

Some New Aspects of the Photoreactions of Platinum Metals Complexes

By Liu Weiping, Yang Yikun and Xiong Huizhou

Institute of Precious Metals, Kunming, P. R. China

and Fu Wenfu

Department of Chemistry, Yunnan Teacher's University, Kunming, P. R. China

Photochemical reactions of platinum metals complexes are of great importance in contributing to the understanding of the chemical reactivity and catalytic properties of platinum metals catalysts. This paper reviews some new aspects of this photochemistry and discusses potential applications in synthesising novel complexes and in exploiting platinum metals-containing catalysts. Among aspects examined are recent trends in the photochemistry of co-ordination compounds, particularly photointramolecular rearrangements, photoredox elimination and addition reactions, and the photoredox reactions of polynuclear complexes.

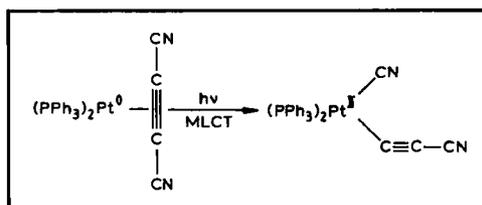
The photochemistry of co-ordination compounds, particularly of the platinum metals complexes, is regarded as an important area of chemical research (1). The photochemistry of platinum metals complexes has been studied since 1962 when the photochemical behaviour of PtCl_4^{2-} was first reported (2). Previously, researchers in this area concentrated mainly on classical platinum metals complexes, and identified three typical types of photoreactions: photosubstitution, photoisomerisation and photoredox reactions (3). Recently, however, some new types of photoreactions, such as photointramolecular rearrangements, photoredox elimination and addition reactions, and photoredox reactions of polynuclear complexes, have been identified and investigated. These interesting reactions may contribute to the understanding of the reactivity of chemical compounds, and to the exploitation of novel catalytic processes. This increased interest in these new photoreactions of the platinum metals complexes is reviewed here briefly.

Photointramolecular Rearrangements

Photointramolecular rearrangements consist mainly of redox and non-redox isomerisations. Photoredox intramolecular isomerisations of

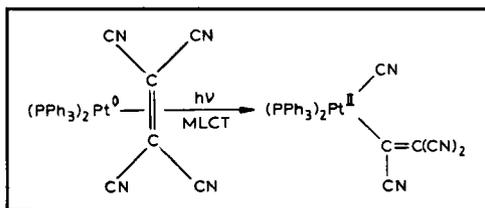
platinum metals complexes are reactions in which the molecular formula of the complex is preserved, but the composition of the individual ligands, the oxidation number of the central atom and also, in some instances, the co-ordination number of the central atom are changed.

A photoredox rearrangement reaction is frequently one of the steps that occurs in the mechanism of catalytic processes and syntheses of organometallic compounds (4). For example, the photochemical transformation of the π -complex, $[\text{Pt}^0(\text{PPh}_3)_2(\text{NCC}_2\text{CN})]$, gives rise to a reactive Pt(II) intermediate which can be isolated. The intermediate, which is prepared by continuous photolysis of the π -complex, is also the first example of a complex that contains a $-\text{CC}\equiv\text{CN}$ group as a ligand (4).



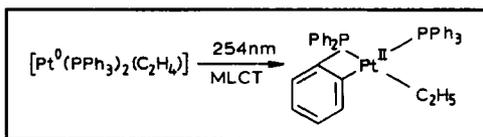
Upon irradiation of the related tetracyanoethylene platinum(0) π -complex, the reaction

below has been observed (5):

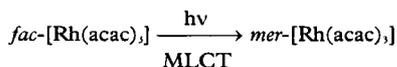
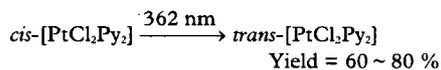
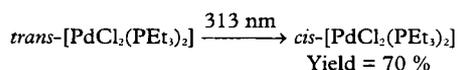


These reactive Pt(II) intermediates may release radicals $\cdot\text{CN}$, $\cdot\text{C}\equiv\text{CCN}$ or $\cdot\text{C}(\text{CN})=\text{C}(\text{CN})_2$ which can be further reacted with other compounds to form desired products, such as R-CN , $\text{R-C}\equiv\text{C-CN}$ or $\text{R-C}(\text{CN})=\text{C}(\text{CN})_2$.

Continuous photolysis of $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$ at 254 nm also results in a photoredox intramolecular rearrangement, forming a tetra co-ordinated π -complex (6). This is an interesting and potentially useful photochemical transformation of an olefin complex into an ethyl complex. This phototransformation may hold promise for the hydrogenation of olefinic compounds.

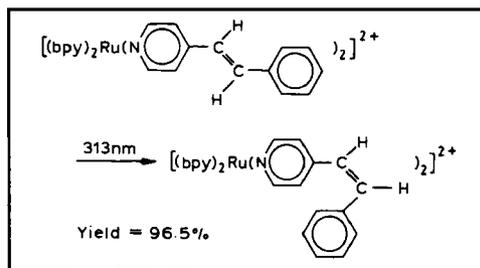


Photoisomerisation reactions of geometrical isomers are non-redox intramolecular rearrangements. So far, studies have been directed particularly towards photochemical *cis* \leftrightarrow *trans* and *mer* \leftrightarrow *fac* conversions of platinum metals complexes. This type of photoconversion has been used as a method to synthesise isomers which are difficult to obtain via thermal reactions, as shown in the following Equations (3, 7, 8):

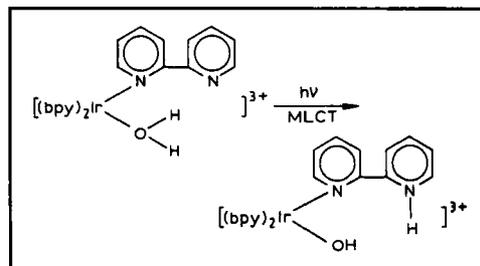


Another type of non-redox intramolecular rearrangement is the photoisomerisation of

co-ordinated ligands, such as the thermally stable *trans*-4-styrylpyridine to the *cis*-form (9):



In some cases, intramolecular rearrangement involves proton transfer between two co-ordinated ligands, as is observed during the irradiation of $[\text{Ir}(\text{bpy})_3\cdot\text{H}_2\text{O}]^{3+}$ in which one of the 2,2'-bipyridine ligands is bonded monofunctionally (10).



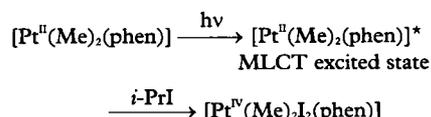
For reactions of this type, a knowledge of the photochemical generation of reactive intermediates may possibly be applied to the catalytic processes in organic syntheses, where the complex can activate the shift of hydrogen from the water molecules to other compounds under irradiation.

Photoredox Elimination and Addition Reactions

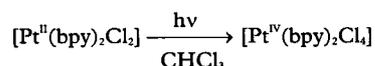
Photoredox elimination and addition reactions are characterised by changes both in the oxidation number of the central atom and in the co-ordination number of the platinum metal complex. Photoredox reactions depend on the nature of the excited states. In the case of metal-to-ligand charge-transfer (MLCT) excitation, the nature of the excited state will determine the process of the reaction (11). An increase in the oxidation number is usually accompanied

by an increase in the co-ordination number and vice versa. The former reactions are called oxidative addition and the latter reductive elimination.

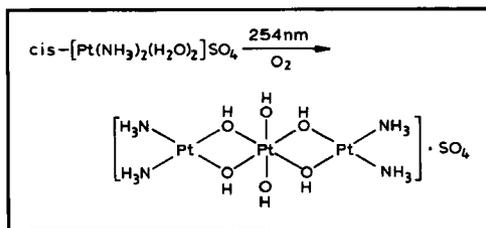
The localisation of the excited electron in the ligand π^* orbital causes a decrease in the electron density on the metal centre and an increase in electrophilicity, which will promote nucleophilic attack on the metal centre, that is, oxidative addition. The reactive part of the ligand, particularly organic compounds, bonds to the vacant, unoccupied site on the central atom with simultaneous oxidation of the central atom, for example (12, 13):



phen = 1,10-phenanthroline $i\text{-Pr}$ = isopropane



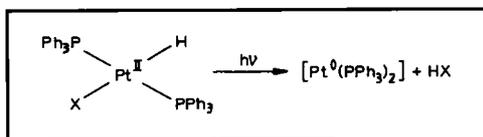
The photoredox addition reaction has been successfully used to synthesise platinum blue (14–15):



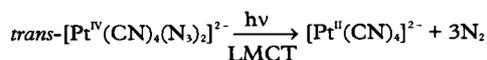
Ligand-to-metal charge-transfer (LMCT) states involve electronic transitions from a ligand orbital to a metal orbital. The elimination reactions of LMCT states are different from those of MLCT states since a decrease in the oxidation number of the central atom is usually accompanied by the release of the co-ordinated ligands.

The electronic transitions of the LMCT excited state are usually observed at a high energy band in organometallic complexes. The metal centre is in a high oxidation state and delocalisation of the electron density from the occu-

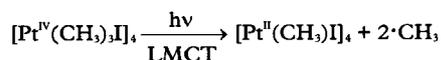
ried ligand orbital to an empty metal orbital may occur in such an excitation. For example, irradiation of *trans*-[PtHX(PPh₃)₂], where X = CH₂CN or CF₃, produces free HX (16):



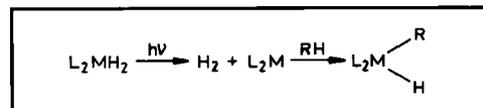
The release of nitrogen from *trans*-[Pt^{IV}(CN)₄(N₃)₂]²⁻ during irradiation at 254 nm is another example of reductive elimination (17):



The tetrameric complex [Pt(CH₃)I]₄ consists of monomeric components which undergo a photochemical reductive elimination releasing methyl radicals (18):



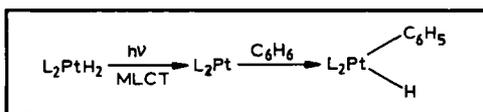
The photoinduced elimination of H₂ can occur from some platinum hydrides (19). Upon irradiation, the MLCT excited states quickly release H₂, leaving behind L₂M fragments, which are co-ordinatively and electronically unsaturated species. These react with organic substrates to give insertion products, as illustrated by the following reactions:



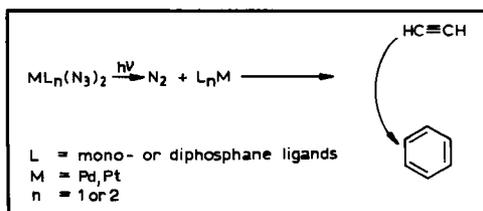
This is, in fact, a photoinduced activation of C-H bonds. C-H bond activation is very important for a number of industrial processes which cleave C-H bonds (20). For example, L₂PtH₂, where L is (*t*-Bu)₂P(CH₂)₂P(*t*-Bu)₂ or (Men)₂P(CH₂)₂P(Men)₂ (Men = menthane) is thermally stable and shows no tendency to lose hydrogen.

However, it is quite photoactive, and irradiation in benzene leads to reductive elimination of hydrogen to generate [L₂Pt] fragments which produce L₂Pt(Ph)H as the exclusive oxidative

product (21). As a result, benzylic C-H bonds have been activated.

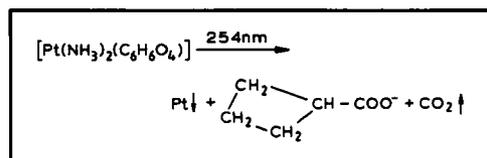


Irradiation of mixed ligand azido complexes of Pd(II) and Pt(II) in MLCT processes produces L_nM^0 where $n = 1, 2$ with the release of N_2 , followed by L_nM activation of C-C bonds, which catalyses the oligomerisation and cyclisation of acetylene and derivatives (22, 23).



In particular, the very convenient photochemical generation of the catalytically active species L_nM should be stressed. Compared with thermal reaction pathways, catalysts are formed photochemically in one reaction step and hence with high selectivity (24). As selectivity is the essence of catalysis, its achievement is central to chemical research. Furthermore, the population of different electronically excited states, depending upon the wavelength of the radiation, provides a method of tuning between different reaction pathways (25).

Solvent effects play an important role in a number of photoinduced electron-transfer reactions. In some aerated solvent systems, such as CHCl_3 , which contain $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ or $[\text{Ru}(\text{bpy})_2\text{Cl}_2]^+$, irradiation causes transformation to the other complex, induced by a solvent-initiated radical chain reaction (26, 27). The photolysis of aqueous Carboplatin, see below, demonstrates that under a nitrogen atmosphere at 254 nm irra-



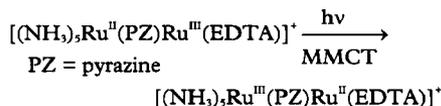
diation, a photoredox reaction occurs to produce platinum (28, 29).

Thus, studies of photoredox elimination and addition reactions are very promising, as the formation of the intermediates as well as the final stable products may find practical application.

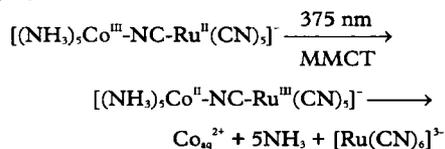
Photoredox Reactions of Polynuclear Complexes

Polynuclear complexes of the platinum metals undergo redox reactions different from those of mononuclear complexes where charge transfer usually occurs between the central atom and the ligands. Irradiation of a polynuclear complex involves an intramolecular electron-transfer reaction between the central atoms, which are connected by a bridging ligand (30, 31).

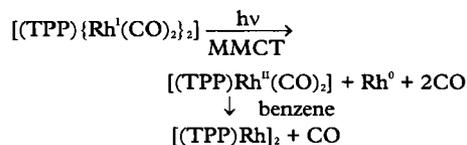
Photoredox reactions of ligand-bridged metal complexes induced by metal-to-metal charge transfer (MMCT) excitation have been investigated extensively (31):



If a binuclear complex has at least one central atom which forms kinetically labile complexes during irradiation, decomposition of the complex from the MMCT excited state can happen (32).

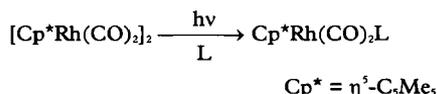


The dinuclear rhodium complex, (μ -tetraphenylporphinato)bis(dicarbonyl)rhodium(I) $[(\text{TPP})\{\text{Rh}^{\text{I}}(\text{CO})_2\}_2]$ also undergoes a photodecomposition reaction (33):

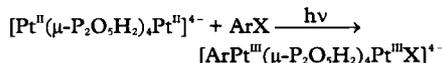


Irradiation of the complex $[\text{Cp}^*\text{Rh}(\text{CO})_2]$ in the presence of L (L = tetracyanoethylene)

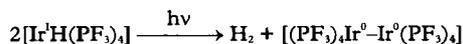
causes a dissociative reaction, to give a mono-nuclear product (34).



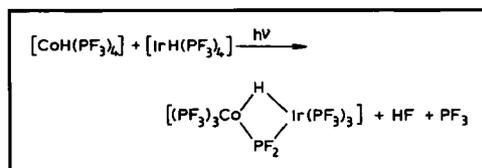
Oxidative addition of ArX (Ar = aryl, X = Br, I) to the excited state of $[\text{Pt}^{\text{II}}(\mu\text{-P}_2\text{O}_5\text{H}_2)_4]^{4+}$ can be observed, giving the axially distributed complex (35, 36).



Photoexcitation of mononuclear complexes may result in the production of polynuclear complexes. The composition of the product and its structure depend on the properties of the central atom. With $[\text{IrH}(\text{PF}_3)_4]$, a complex with a metal-metal single bond is formed:



While a double-bridged compound is produced from a mixture of $[\text{IrH}(\text{PF}_3)_4]$ and $[\text{CoH}(\text{PF}_3)_4]$ (37):



These different photoreactions of various platinum group metals complexes could open up pathways to the formation of further interesting complexes, and the increasing knowledge of the photochemical behaviour of polynuclear complexes may indeed lead to the development of new types of platinum metals catalysts.

References

- 1 F. Basolo, *Coord. Chem. Rev.*, 1993, **125**, 13
- 2 J. R. Perumareddi, PhD Dissertation, UCLA, 1962
- 3 Liu Weiping and Yang Yikun, *Precious Metals (China)*, 1997, **18**, (2), 53
- 4 F. W. Grevels and E. Koerner, *Ann. Chem.*, 1975, 547
- 5 O. Traverso, V. Carassiti, and M. Graziani, *J. Organomet. Chem.*, 1973, **57**, C22
- 6 P. Bergamini and E. Costa, *Coord. Chem. Rev.*, 1993, **125**, 53
- 7 N. W. Alcock and T. J. Kemp, *Inorg. Chim. Acta*, 1980, **44**, LZ54
- 8 N. W. Alcock and T. J. Kemp, *J. Chem. Soc., Dalton Trans.*, 1981, 635
- 9 P. P. Zarnegar, C. R. Bock and D. G. Whitten, *J. Am. Chem. Soc.*, 1975, **79**, 2073
- 10 R. J. Watts and S. F. Bergeron, *J. Phys. Chem.*, 1979, **83**, 424
- 11 C. A. Bignozzi and C. Chiorboli, *Inorg. Chem.*, 1993, **32**, 1036
- 12 R. H. Hill and R. J. Puddephatt, *J. Am. Chem. Soc.*, 1985, **107**, 1218
- 13 A. Vogler and H. Kunkely, *Angew. Chem.*, 1984, **94**, 217
- 14 C. A. Bignozzi and C. Bartocci, *Inorg. Chim. Acta*, 1982, **62**, 187
- 15 B. Lipper, *J. Clin. Hemat. Onc.*, 1979, **7**, 26
- 16 M. Hackett, *J. Am. Chem. Soc.*, 1986, **108**, 8094
- 17 W. Webber and R. V. Eldik, *Inorg. Chim. Acta*, 1986, **111**, 129
- 18 H. Kunkely and A. Vogler, *Coord. Chem. Rev.*, 1991, **111**, 15
- 19 G. L. Geoffroy and M. S. Wrighton, *Organometallic Photochemistry*, Academic Press, 1977
- 20 J. P. Colman and L. S. Hegedus, "Principles and Applications of Organometallic Chemistry", University Science Book, California, 1980
- 21 P. Bergamini and S. Sostero, "Polynuclear Inorganic Compounds", Venezia, 1981, 1311
- 22 H. Henning, R. Stich and H. Knoll, *Z. Anorg. Allg. Chem.*, 1989, **572**, 139
- 23 H. Knoll, R. Stich and H. Henning, *Inorg. Chim. Acta*, 1990, **178**, 71
- 24 W. D. Jones, in "Activation and Functionalization of Alkanes", ed. G. L. Hills, John Wiley, 1989
- 25 H. Henning and R. Billing, *Coord. Chem. Rev.*, 1993, **125**, 89
- 26 N. Sonoyana and O. Karasawa, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 437
- 27 C. C. Tong, M. Winkelmann and A. Jain, *Inorg. Chim. Acta*, 1994, **226**, 247
- 28 W. P. Liu, Y. K. Yang and Z. H. Que, *Science in China, Series B*, 1994, **37**, 799
- 29 W. P. Liu, Y. K. Yang and Z. H. Que, *Acta Pharm. Sinica*, 1996, **31**, (1), 74
- 30 H. Kunkely and A. Vogler, *Inorg. Chim. Acta*, 1993, **209**, 93
- 31 H. Kunkely, A. Pawlowski and A. Vogler, *Inorg. Chim. Acta*, 1994, **225**, 327
- 32 C. J. Curtis and J. S. Bernstein, *Chem. Phys. Lett.*, 1981, **81**, 48
- 33 M. Hoshino and K. Yasufuku, *Inorg. Chem.*, 1985, **24**, 4408
- 34 F. Pradella and M. Scoponi, *J. Organomet. Chem.*, 1993, **77**, C273
- 35 J. Kruck and R. Kobet, *Chem. Ber.*, 1982, **105**, 3765
- 36 Y. Honkay, C. M. Che and Z. T. Zhou, *J. Chem. Soc., Chem. Commun.*, 1992, **18**, 1369
- 37 D. M. Roundhill, *J. Am. Chem. Soc.*, 1985, **107**, 4354