn]⁻,³⁶⁰ the absorption spectra of metallo-TPP compounds in SF₆, Ar, and n-octane matrices,³⁶¹ the Zeeman effect in the absorption spectra of Pd-porphin in n-octane single crystals,³⁶² the electronic spectra of Cu^{II}- and Ni^{II}-corrin derivatives,³⁶³ m.c.d. studies on porphyrins,^{364, 365} photoelectron spectra of porphyrins and pyrroles,³⁶⁶ and quantum mechanical calculations on porphyrins.^{367, 368}

³⁴⁹ D. Magde, M. W. Windsor, D. Holten, and M. Gouterman, *Chem. Phys. Letters*, 1974, **29**, 183.

³⁵⁰ B. M. Dzhagarov, G. P. Gurinovich, and A. M. Simonov, *Optika i Spektroskopiya*, 1974, **37**, 254.

³⁵¹ V. V. Sapunov, K. N. Solovev, and M. P. Tsvirko, *Zhur. priklad. Spektroskopii*, 1974, **21**, 667.

³⁵² R. P. Burgner and A. M. Ponte Goncalves, *J. Chem. Phys.*, 1974, **60**, 2942.

³⁵³ R. H. Clarke and R. E. Connors, *J. Chem. Phys.*, 1975, **62**, 1600.

³⁵⁴ H. Levanon and S. Vega, *J. Chem. Phys.*, 1974, **61**, 2265.

³⁵⁵ A. M. Ponte Goncalves and R. P. Burgner, *J. Chem. Phys.*, 1974, **61**, 2975.

³⁵⁶ S. R. Langhoff, E. R. Davidson, M. Gouterman, W. R. Leenstra, and A. L. Kwiram, *J. Chem. Phys.*, 1975, **62**, 169.

³⁵⁷ W. G. van Dorp, M. Soma, J. A. Kooter, and J. H. Van der Waals, *Mol. Phys.*, 1974, **28**, 1551.

³⁵⁸ B. M. Hoffman, *J. Amer. Chem. Soc.*, 1975, **97**, 1688.

³⁵⁹ R. H. Clarke and R. E. Connors, *Chem. Phys. Letters*, 1975, **33**, 365.

³⁶⁰ V. G. Maslov, *Optika i Spektroskopiya*, 1974, **37**, 1010.

³⁶¹ J. J. Leonard and F. R. Longo, *J. Phys. Chem.*, 1975, **79**, 62.

³⁶² G. W. Canters, M. Noort, and J. H. Van der Waals, *Chem. Phys. Letters*, 1975, **30**, 1.

³⁶³ N. S. Hush, J. M. Dyke, M. L. Williams, and I. S. Woolsey, *J.C.S. Dalton*, 1974, 395.

³⁶⁴ G. Barth, R. E. Lindner, E. Bunnenberg, C. Djerassi, L. Seamans, and A. Moscowitz, *J.C.S. Perkin II*, 1974, 1706.

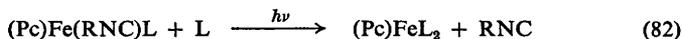
³⁶⁵ R. E. Lindner, G. Barth, E. Bunnenberg, C. Djerassi, L. Seamans, and A. Moscowitz, *J.C.S. Perkin II*, 1974, 1712.

³⁶⁶ H. Falk, O. Hofer, and H. Lehner, *Monatsh.*, 1974, **105**, 366.

³⁶⁷ J. Almlof, *Internat. J. Quantum Chem.*, 1974, **8**, 915.

³⁶⁸ G. M. Maggiora and L. J. Weimann, *Internat. J. Quantum Chem., Quantum Biol., Symp.*, 1974, **1**, 179.

The photosubstitution reaction (82) of the phthalocyanine (Pc) complex (Pc)Fe(RNC)L (L = py, piperidine, or methylimidazole) proceeds efficiently,



whereas the back reaction is favoured in the dark.³⁶⁹ The system displays useful photochromic properties as the system may be cycled several hundred times without loss in reversibility. Other publications concerned with phthalocyanine photophysics discuss the determination of Φ_{ISC} for 4-t-butylphthalocyanine and its metal derivatives,³⁷⁰ the phosphorescence of Pt-phthalocyanine single crystals at 4 K,³⁷¹ the line spectra of Mg- and Zn-phthalocyanines in n-decane at 4 K,³⁷² m.c.d. of phthalocyanines,³⁷³ and the fluorescence and absorption spectra of Zn- and Pd-azaporphyrins.³⁷⁴

Chlorophylls.—Aspects of the primary processes of photosynthesis which have recently been reviewed include excitation energy transfer in photosynthesis,³⁷⁵ primary photochemical reactions in chloroplast photosynthesis,³⁷⁶ light-induced paramagnetism in photosynthetic systems,³⁷⁷ and photosynthetic reaction centres and primary photochemical reactions.³⁷⁸

Fong³⁷⁹ has presented a new theory to explain the function of light in the photo-oxidation of water in the chloroplast. The reaction centre is assumed to be the dimeric species $(\text{Chl.H}_2\text{O})_2$. It is further predicted that the triplet state of this complex will have an anomalously long lifetime. Transfer of energy from the singlet state of the 'antenna' chlorophyll to this state will produce a triplet CT state, in which the photo-oxidation of water may occur. It has recently been proposed that the 'antenna' chlorophyll-a molecules in the chloroplast have an oligomeric form similar to that observed for chlorophyll-a in non-polar solvents such as hexane, *i.e.* $(\text{Chl}_2)_n$.³⁸⁰ ¹H N.m.r. has been used to obtain structural information about the dimers of chlorophyll-a formed in CCl_4 and benzene solutions,³⁸¹ and ¹³C and ¹⁵N n.m.r. spectra of chlorophyll-a have been assigned.³⁸²

Photoconductivity has been induced both in microcrystalline chlorophyll-a on laser excitation,³⁸³ and in ether solutions after flash photolysis.³⁸⁴ In a publication which was incorrectly abstracted in last year's Report, it has been shown

³⁶⁹ D. V. Stynes, *J. Amer. Chem. Soc.*, 1974, **96**, 5942.

³⁷⁰ A. V. Butenin, B. Y. Kogan, E. A. Luk'yanets, and L. I. Molchanova, *Optika i Spektroskopiya*, 1974, **37**, 696.

³⁷¹ K. Kaneto, K. Yoshino, and Y. Inuishi, *J. Phys. Soc. Japan*, 1974, **37**, 1297.

³⁷² O. N. Korotaev and R. I. Personov, *Optika i Spektroskopiya*, 1974, **37**, 886.

³⁷³ (a) M. J. Stillman and A. J. Thomson, *J.C.S. Faraday II*, 1974, **70**, 790; (b) M. J. Stillman and A. J. Thomson, *ibid.*, p. 805.

³⁷⁴ V. A. Mashenkov, K. N. Solovov, A. E. Turkova, and N. A. Yushkevich, *Zhur. priklad. Spektroskopii*, 1974, **21**, 73.

³⁷⁵ A. Y. Borisov and V. I. Gokid, *Biochim. Biophys. Acta*, 1973, **301**, 227.

³⁷⁶ A. J. Bearden and R. Malkin, *Quart. Rev. Biophys.*, 1974, **7**, 131.

³⁷⁷ J. T. Warden and J. R. Bolton, *Accounts Chem. Res.*, 1974, **7**, 189.

³⁷⁸ B. Ke, *Photochem. and Photobiol.*, 1974, **20**, 542.

³⁷⁹ (a) F. K. Fong, *J. Theor. Biol.*, 1974, **46**, 407; (b) F. K. Fong, *Proc. Nat. Acad. Sci. U.S.A.*, 1974, **71**, 3692; (c) F. K. Fong, *Appl. Phys.*, 1975, **6**, 151.

³⁸⁰ T. M. Cotton, A. D. Trifunac, K. Ballschmitter, and J. J. Katz, *Biochim. Biophys. Acta*, 1974, **368**, 181.

³⁸¹ A. D. Trifunac and J. J. Katz, *J. Amer. Chem. Soc.*, 1974, **96**, 5233.

³⁸² S. G. Boxer, G. L. Closs, and J. J. Katz, *J. Amer. Chem. Soc.*, 1974, **96**, 7058.

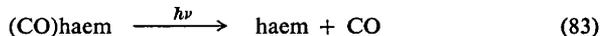
³⁸³ A. Bromberg, C. W. Tang, and A. C. Albrecht, *J. Chem. Phys.*, 1974, **60**, 4058.

³⁸⁴ N. D. Gudkov, Y. M. Stolovitskii, and V. B. Evstigneev, *Biofizika*, 1973, **18**, 807.

that photolysis of chlorophyll-a in ethanol at low temperatures produces Chl^{\dagger} in the absence of quinone.³⁸⁵ The photochemical interaction of chlorophylls and related compounds with quinones has been studied by e.s.r. techniques,³⁸⁶⁻³⁹⁰ and by measurement of pH³⁹¹ and electrode potential³⁹² changes during irradiation. Electron transfer has also been observed between chlorophyll and quinones in lecithin matrices.³⁹³ Photo-oxidation of chlorophyll-a by oxygen^{394, 395} and the photoreduction of chlorophylls and related compounds by various reagents³⁹⁶⁻³⁹⁸ have been discussed. Chlorophyll-a in monomolecular layers³⁹⁹ or adsorbed on nylon⁴⁰⁰ or other polymers⁴⁰¹ photosensitizes the reduction of methyl red. Other chlorophyll-sensitized reactions include the photoreduction of ferredoxin⁴⁰² and of cytochrome *c*.⁴⁰³

Reports on chlorophyll fluorescence,⁴⁰⁴⁻⁴⁰⁸ phosphorescence,⁴⁰⁹ and photochemiluminescence^{410, 411} have been published. The properties of the triplet state of chlorophyll have been studied by e.s.r.⁴¹²⁻⁴¹⁵ and by optically detected magnetic resonance.^{416, 417}

Haem.—The photodissociation of carbonylhaem (83) and its subsequent reformation have been studied in 80% ethylene glycol: water and in glycerol solutions

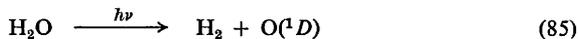


- ³⁸⁵ J. R. Harbour and G. Tollin, *Photochem. and Photobiol.*, 1974, **19**, 69.
³⁸⁶ V. M. Voznyak, I. I. Proskuryakov, and V. B. Evstigneev, *Biofizika*, 1974, **19**, 815.
³⁸⁷ A. P. Kostikov, N. A. Sanovnikova, V. B. Evstigneev, and L. P. Kayushin, *Biofizika*, 1974, **19**, 244.
³⁸⁸ A. P. Kostikov, L. P. Kayushin, L. N. Chekulaeva, N. A. Sadovnikova, and V. B. Evstigneev, *F.E.B.S. Letters*, 1974, **48**, 149.
³⁸⁹ V. A. Kim, V. M. Voznyak, and V. B. Evstigneev, *Biofizika*, 1974, **19**, 992.
³⁹⁰ (a) J. R. Harbour and G. Tollin, *Photochem. and Photobiol.*, 1974, **19**, 163; (b) J. R. Harbour and G. Tollin, *ibid.*, 1974, **20**, 271.
³⁹¹ V. B. Evstigneev and V. S. Chudar, *Biofizika*, 1974, **19**, 425; 1974, **19**, 997.
³⁹² V. B. Evstigneev, A. A. Kazakova, and B. A. Kiselev, *Biofizika*, 1974, **19**, 810.
³⁹³ G. S. Beddard, G. Porter, and G. M. Weese, *Proc. Roy. Soc. (A)*, 1974, **342**, 317.
³⁹⁴ A. A. Krasnovskii, M. G. Shaposhnikova, and F. F. Litvin, *Biofizika*, 1974, **19**, 650.
³⁹⁵ J. P. Chauvet, R. Journeaux, R. Viovy, and F. Villain, *J. Chim. phys.*, 1974, **71**, 879.
³⁹⁶ H. Scheer and J. J. Katz, *Proc. Nat. Acad. Sci. U.S.A.*, 1974, **71**, 1626.
³⁹⁷ E. V. Pakshina and A. A. Krasnovskii, *Biofizika*, 1974, **19**, 238.
³⁹⁸ V. P. Suboch, A. P. Losev, and G. P. Gurinovich, *Photochem. and Photobiol.*, 1974, **20**, 183.
³⁹⁹ S. M. de B. Costa and G. Porter, *Proc. Roy. Soc.*, 1974, **A341**, 167.
⁴⁰⁰ N. I. Loboda, L. I. Nekrasov, and N. A. Shchegoleva, *Zhur. fiz. Khim.*, 1974, **48**, 338.
⁴⁰¹ I. G. Nazarova and V. B. Evstigneev, *Biofizika*, 1974, **19**, 178.
⁴⁰² E. N. Mukhin, N. F. Neznaiko, A. Y. Shkuropatov, Y. M. Stokovitskii, and V. B. Evstigneev, *Doklady Akad. Nauk S.S.S.R.*, 1975, **220**, 978.
⁴⁰³ A. A. Krasnovskii and E. S. Mikhailova, *Doklady Akad. Nauk S.S.S.R.*, 1974, **215**, 727.
⁴⁰⁴ M. Kaplanova and K. Vacek, *Photochem. and Photobiol.*, 1974, **20**, 371.
⁴⁰⁵ K. Vacek, E. Vavrinc, V. Cerna, O. Vinduskova, J. Naus, and P. Lokaj, *Stud. Biophys.*, 1974, **44**, 155.
⁴⁰⁶ R. M. Leblanc, G. Galinier, A. Tessier, and L. Lemieux, *Canad. J. Chem.*, 1974, **52**, 3723.
⁴⁰⁷ L. V. Levshin, T. D. Slavnova, and V. I. Yuzhakov, *Biofizika*, 1975, **20**, 150.
⁴⁰⁸ E. R. Menzel and J. S. Polles, *Chem. Phys. Letters*, 1974, **24**, 545.
⁴⁰⁹ A. A. Krasnovskii, N. N. Lebedev, and F. F. Litvin, *Doklady Akad. Nauk S.S.S.R.*, 1974, **216**, 1406.
⁴¹⁰ A. A. Krasnovskii and F. F. Litvin, *Photochem. and Photobiol.*, 1974, **20**, 133.
⁴¹¹ A. A. Krasnovskii and M. G. Shaposhnikova, *Mol. Biol. (Moscow)*, 1974, **8**, 666.
⁴¹² J. F. Kleibecker and T. J. Schaafsma, *Chem. Phys. Letters*, 1974, **29**, 116.
⁴¹³ H. Levanon and A. Scherz, *Chem. Phys. Letters*, 1975, **31**, 119.
⁴¹⁴ J. R. Norris, R. A. Uphaus, and J. J. Katz, *Chem. Phys. Letters*, 1975, **31**, 157.
⁴¹⁵ R. A. Uphaus, J. R. Norris, and J. J. Katz, *Biochem. Biophys. Res. Comm.*, 1974, **61**, 1057.
⁴¹⁶ R. H. Clarke and R. H. Hofeldt, *J. Chem. Phys.*, 1974, **61**, 4582.
⁴¹⁷ R. H. Clarke and R. H. Hofeldt, *J. Amer. Chem. Soc.*, 1974, **96**, 3005.

over a range of pressures (1—2760 bar) using a laser flash photolysis apparatus.⁴¹⁸ For glycerol the viscosity is markedly pressure dependent, and in this way it has been possible to show that the quantum yield for the photodissociation reaction falls off markedly with increasing viscosity. The same apparatus has been employed in a study of the binding of O₂ and CO to haemoglobin and myoglobin.⁴¹⁹ Investigation of the processes following photodissociation of CO from carbonylhaemoglobin and related compounds has provided useful information for the formulation of theories of the reactivity of these species.^{420–429} Similarly the dissociation of CO and O₂ from their complexes with cobalt-myoglobin and -haemoglobin^{430, 431} and of NO from nitrosyl-manganese-haemoglobin⁴³² have been described. The photoreduction of cytochrome *c*⁴³³ and a comparison of the photoactivity of low-spin myoglobins with that of the high-spin species⁴³⁴ have been the subjects of recent reports.

4 Water, Hydrogen Peroxide, and Anions

The relative importance of the processes (84) and (85) in the gas phase has been determined directly using a flash photolysis–resonance fluorescence method.⁴³⁵ It was established that at 105 < λ < 145 nm, the relative efficiencies for reactions (84) and (85) are 0.89 and 0.11, whereas for 145 < λ < 185 nm reaction (85) is of negligible importance (<1%).



In another study it has been shown that 23% of the hydrogen formed on irradiation of water at 147 nm is produced *via* step (85).⁴³⁶ The new technique of polarized photofluorescence excitation spectroscopy has been applied to the OH radicals produced by reaction (86) on irradiation at λ ≈ 130 nm.⁴³⁷ The



⁴¹⁸ E. F. Caldin and B. B. Hasinoff, *J.C.S. Faraday I*, 1975, **71**, 515.

⁴¹⁹ B. B. Hasinoff, *Biochemistry*, 1974, **13**, 3111.

⁴²⁰ M. Brunori, B. Giardina, and E. E. Di Iorio, *F.E.B.S. Letters*, 1974, **46**, 312.

⁴²¹ P. H. Fang, *Phys. Rev. Letters*, 1974, **33**, 1515.

⁴²² R. H. Austin, K. Beeson, L. Eisenstein, H. Frauenfelder, and I. C. Gunsalus, *Phys. Rev. Letters*, 1975, **34**, 845.

⁴²³ E. Chiancone, N. M. Anderson, E. Antonini, J. Bonaventura, C. Bonaventura, M. Brunori, and C. Spagnuolo, *J. Biol. Chem.*, 1974, **249**, 5689.

⁴²⁴ Y. A. Ermakov, V. I. Pasechnik, and S. V. Tulsikii, *Biofizika*, 1975, **20**, 153.

⁴²⁵ R. D. Gray, *J. Biol. Chem.*, 1975, **250**, 790.

⁴²⁶ E. Whitehead, *Biophys. Chem.*, 1974, **2**, 377.

⁴²⁷ V. N. Kulakov, A. L. Lyubarskii, E. E. Fesenko, and M. V. Vol'kenshtein, *Stud. Biophys.*, 1974, **42**, 55.

⁴²⁸ T. Iizuka, H. Yamamoto, M. Kotani, and T. Yonetani, *Biochim. Biophys. Acta*, 1974, **371**, 126.

⁴²⁹ P. Debey and P. Douzou, *F.E.B.S. Letters*, 1974, **39**, 271.

⁴³⁰ T. Yonetani, H. Yamamoto, and T. Iizuka, *J. Biol. Chem.*, 1974, **249**, 2168.

⁴³¹ T. Iizuka, H. Yamamoto, M. Kotani, and T. Yonetani, *Biochim. Biophys. Acta*, 1974, **351**, 182.

⁴³² Q. H. Gibson, B. M. Hoffman, R. H. Crepeau, S. J. Edelstein, and C. Bull, *Biochem. Biophys. Res. Comm.*, 1974, **59**, 146.

⁴³³ W. P. Vorkink and M. A. Cusanovich, *Photochem. and Photobiol.*, 1974, **19**, 205.

⁴³⁴ M. Folin, G. Gennari, and G. Jori, *Photochem. and Photobiol.*, 1974, **20**, 357.

⁴³⁵ L. J. Stief, W. A. Payne, and R. B. Klemm, *J. Chem. Phys.*, 1975, **62**, 4000.

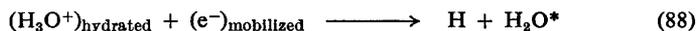
⁴³⁶ A. Y. M. Ung, *Chem. Phys. Letters*, 1974, **28**, 603.

⁴³⁷ G. A. Chamberlain and J. P. Simons, *Chem. Phys. Letters*, 1975, **32**, 355.

results are consistent with the excited OH radical being formed by the predissociation of a vibronic 1B_1 state, probably the 1A_2 electronic state carrying one quantum of the antisymmetric stretching frequency $\nu_3(b_2)$. The quantum yield for the mercury-sensitized emission of water vapour ($\lambda_{\text{max}} = 283 \text{ nm}$), produced by the bimolecular process (87), is 0.28 at 293 K.⁴³⁸

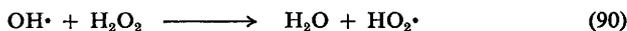


Emission ($\lambda_{\text{max}} = 380 \text{ nm}$), assigned to that from the lowest triplet state of water, has been observed following either γ -irradiation or mercury sensitization of crystalline H_2O or D_2O .⁴³⁹ For the mercury sensitization a triplet energy-transfer mechanism appears to be operative, while for the γ -irradiation the excited state is formed *via* reaction (88). Photolysis of water adsorbed on various organic materials is observed with short-wavelength u.v. light ($\lambda < 250 \text{ nm}$).⁴⁴⁰

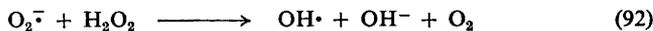
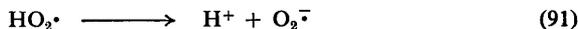


The results of electron impact studies with water are consistent with a vertical excitation energy of 7.4 eV for the 3B_1 state of water,⁴⁴¹ and this has been confirmed by recent calculations on H_2O .^{442–445}

It is well established that photolysis of H_2O_2 in aqueous solution leads to $\text{OH}\cdot$ and $\text{HO}_2\cdot$ radicals *via* steps (89) and (90). The adducts of both these radicals



with spin-traps, 5,5-dimethyl-1-pyrroline-1-oxide (66) and phenyl-*t*-butylnitron, have now been identified by e.s.r.⁴⁴⁶ In neutral solution $\text{HO}_2\cdot$ rapidly deprotonates yielding $\text{O}_2^{\cdot-}$. The rate constant for the reaction of this ionic species with H_2O_2 has recently been redetermined.⁴⁴⁷ Studies of the photolysis of H_2O_2 in the presence of *p*-nitrosodimethylaniline,⁴⁴⁸ β -ammonioalcohols,⁴⁴⁹ and propan-2-ol⁴⁵⁰ have been reported.



The absorption spectra of iodine-solvent complexes have been recorded following nanosecond laser flash photolysis of I^- in MeCN, EtCN, Pr^nCN ,

⁴³⁸ A. B. Callear and J. H. Connor, *J.C.S. Faraday II*, 1974, **70**, 1767.

⁴³⁹ A. Bernas and T. B. Truong, *Chem. Phys. Letters*, 1974, **29**, 585.

⁴⁴⁰ L. L. Basov, Y. P. Efimov, and Y. P. Solonitsyn, *Uspekhi Fotoniki*, 1974, **4**, 12.

⁴⁴¹ E. N. Lassette and A. Skerbele, *J. Chem. Phys.*, 1974, **60**, 2464.

⁴⁴² D. Yeager, V. McKoy, and G. A. Segal, *J. Chem. Phys.*, 1974, **61**, 755.

⁴⁴³ R. J. Buenker and S. D. Peyerimhoff, *Chem. Phys. Letters*, 1974, **29**, 253.

⁴⁴⁴ N. W. Winter, W. A. Goddard, and F. W. Bobrowicz, *J. Chem. Phys.*, 1975, **62**, 4325.

⁴⁴⁵ C. Peterson and G. V. Pfeiffer, *Theor. Chim. Acta*, 1974, **33**, 115.

⁴⁴⁶ J. R. Harbour, V. Chow, and J. R. Bolton, *Canad. J. Chem.*, 1974, **52**, 3549.

⁴⁴⁷ V. D. Maiboroda, E. P. Petryaev, V. M. Byakov, and L. F. Ivashkevich, *Khim. vysok. Energii*, 1974, **8**, 284.

⁴⁴⁸ M. Hatada, I. Kraljic, A. El Samahy, and C. N. Trumbore, *J. Phys. Chem.*, 1974, **78**, 888.

⁴⁴⁹ T. Foster and P. R. West, *Canad. J. Chem.*, 1974, **52**, 3589.

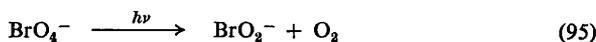
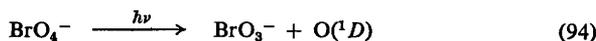
⁴⁵⁰ S. Paszyc and H. Zalecka, *Bull. Acad. polon. Sci., Ser. Sci. chim.*, 1974, **22**, 695.

MeOH, PrⁱOH, or MeO(CH₂)₂OMe.^{451a} Similarly, the corresponding Br-H₂O and Cl-H₂O complexes have been observed on laser photolysis of Br₂ and Cl₂ in water.^{451b} The primary photoprocess following nitrogen-laser irradiation of I₃⁻ is (93).⁴⁵² However, for solutions in various alcohols it has been shown that I₄⁻ is produced on laser flash photolysis of I₂/I⁻ mixtures.⁴⁵³ This species is formed by reaction of iodine atoms, formed on photolysis of I₂, with I₃⁻. I₄⁻ has also been observed following γ-irradiation of I₂ in methyltetrahydrofuran.⁴⁵⁴

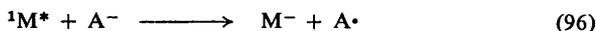


Exchange of hydrogen between benzene and acidified water has been induced by photolysis of the mixture in the presence of I⁻.⁴⁵⁵ The active species involved are hydrogen atoms formed from the hydrated electrons liberated by I⁻. The reaction of hydrated electrons, formed by photolysis of I⁻, with alkyl halides has also been studied.⁴⁵⁶

The photochemical behaviour of BrO₄⁻ differs from that of other oxyhaloanions XO_n⁻.⁴⁵⁷ Thus photolysis in NaOH glasses at 77 K and flash photolysis in aqueous solution provided evidence for participation of reactions (94) and (95) but not for O⁻ or O(³P) production. The absence of O⁻ is attributed to the low stability of BrO₃. The photolysis of powdered samples of NaClO₃, both with and without previous γ-irradiation, has been investigated.⁴⁵⁸



The mechanism for the quenching of singlet states of aromatic hydrocarbons by inorganic anions has been investigated both by fluorescence studies^{459a} and by flash photolysis.^{459b} It has been shown that although the quenching rate constant parallels the ease of oxidation of the anion, in most cases electron-transfer processes (96) are not important. Further the flash photolysis experi-



ments indicate that the triplet state is formed in high yield after the quenching process, and it is proposed that the singlet state deactivation involves an efficient radiationless conversion into the triplet state, induced by coupling of higher-lying electron-transfer states within the collision complex (¹M*...A⁻). Evidence has also been reported for enhanced intersystem crossing from the singlet state of azastilbenes in the presence of inorganic anions.⁴⁶⁰

⁴⁵¹ (a) A. Treinin and E. Hayon, *Internat. J. Radiation Phys. Chem.*, 1975, 7, 387; (b) A. Treinin and E. Hayon, *J. Amer. Chem. Soc.*, 1975, 97, 1716.

⁴⁵² A. Barkatt and M. Ottolenghi, *Mol. Photochem.*, 1974, 6, 253.

⁴⁵³ P. Fournier de Violet, R. Bonneau, and J. Jousot-Dubien, *Chem. Phys. Letters*, 1974, 28, 569.

⁴⁵⁴ T. Shida, Y. Takahashi, H. Hatano, and M. Imamura, *Chem. Phys. Letters*, 1975, 33, 491.

⁴⁵⁵ V. Gold, M. A. Major, and M. J. Gregory, *J.C.S. Faraday I*, 1974, 70, 965.

⁴⁵⁶ S. R. Logan and P. B. Wilmot, *Internat. J. Radiation Phys. Chem.*, 1974, 6, 1.

⁴⁵⁷ U. K. Klaening, K. J. Olsen, and E. H. Appelman, *J.C.S. Faraday I*, 1975, 71, 473.

⁴⁵⁸ P. J. Herley and P. W. Levy, *J. Chem. Phys.*, 1975, 62, 177.

⁴⁵⁹ (a) A. R. Watkins, *J. Phys. Chem.*, 1974, 78, 2555; (b) A. R. Watkins, *ibid.*, p. 1885.

⁴⁶⁰ P. Bortolus, G. Bartocci, and U. Mazzucato, *J. Phys. Chem.*, 1975, 79, 21.

Other reports consider the gas-phase photodecomposition of CO_3^{2-} ,⁴⁶¹ the photoformation of CO_3^{2-} from CO_3^- and K atoms in argon matrices at 14 K,⁴⁶² and the catalysis of the photo-initiated autoxidation of SO_3^{2-} by Fe^{3+} .⁴⁶³

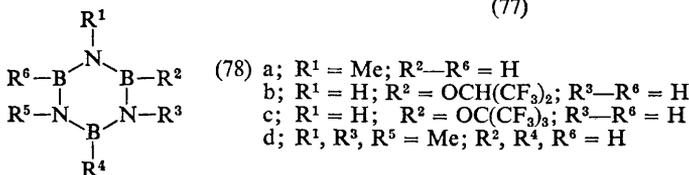
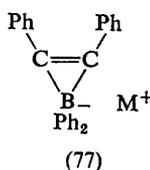
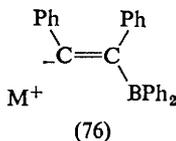
5 Main-group Elements

Magnesium.—Excitation of the Grignard reagents (75; $\text{R}^1 = \text{PhCH}_2$, $\text{R}^2 = \text{H}$; $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Me}$) in bands assigned to the C—Mg chromophore causes the β -elimination reaction represented in equation (97).⁴⁶⁴ HMgX subsequently disproportionates to yield MgX_2 and MgH_2 .



Chemiluminescence is observed during the reactions of aryl Grignard reagents with oxygen^{465a} or with aryl peroxides.^{465b} Analysis of the luminescence spectrum and e.s.r. data indicates that for the oxygen-induced reaction brominated biphenyls are the emitters, whereas in the peroxide case triphenylmethane is the luminescent species.

Boron.—The principal reaction on photolysis of $\text{Na}^+[\text{BPh}_4]^-$ in tetrahydrofuran or dimethoxyethane solution is formation of biphenyl and $\text{Na}^+[\text{BPh}_2]^-$.⁴⁶⁶ This latter species exhibits carbenoid-like activity and reacts with diphenylacetylene to give an equilibrating mixture of (76) and (77). Radical formation on irradiation of MPh_3 ($\text{M} = \text{B}$, Al , or Ga) at 77 K has been discussed.⁴⁶⁷



Photolysis (at 1849 nm) of *N*-methylborazine (78a) produces H_2 , CH_4 , and borazanaphthalene derivatives.⁴⁶⁸ The initial reaction appears to be decomposition of the excited borazine into H_2 or CH_4 and the corresponding borazyne compound. This benzyne analogue then reacts with another borazine molecule

⁴⁶¹ J. T. Moseley, R. A. Bennett, and J. R. Peterson, *Chem. Phys. Letters*, 1974, **26**, 288.

⁴⁶² M. E. Jacox and D. E. Milligan, *J. Mol. Spectroscopy*, 1974, **52**, 363.

⁴⁶³ J. Veprek-Siska, S. Lunak, and A. El-Wakil, *Z. Naturforsch.*, 1974, **29b**, 812.

⁴⁶⁴ B. O. Wagner and G. S. Hammond, *J. Organometallic Chem.*, 1975, **85**, 1.

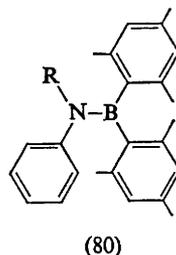
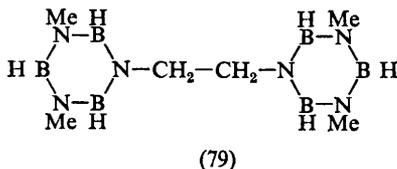
⁴⁶⁵ (a) P. H. Bolton and D. R. Kearns, *J. Amer. Chem. Soc.*, 1974, **96**, 4651; (b) P. H. Bolton and D. R. Kearns, *J. Phys. Chem.*, 1974, **78**, 1896.

⁴⁶⁶ J. J. Eisch, K. Tamao, and R. J. Wilcsek, *J. Amer. Chem. Soc.*, 1975, **97**, 895.

⁴⁶⁷ K. L. Rogozhin, A. N. Rodionov, D. N. Shigorin, N. I. Sheverdina, and K. A. Kocheshkov, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1974, 2740.

⁴⁶⁸ L. J. Turbini and R. F. Porter, *Inorg. Chem.*, 1975, **14**, 1252.

to yield the borazanaphthalene. Irradiation of hexafluoroacetone and borazine, under conditions where the hexafluoroacetone absorbs the light, gives (78b) and (78c).⁴⁶⁹ Compound (79) has been isolated following the mercury-sensitized photolysis of H_2 in the presence of (78d).⁴⁷⁰



The emission properties of anilindimesitylboranes (80) have been investigated.⁴⁷¹ These compounds show very large Stokes' shifts ($148\text{--}258\text{ kJ mol}^{-1}$) and the position of the fluorescence band is markedly solvent dependent. From these observations it has been concluded that the lowest excited singlet state has very pronounced $\bar{B}=\bar{N}^+$ character. By contrast, other aminoboranes exhibit only slight Stokes' shifts (*ca.* 34 kJ mol^{-1}), and in this case the emission has been characterized as that from a polar $\pi\pi^*$ excited state.⁴⁷² The anomalously large Stokes' shifts for the anilindimesitylboranes is attributed to steric hindrance which causes the ground-state to adopt sp^3 hybridization around the N atom.

Several i.r. laser-induced reactions of boron compounds have been observed.^{473–476} Thus $B_{20}H_{16}$ is formed as the main product on irradiation of B_2H_6 using a CO_2 laser.⁴⁷³ Excitation of BCl_3 in the presence of H_2S causes enrichment of ^{10}B ($^{10}B : ^{11}B$ from 0.242 to 0.413) for $10.55\text{ }\mu\text{m}$ radiation, while photolysis at $10.18\text{ }\mu\text{m}$ leads to a decrease of the $^{10}B : ^{11}B$ ratio to 0.169.⁴⁷⁴ The decomposition of H_3BPF_3 to B_2H_6 and PF_3 has also been stimulated by CO_2 laser irradiation but in this case no isotope effect was observed.⁴⁷⁵ Visible luminescence of BCl_3 has been induced using a CO_2 laser.⁴⁷⁶ The absorption and emission spectra of BI have been recorded following flash photolysis of BI_3 .⁴⁷⁷

Aluminium, Gallium, Indium, and Thallium.—The phosphorescence spectra of the acetylacetonates of Mg, Al, Ga, and In in EPA at 77 K have been recorded.⁴⁷⁸

The oxidation of Mn^{2+} or Fe^{2+} and the reduction of Co^{3+} by Tl^{2+} have been studied following the generation of Tl^{2+} by flash photolysis of Tl^{3+} .⁴⁷⁹ U.v.

⁴⁶⁹ L. J. Turbini, G. M. Golenwsky, and R. F. Porter, *Inorg. Chem.*, 1975, 14, 691.

⁴⁷⁰ L. J. Turbini, T. J. Mazanec, and R. F. Porter, *J. Inorg. Nuclear Chem.*, 1975, 37, 1129.

⁴⁷¹ M. E. Glogowski, P. J. Gridale, J. L. R. Williams, and L. Costa, *J. Organometallic Chem.*, 1974, 74, 175.

⁴⁷² K. G. Hancock, Y. Ko, D. A. Dickinson, and J. D. Kramer, *J. Organometallic Chem.*, 1975, 90, 23.

⁴⁷³ H. R. Bachmann, H. Noeth, R. Rinck, and K. L. Kompa, *Chem. Phys. Letters*, 1974, 29, 627.

⁴⁷⁴ S. M. Freund and J. J. Ritter, *Chem. Phys. Letters*, 1975, 32, 255.

⁴⁷⁵ E. R. Lory, S. H. Bauer, and T. Manuccia, *J. Phys. Chem.*, 1975, 79, 545.

⁴⁷⁶ R. V. Ambartzumian, N. V. Chekalin, V. S. Doljikov, V. S. Letokhov, and E. A. Ryabov, *Chem. Phys. Letters*, 1974, 25, 515.

⁴⁷⁷ J. Lebreton, J. Ferran, A. Chatalic, D. Iacocca, and L. Marsigny, *J. Chim. phys.*, 1974, 71, 587.

⁴⁷⁸ R. H. Clarke and R. E. Connors, *Spectrochim. Acta*, 1974, 30A, 2063.

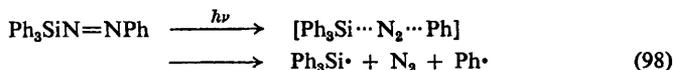
⁴⁷⁹ B. Falcinella, P. D. Felgate, and G. S. Laurence, *J.C.S. Dalton*, 1975, 1.

irradiation of $\text{Ti}(\text{OAc})_3$ in 10% sulphuric acid at 77 K produces methyl radicals.⁴⁸⁰ The effect of chloride ion on the luminescence of Ti^{I} in solution has been discussed.^{481, 482}

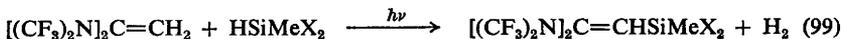
Silicon.—Organic aspects of the photochemistry of silicon-containing compounds are discussed in Part III, Chapter 6, Section 3. A review of the photochemistry of polysilanes has been published.⁴⁸³

The luminescence properties of Group IV metal tetraphenyl compounds have been discussed.^{484, 485} Other authors have considered the assignment of electronic transitions in polysilanes,⁴⁸⁶ the nature of the long-wavelength u.v. transitions in acylsilanes,⁴⁸⁷ the extent of (*p-d*) π -bonding in PhMMe_3 ($\text{M} = \text{Si}, \text{Ge}, \text{or Sn}$),⁴⁸⁸ and the assignment of the photoelectron spectra of $\text{M}(\text{CH}_2\text{SiMe}_3)_4$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}, \text{Ge}, \text{or Sn}$).⁴⁸⁹

The photochemical decomposition of $\text{Ph}_3\text{SiN}=\text{NPh}$ is presumed to proceed *via* reaction (98).⁴⁹⁰ However, although $\text{Ph}\cdot$ could be spin-trapped by αN -diphenylnitron, the corresponding adduct could not be observed for the $\text{Ph}_3\text{Si}\cdot$ species.



Reaction (99) proceeds in high yield, but low conversion, following the photolysis of the Si—H bond in HSiMeX_2 ($\text{X} = \text{Me}$ or Cl).⁴⁹¹ Addition of SiCl_3 , formed on photolysis of HSiCl_3 , to halogenated olefins,⁴⁹² and formation of $(\text{MeO})_2(\text{Me})\text{Si}-\text{Si}(\text{Me})(\text{OMe})_2$ from $(\text{MeO})_2(\text{Me})\text{SiH}$,⁴⁹³ have been reported.



Insertion of the carbene $\text{Me}_3\text{SiCH}:$ into C—H and Si—H bonds has been investigated following photolysis of $\text{Me}_3\text{SiCHN}_2$.⁴⁹⁴ Other photochemically induced reactions include the addition of H_2S to dimethyldiallylsilane,⁴⁹⁵ and the chlorination of alkyltrichlorosilanes.⁴⁹⁶

⁴⁸⁰ C. T. Cazianis and D. R. Eaton, *Canad. J. Chem.*, 1974, **52**, 2471.

⁴⁸¹ M. U. Belyi, N. G. Musienko, and B. A. Okhrimenko, *Ukrain fiz. Zhur.*, 1974, **19**, 1460.

⁴⁸² P. J. Mayne and G. P. Kirkbright, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1527.

⁴⁸³ M. Kumada, M. Ishikawa, H. Okinoshima, and K. Yamamoto, *Ann. New York Acad. Sci.*, 1974, **239**, 32.

⁴⁸⁴ M. Gouterman and P. Sayer, *J. Mol. Spectroscopy*, 1974, **53**, 319.

⁴⁸⁵ T. S. Lin, *Chem. Phys.*, 1974, **6**, 235.

⁴⁸⁶ B. G. Ramsey, *J. Organometallic Chem.*, 1974, **67**, C67.

⁴⁸⁷ B. G. Ramsey, A. Brook, A. R. Bassindale, and H. Bock, *J. Organometallic Chem.*, 1974, **74**, C41.

⁴⁸⁸ P. K. Bischof, M. J. S. Dewar, D. W. Goodman, and T. B. Jones, *J. Organometallic Chem.*, 1974, **82**, 89.

⁴⁸⁹ M. F. Lappert, J. B. Pedley, and G. Sharp, *J. Organometallic Chem.*, 1974, **66**, 271.

⁴⁹⁰ H. Watanabe, Y. Cho, Y. Ide, M. Matsumoto, and Y. Nagai, *J. Organometallic Chem.*, 1974, **78**, C4.

⁴⁹¹ D. H. Coy, F. Fitton, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, *J.C.S. Dalton*, 1974, 1852.

⁴⁹² W. I. Bevan, R. N. Haszeldine, J. Middleton, and A. E. Tipping, *J.C.S. Dalton*, 1974, 2305.

⁴⁹³ M. E. Childs and W. P. Weber, *J. Organometallic Chem.*, 1975, **86**, 169.

⁴⁹⁴ R. N. Haszeldine, D. Scott, and A. E. Tipping, *J.C.S. Perkin I*, 1974, 1440.

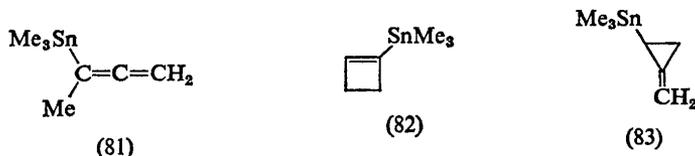
⁴⁹⁵ K. E. Koenig, R. A. Felix, and W. P. Weber, *J. Org. Chem.*, 1974, **39**, 1539.

⁴⁹⁶ (a) T. Burton and A. Bruylants, *J. Organometallic Chem.*, 1974, **69**, 397; (b) T. Burton and A. Bruylants, *Bull. Soc. chim. belges*, 1973, **82**, 737.

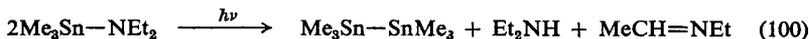
Germanium and Tin.—A general photochemical method for the preparation of metal-centred radicals $(R_2CH)_3M^1$ and $(R_2N)_3M^2$ ($R = SiMe_3$; $M^1 = Si, Ge,$ or Sn ; $M^2 = Ge$ or Sn) from the corresponding $(R_2CH)_2M^1$ or $(R_2N)_2M^2$ has been described.⁴⁹⁷ The radical species, which have been characterized by e.s.r., have lifetimes at room temperature of from 10 min [for $(R_2CH)_3Si$] to > 5 months [for $(R_2N)_3Ge$]. R_1^3Ge radicals ($R^1 = Ph, Me, Et, Pr^n, Pr^l,$ or Bu^n) have been identified by e.s.r. following reactions of photochemically generated Me_3CO^{\cdot} radicals with GeR^1_3H .⁴⁹⁸ I.r. spectra have been recorded for the free-radical species formed from GeH_nCl_{4-n} ($n = 0-4$), GeH_3Br , and GeH_2Br_2 on photolysis in argon and carbon monoxide matrices at 4 and 24 K.⁴⁹⁹

The photochemical decomposition of $[Ge^{IV}(ox)_3]^{2-}$,⁵⁰⁰ and the light-induced reactions of $Et_3MC\equiv CH$ ($M = Ge$ or Sn) with Bu^nSH ⁵⁰¹ have been discussed.

In contrast with their behaviour on heating, *cis*- and *trans*-penta-1,3-dienes produce the 1,4-addition products *cis*- and *trans*- $Me_3SnCH_2C=CHEt$ on photolysis in Me_3SnH .⁵⁰² No products arising from $Sn-C$ bond rupture could be observed after irradiation of 2-trimethylstannylbuta-1,3-diene, and the main products found were the isomers (81)—(83).⁵⁰³



Evidence for the photochemical cleavage of the $Sn-N$ bond as the primary step in reaction (100) has been adduced from CIDNP experiments.⁵⁰⁴ The reactions



of alkyl halides with R_3Sn ($R = Ph$ or Bu^n), produced on photolysis of Sn_2R_6 ,⁵⁰⁵ and the light-induced free-radical reactions of organotin alkoxides with polyhalogenomethanes have been investigated.⁵⁰⁶

Lead.—Recent reports on solid-state photoprocesses of Pb^{IV} compounds include investigations in the far-⁵⁰⁷ and near-i.r.⁵⁰⁸ of the effect of photodecomposition of $Pb(N_3)_2$, the low-temperature photoluminescence of $Pb(N_3)_2$,⁵⁰⁹ photoproduction of disorder in $Pb(N_3)_2$ and $Tl(N_3)_2$,⁵¹⁰ studies of the photolysis of $PbCl_2$

⁴⁹⁷ J. D. Cotton, C. S. Cundy, D. H. Harris, A. Hudson, M. F. Lappert, and P. W. Lednor, *J.C.S. Chem. Comm.*, 1974, 651.

⁴⁹⁸ H. Sakurai, K. Mochida, and M. Kira, *J. Amer. Chem. Soc.*, 1975, **97**, 929.

⁴⁹⁹ W. A. Guillory, R. J. Isabel, and G. R. Smith, *J. Mol. Structure*, 1973, **19**, 473.

⁵⁰⁰ E. L. J. Breet and R. van Eldik, *Inorg. Chim. Acta*, 1974, **9**, 177, 183.

⁵⁰¹ M. G. Voronkov, R. G. Mirskov, and V. I. Rakhlin, *Zhur. obschei Khim.*, 1974, **44**, 954.

⁵⁰² M. Bigwood and S. Boue, *J.C.S. Chem. Comm.*, 1974, 529.

⁵⁰³ P. Vanderlinden and S. Boue, *J. Organometallic Chem.*, 1975, **87**, 183.

⁵⁰⁴ M. Lehnig, *Tetrahedron Letters*, 1974, 3323.

⁵⁰⁵ H. G. Kuivila and C. C. H. Pian, *J.C.S. Chem. Comm.*, 1974, 369.

⁵⁰⁶ J.-C. Pommier and D. Chevolleau, *J. Organometallic Chem.*, 1974, **74**, 405.

⁵⁰⁷ S. P. Varma, F. Williams, and K. D. Moeller, *J. Chem. Phys.*, 1974, **60**, 4950.

⁵⁰⁸ S. P. Varma and F. Williams, *J. Chem. Phys.*, 1974, **60**, 4955.

⁵⁰⁹ J. Schanda, B. Baron, and F. Williams, *J. Luminescence*, 1974, **9**, 338.

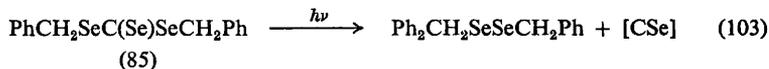
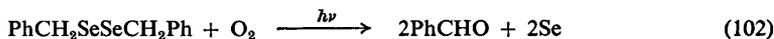
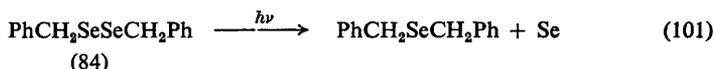
⁵¹⁰ D. A. Wiegand, *Phys. Rev. (B)*, 1974, **10**, 1241.

crystal surfaces,⁵¹¹ photolysis of PbBr_2 ,^{512, 513} and photoluminescence of PbI_2 at 4.2 K.⁵¹⁴

Phosphorus.—E.s.r. data have been presented as evidence for formation of $\text{PPh}_2\cdot$ on u.v. irradiation of crystalline PPh_3 ⁵¹⁵ or PPh_2H .⁵¹⁶ Other publications discuss the fluorescence spectra of triarylphosphines,⁵¹⁷ and the correlation with Hammett σ values of the rate constants for quenching of the singlet states of substituted anthracenes by PPh_3 .⁵¹⁸

U.v. irradiation of PF_2Cl yields $\text{PF}_2\cdot$,⁵¹⁹ whereas photolysis of PF_3 in the presence of F_2O or ROOR produces $\text{PF}_4\cdot$ and $\text{PF}_3\text{OR}\cdot$ respectively.⁵²⁰ The photoaddition of P_2F_4 to olefins has preparative applications.⁵²¹

Other Elements.—The photochemical transformations of the organoselenium compounds (84) and (85) have been described.⁵²² Photo-induced rupture of the



S_8 rings leads to the polymerization of sulphur.⁵²³ Photochemical preparations of SO_3F_2 , $\text{S}_2\text{O}_5\text{F}_2$,⁵²⁴ and of $\text{SF}_4\text{OR}\cdot$ ⁵²⁵ have been reported.

Photo-induced reactions in inert matrices continue to be very useful techniques for the synthesis of novel small molecules. Thus photolysis ($\lambda < 240$ nm) of F_3NO in argon matrices at 8 K produces FNO ,⁵²⁶ and similarly the main primary product on irradiation of CF_3OF or CF_3OCl is F_2CO .⁵²⁷ $\text{NF}_2\cdot$ is formed on photolysis of NF_3 in argon or carbon monoxide matrices.⁵²⁸ Irradiation of mixtures of F_2 and NO_2 in nitrogen matrices at 8 K gives FNO_2 .^{529a} On warming

⁵¹¹ J. F. Reber and R. Steiger, *Surface Sci.*, 1975, 49, 236.

⁵¹² M. T. Kostyshin and E. V. Mikhailovskaya, *Ukrain. fiz. Zhur.*, 1974, 19, 507.

⁵¹³ M. T. Kostyshin, E. V. Mikhailovskaya, and V. M. Sharyi, *Ukrain. fiz. Zhur.*, 1974, 19, 1327.

⁵¹⁴ (a) F. Levy, A. Mercier, and J. P. Voitchovsky, *Helv. Phys. Acta*, 1974, 47, 440; (b) F. Levy, A. Mercier, and J. P. Voitchovsky, *Solid State Comm.*, 1974, 15, 819.

⁵¹⁵ W. T. Cook, J. S. Vincent, I. Bernal, and F. Ramirez, *J. Chem. Phys.*, 1974, 61, 3479.

⁵¹⁶ M. Geoffroy, E. A. C. Lucken, and C. Mazeline, *Mol. Phys.*, 1974, 28, 839.

⁵¹⁷ N. A. Rozanel'skaya, A. I. Bokanov, B. M. Uzhinov, and B. I. Stepanov, *Zhur. obshchei Khim.*, 1975, 45, 277.

⁵¹⁸ M. E. R. Marcondes, V. G. Toseano, and R. G. Weiss, *Tetrahedron Letters*, 1974, 4053.

⁵¹⁹ A. J. Colussi, J. R. Morton, K. F. Preston, and R. W. Fessenden, *J. Chem. Phys.*, 1974, 61, 1247.

⁵²⁰ A. J. Colussi, J. R. Morton, and K. F. Preston, *J. Phys. Chem.*, 1975, 79, 651.

⁵²¹ J. G. Morse and K. W. Morse, *Inorg. Chem.*, 1975, 14, 565.

⁵²² W. Stanley, M. R. Van De Mark, and P. L. Kumler, *J.C.S. Chem. Comm.*, 1974, 700.

⁵²³ T. Nakayama, T. Nose, H. Kokada, and E. Inoue, *J. Chem. Letters*, 1974, 287.

⁵²⁴ M. Gambaruto, J. E. Sicre, and H. J. Schumacher, *J. Fluorine Chem.*, 1975, 5, 175.

⁵²⁵ A. R. Gregory, S. E. Kavelas, J. R. Morton, and K. F. Preston, *J. Amer. Chem. Soc.*, 1975, 97, 2206.

⁵²⁶ R. R. Smardzewski and W. B. Fox, *J. Chem. Phys.*, 1974, 60, 2193.

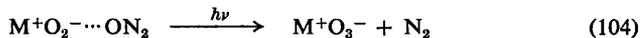
⁵²⁷ R. R. Smardzewski and W. B. Fox, *J. Phys. Chem.*, 1975, 79, 219.

⁵²⁸ M. E. Jacox, D. E. Milligan, W. A. Guillery, and J. J. Smith, *J. Mol. Spectroscopy*, 1974, 52, 322.

⁵²⁹ (a) R. R. Smardzewski and W. B. Fox, *J. Chem. Phys.*, 1974, 60, 2980; (b) R. R. Smardzewski and W. B. Fox, *ibid.*, 1974, 61, 4933.

the matrix to 20 K further fluorine atoms diffuse through the matrix and react with NO₂ to give ONOF. This compound on further irradiation isomerizes to the more stable FNO₂. Small amounts of OF are also found during this matrix reaction and it is suggested that these arise from combination of O and F atoms formed respectively from NO₂ and F₂.^{529b} Noble gas dihalides have been synthesized on photolysis of mixtures of Kr and F₂, or Xe and F₂, Cl₂ or ClF in low-temperature matrices,⁵³⁰ and of Xe and F₂ at 77 K.⁵³¹

It is proposed that the production of M⁺O₃⁻ on photolysis of alkali-metal atoms M, O₂, and N₂O in argon matrices involves reaction (104).⁵³² Similarly, nitrites are formed by process (105) when NO is substituted for O₂. The



fluorescence spectra of ClO₂⁵³³ and of ICl⁵³⁴ in noble-gas matrices have been reported.

6 Surface Photochemistry and Miscellaneous Topics

A review (in Japanese) of the photochemistry of TiO₂ has been published.⁵³⁵

Irradiation of high-purity ZnO in aqueous solution produces e.s.r. signals which have been assigned to unpaired electrons both in the conduction band of the bulk ZnO and in partially ionized donors (*e.g.* Zn⁺) near the surface.⁵³⁶ Illumination of the TiO₂ plate in a TiO₂ electrolyte Pt cell induces photocurrents with low efficiency ($\Phi = 10^{-3}$).⁵³⁷ The photoreduction of methyl viologen in the presence of TiO₂ has been reported.⁵³⁸ Other studies deal with the photoreduction of TiO₂ in organic media,⁵³⁹ and the photocatalytic deposition of Pd on TiO₂.⁵⁴⁰

The photo-oxidation of SO₂ to SO₃⁻ in the presence of H₂O and O₂ or N₂O has been monitored by e.s.r.⁵⁴¹ The photo-oxidation of carbon monoxide by oxygen may be catalysed by illumination of a number of inorganic oxides,⁵⁴² and in another study it has been shown that the catalytic activity of ZnO for this reaction depends on the contact time of the catalyst with the gases prior to irradiation.⁵⁴³ Flash illumination of TiO₂ initiates the dehydrogenation of methanol or ethanol to formaldehyde and acetaldehyde, respectively.⁵⁴⁴ The oxidation of paraffins and olefins to ketones takes place on irradiation of TiO₂ in the presence of these

⁵³⁰ W. F. Howard and L. Andrews, *J. Amer. Chem. Soc.*, 1974, **96**, 7864.

⁵³¹ A. I. Malkova, V. I. Tupikov, I. V. Isakov, and V. Y. Dudarev, *Zhur. neorg. Khim.*, 1974, **19**, 1729.

⁵³² L. Andrews and T. E. Tevault, *J. Mol. Spectroscopy*, 1975, **55**, 452.

⁵³³ F. K. Chi and L. Andrews, *J. Mol. Spectroscopy*, 1974, **52**, 82.

⁵³⁴ V. E. Bondybey and L. E. Brusik, *J. Chem. Phys.*, 1975, **62**, 620.

⁵³⁵ H. Mimuro, *Shikizai Kyokaiishi*, 1974, **47**, 605.

⁵³⁶ J. Cunningham and S. Corkery, *J. Phys. Chem.*, 1975, **79**, 933.

⁵³⁷ T. Ohnishi, Y. Nakato, and H. Tsubomura, *Ber. Bunsengesellschaft phys. Chem.*, 1975, **79**, 523.

⁵³⁸ A. A. Krasnovskii and G. P. Brin, *Doklady Akad. Nauk S.S.S.R.*, 1973, **213**, 1431.

⁵³⁹ V. S. Il'enko and A. V. Uvarov, *Kinetika i Kataliz*, 1974, **15**, 543.

⁵⁴⁰ F. Moellers, H. J. Tolle, and R. Memming, *J. Electrochem. Soc.*, 1974, **121**, 1160.

⁵⁴¹ M. J. Lin and J. H. Lunsford, *J. Phys. Chem.*, 1975, **79**, 892.

⁵⁴² L. V. Lyashenko and Y. B. Gorokhovatskii, *Teor. i eksp. Khim.*, 1974, **10**, 186.

⁵⁴³ V. S. Zakharenko, A. E. Cherkashin, and N. P. Keier, *React. Kinet. Catal. Letters*, 1974, **1**, 381.

⁵⁴⁴ J. Cunningham, E. Finn, and A. L. Penny, *Chemica Scripta*, 1974, **6**, 87.

substrates and oxygen,⁵⁴⁵ and in the case of isobutane it has been shown that excited atomic oxygen is the active species.⁵⁴⁶ From e.s.r. measurements it has been demonstrated that photolysis of water on silica gel at -170°C yields $\text{OH}\cdot$, while $\cdot\text{CHO}$ is formed from carbon monoxide or carbon dioxide.⁵⁴⁷

A theory for the photocatalysed exchange reaction of deuterium and hydrogen over semiconductors such as ZnO has been presented.⁵⁴⁸ In the photocatalysed exchange of $^{16}\text{O}_2$ and $^{18}\text{O}_2$ over TiO_2 it has been shown that O_3^- is the important intermediate,⁵⁴⁹ and other authors have recorded the e.s.r. signal of this species on irradiating TiO_2 applied on silica gel in the presence of molecular oxygen.^{550, 551}

The binding of methyl radicals to silica gel has been examined for species produced both by γ -irradiation and by photolysis of methyl iodide.⁵⁵² It has been found that the subsequent rates of decay of these radicals depend on the energy with which the species is 'born' and on the specific site on which the methyl iodide is absorbed. Photolysis of butyl methacrylate over Al_2O_3 or Ga_2O_3 gives radical species bonded to the surface, which may then be used to initiate polymerization reactions.⁵⁵³

Other subjects recently discussed include the photoabsorption of carbon monoxide and oxygen on ZnO,⁵⁵⁴ the relative photoabsorption of oxygen and methane over ZnO,⁵⁵⁵ the photocatalytic properties of ZnO and MgO,⁵⁵⁶ the effect of irradiation on the dielectric properties of TiO_2 ,⁵⁵⁷ the photoluminescence of an oxide layer on aluminium,⁵⁵⁸ the singlet-triplet splitting of the free A-exciton in ZnO,⁵⁵⁹ the properties of the photosensitive film of copper in iodine solution,⁵⁶⁰ and the photosensitivity of layers of CuCl_2 and $[\text{Fe}(\text{ox})_3]^{3-}$.⁵⁶¹

⁵⁴⁵ M. Formenti, F. Juillet, P. Meriaudeau, and S. J. Teichner, in 'Catalysis, Proc. International Congress, 5th', ed. J. W. Hightower, North Holland, Amsterdam, 1973, p. 1011.

⁵⁴⁶ S. Bourasseau, J. R. Martin, F. Juillet, and S. J. Teichner, *J. Chim. phys.*, 1974, **71**, 1025.

⁵⁴⁷ S. S. Tseng and S. Chang, *Origins Life*, 1975, **6**, 61.

⁵⁴⁸ F. F. Vol'kenshtein and V. B. Nagaev, *Kinetika i Kataliz*, 1974, **15**, 373.

⁵⁴⁹ K. Tanaka, *J. Phys. Chem.*, 1974, **78**, 555.

⁵⁵⁰ V. V. Nikisha, B. N. Shelimov, and V. B. Kazanskii, *Kinetika i Kataliz*, 1974, **15**, 676.

⁵⁵¹ V. V. Nikisha, S. A. Surin, B. N. Shelimov, and V. B. Kazanskii, *React. Kinet. Catal. Letters*, 1974, **1**, 141.

⁵⁵² G. R. Joppien and J. E. Willard, *J. Phys. Chem.*, 1974, **78**, 1391.

⁵⁵³ V. P. Galkin, V. B. Golubev, and E. V. Lunina, *Zhur. fiz. Khim.*, 1974, **48**, 777.

⁵⁵⁴ J. M. Balois, M. Guelton, and J. P. Bonnelle, *J. Chim. phys.*, 1974, **71**, 431.

⁵⁵⁵ G. N. Kuz'min and Y. P. Solonitsyn, *Kinetika i Kataliz*, 1974, **15**, 700.

⁵⁵⁶ A. A. Lisachenko and F. I. Vilesov, *Uspekhi Fotoniki*, 1974, **4**, 18.

⁵⁵⁷ V. I. Kovalevskii, V. V. Sviridov, and M. S. Mironov, *Izvest. Vyssh. Ucheb. Zaved., Fiz.*, 1974, **17**, 156.

⁵⁵⁸ M. I. Eidel'berg and I. I. Petrenko, *Izvest. Vyssh. Ucheb. Zaved., Fiz.*, 1974, **17**, 135.

⁵⁵⁹ E. Tomzig and R. Helbig, *Solid State Comm.*, 1974, **15**, 1513.

⁵⁶⁰ J. Franco and N. K. Patel, *J. Chem. Phys.*, 1975, **61**, 2169.

⁵⁶¹ L. I. Stepanova and V. V. Sviridov, *Vestsi Akad. Navuk Belarus. S.S.R., Ser. khim. Navuk*, 1974, **38**.

