

Stereochemical Properties of $\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})(\text{PR}_3)\text{R}'$ Complexes ($\text{PR}_3 = \text{PMe}_3, \text{PMe}_2\text{Ph}$; $\text{R}' = \text{Br}, \text{C}_2\text{H}_5, \text{C}(\text{O})\text{C}_2\text{H}_5, \text{CHO}$) and Steric Inhibition of Tripodal Rotation

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Summary: Clockwise or counterclockwise arrays of the phenyl substituents of the C_5Ph_5 ligand associated with a chiral tripodal iron center give rise to the presence of two diastereoisomers in the solid state; this bulky ligand allows the observation of the steric inhibition of the tripodal rotation at low temperature in solution and permits the isolation of the first thermally stable neutral iron formyl complex, $\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})(\text{PMe}_3)\{\text{C}(\text{O})\text{H}\}$.

The chiral auxiliaries $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{NO})]^1$ and $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)]^2$ have been shown to exert powerful stereocontrol in a wide variety of reactions of coordinated ligands. Likewise, the metallocenic chirality arising from a clockwise or counterclockwise canting arrangement of alkyl substituents around the ring in per-alkylated planar cyclic ligands has also been widely investigated.³ The combination of these two sources of chirality in the same molecule should open new areas in molecular topology. In connection with this new concept, we have investigated the synthesis of the conformational diastereoisomeric complexes $\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})(\text{PR}_3)\text{R}'$ and report that, in addition to the stereochemical aspects, the bulky C_5Ph_5 ligand also permits the exploration of the steric inhibition of the tripodal rotation in the 5-fold axis planar C_5R_5 series. The R' fragments ($\text{R}' = \text{Br}, \text{C}(\text{O})\text{C}_2\text{H}_5, \text{C}_2\text{H}_5, \text{C}(\text{O})\text{H}$) were chosen for their synthetic and fundamental interest.⁴

Results and Discussion

The bromo complex $\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}^5$ (1) reacted with a slight excess of PMe_3 (1.25 equiv, toluene, 20 °C, 48 h) to give pure $[\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})(\text{PMe}_3)\text{Br}]^6$ (2) in 80% yield (Scheme I). The alkyl compound $\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2(\text{C}_2\text{H}_5)$ (3), prepared from 1 by a previously described procedure,⁵ cleanly afforded the orange crystalline acyl derivatives $\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})(\text{PR}'_3)\{\text{C}(\text{O})\text{C}_2\text{H}_5\}^6$ (4, $\text{PR}'_3 = \text{PMe}_3$; 5, $\text{PR}'_3 = \text{PMe}_2\text{Ph}$) in 80% yield upon reaction with a 3-fold excess of PMe_3 or PMe_2Ph for 40 h at 20 °C.

(1) (a) Merrifield, J. H.; Lin, H.-Y.; Kiel, W. A.; Gladysz, J. A. *J. Am. Chem. Soc.* 1983, 105, 5811. (b) O'Connor, E. J.; Kobayashi, M.; Loss, H. G.; Gladysz, J. A. *J. Am. Chem. Soc.* 1987, 109, 4837. (c) Senn, D. R.; Wong, A.; Patton, A. T.; Marsi, M.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* 1988, 110, 6096.

(2) Davies, S. G.; Dordor-Hedgecock, I. M.; Sutton, K. H.; Whittaker, M. *J. Am. Chem. Soc.* 1987, 109, 5711.

(3) (a) Brunner, H. *Adv. Organomet. Chem.* 1980, 18, 151. (b) Berg, U.; Libjefors, T.; Roussel, C.; Sandström, L. *Acc. Chem. Res.* 1985, 18, 80. (c) Mislow, K. *Chimia* 1986, 40, 395. (d) Schuster, I. I.; Weissensteiner, W.; Mislow, K. *J. Am. Chem. Soc.* 1986, 108, 6661. (e) Gloguen, B.; Astruc, D. *J. Am. Chem. Soc.* 1990, 112, 4607. (f) Mailvaganam, B.; Mailvaganam, B.; Sayer, B. G.; McGlinchey, M. *J. Organometallics* 1990, 9, 1089. (g) Frampton, C. S.; Top, S.; Sayer, B. G.; McGlinchey, M. *J. Am. Chem. Soc.* 1991, 113, 1177.

(4) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980.

(5) (a) Vey, S. M.; Pauson, P. L. *J. Chem. Soc.* 1965, 4312. (b) Brégaint, P.; Hamon, J.-R.; Lapinte, C. *J. Organomet. Chem.* 1990, 398, C25.

(6) Connelly, N. G.; Manners, I. *J. Chem. Soc., Dalton Trans.* 1989, 283.

Scheme I

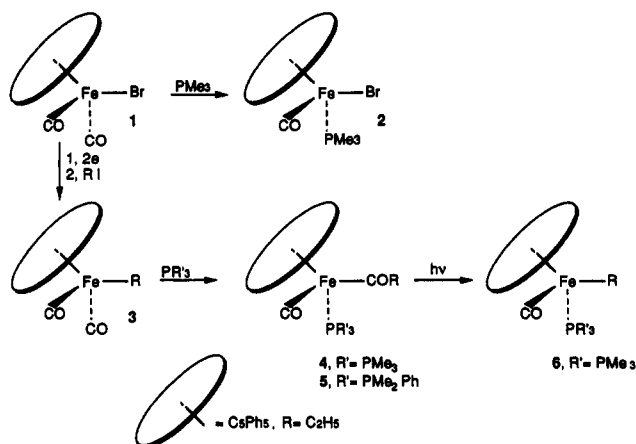


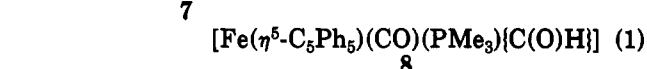
Table I. IR Data for $[\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})(\text{PR}_3)\text{R}']$ in the Solid State and in Solution

complexes	solid state ^a	soln ^b
2: $\text{R}' = \text{Br}, \text{PR}_3 = \text{PMe}_3$	1946, 1930	1942
4: $\text{R}' = \text{C}(\text{O})\text{C}_2\text{H}_5, \text{PR}_3 = \text{PMe}_3$	1897, 1607, 1600	1903, 1603
5: $\text{R}' = \text{C}(\text{O})\text{C}_2\text{H}_5, \text{PR}_3 = \text{PMe}_2\text{Ph}$	1907, 1906, 1612, 1602	1906, 1607
6: $\text{R}' = \text{C}_2\text{H}_5, \text{PR}_3 = \text{PMe}_3$	1898, 1890	1893
8: $\text{R}' = \text{C}(\text{O})\text{H}, \text{PR}_3 = \text{PMe}_3$	1929, 1920, 1597, 1587	1931, 1586

^a Nujol mull. ^b CH_2Cl_2 solution.

Irradiation ($\lambda > 360$ nm) of a toluene solution of 4 afforded the alkyliron complex $\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})(\text{PMe}_3)(\text{C}_2\text{H}_5)$ (6), isolated as red crystals in 95% yield. Solution NMR spectra recorded at room temperature for the chiral complexes 2 and 4-8 exhibited a single set of signals, indicating that the phenyl substituents of the C_5Ph_5 ligand rotate rapidly on the NMR time scale.⁶

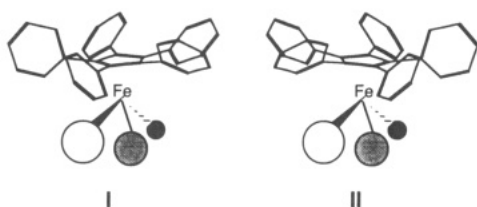
The iron formyl complex $[\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})(\text{PMe}_3)\{\text{C}(\text{O})\text{H}\}]$ (8) was obtained as orange crystals in 88% yield by sodium borohydride reduction of the cationic precursors⁵ $[\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2(\text{PMe}_3)]\text{PF}_6$ (7), following a known procedure^{7a} (eq 1). The ¹H NMR spectrum (20



°C, C_6D_6) of 8 shows the proton resonance of the formyl ligand as a doublet at δ 15.27 ($^3J_{\text{PH}} = 2.3$ Hz).⁷ Compound 8 is a rare example of a neutral first-row transition-metal formyl complex to be isolated and is the first to be stable at room temperature.⁷ The C_5H_5 and C_5Me_5 formyl analogues have been spectroscopically characterized in solu-

(7) (a) Asdar, A.; Lapinte, C. *Organometallics* 1989, 8, 2708. Gibson, D. H.; Mandal, S. K.; Owens, K.; Sattich, W. E.; Franco, J. O. *Organometallics* 1989, 8, 1114. (b) Lapinte, C.; Catheline, D.; Astruc, D. *Organometallics* 1988, 7, 1683, and refs 1-20 therein.

Chart I. Schematic View of One Pair of Diastereoisomers



tion, but their isolation was precluded by thermal instability. The important increase of stability associated with the C_5Ph_5 ligand should be both kinetic and thermodynamic in origin. The bulky and electron-withdrawing phenyl groups sterically protect the labile formyl fragment and also lower the electron density on the formyl carbon atom, demonstrated by a shielding shift of more than 30 ppm in the ^{13}C NMR spectrum with respect to the spectrum for the C_5Me_5 analogue.⁷

The solid-state IR spectra obtained from bulk material of the compounds 2, 4–6, and 8 in Nujol mulls shows a splitting of the C–O stretching absorptions observed in solution (Table I), in contrast with the previously reported compounds in the $Fe(\eta^5-C_5Ph_5)(CO)_2$ series with a prochiral iron atom, for which the solid-state and solution IR spectra are identical.⁵ The solubility of all these solid complexes in Nujol is low, and the mull spectra are those of the solid state. These spectra indicate the creation of a new source of molecular asymmetry in the C_5Ph_5 pentacycle during crystallization, giving rise to two diastereoisomers.⁸ A chiral array of the C_5Ph_5 ligand has already been observed in half-sandwich complexes (e.g. $Co(\eta^5-C_5Ph_5)(CO)_2$,^{9a} $Fe(\eta^5-C_5Ph_5)(CO)_2Br$,^{9b} and $Ru(\eta^5-C_5Ph_5)(CO)(PPh_3)Br$ ^{9c}), and preliminary X-ray data for the formyl compound 8 unambiguously establish that the observed diastereoisomerism comes from the two opposite canting modes of all the five phenyl groups around the C_5 ring.¹⁰

Dynamic ^{13}C NMR data for 5, from +20 to –110 °C (the lowest accessible temperature owing to poor solubility), in a 4:1 mixture of CD_2Cl_2 and $CFCl_3$ revealed a decoalescence phenomenon whereby the single resonance of the C_5 ring yielded ultimately four distinct signals in the ratio 1:2:1:1 (Figure 1). This splitting is in complete agreement with the cessation of tripodal rotation on the NMR time scale. This behavior is unprecedented in persubstituted half-sandwich C_5 ring molecules and is related to the work of McGlinchey on (arene)chromium piano-stool complexes.¹¹ The CPMAS ^{13}C NMR spectrum obtained from a solid sample of 5 generally correlates well with the limiting low-temperature ^{13}C NMR solution spectrum.

The solid-state ^{13}C NMR spectrum of $Fe(\eta^5-C_5Ph_5)(CO)(PMe_3)(C_2H_5)$ (6) has also been recorded. In the phenyl region, the spectrum can only be interpreted in terms of 30 distinct carbon atoms; the five ipso carbons were differentiated from the CH resonances by a DEPT experiment. The two diastereoisomers are not separated

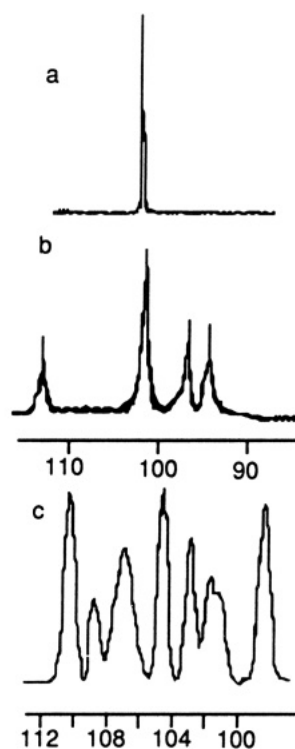


Figure 1. ^{13}C NMR spectra in the C_5 ring region of $Fe(C_5Ph_5)(CO)(PMe_3)(C_2H_5)$: (a) in 4:1 CD_2Cl_2 – $CFCl_3$ solution at 20 °C; (b) as in (a) except at –100 °C; (c) in the solid state.

in this region of the spectrum, but the o,o' and m,m' carbon atoms of each phenyl group are differentiated. In contrast, the C_5 ring gives rise to a 1:1:2:1:1:1:1:2 peak pattern corresponding to 10 distinct carbon atoms, in agreement with the presence of two diastereoisomers in the solid. It is clear that, in the solid state, the rotations of the tripod and of the phenyl groups are hindered. It appears from our preliminary data that the barrier to tripodal rotation seems higher than that to the phenyl rotation. However, a gearlike interaction between the phenyl groups and the tripod cannot be excluded at the present time. Further synthetic and structural studies of these compounds are presently underway.

Experimental Section

General Data. Reagent grade tetrahydrofuran (THF), diethyl ether, toluene, and pentane were predried and distilled over sodium benzophenone ketyl prior to use. Photolyses were performed with a Hanovia lamp (450 W, 250 nm) equipped with a quartz jacket, at room temperature under a stream of argon. 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) experiments were performed on a multinuclear Bruker 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 spectrometer, and the data are reported in Table I. The CPMAS spectra were recorded with a 400-MHz Bruker instrument and the relative weights of the peaks estimated with Bruker software. Elemental analyses were performed at the Center for Microanalyses of the CNRS at Lyon-Villeurbanne, France.

1. Synthesis of $Fe(\eta^5-C_5Ph_5)(CO)(PMe_3)Br$ (2). To a red toluene solution (100 mL) of 0.064 g (0.1 mmol) of **1**⁵ was added 13 μ L (0.125 mmol) of PMe_3 . After the mixture was stirred 2 days the solvent was removed under vacuum and the solid residue extracted with 20 mL of diethyl ether. After 20 mL of pentane was added, the solution was stored at –25 °C for 2 days. Brown microcrystals of **2** were recovered by filtration in 83% yield (0.057

(8) Spectroscopic data for a crystalline material are a reflection of the space group and the contents of the unit cell rather than that of the point group of the isolated molecule. In the solid, there are eight molecules of 8 per unit cell (monoclinic crystal system, space group $C2/c$).¹²

(9) (a) Chambers, J. W.; Baskar, A. J.; Bott, S. G.; Atwood, J. L.; Rausch, M. D. *Organometallics* 1986, 5, 1635. (b) Field, L. D.; Hambley, T. W.; Lindall, C. M.; Masters, A. F. *Polyhedron* 1989, 8, 2425. (c) Adams, H.; Bailey, N. A.; Browning, A. F.; Ramsden, J. A.; White, C. J. *J. Organomet. Chem.* 1990, 387, 305.

(10) Bregaint, P.; Toupet, L.; Hamon, J.-R.; Lapinte, C. Work in progress.

(11) Downton, P. A.; Mailvaganam, B.; Frampton, C. S.; Sayer, B. G.; McGlinchey, M. J. *J. Am. Chem. Soc.* 1990, 112, 27.

(12) Childs, R. F.; Varadarajan, A.; Lock, C. J. L.; Faggiani, R.; Fyfe, C. A.; Wasylishen, R. E. *J. Am. Chem. Soc.* 1982, 104, 2452.

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 $Fe(\eta^5-C_5Ph_5)(CO)(PMe_3)(C(O)C_2H_5)$ (4). To 7 mL of CH_2Cl_2 was added 0.050 g of **3** and 30 μ L (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 $Fe(\eta^5-C_5Ph_5)(CO)(PMe_2Ph)(C(O)C_2H_5)$ (5). By the procedure described for **4**, complex **5** was isolated as orange crystals in 80% yield. Anal. Calcd for $C_{47}H_{41}FeO_2P \cdot C_7H_8$: 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-C₅); 133.1 (s, m Ph-C₅); 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-C₅); 127.0 (s, p Ph-C₅); 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 $Fe(\eta^5-C_5Ph_5)(CO)(PMe_3)(C_2H_5)$ (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, $J_{HH} = 7.5$ Hz, $J_{HH} = 7.3$ 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 $Fe(\eta^5-C_5Ph_5)(CO)(PMe_3)(CHO)$ (8). In a mortar 0.194 g (0.25 mmol) of **7** 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).

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

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Summary: The hydride complexes $Mo(Cp^*)(CO)_2(PR_3)H$ (**2**, $PR_3 = PMe_3$; **3**, $PR_3 = PPh_2$; **4**, $PR_3 = PPh_3$; **5**, $PR_3 = P(OMe)_3$; **6**, $PR_3 = P(OPh)_3$) are prepared from $Mo(Cp^*)(CO)_3H$ (**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**, $PR_3 = PPh_2$) in the presence of free PR_3 to give $Mo(Cp^*)(CO)(PR_3)_2H$ (**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 im-

portant 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.