

Preliminary communication

PHOTOCHEMISTRY OF PHOSPHINE HYDRIDE COMPLEXES OF IRON GROUP METALS

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Summary

On photolysis *cis*-[MH₂(DMPE)₂] (M = Fe, Ru, Os; DMPE = Me₂PCH₂CH₂-PMe₂) and *cis*-[MH₂(DPPE)₂] (M = Fe, Ru, Os; DPPE = Ph₂PCH₂CH₂PPh₂) readily lose H₂ by concerted coupling of the two hydrogen atoms. The photo-reactions generate the extremely reactive intermediates [M(DMPE)₂] and [M(DPPE)₂] which react with tetracyanoethylene (TCNE) to form metal(II) complexes: [C₂(CN)₃M(DMPE)₂CN], [C₂(CN)₃M(DPPE)₂CN] via free-radical oxidative addition processes. The reactive species may be trapped to give zero-valent compounds upon irradiation of the title compounds in the presence of Lewis ligand L (e.g. [LM(DMPE)₂], [LM(DPPE)₂]; L = CO, C₂H₄).

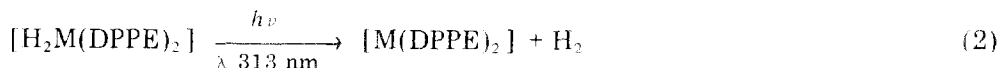
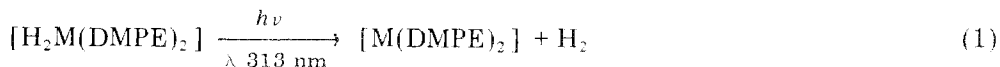
Transition metal hydrides have played an important role in the development of organometallic chemistry. They have shown to be useful in numerous synthetic transformations and are of great importance in many transition metal assisted or catalyzed reactions [1]. As part of our continuing study [2–4] of the photochemistry of transition metal hydride complexes of the iron group metals bearing phosphorus ligands, we have now investigated the photoinduced elimination of H₂ from *cis*-[MH₂(DMPE)₂] and *cis*-[MH₂(DPPE)₂] (M = Fe, Ru, Os; DMPE = dimethylphosphinoethane; DPPE = diphenylphosphinoethane) with the following aims: (i) to see which pathways are available for photo-induced H₂ evolution; (ii) to study the photochemical synthesis of very reactive, low valent phosphine complexes of Fe, Ru and Os, which might enter into important reactions such as N₂ or CO₂ fixation and saturated C—H bond activation; and (iii) to observe the reactivities of the photogenerated coordinatively unsaturated species [M(DMPE)₂] and [M(DPPE)₂] in processes involving electron transfer; e.g. oxidative addition reactions.

Experimental

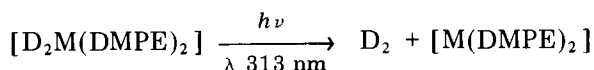
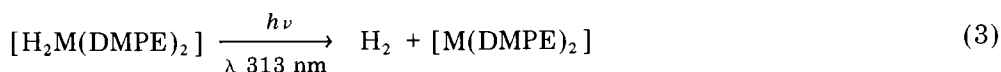
The complexes used were prepared as previously described [5,6]. All operations were carried out under purified N₂ or argon. Photolysis experiments were carried out by our usual techniques [2-4], with the addition of an irradiation cell for direct photolysis in the ESR cavity. Analysis of the gases above the irradiated solutions was by linked GLC-mass spectrometry or GLC.

Results and discussion

Intramolecular reductive elimination. Irradiation (λ 313 nm) of degassed toluene solutions of *cis*-[H₂Fe(DMPE)₂] (1), *cis*-[H₂Ru(DMPE)₂] (2) and *cis*-[H₂Os(DMPE)₂] (3) results in a rapid color change from orange to dark red, and red-brown precipitates are obtained after prolonged (3 h) photolysis. During the radiation there is a smooth fall in intensity of the characteristic ν (M-H) bands of [H₂M(DMPE)₂] at 1770 cm⁻¹ (1), 1775 cm⁻¹ (2), 1786 cm⁻¹ (3) and no new vibrations appear in the ν (M-H) region. The ¹H NMR and ³¹P NMR spectra of the red-brown precipitates suggest that they are the [M₂(DMPE)₅] compounds described by Tolman [7]. The *cis*-[MH₂(DPPE)₂] (4, M = Fe; 5, M = Ru) complexes also lose H₂ upon photolysis, in this case generating stable [MH(C₆H₄PPhCH₂CH₂PPh₂)(DPPE)] complexes containing an *ortho*-metalated phosphine ligand [3,8] (4a, M = Fe; 5a, M = Ru). Mass spectral analysis of the gases above irradiated toluene-*d*₈ solutions of [MH₂(DMPE)₂] and [MH₂(DPPE)₂] showed the presence of a considerable amount of H₂ with little HD (3%) present. Since toluene is an efficient hydrogen atom scavenger, the absence of a significant amount of HD indicated that free hydrogen atoms are not produced in the photolysis and an intramolecular elimination process is suggested. Low temperature (-50°C) photolysis of complexes 1-5 in the ESR cavity in the presence of phenyl butyl nitrene (PBN) as scavenger of H[•] does not produce any hydrogen atom spin adduct. Since the toluene solution photolysis and ESR experiments showed that the free hydrogen atoms are apparently not produced, and since heterolytic cleavage of a M-H bond is unlikely [1,4], the substantial amount of H₂ must arise from concerted elimination of H₂ to generate the coordinatively unsaturated species M(DMPE)₂ (1a, M = Fe; 2a, M = Ru; 3a, M = Os), eq. 1; and [M(DPPE)₂] (4a, M = Fe; 5a, M = Ru), eq. 2.

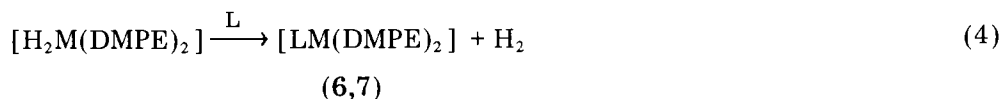


Deuterium labeling experiments, e.g. crossover experiments (eq. 3), confirm that photoinduced loss of H₂ is predominantly intramolecular. A mixture of complex 1 and [D₂M(DMPE)₂] when irradiated gave mainly H₂ and D₂ with only a small quantity of HD. Some crossover (~3%) was observed in the products from the [H₂Ru(DMPE)₂] experiments. However, the mass spectrum of recovered starting material indicates that this scrambling occurs prior to the photochemical reaction.



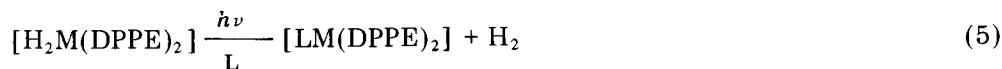
The same behavior was observed for mixtures of $[\text{H}_2\text{M}(\text{DPPE})_2]$ and $[\text{D}_2\text{M}(\text{DPPE})_2]$.

Photochemical reactions of complexes 1–5 with Lewis base ligands. Irradiation of complexes 1–5 (in C_6D_6) in the presence of Lewis base ligands leads to near quantitative formation [9] of the $[\text{LM}(\text{DMPE})_2]$ adducts, eq. 4:



(6, L = CO; M = Fe (^{31}P NMR: -63.5s ; $\nu(\text{CO})$: 1812 cm^{-1});
7, L = C_2H_4 ; M = Ru (^1H NMR: 0.59qu , coordinated C_2H_4))

and $[\text{LM}(\text{DPPE})_2]$ adducts, eq. 5.



(8, L = CO; M = Fe (^{31}P NMR: -95s ; $\nu(\text{CO})$: 1835 cm^{-1});
9, L = C_2H_4 ; M = Fe (^1H NMR: 0.75 qu , coordinated C_2H_4));

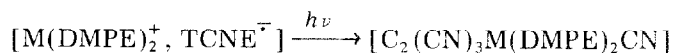
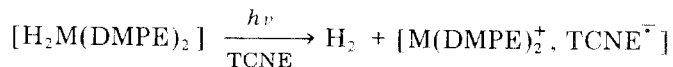
The fact that complexes 6–9 are formed in the photoreactions of 1–5 with L indicates that $[\text{M}(\text{DMPE})_2]$ and $[\text{M}(\text{DPPE})_2]$ are the primary products of eq. 1 and 2.

The unusual spectroscopic properties, extremely low $\nu(\text{CO})$ when L = CO and a high field ^1H NMR shift of the ethylenic protons when L = C_2H_4 , imply a very high electron density on the metal [7].

Photoreactions involving electron transfer. Photolysis of complexes 1, 2, 4 and 5 in C_6H_6 in the presence of tetracyanoethylene (TCNE) at ambient temperature for 2 h results in the formation of cyanovinylmetal(II) cyanide compounds: $[\text{C}_2(\text{CN})_3\text{M}(\text{DMPE})_2\text{CN}]$ (10, M = Fe: $\nu(\text{CN})$ 2210, 2170, 2160 cm^{-1} ; $\nu(\text{CN}^-)$ 2075 cm^{-1} ; $\nu(\text{C}=\text{C})$ 1425 cm^{-1} ; 11, M = Ru: $\nu(\text{CN})$ 2214, 2175, 2165 cm^{-1} , $\nu(\text{CN}^-)$ 2080 cm^{-1} , $\nu(\text{C}=\text{C})$ 1431 cm^{-1}); $[\text{C}_2(\text{CN})_3\text{Fe}(\text{DPPE})_2\text{CN}]$ (12, $\nu(\text{CN})$ 2200, 2170, 2155 cm^{-1} ; $\nu(\text{CN}^-)$ 2095 cm^{-1} , $\nu(\text{C}=\text{C})$ 1428 cm^{-1}). These compounds are formally similar to the product of photochemical rearrangement of the $[(\text{PPh}_3)_2\text{Pt} \cdot \text{TCNE}]$ complex [10].

These reactions are oxidative addition processes involving the TCNE^- radical anion (ESR, UV-visible spectra). This indicates that the oxidative addition reaction is initiated by a photoinduced single electron transfer from the donor intermediates $[\text{M}(\text{DMPE})_2]$ and $[\text{M}(\text{DPPE})_2]$ to the acceptor TCNE with formation of TCNE^- radical anions and the oxidized metal complexes. Nucleophilic attack by TCNE^- on the oxidized metal complexes then leads to the products (Scheme 1).

SCHEME 1



As well as revealing new donor—acceptor reactions these investigations give some indication of the utility of the electron reservoir complexes $[\text{M}(\text{DMPE})_2]$ and $[\text{M}(\text{DPPE})_2]$ as electron transfer reagents. Related studies involving C—H activation and C—C bond formation are in progress.

References

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- 9 In the photochemical reaction under N_2 of complex 4 with C_2H_4 there are two more minor products: one is $[\text{Fe}(\text{N}_2)(\text{DPPE})_2]$ ($\nu(\text{N}_2)$ 2120 cm^{-1}) and the other is unidentified. Further related photoreactions are under investigation.
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