mg). Anal. Calcd for $C_{39}H_{34}FeOPBr$: C, 68.34; H, 5.00. Found: C, 68.28; H, 5.11. ^1H NMR (C_6D_6, 20 °C; δ): 7.41, 7.16, 6.89 (m, C_5Ph_5, 25 H); 1.29 (d, PMe_3, 9 H, $^2J_{PH}$ = 8.8 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C; δ): 222.8 (d, CO, $^2J_{CP}$ = 37 Hz); 130.6 (s, ipso Ph); 129.6 (s, m Ph); 128.4 (s, o Ph); 127.1 (s, p Ph); 97.8 (s, C_5Ph_5); 18.2 (d, PMe_3, J_{CP} = 30 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C; δ): 17.8 (PMe_3).

2. Synthesis of Fe(η^5-C_5Ph_5)(CO)(PMe_3)\{C(O)C_2H_5\} (4). To 7 mL of CH_2Cl_2 was added 0.050 g of 3[5] and 30 μL (0.29 mmol) of PMe_3. The solution was stirred in the dark and was kept at 18 °C for 40 h. The solvent was removed under vacuum and the solid residue washed with diethyl ether (2 × 20 mL). Recrystallization from a toluene–pentane solution afforded 0.045 g (87%) of orange crystals of 4. Anal. Calcd for $C_{42}H_{39}FeO_2P\cdot C_7H_8$: C, 77.98; H, 6.28; Fe, 7.40; P, 4.10. Found: C, 78.17; H, 6.17; Fe, 7.62; H, 4.11. ^1H NMR (CD_2Cl_2, 20 °C; δ): 7.11, 7.03, 6.96 (m, C_5Ph_5, 25 H); 3.5 (m, CH_2, H_a); 3.1 (m, CH_2, H_b); 1.30 (d, PMe_3, 9 H, $^2J_{PH}$ = 9.2 Hz); 0.81 (m, CH_3, 3 H, $^3J_{HH}$ = 6.6, 6.4 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C; δ): 276.7 (d, C(O)Et, $^2J_{CP}$ = 38 Hz); 223.3 (d, CO, $^2J_{CP}$ = 37 Hz); 134.0 (s, ipso Ph); 131.0 (s, m Ph); 127.4 (s, o Ph); 127.0 (s, p Ph); 101.6 (s, C_5Ph_5); 59.3 (s (t in the undecoupled spectrum, $^1J_{CH}$ = 126 Hz), CH_2); 17.7 (d, PMe_3, $^1J_{CP}$ = 28 Hz); 10.9 (s, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C; δ): 31.5 (s, PMe_3).

3. Synthesis of Fe(η^5-C_5Ph_5)(CO)(PMe_2Ph)\{C(O)C_2H_5\} (5). By the procedure described for 4, complex 5 was isolated as orange crystals in 80% yield. Anal. Calcd for $C_{47}H_{41}FeO_2P$: C, 77.90; H, 5.70. Found: C, 78.09; H, 6.06. ^1H NMR (CD_2Cl_2, 20 °C; δ): 7.56, 7.29, 7.00 (m, C_5Ph_5, PPh, 30 H); 3.35 (m, CH_2, H_a); 2.45 (m, CH_2, H_b); 1.71, 1.60 (dd, PMe_2, 9 H), 0.71 (m, CH_3, 3 H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C; δ): 276.0 (d, COEt, $^2J_{CP}$ = 25 Hz); 223.3 (d, CO, $^2J_{CP}$ = 35 Hz); 138.9 (d, ipso C–P, $^1J_{PC}$ = 42 Hz); 133.8 (s, ipso C–C_5); 133.1 (s, m Ph–C_5) 131.3 (d, m Ph–P, $^2J_{PC}$ = 7 Hz); 129.5 (s, p Ph); 128.2 (d, o Ph, $^2J_{PC}$ = 8.3 Hz); 127.4 (s, o Ph–C_5); 127.0 (s, p Ph–C_5); 101.6 (s, C_5Ph_5); 58.6 (d, CH_2, $^3J_{PC}$ = 7 Hz); 17.2 (d, PMe, J_{CP} = 28 Hz); 15.0 (d, PMe, J_{CP} = 26 Hz); 11.1 (s, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C; δ): 38.3 (s, PMe_3).

4. Synthesis of Fe(η^5-C_5Ph_5)(CO)(PMe_3)(C_2H_5) (6). To 7 mL of toluene was added 0.050 g (0.085 mmol) of 4, and the resulting orange solution was irradiated with a Pyrex filter for 3 h. After concentration of the solution under vacuum (2 mL) and slow diffusion of pentane (2 mL) 0.051 g of red crystals of 6 (94% yield) was recovered. Anal. Calcd for $C_{41}H_{39}FeOP$: C, 77.60; H, 6.19; Fe, 8.8; P, 4.88. Found: C, 77.29; H, 6.25; Fe, 8.32; H, 4.78. ^1H NMR (C_6D_6, 20 °C; δ): 7.20, 7.16, 6.93 (m, C_5Ph_5, 25 H); 2.32 (m, 1 H, CH_2); 1.72 (m, CH_3, 3 H, J_{HH_a} = 7.5 Hz, J_{HH_b} = 7.3 Hz); 1.21 (d, PMe_3, 9 H, $^2J_{PH}$ = 9.2 Hz); 0.73 (m, CH_2, 1 H). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C; δ): 223.2 (d, CO, $^2J_{CP}$ = 42 Hz); 135.0 (s, ipso Ph); 131.1 (s, m Ph); 128.4 (s, o Ph); 127.0 (s, p Ph); 100.0 (s, C_5Ph_5); 22.9 (s, CH_3); 17.2 (d, PMe_3, $^1J_{CP}$ = 27 Hz); 0.23 (d, CH_2, $^2J_{CP}$ = 29 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C; δ): 31.6 (s, PMe_3).

5. Synthesis of Fe(η^5-C_5Ph_5)(CO)(PMe_3)(CHO) (8). In a mortar 0.194 g (0.25 mmol) of 7[5] and 0.028 g (0.75 mmol) of $NaBH_4$ were carefully ground before being placed in a Schlenk tube. The solid mixture was deaerated in vacuo for 5 min before being cooled at 0 °C. Then, a cold mixture (0 °C) of 25 mL of CH_2Cl_2 and 0.5 mL of CH_3OH was added and the suspension stirred for 1 h. The solvents were removed under vacuum and the solid residue was extracted with CH_2Cl_2 (3 × 15 mL) and crystallized by addition of an excess of pentane. The complex 8 was isolated as yellow crystals in 88% yield (0.140 g). Anal. Calcd for $C_{40}H_{35}FeO_2P$: C, 75.72; H, 5.56. Found: C, 75.68; H, 5.82. ^1H NMR (C_6D_6, 20 °C; δ): 15.27 (d, CHO, 1 H, $^3J_{PH}$ = 2.3 Hz); 7.23, 7.15, 6.88 (m, C_5Ph_5, 25 H); 1.14 (d, 9 H, PMe_3, $^2J_{PH}$ = 8.3 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, δ): 272.2 (d, CHO, $^2J_{CP}$ = 27 Hz); 220.4 (d, CO, $^2J_{CP}$ = 35 Hz); 129.0 (m, Ph, other phenyl resonances are masked by the solvent); 102.5 (s, C_5Ph_5); 18.1 (d, PMe_3, J_{CP} = 29 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C; δ): 27.1 (s, PMe_3).

Acknowledgment. We thank Drs. S. Sinbandhit (CRMPO, Rennes, France) for helpful discussions and F. Taulelle (Bruker Analytische Messtechnik GmbH, Rheinstetten, Germany) for CPMAS NMR assistance.

Registry No. 1, 12150-67-3; 2, 138855-94-4; 3, 132081-00-6; 4, 138855-95-5; 5, 138855-96-6; 6, 138855-97-7; 7, 132081-12-0; 8, 138855-98-8.

Synthesis of Molybdenum Hydride Complexes via an Electron-Transfer Mechanism and CO Exchange by Phosphine in the 17-Electron Intermediates

Marie-José Tudoret, Marie-Laure Robo, and Claude Lapinte*

Laboratoire de Chimie des Complexes de Métaux de Transition et Synthèse Organique,
URA CNRS 415, Université de Rennes I, 35042 Rennes Cedex, France

Received October 9, 1991

Summary: The hydride complexes Mo(Cp*)$(CO)_2(PR_3)$H (**2**, PR_3 = PMe_3; **3**, PR_3 = $PMePh_2$; **4**, PR_3 = PPh_3; **5**, PR_3 = $P(OMe)_3$; **6**, PR_3 = $P(OPh)_3$) are prepared from Mo(Cp*)$(CO)_3$H (**1**) by thermal substitution of a CO ligand by the corresponding phosphine or phosphite. $LiAlH_4$ reacts with [Mo(Cp*)$(CO)_3PR_3$]PF_6 (**7**, PR_3 = PMe_3; **8**, PR_3 = $PMePh_2$) in the presence of free PR_3 to give Mo(CP*)(CO)$(PR_3)_2$H (**9**, PR_3 = PMe_3; **10**, PR_3 = PPh_2Me), via an electron-transfer mechanism, CO exchange by PMe_3 and PPh_2Me at the 17-electron species, and subsequent H-atom capture.

Transition-metal hydride complexes constitute an important class of compounds because of their involvement in catalytic and stoichiometric processes such as hydrogenation and hydroformylation.[1] It is now well recognized that several transition monohydrides act as hydrogen-atom donors, and fundamental investigations were recently done on the thermodynamic driving force for H* atom transfer to organic substrates.[2] We wish to report the synthesis

---

[1] (a) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Metal Chemistry*; University Science Books: Mill Valley, CA, 1985; pp 256–259. (b) Catalytic Transition Metal Hydrides. In *Annals of the New York Academy of Sciences*; Slocum, D. W., Moser, W. R., Eds.; New York Academy of Sciences: New York, 1983; Vol. 415, pp 1-324. (c) Pearson, R. G. *Chem. Rev.* 1985, *85*, 41.

0276-7333/92/2311-1419\$03.00/0 © 1992 American Chemical Society

of several new, electron-rich molybdenum hydrides (**9**, $PR_3 = PMe_3$; **10**, $PR_3 = PPh_2Me$) with formation of the M–H bonds via an electron-transfer (ET) pathway, associated with carbonyl ligand displacement and H$^•$ atom abstraction.

Results and Discussion

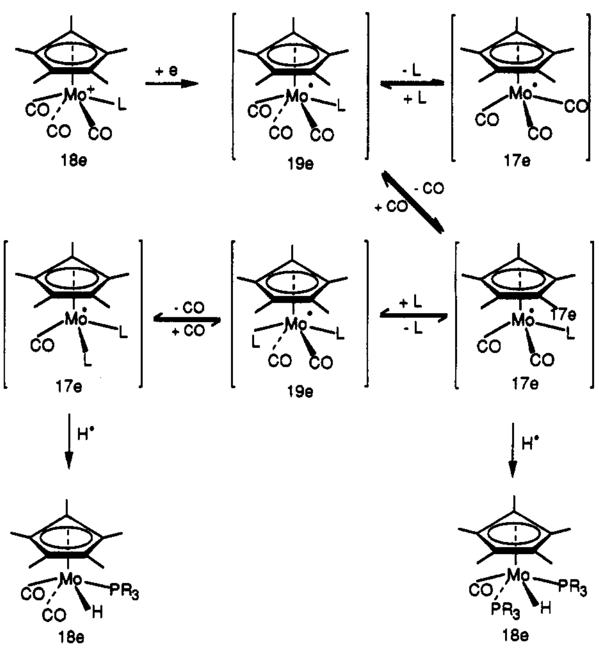
1. Synthesis and Characterization of Mo(Cp*)(CO)$_2$(PR$_3$)H. The molybdenum hydride Mo(Cp*)(CO)$_3$H[3] (**1**) reacts with 1 equiv of PR_3 in toluene to give pure Mo(Cp*)(CO)$_2$(PR$_3$)H (**2**, $PR_3 = PMe_3$; **3**, $PR_3 = PMePh_2$; **4**, $PR_3 = PPh_3$; **5**, $PR_3 = P(OMe)_3$; **6**, $PR_3 = P(OPh)_3$) isolated in 55–90% yield after crystallization from pentane (eq 1). The PR_3 ligands readily displace the carbon monoxide in less than 1 h at 20 °C, except in the case of PPh_3 for which 24 h at 65 °C is necessary. Compounds **2–6** were obtained in analytically pure form as single isomers with the cis geometry defined on the basis of the large $^1J_{PH}$ coupling constant observed for the high-field ^1H NMR signal[5] and the two ν_{CO} absorptions in the IR spectra with a more intense higher frequency band.[3] The ^{13}C NMR spectra display one broad signal in the region corresponding to the CO resonance, suggesting a fluxional behavior for these molybdenum hydride complexes[4] as already noted for the Cp analogues.[5]

$$\mathrm{Mo(Cp^*)(CO)_3H + PR_3 \rightarrow Mo(Cp^*)(CO)_2(PR_3)H + CO} \quad (1)$$

Treatment of compounds **2–6** with 1 equiv of PR_3 in refluxing toluene for 48 h does not provide any NMR-detectable traces of bis(phosphine) hydride complexes Mo(Cp*)(CO)(PR$_3$)$_2$H.

2. Synthesis and Characterization of Mo(Cp*)(CO)(PR$_3$)$_2$H. When the molybdenum salts [Mo(Cp*)(CO)$_3$PR$_3$]PF$_6$ (**7**, $PR_3 = PMe_3$; **8**, $PR_3 = PMePh_2$) are treated with an excess of $LiAlH_4$ in THF at 20 °C, the yellow solutions turn immediately orange to brown and yellow powders containing the novel molybdenum hydride complexes Mo(Cp*)(CO)(PR$_3$)$_2$H (**9**, $PR_3 = PMe_3$; **10**, $PR_3 = PMePh_2$) which are obtained in higher than 50% overall yield respectively together with the hydride compounds **2** or **3** as minor products (see Experimental Section). The yields of bis(phosphine) hydride complexes are improved by adding 1 equiv of PR_3 to the solutions before introducing $LiAlH_4$. Purification of hydride **10** was achieved by chromatography on an alumina column, whereas compound **9** decomposed by the same procedure. The magnetic equivalency of the two phosphorus atoms and the large $^2J_{PH}$ value establish the cis position of the two phosphine ligands with respect to the hydrogen atom bounded to the metal. In the case of the more bulky PPh_3 ligand,[5] the organometallic salt [Mo(Cp*)(CO)$_3$PPh$_3$]PF$_6$ (**11**) is reduced with $LiAlH_4$ to produce in 1 h at 20 °C the corresponding metal hydride Mo(Cp*)(CO)$_2$(PPh$_3$)H (**4**), isolated in 75% yield as the single product. The reduction of [Mo(Cp*)(CO)$_3$PR$_3$)]PF$_6$ (**12**, $PR_3 = P(OMe)_3$; **13**, $PR_3 = P(OPh)_3$) also affords only the pure hydride complexes **5** and **6** in 90% yield. To summarize, the one-pot syntheses of the electron-rich bis(phosphine) hydride complexes in Cp* series is an unprecedented and novel route to such compounds. However, the scope of this reaction to prepare the bis(phosphine) hydride complexes Mo(Cp*)(CO)(PR$_3$)$_2$H is strongly limited by steric factors as well as the electronic properties of the phosphorus ligands.

Scheme I



3. Evidence for an ET Mechanism and Paramagnetic Intermediates. In view of the strong dependence of both the steric and electronic character of the incoming ligand and the absence of metal–alkyl compounds even as trace product resulting from main-group metal hydride reduction of coordinated carbon monoxide,[6] we have investigated the possibility of an ET path. Indeed, mixing $LiAlH_4$ and [Mo(Cp*)(CO)$_3$L]PF$_6$ (**7**, L = PMe_3; **14**, L = CO; **15**, L = CH_3CN) in the solid state followed by introduction of THF at −80 °C results in the appearance of an orange color. The EPR spectrum of the reaction mixture frozen at 140 K displays three signals close to **g** = 2, indicating the presence of Mo^I unpaired electron species.[7,8] In the case of the tetracarbonylmetal compound, the low resolution of the spectrum does not permit determination of the components of the **g** tensor. In contrast three **g**-tensor components are observed for possible Mo^I transient intermediates resulting from the reduction of **7** (1.9203, 2.0194, 2.0628) and **13** (1.9760, 2.0110, 2.0708). In addition, an isotropic hyperfine interaction of the unpaired electron with a single ^{31}P ($I = ^1/_2$) nucleus is evidenced by a 43 G doublet separation, similar to the value observed for the stable isostructural radical [Cr(Cp*)(CO)$_2$(PMe$_3$)]$^•$.[8] Thus, whether a 17- or a 19-electron intermediate or both are present remains open to question.

---

(2) (a) Eisenberg, D. C.; Lawrie, C. J. C.; Moody, A. E.; Norton, J. R. *J. Am. Chem. Soc.* **1991**, *113*, 4888. (b) Feder, H. M.; Halpern, J. *J. Am. Chem. Soc.* **1975**, *97*, 7186. Sweany, R. L.; Butler, S. C.; Halpern, J. *J. Organomet. Chem.* **1981**, *213*, 487. (c) Connolly, J. W. *Organometallics* **1984**, *3*, 1333. (d) Wright, S. C.; Gillis, D. J.; Baird, M. C. *J. Am. Chem. Soc.* **1987**, *109*, 1995. (e) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711. (f) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2843. (g) Kiss, G.; Zhang, K.; Mukerjee, S. L.; Hoff, C. D. *J. Am. Chem. Soc.* **1990**, *112*, 5657. (h) Bullock, R. M.; Samsel, E. G. *J. Am. Chem. Soc.* **1990**, *112*, 6886.

(3) Asdar, A.; Tudoret, M.-J.; Lapinte, C. *J. Organomet. Chem.* **1988**, *349*, 353.

(4) Tudoret, M.-J.; Robo, M.-L.; Lapinte, C. Work in progress.

(5) Kalck, P.; Pince, R.; Poilblanc, R.; Roussel, J. *J. Organomet. Chem.* **1970**, *24*, 445. Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852.

(6) Lapinte, C.; Catheline, D.; Astruc, D. *Organometallics* **1988**, *7*, 1683 and references therein.

(7) Symons, M. C. R.; Bratt, S. W.; Wyatt, J. L. *J. Chem. Soc., Dalton Trans.* **1983**, 1377.

(8) Fortier, S.; Baird, M. C.; Preston, K. F.; Morton, J. R.; Ziegler, T.; Jaeger, T. J.; Watkins, W. C.; MacNeil, J. H.; Watson, K. A.; Hensel, K.; Le Page, Y.; Charland, J.-P.; Williams. A. J. *J. Am. Chem. Soc.* **1991**, *113*, 542.

A possible mechanism is outlined in Scheme I. In the initial step of the reaction, the 19-electron radical $[Mo(Cp^*)(CO)_3PR_3]^\bullet$ should be formed by electron transfer from $LiAlH_4$ to $[Mo(Cp^*)(CO)_3PR_3]PF_6$.[9,10] The kinetically favored evolution of the 19-electron radical should be the decoordination of the PR_3 ligand to produce the 17-electron intermediate $[Mo(Cp^*)(CO)_3]^\bullet$. Such a behavior is in agreement with cyclic voltammetry studies, which have shown that the reduction of $[Mo(Cp^*)(CO)_3PR_3]PF_6$ is a 2-electron irreversible process which leads through an ECE mechanism to the anionic complex $[Mo(Cp^*)(CO)_3]^-$.[3] The intermediate radical $[Mo(Cp^*)(CO)_3]^\bullet$ is trapped on the electrode by a second 1-electron reduction. The formation of $[Mo(Cp^*)(CO)_3]^\bullet$ in an early stage of the $LiAlH_4$ reduction reactions is strongly supported by cross experiments. Thus, the $LiAlH_4$ reduction of $[Mo(Cp^*)(CO)_4]PF_6$ in the presence of 1 equiv of PMe_3 affords the bis(trimethylphosphine) hydride complex **9**. Moreover the reduction of $[Mo(Cp^*)(CO)_3(PPh_2Me)]PF_6$ under identical conditions gives rise to a mixture of the five hydride complexes **2**, **3**, **9**, **10**, and $Mo(Cp^*)(CO)(PMe_3)(PPh_2Me)H$ (**16**). Whereas the chiral hydride complex **16**, obtained in 50% yield, is the major product, the formation of complexes **2** and **3** in the same molar ratio (5%) and the presence of **9** (15%) imply the decoordination of the PPh_2Me in the 19-electron intermediate shown in Scheme I.

On the other hand, incorporation of one or two PR_3 groups indicates that facile CO exchange by phosphine occurs at the 17-electron species, whereas the second substitution of CO by PR_3 is not observed at the 18-electron complexes (vide supra). Thus, the 17-electron $[Mo(Cp^*)(CO)_2(PR_3)]^\bullet$ and $[Mo(Cp^*)(CO)(PR_3)_2]^\bullet$ species are more stable than $[Mo(Cp^*)(CO)_3]^\bullet$, presumably because of the steric protection offered the metal-centered radical by the phosphine.[11] Fast ligand substitution in 17-electron radicals via an associative pathway is well established, and it has been shown that these reactions proceed 10^6–10^{10} times faster than similar reactions of the isostructural 18-electron compounds.[11-13] It was also recognized that several 17-electron radicals generated by photolysis of metal–metal-bonded dimer undergo CO phosphite or phosphine ligand substitution via 19-electron intermediates.[12] It is likely that 19-electron species are formed in the presence of a ligand in the reactions involving 17-electron radicals that are not overcrowded.[11] Thus, the PPh_3 ligand should be too bulky to produce $[Mo(Cp^*)(CO)(PPh_3)_2]^\bullet$.

4. Formation of Hydride Complexes. In 19-electron complexes, H-atom transfer from $LiAlH_4$ or AlH_3 can proceed at a CO ligand,[11,12] but in our case, no formyl complexes were detected. Thus, the possibility that this path is operative in the formation of the hydride complexes seems to be very unlikely. The aluminum hydrides together with THF are good sources of hydrogen atom, and the molybdenum hydrides could result from a coupling reaction between a hydrogen-atom donor and a 17-electron radical. Moreover, hydrogen-atom-transfer reactions of transition-metal hydrides are common,[2] and reactions between the in situ generated molybdenum hydride complexes and 17-electron intermediates would take place as depicted by eq 2. Similarly, Baird has reported the recent

$$Mo(Cp^*)(CO)_2(PR_3)H + [Mo(Cp^*)(CO)_3]^\bullet \rightleftharpoons Mo(Cp^*)(CO)_3H + [Mo(Cp^*)(CO)_2(PR_3)]^\bullet \quad (2)$$

observation that $H^\bullet$ transfer between $Cr(C_5H_5)(CO)_3H$ and $[Cr(C_5H_5)(CO)_3]^\bullet$ is rapid on the NMR time scale.[13] It has been established that the M–H bond dissociation energy would be quite insensitive to phosphine substitution,[2e-g] thus the position of the equilibrium 2 would be controlled by the relative stability of the 17-electron species.

5. Concluding Remarks. Similar reductions of cationic carbonylmetal complexes are closely related to these observations. Kochi et al. have prepared $HMn(CO)_3(PPhMe_2)_2$ by electroreduction of $Mn(CO)_6^+$ in the presence of 20 equiv of $PPhMe_2$; the supporting electrolyte was the hydrogen-atom donor.[14d] Single-electron reduction of $[Fe(Cp^*)(\eta^2\text{-dppe})(CO)]PF_6$ by $LiAlH_4$ yields the hydride $Fe(Cp^*)(\eta^1\text{-dppe})(CO)H$ via the 19-electron species $[Fe(Cp^*)(\eta^2\text{-dppe})(CO)]^\bullet$, which rapidly decoordinates a phosphorus atom to give the 17-electron species $[Fe(Cp^*)(\eta^1\text{-dppe})(CO)]^\bullet$.[6] While selective exchange of carbonyl ligands in bimetallic complexes and clusters has been carried out via rapid 17- to 19-electron interconversion, by applying a cathodic current,[15] the simple exchange of a π-acid CO ligand at a 17-electron mononuclear species is less usual.[11,14] It was observed that the yield of substitution products correlated with the lifetime of the unpaired electron species.[11b,15] The different behavior observed in the Fe and Mo series should be attributed to a very short lifetime of the Fe^I species, the lifetime for the Mo^I radicals being sufficient to be intercepted by the free P-ligands.

Experimental Section

General Data. Reagent grade tetrahydrofuran (THF), diethyl ether, toluene, and pentane were predried and distilled over sodium benzophenone ketyl prior to use. All the manipulations were carried out under an argon atmosphere using Schlenk techniques or in a Jacomex 532 drybox filled with nitrogen. Routine NMR spectra were recorded using a Bruker AW 80-MHz instrument. High-field NMR (300 MHz) spectra experiments were performed on a multinuclear Brucker instrument. Chemical shifts are given in parts per million relative to tetramethylsilane (TMS) for ^1H and ^{13}C NMR spectra and H_3PO_4 for ^{31}P NMR spectra. IR spectra were recorded on a Nicolet 205 FT instrument. Elemental analyses were performed at the Center for Microanalyses of the CNRS at Lyon-Villeurbanne.

1. Synthesis of $Mo(C_5Me_5)(CO)_2(PR_3)H$ (2, $PR_3 = PMe_3$; 3, $PR_3 = PMePh_2$; 4, $PR_3 = PPh_3$; 5, $PR_3 = P(OMe)_3$; 6, $PR_3 = P(OPh)_3$). General Procedure. To 20 mL of toluene were added 0.620 g (2 mmol) of $Mo(Cp^*)(CO)_3H$ (1) and 2 mmol of the P-ligands. The resulting yellow solution was stirred for *t*

---

(9) (a) Michaud, P.; Astruc, D.; Ammeter, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 3755. (b) Ashby, E. C.; Goel, A. B.; de Priest, R. N. *J. Am. Chem. Soc.* **1980**, *102*, 7779. (c) Jones, W. D.; Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* 1981, *103*, 4415.

(10) Lapinte, C.; Catheline, D.; Astruc, D. *Organometallics* **1984**, *3*, 817.

(11) (a) Astruc, D. *Chem. Rev.* **1988**, *88*, 1189. (b) Astruc, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 643.

(12) (a) Narayanan, B. A.; Amatore, C. A.; Kochi, J. K. *Organometallics* **1986**, *5*, 926. (b) Narayanan, B. A.; Kochi, J. K. *J. Organomet. Chem.* **1984**, *272*, C49. (c) Narayanan, B. A.; Amatore, C. A.; Kochi, J. K. *Organometallics* **1984**, *3*, 802. (d) Symons, M. C. R.; Bratt, S. W. *J. Chem. Soc., Dalton Trans.* **1979**, 1739. Madonik, A. M.; Astruc, D. *J. Am. Chem. Soc.* **1984**, *106*, 2437.

(13) Cooley, N. A.; Watson, K. A.; Fortier, S.; Baird, M. C. *Organometallics* **1986**, *5*, 2563.

(14) (a) Nappa, M. J.; Santi, R.; Halpern, J. *Organometallics* **1985**, *4*, 34. (b) Fawcett, J. P.; Jackson, R. A.; Poë, A. *J. Chem. Soc., Chem. Commun.* **1975**, 733. (c) Therien, M. J.; Ni, C. L.; Anson, F.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 4037. (d) Kuchynka, D. J.; Amatore, C.; Kochi, J. K. *Inorg. Chem.* **1986**, *25*, 4087. (e) Hershberger, J. W.; Klinger, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 3034. (f) For relevant reviews, see: *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: Amsterdam, 1990.

(15) (a) Bezems, G. J.; Rieger, P. H.; Visco, S. *J. Chem. Soc., Chem. Commun.* 1981, 265. (b) Arewgoda, M.; Rieger, P. H.; Robinson, B. H.; Simpson, J.; Visco, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 5633. (c) Ohst, H. H.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1986**, 121. (d) Ohst, H. H.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 2897. (e) Lhadi, E. K.; Patin, H.; Darchen, A. *Organometallics* **1984**, *3*, 1128.

minutes at T °C before removing the solvent under vacuum. The crude residue was crystallized from a minimum amount of pentane, and the hydride compounds **2**–**6** were recovered as pure yellow powders in y % yields. [**2**, $PR_3 = PMe_3$, $t = 5$, $T = 20$, $y = 90$ (0.655 g); **3**, $PR_3 = PMePh_2$, $t = 20$, $T = 20$, $y = 82$ (0.800 g); **4**, $PR_3 = PPh_3$, $t = 1440$, $T = 65$, $y = 55$ (0.605 g); **5**, $PR_3 = P(OMe)_3$, $t = 5$, $T = 20$, $y = 94$ (0.775 g); **6**, $PR_3 = P(OPh)_3$, $t = 60$, $T = 20$, $y = 88$ (1.052 g)].

2: IR (cm^{-1}, Nujol) 1960, 1860 (s, ν_{CO}); ^{1}H NMR (C_6D_6, 25 °C) δ 1.93 (s, 15 H, Cp*), 1.66 (d, 9 H, $^2J_{PH} = 8$ Hz, PMe_3), −5.81 (d, 1 H, $^2J_{PH} = 63$ Hz, H); {^{1}H} ^{13}C NMR (C_6D_6, 25 °C) δ 243.0 (broad m, CO), 102.6 (s, Cp*), 22.8 (d, $^2J_{PC} = 27$ Hz, PMe_3), 11.6 (s, Cp*); ^{31}P NMR (C_6D_6, 25 °C) δ 19.2 (s, PMe_3). Anal. Calcd for $C_{15}H_{25}MoO_2P$: C, 49.46; H, 6.92. Found: C, 49.4; H, 7.13.

3: IR (cm^{-1}, Nujol) 1945, 1865 (s, ν_{CO}); ^{1}H NMR (C_6D_6, 25 °C) δ 7–7.5 (m, 10 H, Ph), 2.31 (d, 3 H, $^2J_{PH} = 4$ Hz, PMe_3), 1.71 (s, 15 H, Cp*), −5.13 (d, 1 H, $^2J_{PH} = 62$ Hz, H); {^{1}H} ^{13}C NMR (C_6D_6, 25 °C) δ 247.8 (broad m, CO), 139.5 (d, $^1J_{CP} = 40.8$ Hz, C_{ipso}), 132.4 (d, $^2J_{CP} = 11$ Hz, C_{ortho}), 129.4 (s, C_{para}), 128.4 (d, $^3J_{CP} = 9$ Hz, C_{meta}), 102.7 (s, Cp*), 23.1 (d, $^2J_{PC} = 30$ Hz, PMe), 11.4 (s, Cp*), ^{31}P NMR (C_6D_6, 25 °C) δ 52.9 (s, $PMePh_2$). Anal. Calcd for $C_{25}H_{29}MoO_2P$: C, 61.48; H, 5.98. Found: C, 61.4; H, 5.9.

4: IR (cm^{-1}, Nujol) 1950, 1875 (s, ν_{CO}); ^{1}H NMR (C_6D_6, 25 °C) δ 7.5 (m, 15 H, Ph), 1.85 (s, 15 H, Cp*), −4.73 (d, 1 H, $^2J_{PH} = 64$ Hz, H); {^{1}H} ^{13}C NMR (C_6D_6, 25 °C) δ 242.5 (broad m, CO), 132.8 (d, $^1J_{CP} = 41$ Hz, C_{ipso}); 133.6 (d, $^2J_{CP} = 12$ Hz, C_{ortho}), 129.6 (s, C_{para}), 128.2 (d, $^3J_{CP} = 9$ Hz, C_{meta}), 102.7 (s, Cp*), 11.4 (s, Cp*); ^{31}P NMR (C_6D_6, 25 °C) δ 73.7 (s, PPh_3). Anal. Calcd for $C_{30}H_{31}MoO_2P$: C, 65.46; H, 5.68. Found: C, 65.4; H, 5.9.

5: IR (cm^{-1}, Nujol) 1947, 1876 (s, ν_{CO}); ^{1}H NMR (C_6D_6, 25 °C) δ 3.31 (d, 9 H, $^2J_{PH} = 12$ Hz, Me), 1.88 (s, 15 H, Cp*), −6.27 (d, 1 H, $^2J_{PH} = 70$ Hz, H). {^{1}H} ^{13}C NMR (C_6D_6, 25 °C) δ 240.0 (broad m, CO), 103.4 (s, Cp*), 51.7 (d, $^2J_{PC} = 4$ Hz, Me), 11.4 (s, Cp*); ^{31}P NMR (C_6D_6, 25 °C) δ 193.1 (s, $P(OMe)_3$). Anal. Calcd for $C_{15}H_{25}MoO_5P$: C, 43.70; H, 6.11. Found: C, 43.91; H, 6.11.

6: IR (cm^{-1}, Nujol) 1961, 1876 (s, ν_{CO}); ^{1}H NMR (C_6D_6, 25 °C) δ 7.5 (m, 15 H, Ph), 1.82 (s, 15 H, Cp*), −5.92 (d, 1 H, $^2J_{PH} = 79$ Hz, H). {^{1}H} ^{13}C NMR (C_6D_6, 25 °C) δ 237.4 (broad m, CO), 152.7 (d, $^2J_{CP} = 9$ Hz, C_{ipso}), 128.8 (d, $^3J_{CP} = 9$ Hz, C_{meta}), 122.7 (s, C_{para}), 122.4 (d, $^3J_{CP} = 4$ Hz, C_{ortho}), 103.7 (s, Cp*), 11.4 (s, Cp*). ^{31}P NMR (C_6D_6, 25 °C) δ 176.3 (s, $P(OPh)_3$). Anal. Calcd for $C_{30}H_{31}MoO_5P$: C, 60.21; H, 5.22. Found: C, 60.0; H, 5.28.

2. Reaction of $Mo(C_5Me_5)(CO)_2(PR_3)H$ (2–6) with PR_3. To 20 mL of toluene were added 2 mmol of $Mo(Cp^*)(CO)_2(PR_3)H$ (**2**–**6**) and 2 mmol of the corresponding P-ligands. The resulting yellow solution was stirred under reflux for 48 h before removal of the solvent under vacuum. The crude residue was shown by ^{1}H NMR spectroscopy to contain only the starting material, recovered in a quantitative yield.

3. Reduction of $[Mo(Cp^*)(CO)_3PR_3]PF_6$ (7, $PR_3 = PMe_3$; 8, $PR_3 = PMePh_2$) with $LiAlH_4$. A. To 1 mmol of $[Mo(Cp^*)(CO)_3PR_3]PF_6$ (**7**, 0.536 g; **8**, 0.660 g) and 4 mmol of $LiAlH_4$ was added 20 mL of THF at −20 °C. After stirring for 1 h, hydrolysis was carried out by addition of 0.5 mL of water. The solvent was removed under vacuum, and the solid residue was extracted with pentane. The yellow powder obtained after removing the pentane was identified by ^{1}H NMR spectroscopy as a mixture of **2** and **9** [60% (0.240 g) overall yield] or **3** and **10** [65% (0.300 g) overall yield] in a 3/7 ratio.

B. Following the same procedure, the reductions of **7** and **8** were carried out with 1 mmol of PR_3. The ^{1}H NMR analysis of the resulting yellow powder revealed a mixture of **2** and **9** [70% (0.282 g) overall yield] or **3** and **10** [82% (0.513 g) overall yield] in a 2/8 ratio. Compounds **3** and **10** were separated on an alumina column. **3** was eluted with pure pentane, and a mixture pentane/diethyl ether, 80/20, was used to elute **10** (40%, 0.250 g).

9: IR (cm^{-1}, Nujol) 1800 (s, ν_{CO}); ^{1}H NMR (C_6D_6, 25 °C) δ 1.79 (s, 15 H, Cp*), 1.30 (d, 18 H, $^2J_{PH} = 4$ Hz, PMe_3), −6.84 (t, 1 H, $^2J_{PH} = 77$ Hz, H); {^{1}H} ^{13}C NMR (C_6D_6, 25 °C) δ 275.0 (t, $^2J_{PC} = 26$ Hz, CO), 102.8 (s, Cp*), 25.1 (d, $^2J_{PC} = 27$ Hz, PMe_3), 11.8 (s, Cp*); ^{31}P NMR (C_6D_6, 25 °C) δ 19.6 (s, PMe_3). Anal. Calcd for $C_{15}H_{25}MoO_2P$: C, 49.46; H, 6.92. Found: C, 49.4; H, 7.13.

10: IR (cm^{-1}, Nujol) 1825 (s, ν_{CO}); ^{1}H NMR (C_6D_6, 25 °C) δ 7–7.5 (m, 20 H, Ph), 1.75 (s, 15 H, Cp*), 1.5 (d, 6 H, $^2J_{PH} = 8$ Hz, PMe), −5.05 (t, 1 H, $^2J_{PH} = 77$ Hz, H); {^{1}H} ^{13}C NMR (C_6D_6, 25 °C) δ 253.2 (7, $^2J_{PC} = 26$ Hz, CO), 142.1 (d, $^1J_{CP} = 45$ Hz, $^3J_{CP} = 32$ Hz C_{ipso}), 132.7 (d, $^2J_{CP} = 11$ Hz, C_{ortho}), 132.2 (d, $^3J_{PC} = 10$ Hz, C_{meta}), 130.9 (d, $^4J_{CP} = 7$ Hz, C_{para}), 101.1 (s, Cp*), 22.1 (d, $^1J_{PC} = 32$ Hz, PMe), 11.4 (s, Cp*). ^{31}P NMR (C_6D_6, 25 °C) δ 63.1 (s, $PMePh_2$). Anal. Calcd for $C_{37}H_{42}MoOP_2$: C, 67.37; H, 6.27. Found: C, 67.0; H, 6.2.

4. Reduction of $[Mo(Cp^*)(CO)_3PR_3]PF_6$ (11, $PR_3 = PPh_3$; 12, $PR_3 = POMe_3$, 13, $PR_3 = POPh_3$) with $LiAlH_4$. To 1 mmol of $[Mo(Cp^*)(CO)_3PR_3]PF_6$ (**11**, 0.668 g; **12**, 0.530 g; **13**, 0.716 g) and 4 mmol of $LiAlH_4$ was added 20 mL of THF at −20 °C. After stirring for 1 h, hydrolysis was carried out by addition of 0.5 mL of water. The solvent was removed under vacuum and the solid residue was extracted with pentane. The yellow powder obtained after removing the pentane was identified, after crystallization, by ^{1}H NMR spectroscopy, as the pure hydride **4** (75% yield), **5** (100% yield), and **6** (98% yield).

5. EPR Monitoring of the Reaction of $[Mo(Cp^*)(CO)_3L]PF_6$ (7, L = PMe_3; 14, L = CO; 15, L = CH_3CN) with $LiAlH_4$. Into a 2-mm quartz tube was added 10 mg of a mixture of **7**, **14**, or **15** and $LiAlH_4$ (1/4 molar ratio) carefully ground in a mortar. Cold THF (−80 °C) was added, and the reaction was immediately quenched by freezing at −196 °C. The EPR spectra were recorded at 133 K.

6. Reduction of $[Mo(Cp^*)(CO)_4]PF_6$ with $LiAlH_4$ in the Presence of PMe_3. To a THF (30 mL) solution were added 1 mmol (0.482 g) of **14** and 2 mmol of PMe_3 (160 mL). The solution was cooled to −20 °C before adding 4 mmol (0.152 g) of $LiAlH_4$. After stirring for 1 h, the solvent was removed under vacuum and the solid residue was extracted with pentane (3 × 20 mL). Recrystallization from pentane afforded a yellow powder identified by ^{1}H NMR spectroscopy as a mixture of **2**/**9** in a 2/1 ratio with an overall yield of 75% (0.282 g).

7. Reduction of $[Mo(Cp^*)(CO)_2(PPh_2Me)]PF_6$ with $LiAlH_4$ in the Presence of PMe_3. To 30 mL of THF were added 1 mmol (0.832 g) of **8** and 1 mmol of PMe_3 (80 μL). The solution was cooled to −20 °C before adding 4 mmol (0.152 g) of $LiAlH_4$. After stirring for 1 h, the solvent was removed under vacuum and the solid residue was extracted with pentane (3 × 20 mL). Recrystallization from pentane afforded a yellow powder identified by ^{1}H NMR spectroscopy as a mixture of **2**, **3**, **9**, **10**, and $MoCp^*(CO)(PMe_3)(PPh_2Me)H$ (**16**) in a 1/1/3/5/10 ratio with an overall yield of 77% (0.542 g).

Acknowledgment. We thank Drs. J.-R. Hamon and S. Sinbandhit (CRMPO, Rennes) for helpful discussions and NMR assistance.

Registry No. **1**, 78003-92-6; **2**, 116000-78-3; **3**, 123124-40-3; **4**, 123124-39-0; **5**, 139012-49-0; **6**, 118332-79-9; **7**, 122474-72-0; **8**, 122474-76-4; **9**, 139012-50-3; **10**, 138899-28-2; **11**, 113693-01-9; **12**, 138899-29-3; **13**, 122474-79-7; **14**, 122474-69-5; **15**, 122474-81-1; **16**, 138899-30-6.

Supplementary Material Available: A figure showing the EPR spectra (1 page). Ordering information is given on any current masthead page.