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Preliminary communication

A new reaction of $[Cp(CO)_2Fe(PPh_2H)]PF_6$ with $NaBH_4$ to give $Cp(CO)(H)Fe(PPh_2H)$ via $Cp(CO)_2FeH$ and PPh_2H

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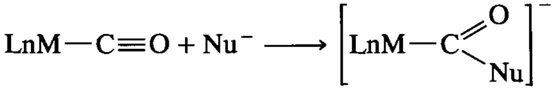
Abstract

$[Cp(CO)_2Fe(PPh_2H)]PF_6$ reacts with $NaBH_4$ to give the intermediates $CpFe(CO)_2H$ and PPh_2H, which are then converted into $Cp(CO)(H)Fe(PPh_2H)$. $[Cp(CO)_2FeL]PF_6$ ($L = P(OMe)_3$, $P(OEt)_3$ and $P(O^iPr)_3$) reacts with $NaBH_4$ to give the product $Cp(CO)(H)FeL$ directly without $Cp(CO)_2FeH$ and L even being formed transiently. The proposed reaction mechanism is that H^- attacks the phosphorus atom to give a metallaphosphorane complex, followed by coupling between a $Cp(CO)_2Fe$ fragment and H on the hypervalent phosphorus.

Reactions of transition-metal complexes containing carbonyl ligands with some Lewis bases have been well investigated with regard to metal carbonyl catalyzed water gas shift (WGS) reactions, which reveal that in general the reaction site is the coordinating carbonyl carbon. For example, the reactions with OR^- [1,2], R^- [3], NR_2^- [2] and OH^- [1,4] give alkoxycarbonyl, acyl(aroyl), carbamoyl and metallacarboxylic acid complexes, respectively.



$$LnM{-}C{\equiv}O + Nu^- \longrightarrow \left[LnM{-}C\overset{\displaystyle O}{\underset{\displaystyle Nu}{\lessgtr}}\right]^-$$

$Nu^- = OR^-, R^-, NR_2^-, OH^-$

We report here a new type of reaction with hydride of iron complexes having carbonyls and a trivalent phosphorus compound as ligands, in which the reaction site is not the carbonyl carbon but the phosphorus atom, and discuss the reaction mechanism involved.

To a suspension of $[Cp(CO)_2Fe(PPh_2H)]PF_6$ * (Cp stands for η^5-C_5H_5) in EtOH were added 2 equiv. of $NaBH_4$ at room temperature to give an orange homogeneous solution. Immediately after the reaction, the solution exhibited two

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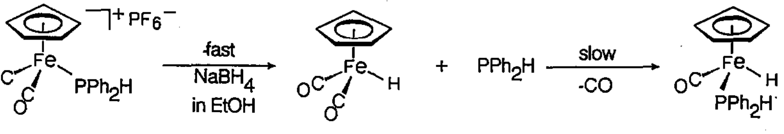
* $[Cp(CO)_2Fe(PPh_2H)]PF_6$ was prepared as a pale yellow powder from $[Cp(CO)_2Fe(THF)]PF_6$ and PPh_2H in CH_2Cl_2 at room temperature. Yield 89%. IR (in CH_2Cl_2) ν(CO) 2062, 2018 cm^{-1}. ^{31}P NMR (in EtOH) δ(ppm) 46.24 (d, J(PH) = 408.9 Hz, PPh_2H), −142.69 (sept, J(PF) = 709.5 Hz, PF_6). ^1H NMR (in acetone-d_6) δ(ppm) 7.60–7.90 (m, 10H, Ph), 7.67 (d, J(PH) = 413.4 Hz, 1H, PH), 5.75 (d, J(PH) = 1.9 Hz, 5H, Cp).

ν(CO) absorptions at 2016 and 1956 cm^{-1} in the IR spectrum, indicating the formation of Cp(CO)$_2$FeH. The ^{31}P{^{1}H} NMR spectrum showed a singlet at -39.36 ppm which became a doublet with a coupling constant of 216.6 Hz without proton irradiation, indicating the formation of a transition-metal free PPh$_2$H. The formation of these compounds were confirmed by comparison of these spectroscopic data with authentic samples. The prolonged reaction resulted in the formation of Cp(CO)(H)Fe(PPh$_2$H) * at the expense of Cp(CO)$_2$FeH and PPh$_2$H (eq. 1). If a hydride anion attacks the carbonyl carbon of [Cp(CO)$_2$Fe(PPh$_2$H)]$^+$, a formyl complex, Cp(CO)Fe{C(O)H}(PPh$_2$H), would be formed. However, no such symptom was observed spectroscopically.



(1)

When [Cp(CO)$_2$Fe{P(OMe)$_3$}]PF$_6$ was treated with NaBH$_4$, [Cp(CO)(H)Fe{P(OMe)$_3$}] ** was formed. In this case, neither Cp(CO)$_2$FeH nor free P(OMe)$_3$ was detected. The reaction looks like a simple substitution of hydride for a carbonyl ligand, but the observation that Cp(CO)$_2$FeH, prepared separately, reacted with P(OMe)$_3$ immediately to afford Cp(CO)HFe{P(OMe)$_3$}, suggests the incipient formation of Cp(CO)$_2$FeH and P(OMe)$_3$ followed by quick substitution of P(OMe)$_3$ for CO in Cp(CO)$_2$FeH (Scheme 1). [Cp(CO)$_2$Fe{P(OEt)$_3$}]PF$_6$ and [Cp(CO)$_2$Fe{P(O^{i}Pr)$_3$}]PF$_6$ behaved similarly.

For the reaction mechanism in which Cp(CO)$_2$FeH is formed from [Cp(CO)$_2$Fe(PPh$_2$H)]PF$_6$ and NaBH$_4$, four mechanisms can be considered, as shown in Scheme 2: (1) attack of H$^-$ at the carbonyl carbon in the starting complex to give a formyl complex [Cp(CO)Fe{C(O)H}(PPh$_2$H)], followed by dissociation of PPh$_2$H and then the carbonyl de-insertion; (2) dissociation of PPh$_2$H to give 16e [Cp(CO)$_2$Fe]$^+$ species, followed by attack of H$^-$ at the iron atom; (3) Cp ring slippage from η^5 to η^3 to give 16e [(η^3-C$_5$H$_5$)(CO)$_2$Fe(PPh$_2$H)]$^+$ species, followed by attack of H$^-$ at the Fe to give (η^3-C$_5$H$_5$)(CO)$_2$(H)Fe(PPh$_2$H), then dissociation of PPh$_2$H and Cp ring slippage from η^3 to η^5; (4) attack of H$^-$ at the phosphorus atom to give a metallaphosphorane complex, Cp(CO)$_2$Fe(PPh$_2$H$_2$), followed by coupling between Cp(CO)$_2$Fe and H on the hypervalent phosphorus.

In order to check the possibility of mechanism 1, [Cp(dppe)Fe(PPh$_2$H)]PF$_6$ (dppe = 1,2-bis(diphenylphosphino)ethane) (^{31}P NMR δ(ppm) 92.01 (d, J(PP) = 51.9 Hz, dppe), 52.42 (dt, J(PP) = 51.9 Hz, J(PH) = 354.0 Hz, PPh$_2$H) having no CO ligand was newly prepared from Cp(dppe)FeCl, PPh$_2$H and NH$_4$PF$_6$, and was treated with H$^-$. The iron complex reacted slowly with NaBH$_4$ in EtOH, and rapidly with LiAlH$_4$ in THF to give Cp(dppe)FeH (^{31}P NMR δ(ppm) 112.62 (d, J(PH) = 73.2 Hz)) and free PPh$_2$H. The results indicate that a carbonyl ligand is

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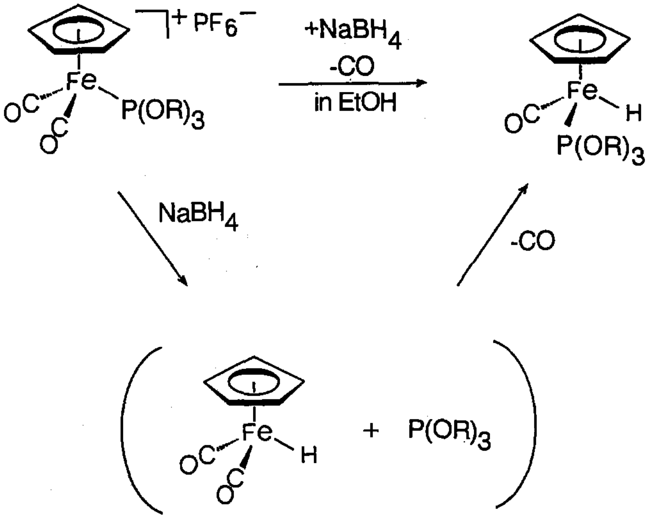
* IR (in EtOH) ν(CO) 1934 cm^{-1}. ^{31}P NMR (in EtOH) δ(ppm) 64.15 (dd, J(PH) = 343.3 and 77.8 Hz). ^{1}H NMR (in C$_6$D$_6$) δ(ppm) 7.00–7.70 (m, 10H, Ph), 6.84 (d, J(PH) = 346.2 Hz, 1H, PH), 4.32 (d, J(PH) = 1.6 Hz, 5H, Cp), -13.0 (d, J(PH) = 78.0 Hz, 1H, FeH).

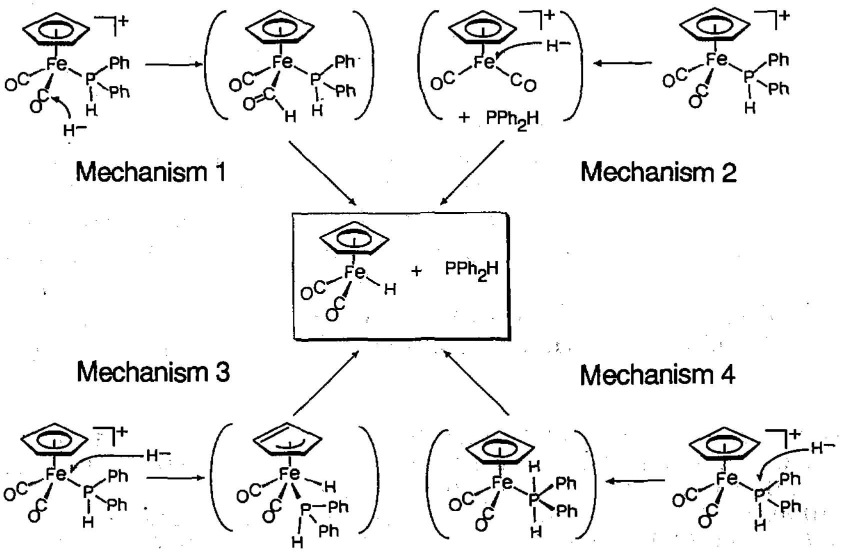
** IR (in EtOH) ν(CO) 1950 cm^{-1}. ^{31}P NMR (in EtOH) δ(ppm) 200.4 (d, J(PH) = 89.3 Hz). ^{1}H NMR (in acetone-d_6) 4.59 (d, J(PH) = 1.0 Hz, 5H, Cp), 3.51 (d, J(PH) = 11.6 Hz, 9H, CH$_3$), -13.7 (d, J(PH) = 90.0 Hz, 1H, FeH).



Scheme 1.

not essential for the substitution of hydride for coordinating PPh_2H, and therefore mechanism 1 can be ruled out. Mechanism 2 can also be ruled out because when $[Cp(CO)_2Fe(PPh_2H)]PF_6$ was treated with PMe_3, being a stronger base than PPh_2H, no reaction occurred, though the formation of $[Cp(CO)_2Fe(PMe_3)]PF_6$ was expected, according to mechanism 2.

Ligand substitution reactions on a transition-metal, accompanied with a change of coordination mode of the Cp ring from η^5 to η^3 or η^1 have been reported [5]. Ligands generally bond more strongly to a central transition-metal in cationic



Scheme 2.

complexes than in neutral complexes. Therefore it is quite difficult for cationic complexes to provide a vacant coordination site by, for example, Cp ring slippage from η^5 to η^3 or ligand dissociation. Actually, Cp ring slippage has only been reported for neutral complexes. We can therefore rule out mechanism 3 in Scheme 2.

Nucleophilic attack of H^- to the phosphorus, as expressed in mechanism 4, is electronically plausible. * Some metallaphosphorane complexes have been reported [6], though they have not been prepared by nucleophilic attack to a coordinating phosphorus atom. In the reaction of phosphenium $[PR_4]^+$, with a Lewis base, a nucleophilic attack of a Lewis base at the phosphorus atom has been suggested to form an intermediate hypervalent phosphorus compound, and the coupling between two substituents out of five has been reported (expressed as ligand coupling) by Oae [7]. We therefore propose mechanism 4 to be the reaction mechanism in the reaction of $[Cp(CO)_2Fe(PPh_2H)]^+$ with H^- *via* a metallaphosphorane complex giving $Cp(CO)_2FeH$. This is the first proposal of ligand coupling taking place between a transition-metal fragment and an organic group on a hypervalent phosphorus atom.

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* The reaction of $[Cp(CO)_2Fe(PPh_2H)]PF_6$ with $NaBD_4$ gave no information about the reaction mechanism because $Cp(CO)_2FeH$ and PPh_2H readily reacted with $NaBD_4$ to give $Cp(CO)_2FeD$ and PPh_2D, respectively.