30.7 (CH_2, t, J_{Cp} = 22), 9.84 (C_5Me_5); IR 1940 (ν_{CO}). Anal. Calcd for $C_{37}H_{29}P_3FeF_6$: C, 59.04; H, 3.86; P, 12.36; Fe, 7.45. Found: C, 59.15; H, 3.88; P, 12.45; Fe, 7.55.

(p) Synthesis of Fp'^-K^+, 16a. Fp'_2, 1 (4.94, 10 mmol), was stirred on a potassium mirror (780 mg, 20 mmol) in 60 mL of THF at room temperature for 2 h. After filtration the THF was removed in vacuo, giving a red powder (85% yield): IR 1870, 1805 (ν_{CO}); Mössbauer, IS = 0.11 mm s^{-1} vs. Fe (77 K), QS = 2.00 mm s^{-1}.

(q) Synthesis of Fp′Me, 17. To a stirred suspension of Fp'^-K^+, **16a**, prepared as in **15**, from 10 mmol of Fp'_2, 1, was added MeI (3.55 g, 25 mmol) by syringe. After evaporation in vacuo, the residue was extracted with 3 × 20 mL of pentane. Evaporation of this solution gave crude **17**, purified by sublimation (70 °C, 1 mmHg), yielding **17**, as yellow microcrystals (80% yield calculated vs. Fp'_2): ^1H NMR (C_6D_6) 1.95 (s, 15 H, C_5Me_5), –0.08 (s, 3 H, FeMe); ^{13}C NMR ($CDCl_3$) 219.5 (CO), 105.2 (C_5Me_5), 9.2 (C_5Me_5), –13.1 (FeMe, J_{CH} = 133 Hz); IR 2040, 1985 (ν_{CO}); Mössbauer, IS = 0.12 mm s^{-1} vs. Fe (77 K), QS = 1.88 mm s^{-1}. Anal. Calcd for $C_{13}H_{18}O_2Fe$: C, 59.57; H, 6.92; Fe, 21.30. Found: C, 59.65; H, 7.02; Fe, 21.38.

(r) Synthesis of $Fp'CH_2OCH_3$, 18. Fp'_2, 1 (980 mg, 2 mmol), was reduced on Na/Hg (5 mmol of Na) in 100 mL of THF over 24 h. The solution was transferred, and 170 mg (2.1 mmol) of chloromethyl methyl ether was added by syringe. After evaporation of the THF the residue was extracted with 3 × 50 mL of pentane. Concentration in vacuo and chromatographic separation on silica plates (1 mm, eluant pentane/ether (95/5), R_f 0.7), yielded **18**, as an orange oil (60% yield: ^1H NMR (C_6D_6) 4.53 (s, 2 H, CH_2), 3.36 (s, 3 H, CH_3), 1.58 (s, 15 H, C_5Me_5); ^{13}C NMR (C_6D_6) 218.7 (CO), 95.5 (C_5Me_5), 61.3 (o-CH_3), 73.3 (CH_2), 9.2 ($C_5\mathit{Me}_5$); IR 2010, 1990, 1940, 1930 (ν_{CO}), 1060 (ν_{C-O}). Anal. Calcd for $C_{14}H_{20}O_3Fe$: C, 57.55; H, 6.90; Fe, 19.11. Found: C, 57.63; H, 6.91; Fe, 19.25.

Acknowledgment. We are grateful to S. Sinbandhit (Centre de Mesures Physiques de l'Ouest) and J.-P. Mariot (Professor F. Varret's Laboratory, Université du Maine) for NMR and Mössbauer assistance and to B.A.S.F. (Ludwigshafen, West Germany) for a generous gift of iron pentacarbonyl.

Registry No. 1, 35344-11-7; **3a**, 89870-08-6; **3b**, 89875-00-3; **3c**, 89875-02-5; **3d**, 89875-04-7; **3e**, 82025-16-9; **3f**, 88250-99-1; **3g**, 89875-06-9; 4, 72303-22-1; **5**, 80409-91-2; **6a**, 89875-07-0; **6b**, 89875-08-1; **6c**, 89875-10-5; **6d**, 89875-12-7; **7**, 89875-14-9; **9**, 86991-88-0; **10**, 86991-90-4; **11**, 86991-92-6; **12**, 86991-96-0; **13**, 89875-16-1; **15**, 88251-02-9; **16a**, 59654-59-0; **17**, 52409-66-2; **18**, 89875-17-2; Cp′H, 4045-44-7; $Fe(CO)_5$, 13463-40-6; $Cp_2Fe^+PF_6^-$, 11077-24-0; Fp_2, 12154-95-9; $Na^{+-}S_2CNMe_2$, 128-04-1; Cp(η^5-$C_6Me_5CH_2$)Fe, 70414-93-6.

Photochemical Hydrogenolysis of the Phosphorus–Cyclopentadienyl Bond of $(CO)_4MnMo(CO)_3[\eta^5\text{-}C_5H_4P(C_6H_4\text{-}p\text{-}CH_3)_2]$ and Formation of the Phosphido-Bridged Metal Hydride Complex $(CO)_4Mn[\mu\text{-}P(C_6H_4\text{-}p\text{-}CH_3)_2](\mu\text{-}H)Mo(CO)_2(C_5H_5)$

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The photolysis of $(CO)_4MnMo(CO)_3[\eta^5\text{-}C_5H_4P(C_6H_4\text{-}p\text{-}CH_3)_2]$, 1, under 1 atm of H_2 results in the formation of $(CO)_4Mn[\mu\text{-}P(C_6H_4\text{-}p\text{-}CH_3)_2](\mu\text{-}H)Mo(CO)_2(C_5H_5)$, 2. Deprotonation of 2 by KOH gives $(CO)_4Mn[\mu\text{-}P(C_6H_4\text{-}p\text{-}CH_3)_2]Mo(CO)_2(C_5H_5)^-$, 3.

We recently reported[1] the synthesis and crystal structure of $(CO)_4MnMo(CO)_3[\eta^5\text{-}C_5H_4P(C_6H_5)_2]$, a heterobimetallic compound in which the two metals are held together through both a metal–metal bond and a heterodifunctional ligand. This compound and a series of related compounds containing Mo–Re,[1] Mo–Rh,[2] and Mo–Ir[2] bonds have been studied as possible precursors to heterobimetallic dihydrides that might serve as reducing agents for polar molecules such as CO.

Reaction of $(CO)_4MnMo(CO)_3[\eta^5\text{-}C_5H_4P(C_6H_5)_2]$ with high pressure of H_2 was investigated as a possible means of cleaving the Mo–Mn bond and of obtaining a heterobimetallic hydride. However, when solutions of $(CO)_4MnMo(CO)_3[\eta^5\text{-}C_5H_4P(C_6H_5)_2]$ under 1200 psi of H_2 at 145 °C were examined by high-pressure infrared spectroscopy, no reaction was observed, and higher temperatures led to decomposition. In a second approach to form heterobimetallic dihydrides, we investigated the reactivity of the related *p*-tolyl compound $(CO)_4MnMo(CO)_3[\eta^5\text{-}C_5H_4P(C_6H_4\text{-}p\text{-}CH_3)_2]$, 1, toward sequential treatment with acid followed by a hydride donor. The Mo–Mn bond of 1 was protonated by CF_3SO_3H, giving a cationic bimetallic bridging hydride. However, reaction of this cation with a hydride donor caused deprotonation rather than dihydride formation.[3]

Here we report an attempted photochemical synthesis of a heterobimetallic dihydride. However, no evidence for

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[†] Procter and Gamble Fellow, 1982–1983.

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(2) Casey, C. P.; Bullock, R. M.; Nief, F. *J. Am. Chem. Soc.* **1983**, *105*, 7574.

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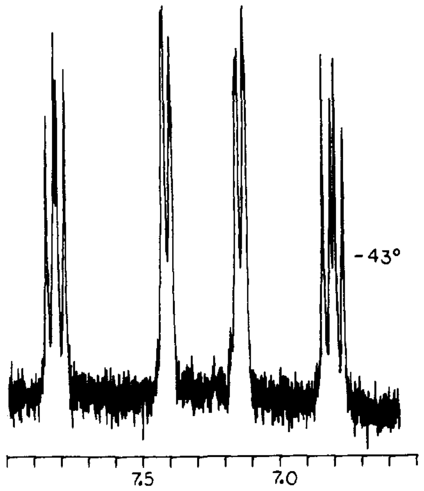
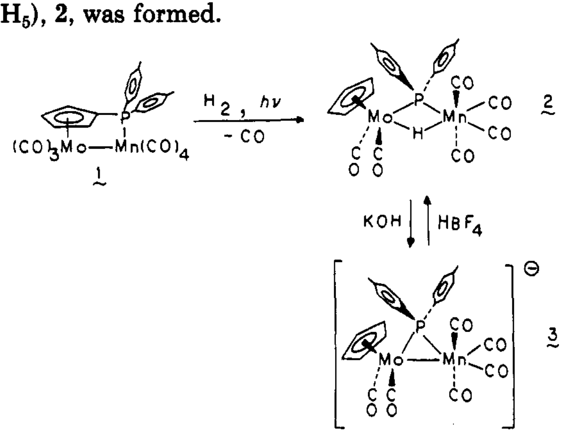


Figure 1. 270-MHz ^1H NMR of the aromatic protons of 2 at -43 °C.

a dihydride was seen. Instead, a novel reaction occurred in which the phosphorus-cyclopentadienyl bond was cleaved and $(CO)_4Mn[\mu\text{-}P(C_6H_4\text{-}p\text{-}CH_3)_2](\mu\text{-}H)Mo(CO)_2(C_5H_5)$, 2, was formed.



Results and Discussion

Photolysis of a toluene solution of 1 under 1 atm of H_2 for 4 days caused a slight color change from red-orange to light orange. Chromatographic purification led to the isolation of 2 as a yellow-orange solid in 60% yield. The elemental composition of 2 was established by mass spectrometry and elemental analysis. The highest mass ion observed in the high resolution mass spectrum was due to $C_{25}H_{20}MnMoO_6P$, indicating the presence of a minimum of six CO ligands and the possible loss of one CO during formation of 2. Since loss of CO upon ionization is a common occurrence in the mass spectra of metal carbonyl complexes, we resorted to elemental analysis to fully establish the number of CO ligands. C and H analyses are too insensitive to distinguish between formulations with six or seven CO ligands since the % C in CO and in the complexes are similar. For example, the C and H analyses obtained were within ±0.30% of the calculated analyses for both $C_{25}H_{20}MnMoO_6P$ and $C_{26}H_{20}MnMoO_7P$. In contrast, the calculated molybdenum analysis differs by 0.71% for the two formulations being considered, and the observed analysis was consistent only with the six CO formulation. This formulation corresponds to loss of one molecule of CO and addition of two hydrogen atoms in the conversion of 1 to 2.

The low-temperature ^1H NMR spectrum of 2 established the presence of a cyclopentadienyl (C_5H_5) ligand, of nonequivalent p-tolyl groups on phosphorus, and of a bridging metal hydride. The 270-MHz ^1H NMR spectrum of 2 at -43 °C in acetone-d_6 exhibits a sharp singlet at δ 5.31 for the cyclopentadienyl ring and a doublet at δ -13.91 for a bridging metal hydride. The ortho protons of the two different p-tolyl rings gave rise to doublets of doublets at δ 7.82 and 6.80, and resonances for the meta protons of the nonequivalent p-tolyl rings were observed at δ 7.41 and 7.14 (Figure 1). The methyl groups of the p-tolyl rings appeared at δ 2.39 and 2.22.

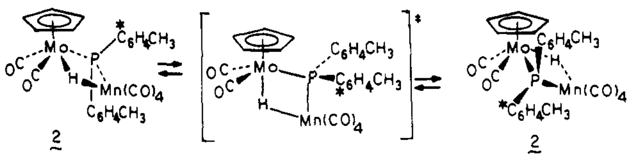


Figure 2.

The $^{13}C\{^1H\}$ NMR spectrum of 2 at -40 °C exhibited a singlet at δ 235.8 for one molybdenum carbonyl and a doublet (J = 27.5 Hz) at δ 242.5 for a molybdenum carbonyl trans to phosphorus. Three resonances were observed for the four manganese carbonyls in an approximately 2:1:1 intensity ratio.

The lowest energy carbonyl band of the five bands observed in the IR spectrum appeared at 1901 cm^{-1}, ruling out the possibility of a bridging carbonyl group. All of this information required that 2 have the assigned bimetallic structure with the two metals joined by a phosphide bridge and a three-center, two-electron Mn-H-Mo bond.

The related symmetric bimetallic compounds $[(CO)_4Mn]_2(\mu\text{-}H)(\mu\text{-}PPh_2)$ (4)[4] and $[C_5H_5(CO)_2Mo]_2(\mu\text{-}H)(\mu\text{-}PMe_2)$ (5)[7] related to Mo-Mn compound 2 have been well characterized. The ^1H NMR parameters of the bridging hydride in Mn-Mn compound 4 (δ -16.18 (J = 35.5 Hz)) and Mo-Mo compound 5 (δ -11.7 (J = 37 Hz)) are similar to those of Mo-Mn compound 2 (δ -13.9 (J = 31 Hz)). Heterobimetallic bridging hydrides related to 2 include $(C_5H_5)(CO)_3Nb(\mu\text{-}H)Nb(CO)(C_5H_5)_2$,[9] $(C_5H_5)(CO)_3V(\mu\text{-}H)Nb(CO)(C_5H_5)_2$,[9] $(CO)_5Cr(\mu\text{-}H)Nb(CO)(C_5H_5)_2$,[9] $(C_5H_5)_2(CO)Nb(\mu\text{-}H)Fe(CO)_4$,[10,11] $(C_5H_5)_2(CO)Ta(\mu\text{-}H)Mn_2(CO)_9$,[12] $[(C_5H_5)_2(CO)Nb]_2(\mu\text{-}H)^+$,[13] $(C_5H_5)_2Nb(\mu\text{-}H)Ni(CO)_3$,[14] and $(C_5H_5)_2(CO)Ta(\mu\text{-}H)M$[15] (M

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[4] Green[5] reported the formation of $[(CO)_4Mn]_2(\mu\text{-}H)(\mu\text{-}PPh_2)$, 4, in low yield from the reaction of $NaMn(CO)_5$ with Ph_2PCl. Later, Hayter[6a] reported an improved synthesis of 4 in 12% yield from the reaction of $Mn_2(CO)_{10}$ with $(Ph_2P)_2$. In both of these reactions the major isolated product was $[(CO)_4Mn(\mu\text{-}PPh_2)]_2$. Mays[6b] has recently reported an 80% yield of 4 from the reaction of $Mn_2(CO)_{10}$ with $HPPh_2$.

[5] Green, M. L. H.; Moelwyn-Hughes, J. T. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem. Biophys., Biol.* **1962**, *17B*, 783.

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[7] Hayter[7] reported the synthesis of $[(CO)_2(C_5H_5)Mo]_2(\mu\text{-}PMe_2)(\mu\text{-}H)$, 5, in 35% yield from $(CO)_3Mo(C_5H_5)^-$ and Me_2PCl, and neutron diffraction studies[8] on 5 conclusively demonstrated the presence of a symmetrically bridged Mo-H-Mo unit. Hayter, R. G. *Inorg. Chem.* **1963**, *2*, 1031.

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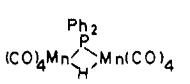
= $Cr(CO)_5$, $Mo(CO)_5$, $W(CO)_5$, and $Mn(CO)_2(C_5H_5)$).



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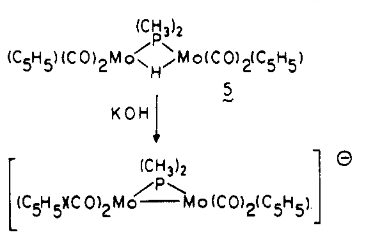

The ^1H NMR spectrum of 2 is temperature dependent and provides evidence for a process that interconverts the environments of the *p*-tolyl groups. At 4 °C in the 270-MHz ^1H NMR, four broad resonances (2 H each) are observed for the aromatic protons, and the *p*-tolyl methyl groups appear as a pair of broad singlets. At 25 °C, these methyl groups give rise to one broad singlet, and the aromatic protons are coalesced into a very broad resonance barely above the base line. The fluxional process responsible for the temperature-dependent NMR spectra (Figure 2) is probably similar to the one we observed[16] for $(CO)_4Fe(\mu\text{-}AsMe_2)Mo(CO)_2(C_5H_5)$, in which the enantiomers of the square-pyramidal molybdenum compounds were interconverted via a symmetric trigonal-bipyramidal intermediate.

In an attempt to form a cationic dihydride, 2 was stirred in diethyl ether solution with an excess of $HBF_4{\cdot}OEt_2$. However, no reaction was observed by IR spectroscopy.

The bridging metal hydride of 2 was reversibly deprotonated by base. Treatment of 2 with KOH in ethanol followed by cation exchange with $N(CH_2CH_3)_4{}^+Br^-$ led to the formation of $N(CH_2CH_3)_4{}^+\{(CO)_4\overline{Mn[\mu\text{-}P\text{-}(C_6H_4PCH_3)_2]Mo}(CO)_2(C_5H_5)\}^-$, 3. The 270-MHz NMR spectrum of 3 at −70 °C in acetone-d_6 exhibited singlets at δ 2.27 and 2.12 for the nonequivalent methyls on the *p*-tolyl groups. As with 2, the ^1H NMR spectrum of 3 was temperature dependent. At 4 °C the methyl groups appeared as a broad singlet; further warming to 48 °C resulted in a sharp singlet for the methyl groups. Changes in the aromatic region were also seen as a function of temperature (Figure 3). A fluxional process analogous to the one discussed above for 2 is presumably responsible for the temperature-dependent NMR spectra observed for 3.

3 was easily protonated to regenerate 2 in 90% isolated yield by treatment of a CH_2Cl_2 solution of 3 with $HBF_4{\cdot}OEt_2$. The procedures we employed for the interconversion of 2 and 3 were modeled after Peterson and Stewart's[17] synthesis of $\{[(C_5H_5)(CO)_2Mo]_2(\mu\text{-}PMe_2)\}^-$ (6) by deprotonation of 5.

The photochemically induced phosphorus–cyclopentadienyl bond cleavage reported here was unexpected and surprising, since we had hoped to form a dihydride from 1. If reactions of this type turn out to be facile, then the use of bimetallic compounds containing the $C_5H_4P(C_6H_4\text{-}p\text{-}CH_3)_2$ ligand in catalysis may be limited. It is not clear what detailed mechanism accounts for the unusual hydrogenolysis of the phosphorus–cyclopentadienyl bond, but several steps must occur, including loss of CO, addition of hydrogen to a metal center, addition of hydrogen to the cyclopentadienyl ring, phosphorus–carbon bond cleavage, and bridging of the phosphorus atom to both metals.

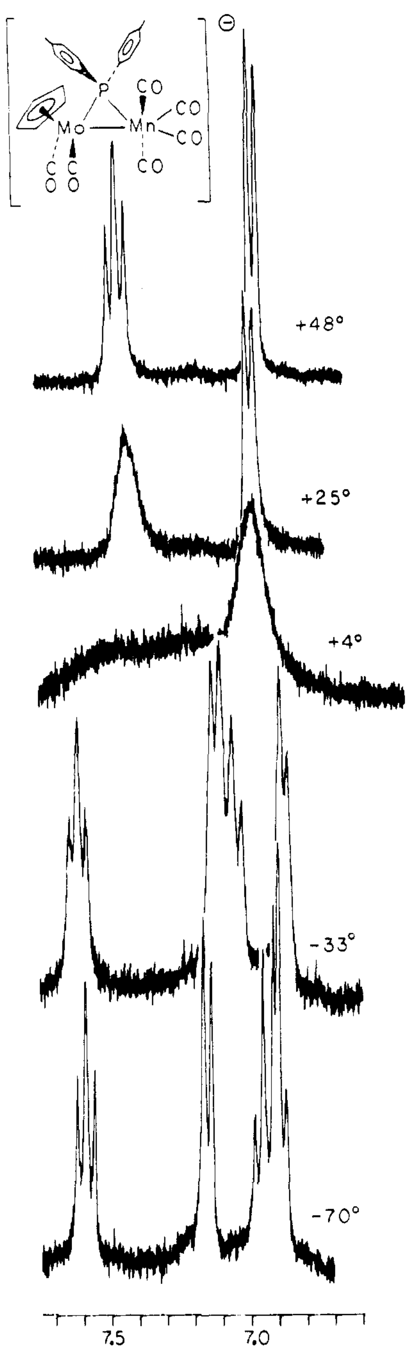

Figure 3. Variable-temperature 270-MHz ^1H NMR spectra of the aromatic protons of 3.

Two reasonable choices for the primary photochemical event are metal–metal bond rupture and metal–carbonyl bond scission. In an attempt to determine whether photoinduced loss of CO occurred readily, a solution of 1 was photolyzed in the presence of ^{13}CO for only 90 min, which led to incorporation of about 0.56 ^{13}CO/molecule. The product was examined by ^{13}C NMR, using appropriate precautions to obtain accurate integrations (see Experimental Section). ^{13}CO was found to be incorporated randomly into 1. The percent ^{13}CO (above natural abundance) was 7.5% for each of two Mo–CO groups and 8.4% for each Mn–CO group. These results are consistent with either negligible site specificity for ^{13}CO incorporation or a fluxional process that randomizes the ^{13}CO between all possible sites in the product.

Studies of a number of diphenylphosphide-bridged compounds have led to a correlation between the ^{31}P chemical shift and the presence or absence of a metal–

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[15] LeBlanc, J. C.; Reynoud, J. F.; Moise, C. *J. Organomet. Chem.* **1983**, *244*, C24.

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metal bond.[18] Phosphido-bridged compounds displaying a downfield chemical shift (δ 200–50) are generally found to have a direct metal–metal bond, while upfield chemical shifts (δ 50 to −200) are typically observed for phosphido-bridged compounds where a metal–metal bond is absent.[18e–h] Thus the ^{31}P NMR chemical shifts of **2** (δ 158.1) and **3** (δ 182.4) support the presence of a molybdenum–manganese bond. However, it is worthwhile to note that while the deprotonation of **2** to **3** was accompanied by a downfield shift of 24.3 ppm, the deprotonation of **5** to **6** was reported to result in an upfield shift in the ^{31}P NMR from δ 146.4 in the hydride **5** to δ 61.6 in the anion **6**.[17] Garrou[19] has noted that while these general trends can be helpful in structural assignments, not enough data have been accumulated to allow definitive structural assignments based on the ^{31}P NMR chemical shift alone, and Jones[20] has pointed out some notable exceptions to the general trend. Thus it is probably inappropriate at this time to attach too much significance to the exact value of the ^{31}P NMR chemical shift in these compounds, except to say that the ^{31}P NMR data, as well as all of the other spectroscopic data, are in accord with the formulation of a three-center two-electron Mo–H–Mn bond in **2** and a molybdenum–manganese bond in **3**.

Experimental Section

All reactions were carried out under nitrogen, using Schlenk glassware or a Vacuum Atmospheres glovebox. Olefin-free hexane, diethyl ether, and toluene were distilled from sodium benzophenone ketyl under a nitrogen atmosphere. CH_2Cl_2 was distilled from CaH_2, CD_2Cl_2 was distilled from P_2O_5, and acetone-d_6 was distilled from B_2O_3.[21] ^1H NMR spectra were recorded on an IBM WP270 (270 MHz); ^{13}C NMR (50.10 MHz) and ^{31}P NMR (80.76 MHz) spectra were recorded on a JEOL FX-200 spectrometer. ^{31}P chemical shifts are referenced in parts per million from 85% H_3PO_4; downfield shifts are recorded as positive. Infrared spectra were recorded on a Beckman 4230 infrared spectrometer. Mass spectra were obtained on an AEI-MS-902 mass spectrometer. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Labs.

$(CO)_4Mn[\mu\text{-}P(C_6H_4\text{-}p\text{-}CH_3)_2](\mu\text{-}H)Mo(CO)_2(C_5H_5)$, 2. A solution of **1** (455.2 mg, 0.729 mmol) in toluene (25 mL) under 1 atm of H_2 in a Vycor tube was photolyzed for 91 h by using a Hanovia 450-W medium-pressure mercury lamp. The solvent was evaporated, and the residue was purified by preparative thin-layer chromatography (silica gel, 1:1 Et_2O/hexane). A band at R_f 0.3 contained 9.2 mg of unreacted **1**, and a band at R_f 0.5 yielded **2** as a yellow-orange solid (259.7 mg, 60%): mp 169–174 °C dec; ^1H NMR (−43 °C, acetone-d_6) δ 7.82 (dd, J_{PH} = 10.5 Hz, J_{HH} = 8.0 Hz, 2 H, ortho), 7.41 (dm, J_{HH} = 7.3 Hz, 2 H, meta), 7.14 (dm, J_{HH} = 7.1 Hz, 2 H, meta), 6.80 (dd, J_{PH} = 12.1 Hz, J_{HH} = 8.0 Hz, 2 H, ortho), 5.31 (s, 5 H, C_5H_5), 2.39 (s, 3 H, CH_3), 2.22 (s, 3 H, CH_3), −13.91 (d, J_{PH} = 31.4 Hz, 1 H, hydride); temperature-dependent ^1H NMR (+4 °C, acetone-d_6) δ 7.81 (br s, 2 H, ortho), 7.39 (br s, 2 H, meta), 7.11 (br s, 2 H, meta), 6.87 (br s, 2 H, ortho), 2.40 (br s, 3 H, CH_3), 2.25 (br s, 3 H, CH_3); ^1H NMR (25 °C, acetone-d_6) δ 7.8 (very broad resonance barely observable above the base line, aromatic), 7.2 (br resonance, aromatic), 2.33 (br s, 6 H, CH_3); ^1H NMR (48 °C, acetone-d_6) δ 7.38 (br s, aromatic), 7.2 (m, aromatic), 2.33 (s, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (−40 °C, acetone-d_6, 0.07 M $Cr(acac)_3$) δ 242.5 (d, J_{PC} = 27.5 Hz, Mo(CO) trans to P), 235.8 (s, Mo(CO)), 219.0 (s), 211.0 (m), 209.2 (m) ($Mn(CO)_4$, approximately 2:1:1 ratio), 140.4 (s, para), 139.0 (s, para), 137.6 (d, J_{PC} = 39.7 Hz, ipso), 136.9 (d, J_{PC} = 42.5 Hz, ipso), 135.1 (d, J_{PC} = 6.1 Hz, ortho), 131.8 (d, J_{PC} = 9.1 Hz, ortho), 129.9 (d, J_{PC} = 9.2 Hz, meta), 129.1 (d, J_{PC} = 9.2 Hz, meta), 92.7 (s, C_5H_5), 21.2 (s, CH_3), 20.9 (s, CH_3); $^{31}P\{^1H\}$ NMR (−70 °C, acetone-d_6) δ 158.1 (s); IR (cyclohexane) 2068 (m), 2001 (m), 1979 (s), 1963 (s), 1901 (m) cm^{-1}. Anal. Calcd for $C_{25}H_{20}MnMoO_6P$: C, 50.19; H, 3.37; Mo, 16.03; *m/e* 599.9433. Found: C, 50.15; H, 3.47; Mo, 16.10; *m/e* 599.9436.

$N(CH_2CH_3)_4{}^+\{(CO)_4\overline{Mn[\mu\text{-}P(C_6H_4\text{-}p\text{-}CH_3)_2]Mo}(CO)_2(C_5H_5)\}$, 3. With a procedure similar to that of Petersen,[17] a solution of KOH in absolute ethanol (0.75 mL of a 0.27 M solution, 0.202 mmol of KOH) was added by syringe to a suspension of **2** (120 mg, 0.201 mmol) in absolute ethanol (5 mL). The reaction mixture was stirred for 18 h, and then a solution of $N(CH_2CH_3)_4Br$ (44 mg, 0.209 mmol) in absolute ethanol (4 mL) was added by syringe. Solvent was evaporated, and the residue was extracted with acetone. Acetone was evaporated, and the residue was recrystallized from CH_2Cl_2/Et_2O to give **3** as an orange solid (100 mg, 68%): mp 179–184 °C dec; ^1H NMR (−70 °C, acetone-d_6) δ 7.60 (pseudotriplet, $J_{PH} \approx J_{HH} \approx$ 9 Hz, 2 H, ortho), 7.15 (d, J_{HH} = 7.6 Hz, 2 H, meta), 6.93 (m, 4 H, ortho + meta), 4.80 (s, C_5H_5, 5 H), 3.42 (br s, 8 H, NCH_2CH_3), 2.27 (s, CH_3), 2.12 (s, CH_3), 1.29 (br s, NCH_2CH_3). In the temperature-dependent ^1H NMR the sharp singlet observed for the C_5H_5 did not vary. The resonances for the CH_2 and CH_3 of the $NEt_4{}^+$ cation underwent an increase in resolution as the temperature was raised, and these signals are reported only for the −70 °C and the +48 °C spectra). (**3**: ^1H NMR (−33 °C, acetone-d_6) δ 7.61 (pseudotriplet, $J_{PH} \approx J_{HH} \approx$ 7 Hz, 2 H, ortho), 7.1 (m, 4 H, ortho + meta), 6.88 (dm, J = 7 Hz, 2 H, meta), 2.28 (br s, 3 H, CH_3), 2.14 (br s, 3 H, CH_3); ^1H NMR (+4 °C, acetone-d_6) δ 7.5 (very broad resonance barely observable above the base line, aromatic), 7.0 (br s, aromatic), 2.22 (br s, 6 H, CH_3); ^1H NMR (+25 °C, acetone-d_6) δ 7.42 (br s, 4 H, ortho), 6.97 (d, J = 7.3 Hz, 4 H, meta), 2.23 (s, 6 H, CH_3); ^1H NMR (48 °C, acetone-d_6) δ 7.46 (t, $J_{PH} \approx J_{HH}$ 8.8 Hz, 4 H, ortho), 6.97 (d, J_{HH} = 7.4 Hz, 4 H, meta), 3.48 (q, J_{HH} = 7.1 Hz, 8 H, NCH_2CH_3), 2.23 (s, CH_3, 6 H), 1.38 (tt, J_{HH} = 7.1 Hz, J_{NH} = 1.8 Hz, 12 H, NCH_2CH_3); $^{13}C\{^1H\}$ NMR (−40 °C, CD_2Cl_2, 0.07 M $Cr(acac)_3$) δ 246.9 (d, J_{PC} = 22.0 Hz, Mo(CO) trans to P), 240.1 (s, Mo(CO)), 232.2 (m), 229.1 (s), 224.4 (br s), 224.1 (br s) ($Mn(CO)_4$), 142.1 (s, para), 141.6 (s, para), 136.3 (d, J_{PC} = 51.3 Hz, ipso carbons of both *p*-tolyls, accidental degeneracy), 134.0 (br s, ortho), 132.1 (br s, ortho), 127.34 (m, all meta carbons), 88.6 (s, C_5H_5), 51.3 (s, NCH_2CH_3), 20.5 (s, CH_3), 6.6 (s, NCH_2CH_3); $^{31}P\{^1H\}$ NMR (−50 °C, acetone-d_6) δ 182.4 (s); IR (CH_2Cl_2), 2004 (m), 1911 (s), 1871 (s), 1778 (w) cm^{-1}. Anal. Calcd for $C_{33}H_{39}MnMoNO_6P$: C, 54.48; H, 5.40. Found: C, 54.13; H, 5.38.

Protonation of 3. $HBF_4{\cdot}OEt_2$ (10 μL, 8.0 × 10^{-5} mol) was added by syringe to a solution of **3** (40 mg, 5.5 × 10^{-5} mol) in CH_2Cl_2 (5 mL). The IR spectrum indicated complete conversion of **3** to **2**. After evaporation of the solvent, the residue was purified by preparative thin layer chromatography (silica gel, 1:1 Et_2O/hexane) to give pure **2** (30 mg, 90%).

^{13}CO Enrichment of 1. A solution of **1** (50 mg) in 1.5 mL of acetone-d_6 was sealed in a 10-mm NMR tube under 1 atm of 90% ^{13}CO (Mound Laboratory). The solution was photolyzed for 90 min by using a Hanovia 450-W medium-pressure Hg lamp. The solvent was evaporated, and $Cr(acac)_3$ (0.07 M) and CD_2Cl_2 were added. A ^{13}C NMR spectrum was recorded at −42 °C by using a pulse angle of 90° and a pulse delay of 5 s. A gated broad-band ^1H decoupling procedure was used in which the decoupler was on during data acquisition and off between pulses. This decoupling procedure[22] serves to negate nuclear Overhauser enhancements if the time between pulses is greater than five times the longest carbon T_1 relaxation time in the molecule; similar procedures have been used to monitor ^{13}CO exchange in other

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transition-metal complexes.[23] The use of $Cr(acac)_3$ as a "shiftless relaxation reagent" reduces carbon T_1 times and also helps suppress nuclear Overhauser enhancements.[24] The spectrum was recorded at low temperature to provide "thermal decoupling".[25] (Since ^{55}Mn is 100% natural abundant with $I = {}^5/_2$, manganese carbonyl resonances are typically very broad at room temperature.) These procedures allowed accurate integrations to be obtained.[26] The intensities of the peaks were measured by planimeter integration, with resonances of the *p*-tolyl and cyclopentadienyl carbons serving as internal standards. The % ^{13}C label per carbonyl site (including natural abundance) was determined to be 8.6% for Mo and 9.5% for Mn. The total % ^{13}C incorporated (above natural abundance) was 7.5% for Mo and 8.4% for Mn.

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Registry No. 1, 83334-34-3; 2, 89828-08-0; 3, 89828-10-4; Mo, 7439-98-7; Mn, 7439-96-5.

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Some Reactions of Tris(2,2,2-trifluoroethyl) Phosphite: A New Ligand for Organometallic Chemistry

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The reactions of $P(OCH_2CF_3)_3$ with three different types of metallocarbonyl compounds $Ni(CO)_4$, $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$, and $(\eta^6\text{-}1,3,5\text{-}(CH_3)_3C_6H_3)Cr(CO)_3$ cleanly form products derived from displacement of CO. The products $(CO)Ni(P(OCH_2CF_3)_3)_3$, $(CO)_2Ni(P(OCH_2CF_3)_3)_2$, $(\eta^5\text{-}C_5H_5)FeI(P(OCH_2CF_3)_3)_2$, and $(\eta^6\text{-}1,3,5\text{-}(CH_3)_3C_6H_3)Cr(CO)_2P(OCH_2CF_3)_3$ are obtained in good yields and are relatively stable. Both thermal and photochemical modes of reaction are observed.

Introduction

When a fluorine atom is substituted in a molecule for another halogen or in particular for a hydrogen atom, significant changes in chemical and physical properties result. With the use of $P(OCH_2CF_3)_3$, we introduce a new ligand into metallochemistry, which allows the incorporation of a large percentage of fluorine into the system so that we can begin to see these changes. We feel that it is important to use these phosphorus(III) compounds, since members of this family have played and still play such an important role in the development of the richness of coordination and organometallic chemistry.[2] Some recent very interesting examples of P(III) usage are to enhance labilization in metal clusters,[3] as substitutional equivalents for carbon monoxide,[4a,b] and for providing the energy for structural reorganization in a cyclopentadienyl metallocarbonyl.[5] These three diverse cases only suggest the scope of possibilities for a new ligand system that contains fluorocarbon moieties in combination with phosphorus(III) which will result in products with significantly different behavior from compounds containing ligands which are derived from hydrocarbon-based starting materials.

While CO is readily substituted by PF_3[6] and fluorophosphine complexes can be converted to fluorophosphite complexes by alcohol solvolysis of metallo derivatives,[7] no direct ligand exchange substitution of CO has been demonstrated by a fluorocarbon derived phosphite prior to our report on the preparation of (η^5-cyclopentadienyl)bis(tris(2,2,2-trifluoroethyl) phosphito)iodoiron(II).[8] The closest example seems to be a displacement by Ruff[9] of $Fe(CO)_5$ from $Fe_2(CO)_9$ forming $(CO)_4FeL$, when $L = F_{3-x}P(OC(CF_3)_2CN)_x$.

We now present evidence for the general use of the title compound as a new, useful ligand in organometallic chemistry.

Results

Reaction of $P(OCH_2CF_3)_3$ with $Ni(CO)_4$. Reaction of 4 equiv of 1 with 2 in pentane gave spontaneous liber-

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[1] The work described herein was accomplished at the University of Idaho where S.M.W. was on sabbatical leave from the University of California, Santa Cruz, CA, 1982–1983 and was presented in part at the 186th National Meeting of the American Chemical Society, August 1983, Washington, D.C.

(2) For some of the scope and variety found from the reactions of P(III) ligands and various organometallic carbonyl compounds see the respective Chapters 10, "Specialist Periodical Reports, Organometallic Chemistry", Royal Society of Chemistry, Publishers, London.

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