$CHCH_2CH(OH)R$ ($R = n\text{-}C_3H_7$), 85520-72-5; (*R*)-$H_2C{=}CHCH_2CH(OH)R$ ($R = i\text{-}C_3H_7$), 88691-75-2; (*R*)-$H_2C{=}CHCH_2CH(OH)R$ ($R = t\text{-}C_4H_9$), 88691-76-3; (*S*)-$H_2C{=}CHCH_2CH(OH)R$ ($R = n\text{-}C_8H_{17}$), 88691-77-4; (*R*)-$H_2C{=}CHCH_2CH(OH)R$ ($R = C_6H_5CH{=}CH$), 88763-79-5; (*R*)-$H_2C{=}CHCH_2CH(OH)R$ ($R = C_6H_5$), 85551-57-1; (–)-2-octyltriphenyltin, 82823-89-0; (+)-2-octylphenyltin dibromide, 96306-48-8; allyl chloride, 107-05-1; triphenyltin chloride, 639-58-7; (2-phenylbutyl)triphenyltin, 96292-71-6; (2-phenylbutyl)triphenyltin dibromide, 96292-72-7; methyltriphenyltin, 1089-59-4; methyldiphenyltin iodide, 1015-39-0; (–)-(2-phenylbutyl)methyldiphenyltin, 96292-73-8; (–)-(2-phenylbutyl)phenylmethyltin iodide, 96306-49-9.

Early–Late Transition Metal Heterobimetallic Compounds Linked by a Heterodifunctional (Diphenylphosphino)cyclopentadienyl-Bridging Ligand

Charles P. Casey* and Francois Nief

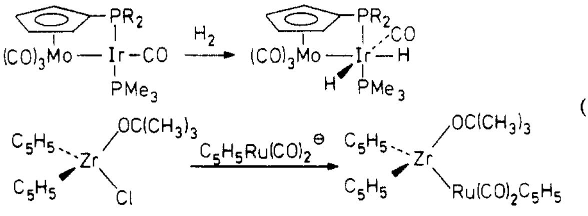
Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Received June 27, 1984

Reaction of $Li^+C_5H_4P(C_6H_5)_2^-$ with $C_5H_5ZrCl_3$ gave $(C_5H_5)[C_5H_4P(C_6H_5)_2]ZrCl_2$, **1**. Reaction of $K^+{}^-OC(CH_3)_3$ with **1** gave $(C_5H_5)[C_5H_4P(C_6H_5)_2]Zr[OC(CH_3)_3]Cl$, **2**. Reaction of $K^+(C_5H_5)Fe(CO)_2^-$ with **2** gave $(C_5H_5)[C_5H_4P(C_6H_5)_2]Zr[OC(CH_3)_3]Fe(CO)_2(C_5H_5)$, **3**. Photolysis of **3** led to expulsion of CO and formation of $(C_5H_5)[C_5H_4P(C_6H_5)_2]Zr[OC(CH_3)_3]Fe(CO)(C_5H_5)$, **4**, in which Zr and Fe are linked by a metal–metal bond and by the heterodifunctional (diphenylphosphino)cyclopentadienyl ligand. Photolysis of **2** and $Na^+Co(CO)_4^-$ led directly to $(C_5H_5)[C_5H_4P(C_6H_5)_2]Zr[OC(CH_3)_3]Co(CO)_3$, **5**.

Introduction

One of our long-range goals is the synthesis of a heterobimetallic dihydride with one hydridic M–H bond to an early transition metal, one acidic M–H bond to a late transition metal, and a heterodifunctional ligand joining the two metals. We believe that such compounds would be powerful reducing agents for polar molecules including CO. Since synthetic methods for preparing the desired precursors with directly bonded early and late transition metals are only in their infancy, we initially concentrated on preparing bimetallic compounds linked by heterodifunctional ligands in which the electronegativities of the metals were similar. In this regard, we prepared a series of Mo–Mn,[1] Mo–Re,[1] Mo–Ir,[2] and Mo–Rh[2] compounds in which the metals were linked by a (di-*p*-tolylphosphino)cyclopentadienyl ligand. Of these compounds, only the Mo–Ir compounds[2] reacted with H_2, and they produced iridium dihydrides instead of the desired heterobimetallic dihydrides. In related work, we have synthesized new compounds with directly bonded Zr–Fe[3] and Zr–Ru[3,4] units, but in these cases the metals were not joined by a heterodifunctional ligand (eq 1).



(1)

Here we report our initial attempts to combine these two approaches by preparing early–late heterobimetallic compounds linked by a heterodifunctional ligand. In this work, we have succeeded in synthesizing new Zr–Fe and Zr–Co complexes linked by a heterodifunctional ligand.

Results

The isolability and stability of compounds with directly bonded Zr–Ru and Zr–Fe units encouraged us to try to synthesize early–late transition metal bonded compounds of zirconium linked by a heterodifunctional ligand. The (diphenylphosphino)cyclopentadienyl ligand was chosen because we had used it successfully to prepare Mo–Mn and Mo–Ir compounds[2,3] and because Rausch[5] and Leblanc[6] had used it as a ligand on titanium. Our first synthetic goal was the synthesis of the zirconium complex **1** possessing one C_5H_5 and one $C_5H_4P(C_6H_5)_2$ ligand. With a sequence of reactions similar to that employed by Rausch[5] for the preparation of $(C_5H_5)[C_5H_4P(C_6H_5)_2]TiCl_2$, we reacted $Li^+C_5H_4P(C_6H_5)_2^-$ with $(C_5H_5)ZrCl_3{\cdot}2THF$ in THF at room temperature and isolated $(C_5H_5)[C_5H_4P(C_6H_5)_2]ZrCl_2$ (**1**) as white crystals in 47% yield.

In earlier work with Zr–Ru and Zr–Fe compounds, we had found that *tert*-butoxy groups on zirconium led to more stable and more easily isolated complexes than derivatives with Zr–Cl or Zr–CH_3 groups.[3] Therefore, we reacted the dichloride complex **1** directly with potassium *tert*-butoxide and isolated white crystalline $(C_5H_5)[C_5H_4P(C_6H_5)_2]Zr[OC(CH_3)_3]Cl$ (**2**) in 45% yield based on $C_5H_5ZrCl_3$.

Reaction of this *tert*-butoxy-substituted zirconium compound **2** with $K^+(C_5H_5)Fe(CO)_2^-$ in THF at room temperature led to the isolation of the directly bonded Zr–Fe compound **3** as bright yellow crystals in 58% yield.

The zirconium atom of **3** is an asymmetric center since it has four different groups bonded to it in a roughly tetrahedral array. Because of this asymmetric zirconium

---

[1] Casey, C. P.; Bullock, R. M.; Fultz, W. C.; Rheingold, A. L. *Organometallics* **1982**, *1*, 1591.

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

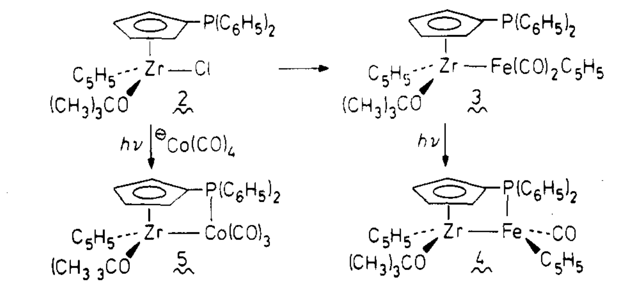
[3] Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 665.

[4] Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *Organometallics* **1984**, *3*, 504.

[5] Rausch, M. D.; Edwards, B. H.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 3882.

[6] Leblanc, J. C.; Moise, C.; Maisonnat, A.; Poilblanc, R.; Charrier, C.; Mathey, F. *J. Organomet. Chem.* **1982**, *231*, C43.

0276-7333/85/2304-1218$01.50/0



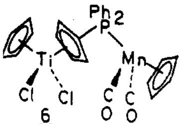
center, the four protons on the $C_5H_4PPh_2$ ligand are all nonequivalent and give rise to four multiplets in the ^1H NMR between δ 6.91 and 6.08. The carbonyl groups on iron are also chemically nonequivalent and give rise to two singlets in the ^{13}C NMR at δ 219.90 and 219.85. The phosphine ligand is not coordinated to a metal as is shown by the ^{31}P NMR chemical shift of δ −17.7. The IR spectrum of 3 has peaks at 1944 and 1892 cm^{-1} which are similar to those seen for $(C_5H_5)_2Zr[OC(CH_3)_3]Fe(CO)_2C_5H_5$; this establishes the presence of a direct Zr–Fe bond.[3] If the compound were joined by a Zr–OC–Fe linkage, the IR bands would have appeared at much lower frequency.

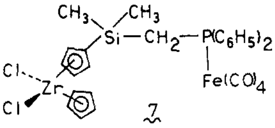
Since **3** did not spontaneously lose CO and form a complex linked by the heterodifunctional ligand, the photolysis of **3** was investigated. Irradiation of **3** in THF for 72 h led to the expulsion of CO and the formation of the bimetallic complex **4** in 84% isolated yield. In **4**, the (diphenylphosphino)cyclopentadienyl ligand bridges the Zr and Fe centers and both metals are asymmetric centers. Although two diastereomers are possible, only a single isomer was observed. Examination of molecular models suggests that the configuration drawn for **4** would be less crowded. Once again, the four protons on the $C_5H_4PPh_2$ ligand are all nonequivalent due to the proximity of the asymmetric zirconium center and give rise to four multiplets in the ^1H NMR between δ 6.09 and 4.82. A single band in the carbonyl region of the IR at 1853 cm^{-1} indicates that one of the two carbonyl groups of **3** was lost in the formation of **4**. The chemical shift of the phosphorus ligand moves 91 ppm downfield to δ 74.0 upon complexation of phosphorus to iron.

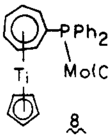
When we tried to make a similar compound by reaction of zirconium complex **2** with $Na^+Co(CO)_4^-$, no reaction was observed in THF at room temperature. However, when this solution was photolyzed for 72 h, the Zr–Co compound **5** was isolated as a yellow solid in 16% yield. In this reaction, the Co–Zr linkage and the Co–P linkage are established in the same process. The four nonequivalent protons of the $C_5H_4P(C_6H_5)_2$ ligand give rise to four multiplets in the ^1H NMR between δ 6.71 and 5.22 for which all coupling constants were assignable (see Experimental Section). The $Co(CO)_3$ unit gives rise to three IR bands at 1986, 1922, and 1890 cm^{-1}. The existence of a P–Co bond is established by the ^{31}P chemical shift of δ 40.23.

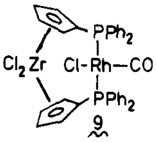
Discussion

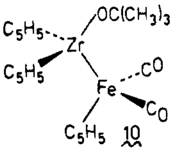
Zr–Fe compound **4** and Zr–Co compound **5** are the first examples of bimetallic compounds in which a group 4 metal and a late transition metal are joined by both a direct metal–metal bond and a heterodifunctional ligand. Examples of early-late transition-metal compounds in which the metals are linked only by a heterodifunctional ligand include Ti,Mn compound **6**,[5] Zr,Fe compound **7**,[7] Ti,Mo compound **8**,[8] and Zr,Rh compound **9**.[6] Examples of early-late transition metal compounds in which the metals are linked only by a metal–metal bond include Zr–Fe compound **10**,[3] Ti–Co compound **11**,[9] and Ta–Co compound **12**.[10] Early-late transition metal compounds in which the metal centers are linked by a metal–metal bond and a bridging ligand include Nb–Co compound **13**[11] and Zr–Co compound **14**.[12]

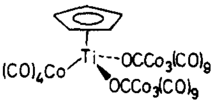

6

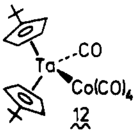

7

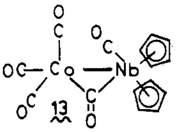

8

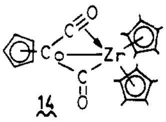

9


10


11


12


13


14

In our synthesis of Zr–Fe compound **3**, metal–metal bond formation occurred readily by a thermal displacement reaction just as in the case of Zr–Fe compound **10**. The displacement of CO by the phosphine ligand in the formation of **4** was accomplished by photolysis of **3**. Presumably, light causes expulsion of CO from the iron center and the coordinatively unsaturated intermediate is trapped intramolecularly by the phosphine ligand.

In the synthesis of Zr–Co compound **5**, no metal–metal bond formation was seen in the absence of light, and photolysis led to both metal–metal bond formation and intramolecular replacement of CO by phosphine. There are several possible explanations of the role of light. First, Zr–Co bond formation may be occurring reversibly with the equilibrium favoring starting materials; photolysis could lead to loss of CO from the Zr–Co intermediate, and phosphine chelation could trap the Zr–Co bonded intermediate. Second, light absorption by the zirconium chromophore of starting material **2** could reduce the hapticity of the Cp–Zr unit and make the zirconium center more reactive toward $Co(CO)_4^-$; subsequent photochemical or thermal loss of CO would then produce **5**. Brubaker has observed photochemical interchange of cyclopentadienyl ligands between $(C_5H_5)_2ZrCl_2$ and $(C_5D_5)_2ZrCl_2$ and has suggested that this is due to an exchange mechanism initiated by photoinduced slippage of an η^5-C_5H_5 ligand to an η^3- or η^1-C_5H_5 ligand.[13] A third possibility is that photolysis of $Co(CO)_4^-$ could lead to formation of a more reactive species capable of replacing a Zr–Cl bond.

Our future plans include studying the thermal and photochemical reactions of these new Zr–Fe and Zr–Co compounds with H_2 and with CO.

Experimental Section

General Data. All manipulations were performed under nitrogen using vacuum line, drybox, and standard Schlenk tech-

---

[7] Schore, N. E. *J. Am. Chem. Soc.* **1979**, *101*, 7410.

[8] Demerseman, B.; Dixneuf, P. H.; Douglade, J.; Mercier, R. *Inorg. Chem.* **1982**, *21*, 3942.

[9] Schmid, G.; Stutte, B.; Boese, R. *Chem. Ber.* **1978**, *111*, 1239.

[10] Moise, C.; Reynoud, J. F.; Leblanc, J. C.; Broussier, R. *J. Organomet. Chem.* **1982**, *240*, C15.

[11] Wong, K. S.; Scheidt, W. R.; Labinger, J. A. *Inorg. Chem.* **1979**, *18*, 1709.

[12] Barger, P. T.; Bercaw, J. E. *J. Organomet Chem.* **1980**, *201*, C39; *Organometallics* **1984**, *3*, 278.

[13] Peng, M. H.; Brubaker, C. H., Jr. *J. Organomet. Chem.* **1977**, *135*, 333.

niques. All solvents used were distilled from potassium–benzophenone. $NaCo(CO)_4$,[14] $KFe(CO)_2(C_5H_5)$,[15] and $LiC_5H_4P(C_6H_5)_2$[1] were obtained as previously described. $(C_5H_5)ZrCl_3$ was prepared by photochlorination of $(C_5H_5)_2ZrCl_2$ in CCl_4 as previously described[16] and was purified by crystallization from THF as an adduct of formula $CpZrCl_3{\cdot}2THF$, as shown by ^1H NMR spectroscopy.[17] Potassium *tert*-butoxide was sublimed in high vacuum and stored in a drybox. ^1H NMR spectra were obtained on Bruker WH-270 or WP-200 spectrometers. ^{13}C and ^{31}P spectra were obtained with a JEOL FX-200 instrument. All NMR spectra were obtained in the THF-d_8; ^{31}P chemical shifts were reported with positive sign downfield from external 85% H_3PO_4. IR spectra were measured on Beckman IR 4230 and Nicolet FT-IR 7199 instruments. Mass spectra were measured on an AEI MS-902 instrument at 30 eV.

$(C_5H_5)[C_5H_5P(C_6H_5)_2]ZrCl_2$, 1. THF (20 mL) was vacuum transferred onto a mixture of $C_5H_5ZrCl_3{\cdot}2THF$[16,17] (400 mg, 1 mmol) and $LiC_5H_4P(C_6H_5)_2$[1] (256 mg, 1 mmol) at −78 °C. The mixture was stirred at room temperature for 0.5 h. THF was evaporated, and toluene was condensed onto the residue. The toluene solution was filtered through Celite and evaporated to dryness. The residue was crystallized from toluene and ether to give 1 (226 mg, 47%) as white crystals: mp 131 °C; ^1H NMR δ 7.33 (d, 3.9 Hz peak separation, 10 H), 6.61 (t, J = 2.6 Hz, 2 H), 6.52 (td, J = 2.6 Hz, J_{PH} = 1.3 Hz, 2 H), 6.35 (s, 5 H); $^{31}P\{^1H\}$ NMR δ −16.7; $^{13}C\{^1H\}$ NMR δ 134.8 (d, J_{PC} = 20.7 Hz, ortho), 129.8 (s, para), 129.2 (d, J_{PC} = 6.9 Hz, meta), 122.7 (d, J_{PC} = 11 Hz, C_2 of C_5H_4P), 118.9 (s, C_3 of C_5H_4P), 117.2 (s, C_5H_5), C_1 of C_5H_5P and C_{ipso} of phenyl were not detected; MS calcd for $C_{22}H_{19}{}^{35}Cl_2P^{90}Zr$ 473.9642, found 473.9643. Anal. Calcd for $C_{22}H_{19}Cl_2PZr$: C, 55.46; H, 4.02. Found: C, 55.58; H, 4.22.

$(C_5H_5)[C_5H_4P(C_6H_5)_2]Zr[OC(CH_3)_3]Cl$, 2. Potassium *tert*-butoxide (123 mg, 1.1 mmol) was added to a crude THF solution of 1 prepared from $C_5H_5ZrCl_3{\cdot}2THF$ (1 mmol) and $LiC_5H_4P(C_6H_5)_2$ (1 mmol). After 4 h, THF was evaporated and the residue was extracted with toluene and filtered. Evaporation of toluene and recrystallization from toluene–hexane gave **2** (230 mg, 45%) as white crystals: mp 113 °C; ^1H NMR δ 7.31 (br s, 10 H), 6.49 (m, 1 H, C_5H_4P), 6.37 (m, 1 H, C_5H_4P), 6.31 (m, 2 H, C_5H_4P), 6.15 (s, 5 H), 1.13 (s, 9 H); $^{13}C\{^1H\}$ NMR δ 139.5 (overlapping doublets, J_{PC} = 9 Hz, ipso of diastereotopic C_6H_5), 134.8 and 134.5 (two d, J_{PC} = 20.6 Hz, ortho of diastereotopic C_6H_5), 129.5 (s, para), 129.1 (d, J = 6.3 Hz, meta), 121.4 and 121.2 (overlapping doublets, J_{PC} = 10 Hz, C_2 and C_2' of C_5H_4P), 116.8 and 116.5 (s, C_3 and C_3' of C_5H_4P), 114.7 (s, C_5H_5), 80.9 (s, $\mathit{C}(CH_3)_3$), 31.5 (s, $C(\mathit{CH}_3)_3$), C_1 of C_5H_4P not observed; $^{31}P\{^1H\}$ NMR δ −17.7; MS calcd for $C_{26}H_{28}{}^{35}ClOP^{90}Zr$ 512.0603, found 512.0609.

$(C_5H_5)[C_5H_4P(C_6H_5)_2][OC(CH_3)_3]ZrFe(CO)_2(C_5H_5)$, 3. A solution of **2** (420 mg, 0.83 mmol) and $K[(C_5H_5)Fe(CO)_2]$ (180 mg, 0.83 mmol) in 25 mL of THF was stirred for 1 h at ambient temperature and evaporated to dryness. The residue was dissolved in toluene and filtered. Addition of hexane precipitated bright yellow crystals which were recrystallized from toluene–hexane to give **3** (310 mg, 50%): mp 161 °C dec; ^1H NMR δ 7.5–7.3 (m, 10 H), 6.91, 6.34, 6.21, 6.08 (multiplets, 1 H each, C_5H_4P), 6.01 (s, C_5H_5Zr), 4.58 (s, 5 H, C_5H_5Fe), 1.13 (s, 9 H); $^{13}C\{^1H\}$ NMR δ 219.90, 219.85 (CO), 139.5–112 (multiplets for C_6H_5 and C_5H_4P), 111.3 (C_5H_5Zr), 82.8 (C_5H_5Fe), 81.2 ($\mathit{C}(CH_3)_3$), 31.5 ($C(\mathit{CH}_3)_3$); $^{31}P\{^1H\}$ NMR δ −17.7; IR (Nujol) 1944 (s), 1892 (s) cm^{-1}; MS, *m/e* (intensity) 626 (24, M − CO), 413 (73), 370 (100). Anal. Calcd for $C_{33}H_{33}FeO_3PZr$: C, 60.45; H, 5.07. Found: C, 60.40; H, 4.82.

$(C_5H_5)[C_5H_4\overline{P(C_6H_5)_2][OC(CH_3)_3]ZrFe}(CO)(C_5H_5)$, 4. A solution of **3** (150 mg, 0.23 mmol) in 20 mL of THF was photolyzed in a Rayonet photolysis reactor equipped with bulbs having maximum emission at 366 nm for 72 h. The solution was evaporated to dryness, and the residue was recrystallized from hexane to give **4** (121 mg, 84%) as a red powder: mp 182 °C; ^1H NMR δ 8.13 (m, 2 H, ortho), 7.49 (m, 3 H, meta and para), 7.40 (m, 2 H, ortho′), 7.28 (m, 3 H, meta′ and para′), 6.18 (s, 5 H, C_5H_5Zr), 6.09, 6.03, 5.85, 4.82 (multiplets, 1 H each, C_5H_4P), 4.30 (d, J_{PH} = 1.1 Hz, C_5H_5Fe), 1.33 (s, 9 H, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR δ 135.8 (J_{PC} = 12.7 Hz, ortho), 133.3 (J_{PC} = 9.5 Hz, ortho′), 130.5 and 129.9 (para and para′), 128.7, 128.5, 128.2, 128.1 (meta and meta′ coupled to P), 118.8 (J_{PC} = 8 Hz, C_2 of C_5H_4P), 115.1 (J_{PC} = 8 Hz, C_2' of C_5H_4P), 107.5 (J_{PC} = 32 Hz, ipso), 106.8 (J_{PC} = 11 Hz, C_3 of C_5H_4P), 104.5 (J_{PC} = 10 Hz, C_3' of C_5H_4P), 110.9 (C_5H_5Zr), 80.6 (C_5H_5Fe), 79.0 ($O\mathit{C}(CH_3)_3$), 33.0 ($OC(\mathit{CH}_3)_3$), ipso carbons of C_6H_5 and CO not observed; $^{31}P\{^1H\}$ NMR δ 74.0; IR (KBr) 1853 cm^{-1}; MS calcd for $C_{32}H_{33}O_2{}^{56}FeP^{90}Zr$ 626.0602, found 626.0607; MS, m/e (intensity) 626 (24), 413 (100).

$(C_5H_5)[C_5H_4\overline{P(C_6H_5)_2][OC(CH_3)_3]ZrCo}(CO)_3$, 5. A solution of **2** (150 mg, 0.29 mmol) and $NaCo(CO)_4$ (60 mg, 0.31 mmol) in 20 mL of THF was photolyzed at 366 nm for 72 h. The solution was evaporated to dryness, and the residue was extracted with toluene, filtered, and evaporated to dryness. The resulting solid was thoroughly extracted with hexane (10 × 10 mL) to leave **5** (30 mg, 16.5%) as a yellow powder: mp 120 °C dec; ^1H NMR δ 7.96 (m, 2 H, ortho), 7.70 (m, 2 H, ortho′), 7.43–7.32 (m, 6 H, meta and para), 6.39 (s, 5 H, C_5H_5), 0.91 (s, 9 H, $C(CH_3)_3$); four multiplets were observed for the nonequivalent C_5H_4P; all coupling constants were obtained by simulation of the spectra; δ 6.71 (m, H_1, J_P = 2.6, J_{12} = 3.0, J_{13} = 3.3, J_{14} = 2.0 Hz), 6.16 (m, H_2, J_P = 2.3, J_{12} = 3.0, J_{23} = 2.3, J_{24} = 3.0 Hz), 5.38 (m, H_3, J_P = 3.3, J_{13} = 3.3, J_{23} = 2.3, J_{34} = 2.2 Hz), 5.22 (m, H_4, J_P = 3.8, J_{14} = 2.0, J_{24} = 3.0, J_{34} = 2.2 Hz); $^{13}C\{^1H\}$ NMR (0.08 M $Cr(acac)_3$, −70 °C) δ 210.7 ($w_{1/2}$ = 10 Hz, CO), 139.9, 139.2, 135.1, 131.9, 129.6, 129.0 (aromatic carbons of nonequivalent phenyl groups), 122.2, 119.3, 108.7, 105.1 (C_5H_4P), 113.3 (C_5H_5Zr), 81.2 ($O\mathit{C}(CH_3)_3$), 31.2 ($OC(\mathit{CH}_3)_3$); $^{31}P\{^1H\}$ NMR δ 40.23; IR (KBr) 1986 (s), 1922 (s), 1890 (vs) cm^{-1}; MS calcd for $C_{29}H_{28}O_4CoP^{90}Zr$ 620.0099, found 620.0093; MS, *m/e* (intensity) 592 (4, M − CO), 564 (17, M − 2CO), 536 (100, M − 3CO), 479 (49, M − 3CO − C_4H_9).

Acknowledgment. Support from the Division of Basic Energy Sciences of the Department of Energy is gratefully acknowledged. F.N. wishes to thank CNRS for financial support and NATO for a fellowship.

Registry No. 1, 96363-99-4; 2, 96364-00-0; 3, 96364-01-1; 4, 96394-16-0; 5, 96394-17-1; $C_5H_5ZrCl_3$, 34767-44-7; $LiC_5H_4P(C_6H_5)_2$, 83272-80-4; $K[(C_5H_5)Fe(CO)_2]$, 60039-75-0; $NaCo(CO)_4$, 14878-28-5.

---

(14) Edgell, W. F.; Lyford, J., IV *Inorg. Chem.* **1970**, *9*, 1932.

(15) Plotkin, J. S.; Shore, S. G. *Inorg. Chem.* **1981**, *20*, 284.

(16) Erker, G.; Berg, K.; Treschanke, L.; Engel, K. *Inorg. Chem.* **1982**, *21*, 1277.

(17) Unpurified material was contaminated with $ZrCl_4$ as shown by subsequent reactions. Recrystallization from THF gave $(C_5H_5)ZrCl_3{\cdot}2THF$ as white crystalline material free of $ZrCl_4$. ^1H NMR (C_6D_6): δ 6.40 (s, 5 H), 3.67 (m, 8 H), 1.28 (m, 8 H).