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Photochemistry of Bis(diphenylphosphino)ethane Hydride Complexes of Iron

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The phoochemistry of transition-metal hydride complexes has recently attracted considerable attention [1] commensurate with their importance in many transition-metal-assisted or -catalyzed organic transformations. Photoinduced elimination of molecular hydrogen seems to be a general reaction for di- and poly-hydride complexes of the transition elements [2, 3]. Photochemical reactions of this type may have considerable potential for hydrogen and energy storage and the present study has been undertaken in order to define the mechanism of dehydrogenation more precisely. This paper reports the photochemistry of [Fe(DPPE)$_2$HCl] and [Fe(DPPE)$_2$H$_2$] (DPPE = bis(diphenylphosphino)ethane) complexes. Reductive elimination of HCl and H$_2$ occurs upon ultraviolet irradiation and the formation of the highly reactive intermediate [Fe(DPPE)$_2$] is observed.

Experimental

[Fe(DPPE)$_2$HCl] (*1*), [Fe(DPPE)$_2$H$_2$] (*2a*) and [Fe(DPPE)$_2$D$_2$] (*2b*) were prepared according the published procedures [4, 5] and characterized by ^{31}P NMR parameters (*1*: δ A, 81.5 ppm downfield of 85% H$_3$PO$_4$); *2a*: δ A, 103 ppm; δ B, 90.2 ppm; JAB: 19.5 Hz).

All operations with these complexes were carried out under argon atmosphere.

Photolysis experiments were carried out using the standard techniques of this laboratory with the addition of an irradiation cell which allowed the solutions to be changed under controlled atmospheres.

The analysis of the gases above irradiated solutions was performed by gas mass spectrometry or by gas chromatography.

Results

The [Fe(DPPE)$_2$HCl] (*1*) complex is thermally resistant to loss of HCl or H$_2$ under vacuum or Ar atmosphere. Irradiation of a thoroughly degassed toluene solution of *1* with 313 nm results in a rapid color change from red-violet to brown. Accompanying the photoreaction is a decrease in intensity of the ν(Fe–H) at 1925 cm^{-1}, and no new vibrations appear in the ν(Fe–H) region. Mass spectral analysis of the gases above irradiated d^8-toluene solutions of *1* showed only HCl, with no being HD detected.

Evaporation of the solvent after prolonged (3 hr) photolysis gave a red-brown solid which showed IR and ^{31}P NMR spectra characteristic of the *ortho*-metallated derivative [5] [Fe(DPPE)H(C$_6$H$_4$PhC$_2$H$_4$-PPh$_2$)] (*3*).

Photochemical reactions of *1* in the presence of CO produced [Fe(DPPE)CO] (*4*), characterized by strong IR bands at 1830 cm^{-1}, 1975 cm^{-1} [ν(C = O), terminal carbonyl [5]) and by ^{31}P NMR spectrum (δ: 96 ppm downfield of 85% H$_3$PO$_4$). In the absence of light complex *1* does not form *4* at room temperature.

The [Fe(DPPE)$_2$H$_2$] (*2a*) and [Fe(DPPE)$_2$D$_2$] (*2b*) complexes are thermally quite stable and show no tendency to lose H$_2$ and D$_2$ under vacuum or Ar atmosphere. Photolysis of degassed toluene solutions of *2a* and *2b* with 313 nm radiation induces a color change from red to brown. Monitoring the photolysis in the IR revealed that the metal–hydride vibrations at 1875, 1825 cm^{-1} (*2a*) and at 1335 cm^{-1} (*2b*) decreased in intensity during irradiation and no new bands appeared in the νFe–H region. Gas chromatographic and mass spectral analysis of gases above the irradiated solutions showed substantial amounts of H$_2$ (*2a*) and D$_2$ (*2b*). Irradiation of an equimolar mixture of *2a* and *2b* gave only H$_2$ and D$_2$ with no being HD detected by mass spectrometry. The photolysis in the E.S.R. cavity of a degassed toluene–methanol solution of *2a* at 290 K containing 5,5′-dimethylpirroline-N-oxide(DMPO) as a spin-trap does not produce any hydrogen atom spin-adduct.

Evaporation of the solvent from the irradiated (3 hr) solution of *2a* gave the *ortho*-metallated product [Fe(DPPE)H(C$_6$H$_4$PPh$_2$)] (*3*). Modification of the reaction course for *2a* can be effected by the presence of additional coordinating ligands. The above photoreaction in the presence of CO yielded the carbonyl derivative *4*. The most interesting modification was that achieved with acetonitrile as solvent upon irradiation at 280 K. A red solid *5* of high thermal reactivity was obtained. ^{31}P NMR (CDCl$_3$, δ 95 ppm downfield of 85% H$_3$PO$_4$) ^{1}H NMR (CDCl$_3$, δ 2.51, CH$_3$) and IR (2235 cm^{-1}, νCN) defined *4* as the [Fe(DPPE)$_2$(CH$_3$CN)] adduct. The increment

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$\Delta\nu$CN = 72 over νCN of free nitrile indicates a coordination of the metal to the lone pair of electrons on the nitrogen [6]. When *5* is allowed to warm up to room temperature, the red adduct loses acetonitrile and the *ortho*-metallated complex *3* is obtained.

Discussion

The steady irradiation experiments show that light induces elimination of HCl and H_2 from the *1* and *2a* complexes to generate $[Fe(DPPE)_2]$ (*6*) as an apparent intermediate. The photogenerated $[Fe(DPPE)_2]$ can be readily trapped by added substrates, and photolysis of *1* and *2a* complexes in the presence of CO and CH_3CN led to formation of the corresponding adducts $[Fe(DPPE)_2CO]$ and $[Fe(DPPE)_2(CH_3CN)]$. The primary photoproduct *6* is a highly reactive intermediate which could undergo reactions with added reagents or *ortho*-metallation if other reagents are not present. Of great importance is the photoelimination reaction mechanism of complexes *1* and *2a*. Heterolytic cleavage of the Fe–H bond to generate H^+ or H^- appeared unlikely in the aromatic solvent employed [2]. Mass spectral analysis of gases over irradiated solutions containing equimolar amounts of *2a* and *2b* gave only H_2 and D_2, with no being HD detected. The absence of HD in gases over irradiated solutions of the mixture indicates a concerted elimination of H_2 since elimination of H^- (D^-) or H^+ (D^+) would lead to a detectable amount of HD. Further evidence of a concerted pathway for the photoinduced elimination of H_2 comes from the E.S.R. experiments in the presence of DNBO in which no hydrogen atom spin adduct is observed. This indicates that hydrogen atoms are not produced to any significant extent in the photoprocesses. A concerted elimination of H_2 has been shown to be the mechanism [7] by which photoinduced loss of H_2 occurs also in $[H_2PtAs(t\text{-}Bu_3)_2]$.

The intermediate *6* can be trapped by added substrates, and photolysis in the presence of CO and CH_3CN leads to the formation of corresponding adducts *4* and *5* (scheme 1).

$$[Fe(DPPE)_2HCl] \xrightarrow{h\nu} [Fe(DPPE)_2] + HCl$$

$$[Fe(DPPE)_2H_2] \xrightarrow{h\nu} [Fe(DPPE)_2] + H_2$$

$$\begin{tikzcd} & {[Fe(DPPE)H(C_6H_4PhPC_2H_4PPl} \\ {[Fe(DPPE)_2]} \arrow[ur] \arrow[r, "CO"] \arrow[dr, "CH_3CN"] & {[Fe(DPPE)_2CO]} \\ & {[Fe(DPPE)_2(CH_3CN)]} \end{tikzcd}$$

Scheme 1

None of the reported reactions occurs thermally, and light is essential to induce HCl and H_2 loss. Systems of this kind appear useful for the production of reactive species in the synthesis of new compounds, and we are at present extending the work in this direction.

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