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Further Perspectives in Organometallic Photochemistry

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Abstract

This article discusses developments in two fields of organometallic chemistry: photochemistry of transition metal hydrides as a route to produce low valent transition metal compounds and the potential of photogenerated coordinatively and electronically unsaturated organometallic species to activate C-H bonds.

1. INTRODUCTION

For some time the field of organometallic chemistry has been of great interest from the fundamental, theoretical and synthetic points of view. New compounds with unusual chemical-physical properties are constantly appearing as organometallic chemists take advantage of the increasingly powerful and sophisticated instruments now available for the structural analysis of organometallic reaction products. At the same time marked progress has been made in understanding the basic processes which lead to the formation of a large number of the known organometallic compounds.

Photochemistry has played a fruitful role in this broad flowering of organometallic chemistry. In fact, today, organometallic photochemistry is a field of intensive, exciting study. This is mainly due to the fact that recent results have indicated that irradiation of organometallic compounds can lead to catalytically and synthetically useful transformations of organic substrates [1-4].

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This communication presents some photochemical studies of organometallic molecules which are of direct relevance to synthesis and catalysis. The specific topics include:

a) Photochemistry of hydride and olefin complexes of transition metals as a tool for preparing low-valent transition metal compounds with unusual physico-chemical properties.
b) Photogeneration of coordinatively and electronically unsaturated intermediates which exhibit selective reactivity toward inert molecules.

2. PHOTOCHEMICAL FORMATION OF LOW-VALENT TRANSITION METAL COMPOUNDS

Low-valent transition metal compounds represent an area of great interest within both the fields of fundamental and applied chemistry. These species are very stimulating not only for their unique reactivity, but also because they represent an ideal model for studying the chemical behaviour of a single centre which compares with a metal surface. This is a problem connected to the relationship between homogeneous and heterogeneous catalysis.

2.1. Photochemistry of hydride complexes

Photoinduced elimination of H_2 is a general reaction for di- and poly-hydrides of all transition elements [1]. It has already been observed for complexes of iron group metals and also for complexes of molybdenum, tungsten, iridium and platinum containing a diverse array of ligands. The reductive elimination of H_2 is a dissociative process originated by MLCT excited states. This has been a much-studied process; only a few exemplary cases are shown here:

$$Cp_2MH_2 \xrightarrow{h\nu} Cp_2M + H_2 \qquad [5,6] \qquad (1)$$

$Cp = \eta^5\text{-}C_5H_5$; M = Mo, W

$$L_2MH_2 \xrightarrow{h\nu} L_2M + H_2 \qquad [7\text{-}9] \qquad (2)$$

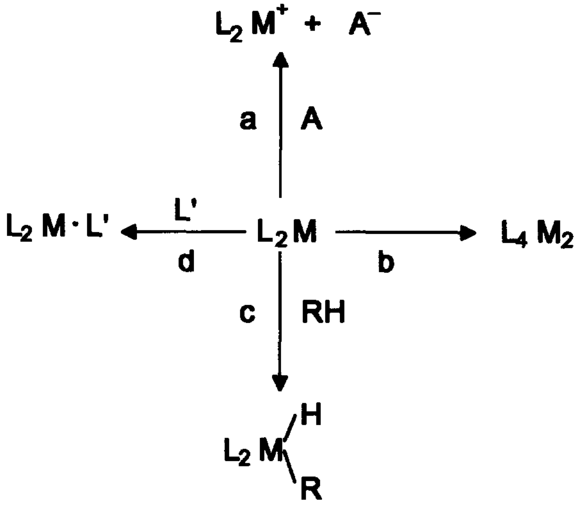
L = phosphine; M = Fe, Ru

$$\mathrm{Cp^*LMH_2} \xrightarrow{h\nu} \mathrm{Cp^*LM} + \mathrm{H_2} \qquad [10\text{-}12] \qquad (3)$$

$\mathrm{Cp^*} = \eta^5\text{-}\mathrm{C_5Me_5}$; L = phosphine; M = Ir, Rh

Upon irradiation, the MLCT excited states of the hydride quickly extrude H_2. This leaves behind electron-rich metal centers which are coordinatively unsaturated. Organometallic fragments exhibit an impressively wide range of chemical behaviours depending on the experimental conditions used.

Figure 1 provides a diagram indicating the various reactions possible for a prototypical L_2M fragment. All of these reactions are known for many different metal centers, though not every metal fragment necessarily exhibits high reactivity with respect to each reaction.



Reaction series a: L=Cp or Cp*; M=Fe, Ru; A=Acceptor
series b: L=Cp; M=Mo
series c: L=Cp or Cp*; M=W
L=Phosphine; M=Fe, Ru
series d: L=Cp' or phosphine; L'=Lewis ligand
M=Mo, W, Fe, Ru, Pt

Figure 1. Possible general reactions of a prototypical metal center.

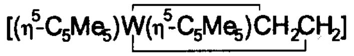
2.2. Selected examples of organometallic center reactivity

2.2.1. Electron transfer

A single electron transfer process between organometallic fragments and organic acceptors results in the formation of precursor complexes with varying degrees of metal-to-ligand charge transfer in the excited state. The metal center is 1e-oxidized and consequently binds, more or less covalently, to the acceptor anion radical. Such cases implicate the involvement of an outer sphere electron transfer mechanism and require suitable donor-acceptor system redox potentials to render the electron transfer process energetically feasible. Some electron transfer reactions, of organometallic centers of central importance in their chemistry, are presented in section 2.2.5.

2.2.2. Recombination

Organometallic fragments formed via photoinduced elimination of H_2 and capable of forming a metal-metal bonded dinuclear species, undergo recombination. The reaction products, however, reflect a steric impediment to recombination due to bulky substituents on the metal. Steric crowding at the metal leads to a weaker metal-metal bond [10]. When the steric requirement is sufficiently large, recombination is prevented. This allows other processes to occur. Of particular interest is the activation of the methyl groups of the C_5Me_5 ligand in the photolysis of $(C_5Me_5)_2WH_2$ [13] in which H_2 loss is followed by formation of the tucked-in compound



$$[(\eta^5\text{-}C_5Me_5)W(\eta^5\text{-}C_5Me_5)CH_2CH_2]$$

This result represents an alternative pathway for C-H bond activation by pentamethylcyclopentadienyl complexes and constitutes an intramolecular insertion into ligand methyl groups compared to the intermolecular reaction with the hydrocarbon substrate.

2.2.3. C-H bond activation

The photogenerated L_2M metal fragments reported in Figure 1 are coordinatively and electronically unsaturated species. The unusual oxidation state of the metal and the ligand environments make these species highly susceptible to easily undergoing oxidative addition reactions. The organometallic fragments react with the organic substrate ultimately forming the insertion product (eq. 4).

$$L_2M + RH \longrightarrow L_2M(R)(H) \qquad (4)$$

The oxidative addition reactions observed with the metal fragment, a carbene-like species, correspond to the so-called insertion reaction that the highly reactive methylene fragment undergoes with C-H bonds [14]. The photoactivation of the C-H bond of aliphatic and aromatic hydrocarbons has recently been achieved by several research groups [15-18]. Low valent rhodium or iridium compounds with tertiary phosphine or carbonyl and pentamethylcyclopentadienyl ligands oxidatively add the C-H bonds of hydrocarbons. This has led to some interesting chemistry and alkanes, arenes and alkenes have all been seen as reactive [19,20,15].

Perhaps the most important feature is the selectivity that the metal fragments show for unhindered C-H bonds and for smaller rings [21]. Selectivity is the essence of catalysis and achieving it is central to chemical research. These photochemical experiments have opened up a highly interesting field of research for both fundamental and applied chemistry. Finding effective methods for utilizing C-H oxidative addition chemistry to achieve efficient catalytic conversions of hydrocarbons into functionalized organic compounds remains a high priority.

2.2.4. C-H bond activation. Platinum phosphine catalysts

Platinum is widely used as a catalyst for a variety of industrial processes that cleave C-H bonds [14]. Insights into the mechanism of hydrocarbon activation by metal (Fe, Ru) phosphine hydrides suggested exploring the potential of phosphine platinum hydrides. Attention was turned to the cis dihydride diphosphine complexes of Pt(II): $[L_2PtH_2]$
$[L=(t\text{-}Bu)_2P(CH_2)_2P(t\text{-}Bu)_2)]$ (1);
$[L=(Men_2)P(CH_2)_2P(Men)_2]$ (2);
$[L=(t\text{-}Bu)_2P(CH_2)_3P(t\text{-}Bu)_2]$ (3).

Complexes 1, 2 and 3 are thermally stable and show no tendency to lose H_2 since the bulky substituents in the phosphine ligands stabilize the cis-coordination. They are quite photosensitive, however, and irradiation in benzene leads to reductive elimination of H_2 to generate the $[L_2Pt]$ fragment which produced $L_2Pt(Ph)(H)$ as the exclusive oxidative addition product [12]. There is no evidence for metalation of the phosphine ligand as found with other metal phosphine complexes (M=Ir, Fe) [8,21]. Insertion of the Pt(O) metal fragment $[L_2Pt]$ must be thermodynamically and kinetically favourable with respect to dimerization and metalation reactions.

Photolysis of the hydrides 1, 2 and 3 in toluene containing the substrate XY (XY=Et_3SiH, CH_3I, C_2H_5I) leads to formation of the products reported in equation 5.

$$[L_2PtH_2] \xrightarrow[-H_2]{h\nu} [L_2Pt] + XY \longrightarrow L_2PtXY \qquad (5)$$

These results can be interpreted in terms of photogenerated $[L_2Pt]$ fragments which oxidatively add XY instead of giving an insertion reaction into C-H bonds of toluene.

In somewhat related experiments, Whitesides [22] observed that a bi-phosphine Pt(O) complex oxidatively added to alkanes under thermal conditions. Heating a cyclopentane solution of L_2Pt (neopentyl)H (L=bis dicyclohexylphosphinoethane) leads to a loss of neopentane and the formation of L_2Pt(cyclopentyl)H. The platinum (0) intermediate (eq. 6) is also able to activate aromatic and benzylic C-H bonds.

$$[L_2Pt(CH_2CMe_3)(H)] \xrightarrow[-CMe_4]{50^\circ C} [L_2Pt] \xrightarrow{RH} L_2Pt(R\text{-}H) \qquad (6)$$

R = Me, Ph, C-pentyl, benzyl.

An interesting and potentially useful photochemical transformation of ethylene has been obtained with the olefin complex $(PPh_3)_2Pt(C_2H_4)$ [15]. Irradiation has proved to induce ortho-metalation of one of the PPh_3 ligands with formation of an ethylene-hydride complex which collapses to the isolated ethyl complex (eq. 7).

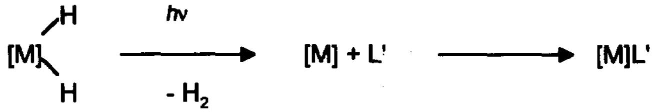
$$[(PPh_3)_2Pt(C_2H_4)] \xrightarrow{h\nu} [(Ph_2PC_6H_4)Pt(PPh_3)(H)(C_2H_4)] \xrightarrow{h\nu}$$

$$\xrightarrow{h\nu} (Ph_2PC_6H_4)Pt(PPh_3)(C_2H_5)] \qquad (7)$$

This result, the first of its kind, represents a special intramolecular case of a photochemical conversion of an ethene complex into an ethyl complex [15].

2.2.5. Formation and properties of charge-transfer complexes

The potential for synthetic utility of photoinduced elimination pathways is illustrated by the observation that the generated organometallic fragments [M] can readily be trapped by a suitable added substrate. Photolythic expulsion of H_2 from the precursor complex, generates a coordinatively unsaturated metal fragment. This fragment reacts with a Lewis ligand L' in a subsequent step, ultimately forming the [M]L' complexes with unusual physico-chemical properties



$$[M]\begin{smallmatrix}H\\H\end{smallmatrix} \xrightarrow[-H_2]{h\nu} [M] + L' \longrightarrow [M]L' \qquad (8)$$

Reaction series: a = [M] = Cp_2W, Cp_2Mo
L' = PPh_3 Ref. 13
L' = TCNE, TCNQ Ref. 23

Reaction series: b = [M] = $[(DIPHOS)_2Fe]$
L' = TCNE, TCNQ Ref. 7

Reaction series: c = [M] = $[(t\text{-}Bu)_2P(CH_2)_2P(t\text{-}Bu)_2]Pt$
L' = TCNE, TCNQ Ref. 9

DIPHOS = Bis(1,2-diphenylphosphino)ethane;
TCNE = Tetracyanoethylene
TCNQ = 7,7,8,8-tetracyanoquinodimethane

Metallocenes have been generated by photolysis of a variety of precursors including the hydrides Cp_2MH_2 (M=Mo, W, Zr). All three have proved to give the adducts Cp_2ML' (L'=CO, C_2H_2, PEt_3 and PPh_3) [13]. The phosphine complexes appear useful as synthetic intermediates because of the lability of the $M\text{-}PR_3$ bond. The photogenerated metallocenes can also be readily trapped by added nitrogen ligands and, in the presence of TCNE and TCNQ, photolysis leads to nearly quantitative formation of the corresponding adducts Cp_2MTCNE and Cp_2MTCNQ.

The excellent capability of the unsaturated nitrogen ligands to stabilize the very reactive Cp_2Mo and Cp_2W metallocene may be attributed to their potential to accommodate spin in their π system. The adducts have an intense transition in the 700-800 nm region. This low-lying band is apparently an MLCT transition typical of a donor-acceptor complex and is a consequence of the exceptional π-acceptor properties of TCNE and TCNQ. The TCNE and TCNQ complexes with metallocenes are "charge-transfer complexes". Understanding the correlation between the staking crystal structure and the electrical and magnetic properties of these molecular compounds is of considerable interest for a rational approach to the synthesis of new advanced materials.

For the organotransition metal compounds with TCNE and TCNQ, magnetic and spectroscopic studies have revealed different extents of electron transfer, depending on the donor capability of the metal fragment. Most useful is the correlation between the charge-transfer absorption energy and the redox potentials of the donor-acceptor system. Other examples of charge transfer complexes can be cited whenever coordinatively and electronically unsaturated fragments react with L (TCNE and TCNQ) to form the corresponding adducts. Following are several examples of this type of reaction. (eq. 9-10).

$$[CpRh(CO)_2]_2 \xrightarrow[L]{h\nu} 2CpRh(CO)_2L \qquad (9)$$

L = TCNE, TCNQ (Ref. 24)

$$[Cp^*Fe(CO)_2]_2 \xrightarrow[L]{h\nu} Cp^*Fe(CO)_2LCp^*Fe(CO)_2 \qquad (10)$$

L = TCNE (Ref. 25)

All charge-transfer complexes show the presence of a charge transfer absorption in the visible region [10,11]. This observation explains, among other things, the special photoreactivity of such compounds. Radical salts with remarkably different magnetic behaviour are obtained. These photoreactions hold a promising future in the synthesis of new magnetic materials.

3. CONCLUSIONS

On the basis of what is presently known about organometallic photochemistry it would appear that photoinduced reductive elimination of H_2 or a two-electron ligand from metal precursors generates metal fragments of relevant interest in synthesis and catalysis. Some of the results reported here suggest that the expansion of reactivity studies of the coordinatively and electronically unsaturated metal fragments could yield catalytic and synthetic dividends.

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