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Synthesis of Molybdenum–Rhodium and Molybdenum–Iridium Compounds Linked by a Heterodifunctional Ligand and Formation of Molybdenum–Iridium Dihydrides by Reaction with Molecular Hydrogen

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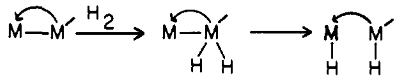
Abstract: A series of Rh–Mo and Ir–Mo compounds linked by a heterodifunctional ligand have been prepared. Li$^+$[η^5-C$_5$H$_4$P(C$_6$H$_4$-*p*-CH$_3$)$_2$]Mo(CO)$_3^-$ (**1**) reacted with the chlorine-bridged rhodium dimer {[(C$_6$H$_4$-*p*-CH$_3$)$_2$PCH$_2$]$_2$RhCl}$_2$ (**2**) to give [(C$_6$H$_4$-*p*-CH$_3$)$_2$PCH$_2$]$_2$RhMo(CO)$_3$[η^5-C$_5$H$_4$P(C$_6$H$_4$-*p*-CH$_3$)$_2$] (**3**). Reaction of **1** with [(CO)$_2$RhCl]$_2$ gave (CO)$_2$RhMo(CO)$_3$[η^5-C$_5$H$_4$P(C$_6$H$_4$-*p*-CH$_3$)$_2$] (**4**). P(C$_6$H$_4$-*p*-CH$_3$)$_3$ or P(CH$_3$)$_3$ reacted with **4** to give phosphine substitution products *trans*-P(C$_6$H$_4$-*p*-CH$_3$)$_3$(CO)RhMo(CO)$_3$[η^5-C$_5$H$_4$P(C$_6$H$_4$-*p*-CH$_3$)$_2$] (**5**) and *trans*-P(CH$_3$)$_3$(CO)RhMo(CO)$_3$-[η^5-C$_5$H$_4$P(C$_6$H$_4$-*p*-CH$_3$)$_2$] (**6**), respectively. None of these rhodium–molybdenum compounds reacted with H$_2$ to form observable metal hydrides. Reaction of **1** with (CO)$_2$IrCl(H$_2$NC$_6$H$_4$-*p*-CH$_3$) provided iridium–molybdenum compound **8**, (CO)$_2$IrMo(CO)$_3$[η^5-C$_5$H$_4$P(C$_6$H$_4$-*p*-CH$_3$)$_2$]. Reaction of **8** with P(CH$_3$)$_3$ or P(C$_6$H$_5$)$_3$ gave phosphine substitution products *trans*-P(CH$_3$)$_3$(CO)IrMo(CO)$_3$[η^5-C$_5$H$_4$P(C$_6$H$_4$-*p*-CH$_3$)$_2$] (**9**) and *trans*-P(C$_6$H$_5$)$_3$(CO)IrMo(CO)$_3$[η^5-C$_5$H$_4$P(C$_6$H$_4$-*p*-CH$_3$)$_2$] (**10**), respectively. Compounds **8**, **9**, and **10** reacted readily with H$_2$ at room temperature and atmospheric pressure to give Mo–IrH$_2$ compounds **11**, **12**, and **13**.

Heterobimetallic[1] metal dihydrides that possess both a hydridic M–H bond and an acidic M–H bond are potentially excellent reducing agents for polar molecules like CO. Compounds possessing a hydridic M–H bond to an early transition metal and an acidic M–H bond to a late transition metal are prime candidates for powerful hydrogenation catalysts and might be available from reaction of H$_2$ with metal–metal bonds. However, since synthetic methods for making the desired precursors with directly bonded early and late transition metals are just beginning to be developed,[2] our early efforts have centered on making bimetallic compounds between metals having smaller electronegativity differences. Our initial approach[3] has been to prepare heterobimetallic compounds linked by a heterodifunctional ligand and to investigate the reactions of these compounds with H$_2$ as a possible route to heterobimetallic dihydrides. Linking the two metal centers through a bridging ligand maximizes the opportunity for the resulting metal hydrides to act cooperatively to reduce polar molecules. Other groups have also employed heterodifunctional ligands in the successful synthesis of heterometallic compounds.[4]



We recently reported[3] the preparation of Li$^+$[η^5-C$_5$H$_4$P-(C$_6$H$_4$-*p*-CH$_3$)$_2$]Mo(CO)$_3^-$ (**1**) which can be viewed as a difunctional chelate ligand with phosphine and metal anion donor groups. The reaction of **1** with [(CO)$_4$MBr]$_2$ (M = Mn, Re) gave (CO)$_4$MMo(CO)$_3$[η^5-C$_5$H$_4$P(C$_6$H$_4$-*p*-CH$_3$)$_2$], in which the two metals are joined together through a metal–metal bond and by the heterodifunctional ligand. Since we are interested in exploring the possibility of using bimetallic compounds for the homogeneous hydrogenation of CO, we were hoping to observe some interaction between the Mo–Mn and Mo–Re complexes and H$_2$. Unfortunately neither of these two compounds formed observable metal hydrides, even under forcing conditions of high temperatures and high hydrogen pressures.

Since these compounds are coordinatively saturated and would have to undergo ligand loss or metal–metal bond rupture in order to react with H$_2$, we decided to prepare new compounds with a metal center capable of undergoing facile oxidative addition of H$_2$. Ideal candidates appeared to be Rh(I)–Mo compounds since there are numerous examples of Rh(I) compounds that oxidatively add H$_2$. In this paper, we report the preparation of a series of Rh(I)–Mo and Ir(I)–Mo compounds and the formation of dihydrides from the oxidative addition of H$_2$ to the Ir(I) centers.

Results and Discussion

Molybdenum–Rhodium Compounds. Reaction of Li$^+$[η^5-C$_5$H$_4$P(C$_6$H$_4$-*p*-CH$_3$)$_2$]Mo(CO)$_3^-$ (**1**) with {[(C$_6$H$_4$-*p*-CH$_3$)$_2$PCH$_2$]$_2$RhCl}$_2$ (**2**) in THF gave a 25% yield of molybdenum–rhodium compound **3**, which was isolated as an orange solid. The ^{31}P NMR of **3** (Figure 1) exhibits eight-line patterns for each of the three nonequivalent phosphines; each phosphorus atom is coupled to the other two phosphorus atoms as well as to the ^{103}Rh atom (I = $^1/_2$, 100% natural abundance).

The molybdenum carbonyls of **3** exhibit ^{13}C NMR resonances at δ 236.9 and 229.7 in a 1:2 intensity ratio. The chemical shifts of the molybdenum carbonyls in **3** are very similar to those ob-

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

(1) For reviews of heterometallic compounds, see: (a) Roberts, D. A.; Geoffroy, G. L.; "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Chapter 40. (b) Bruce, M. I. *J. Organomet. Chem.* **1983**, *242*, 147–204.

(2) Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 665 and references therein.

(3) Casey, C. P.; Bullock, R. M.; Fultz, W. C.; Rheingold, A. L. *Oganometallics* **1982**, *1*, 1591.

(4) (a) Schore, N. E.; Benner, L. S.; LaBelle, B. E. *Inorg. Chem.* **1981**, *20*, 3200. (b) Schore, N. E. *J. Am. Chem. Soc.* **1979**, *101*, 7410. (c) Schore, N. E.; Hope, H. *Ibid.* **1980**, *102*, 4251. (d) Rudie, A. W.; Lichtenberg, D. W.; Katcher, M. L.; Davison, A. *Inorg. Chem.* **1978**, *17*, 2859. (e) Bishop, J. J.; Davison, A. *Ibid.* **1971**, *10*, 826. (f) Bishop, J. J.; Davison, A. *Ibid.* **1971**, *10*, 832. (g) Whitesides, G. M.; Gaasch, J. F.; Stedronsky, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 5258. (h) Hauser, C. R.; Cain, C. E. *J. Org. Chem.* **1958**, *23*, 1142. (i) Pavlik, I.; Handlir, K. *Collect. Czech. Chem. Commun.* **1966**, *31*, 1958. (j) Demerseman, B.; Dixneuf, P. H.; Doublade, J.; Mercier, R. *Inorg. Chem.* **1982**, *21*, 3942. (k) Wrobleski, D. A.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1982**, *104*, 2314. (l) Kraihanzel, C. S.; Sinn, E.; Gray, G. M. *Ibid.* **1981**, *103*, 960. (m) Powell, J.; May, C. J. *Ibid.* **1982**, *104*, 2636. (n) Farr, J. P.; Olmstead, M. M.; Wood, F. E.; Balch, A. L. *Ibid.* **1983**, *105*, 792. (o) Farr, J. P.; Olmstead, M. M.; Balch, A. L. *Ibid.* **1980**, *102*, 6654. (p) Maisonnet, A.; Farr, J. P.; Balch, A. L. *Inorg. Chim. Acta.* **1981**, *53*, L217. (q) Maisonnet, A.; Farr, J. P.; Olmstead, M. M.; Hunt, C. T.; Balch, A. L. *Inorg. Chem.* **1982**, *21*, 3961.

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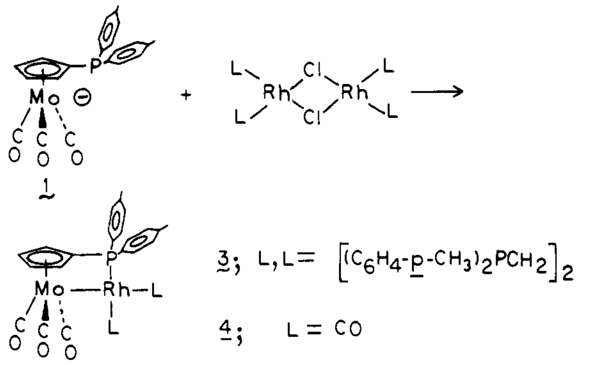
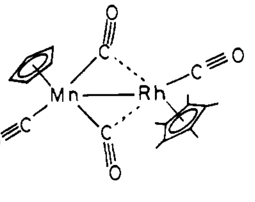
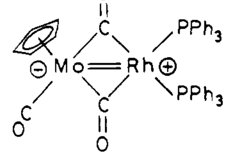


served in $(CO)_4MnMo(CO)_3[\eta^5\text{-}C_5H_4P(C_6H_5)_2]$, for which the X-ray crystal structure indicates conclusively that no bridging carbonyls are present.[3] More importantly, the absence of coupling between the ^{103}Rh and the ^{13}CO indicates that the molybdenum carbonyl does not interact appreciably with the rhodium atom. Stone[5] has synthesized the related manganese–rhodium compound $(C_5H_5)(CO)Mn(\mu\text{-}CO)_2Rh(CO)(C_5Me_5)$, A, in which the presence of two semibridging carbonyls was established by X-ray crystallography. The semibridging carbonyl groups of A showed a 22-Hz coupling to Rh in contrast to the absence of Rh–^{13}C coupling in **3**. Three IR bands were observed for **3** at 1922, 1841, and 1801 cm^{-1}. The band at 1801 cm^{-1} is at surprisingly low energy for a terminal carbonyl and is similar to that seen for the semibridging carbonyls of A. However, the ^{13}C NMR data outlined above indicate that the molybdenum carbonyls do not interact with rhodium. The low-energy IR carbonyl stretches of **3** are probably a result of a highly polarized $^{\delta+}Rh\text{–}Mo^{\delta-}$ bond. This polarization is related to the stability of $(C_5H_5)Mo(CO)_3^-$ anions and L_3Rh^+ cations. As better electron donor ligands are placed on Rh, the metal–metal bond becomes more polarized and the $Mo(CO)_3$ stretches move to lower energy.


A


B

In the absence of the heterodifunctional ligand linking Mo and Rh, Carlton[6] has observed quite different chemistry in the reaction of $Na^+(C_5H_5)(CO)_3Mo^-$ and $RhCl(PPh_3)_3$, which produced $(C_5H_5)(CO)Mo(\mu\text{-}CO)_2Rh(PPh_3)_2$ (B). This compound, which has a metal–metal double bond and two bridging CO ligands, might result from initial formation of $(C_5H_5)(CO)_3Mo\text{–}Rh(PPh_3)_3$ followed by loss of PPh_3 and rearrangement. Examination of the X-ray crystal structure of B indicates that it would be impossible to form a similar compound with a heterodifunctional cyclopentadienylphosphine ligand joining Mo and Rh. A structure similar to B in which the cyclopentadienylphosphine is bonded only to Mo is certainly possible. However, the tendency of the cylopentadienylphosphine ligand to bridge the two metal centers is apparently greater than the tendency to form structures such as B.

Reaction of **1** with $[(CO)_2RhCl]_2$[7] produced the analogous compound **4** with two carbonyl groups bonded to rhodium. The lowest energy band in the IR spectrum of **4** appears at 1867 cm^{-1} and is assigned to carbonyl ligands on molybdenum. This band is 66 cm^{-1} higher in energy than the lowest energy CO band in **3** and indicates that the molybdenum center of **4** is less electron rich than that in **3**. This is consistent with the greater ability of phosphorus donor ligands on **3** to stabilize a polar $^{\delta+}Rh\text{–}Mo^{\delta-}$ bond.

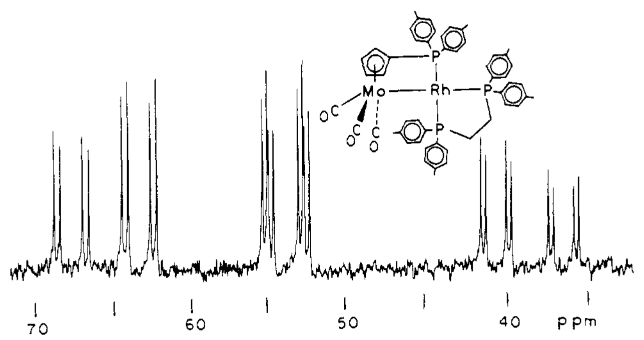
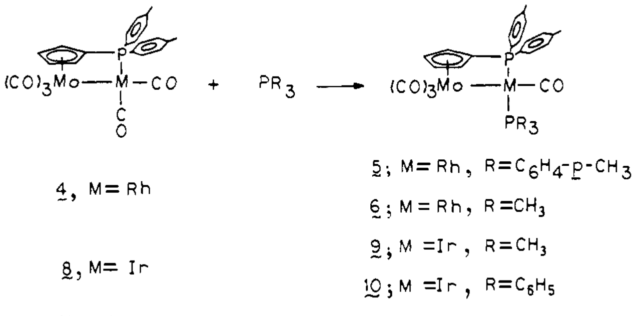


Figure 1. 81-MHz ^{31}P NMR spectrum of **3**.

In order to provide a more sterically crowded and somewhat more electron-rich molybdenum center, we have synthesized the tetramethylcyclopentadienyl compound $Li^+[\eta^5\text{-}C_5(CH_3)_4P(C_6H_4\text{-}p\text{-}CH_3)_2]Mo(CO)_3^-$. Reaction of **2** with this more crowded molybdenum anion produced $[(C_6H_4\text{-}p\text{-}CH_3)_2PCH_2]_2RhMo(CO)_3[\eta^5\text{-}C_5(CH_3)_4P(C_6H_4\text{-}p\text{-}CH_3)_2]$ (**7**). The infrared stretches of the cabronyls on molybdenum in tetramethyl compound **7** were shifted only to slightly lower energy than those in the analogous compound **3**. The major influence of tetramethyl substitution on the cyclopentadiene ring is therefore a steric effect, not an electronic effect.

Reaction of dicarbonylrhodium–molybdenum compound **4** with a slight excess of $P(C_6H_4\text{-}p\text{-}CH_3)_3$ led to substitution of phosphine for one carbonyl group on rhodium and formation of **5**. Similarly, reaction of $P(CH_3)_3$ with **4** led to substitution product **6**. The large $^{31}P\text{–}^{31}P$ coupling constants seen for compounds **5** and **6** (J_{PP} = 332 Hz for **5**, J_{PP} = 348 Hz for **6**) establish the trans relationship of the phosphine ligands. The $^{31}P\text{–}^{31}P$ coupling for cis phosphines is significantly smaller: for **3**, the cis $^{31}P\text{–}^{31}P$ coupling constants are 26 and 32 Hz, while the trans $^{31}P\text{–}^{31}P$ coupling is 345 Hz.



In unsuccessful attempts to form heterobimetallic dihydrides, we studied the stability of **3**, **4**, **5**, and **6** under high hydrogen pressure by heating toluene solutions to successively higher temperatures, cooling the solutions, and examining samples of the solutions at atmospheric pressure. A 6 mM toluene solution of **3** that was heated at 70 °C for 6 h under 1100 psi H_2 underwent approximately 10% decomposition; higher temperatures caused further decomposition. A 6 mM toluene solution of **4** showed no change in its IR spectrum after being heated at 60 °C for 5 h under 1200 psi H_2; more forcing conditions (105 °C, 19 h, 1200 psi H_2) caused 16% decomposition, but no new IR bands were observed. A 3 mM toluene solution of **5** that was heated at 115 °C for 15 h under 1000 psi H_2, showed no decomposition. **6** was similarly unreactive toward H_2 and showed no change after 25.5 h at 115 °C under 1100 psi H_2. Thus, **3**, **4**, **5**, and **6** thermally decompose when heated in the presence of H_2, and no evidence was obtained for formation of any metal hydrides. In an NMR experiment, a 33 mM C_6D_6 solution of **7** was unchanged after heating at 72 °C for 60 days under 650 mm H_2 pressure.

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(5) Aldridge, M. L.; Green, M.; Howard, J. A. K.; Pain, G. N.; Porter, S. J.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1982**, 1333.

(6) Carlton, L.; Lindsell, W. E.; McCullough, K. J.; Preston, P. N.; *J. Chem. Soc., Chem. Commun.* **1982**, 1001.

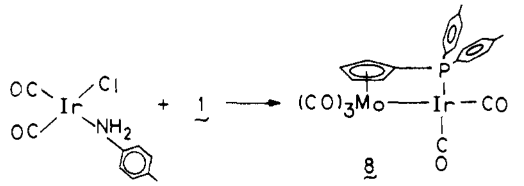
(7) McCleverty, J. A.; Wilkinson, G.; Lipson, L. G.; Maddox, M. L.; Kaesz, H. D. *Inorg. Synth.* **1966**, *8*, 211.

The possibility that **4** and H_2 might react to form a dihydride which is only stable under high pressures of H_2 was investigated by high-pressure infrared spectroscopy. However, no new IR bands were observed as the temperature was raised to 100 °C under 1200 psi H_2. Decomposition of **4** resulted when the temperature was raised to 150 °C under 1250 psi H_2.

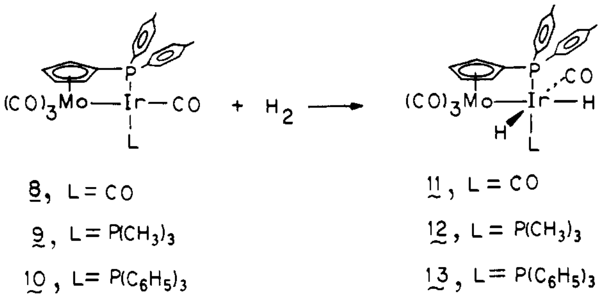
It is not clear whether kinetic or thermodynamic factors are responsible for the failure to observe oxidative addition of H_2 to the 16-electron Rh^I centers in these compounds. **3** may be reacting rapidly and reversibly with H_2 to form a thermodynamically unstable dihydride. Geoffroy reported that the heterobimetallic compound *trans*-$(CO)(PEt_3)_2Rh{-}Co(CO)_4$ also failed to react with H_2 (102 atm) after heating at 90 °C for 6 h.[8]

Iridium–Molybdenum Compounds. Third-row transition metals (such as Ir) normally form stronger bonds to hydrogen than their second-row counterparts (such as Rh). We therefore decided to prepare Ir–Mo compounds in the hope that they would react with H_2 to produce isolable metal hydrides.

The reaction between **1** and $(CO)_2ClIr(H_2NC_6H_4\text{-}p\text{-}CH_3)$[9] in THF gave $(CO)_2IrMo(CO)_3[\eta^5\text{-}C_5H_4P(C_6H_4\text{-}p\text{-}CH_3)_2]$ (**8**) as an orange microcrystalline solid. As in the case of rhodium–molybdenum compound **4**, reaction of $P(CH_3)_3$ with **8** gives the phosphine substitution product **9** in which the $P(CH_3)_3$ is trans to the phosphorus atom of the heterodifunctional ligand. Similarly, reaction of **8** with $P(C_6H_5)_3$ cleanly gave the analogous triphenylphosphine substitution product **10** as orange crystals in 74% yield. The reaction of **1** with *trans*-$Ir(CO)(Cl)[P(C_6H_5)_3]_2$ also gave **10**, but it was difficult to separate **10** from a small amount of an unidentified impurity formed in this preparation.



Molybdenum–Iridium Dihydrides. All three Ir–Mo compounds react readily with hydrogen to form iridium dihydrides **11**, **12**, and **13**.



The stereochemistry of the molybdenum–iridium dihydrides was deduced spectroscopically. The large $^{31}P{-}^{31}P$ couplings seen in the ^{31}P NMR spectra of **12** and **13** (J_{PP} = 308 Hz for **12**, J_{PP} = 312 Hz for **13**) clearly indicate that the two phosphines are trans. The 270-MHz ^1H NMR spectrum of **12** exhibited resonances for the two hydrides at δ −10.43 and −13.81. Each of these resonances is a split into a multiplet by coupling to two different phosphorus atoms and the other metal hydride. Selective decoupling of each hydride resonance enabled the determination of coupling constants. The J_{HH} value of 3.4 Hz is consistent with the cis hydrides, and the J_{PH} values of 11.0, 14.6, 15.6, and 21.6 Hz indicate that each hydride is cis to two phosphines. Much larger J_{PH} values would have been expected if the hydrogens were trans to a phosphine. Although compounds containing hydrogen atoms trans to a phosphine are relatively rare, some examples are known: coupling constants for $[HPt(PPh_3)_3]^+$ are $J_{P_{trans}\text{-}H}$ = 160 Hz and $J_{P_{cis}\text{-}H}$ = 13 Hz.[10] A pattern similar to that seen for **12** was observed for the two hydrides in the ^1H NMR of **13**. The ^1H NMR of **11** exhibited doublets of doublets at δ −11.37 and −11.58, since in this case each hydride is coupled to the other hydride and to one phosphorus atom.

The ^{13}C NMR spectra of **11**, **12**, and **13** also support the assigned structure. The absence of a plane of symmetry gives rise to nonequivalent *p*-tolyl groups. The ^{13}C NMR of the triphenylphosphine-substituted molybdenum iridium dihydride **13** at −30 °C exhibits three equal intensity singlets at δ 233.9, 227.6, and 224.9 assigned to the nonequivalent molybdenum carbonyls. In the room temperature ^{13}C NMR of **13**, these signals appear as a broad resonance barely above the base line. Apparently, there is a fluxional process that interconverts the molybdenum carbonyls at room temperature. Similarly, the ^{13}C resonances due to the $Mo(CO)_3$ units of **11** and **12** are broadened at room temperature.

Although all three of the iridium dihydrides are formed under very mild conditions (≤1 atm H_2, room temperature), their rates of formation are significantly different. In an NMR experiment, a 12 mM C_6D_6 solution of triphenylphosphine-substituted compound **10** reacted with 400 mm H_2 to form **13** with an approximate half-life of 30 min. In contrast, the reaction of the trimethylphosphine-substituted compound **9** (28 mM) with H_2 (396 mm) was complete in less than 6 min at room temperature, and the reaction of dicarbonyliridium compound **8** (44 mM) with H_2 (565 mm) was complete in less than 7 min. The slower reaction of the triphenylphosphine-substituted Ir–Mo compound with H_2 is undoubtedly due to steric retardation since the rate is slower than that of either **9**, which has a better donor $P(CH_3)_3$ ligand on Ir, or **8**, which has a better acceptor CO ligand in place of $P(C_6H_5)_3$.

^1H NMR experiments were carried out that establish the reversibility of the hydrogen addition to **8**, **9**, and **10**. NMR tubes containing C_6D_6 solutions of **11**, **12**, and **13** were allowed to stand at room temperature for 20 h. During this time, all three tubes were periodically frozen and pumped to remove any H_2 formed by reductive elimination. ^1H NMR analysis revealed that 85% of **11** was converted back to **8**; 24% of **13** was converted back to **10**; and 15% of **12** was converted back to **9**. Because of the reversibility of the addition of H_2 to iridium–molybdenum compounds **8**, **9**, and **10**, we have not been able to isolate completely pure **11** or **13**. However, since the trimethylphosphine-substituted molybdenum iridium dihydride **12** is somewhat more stable, we were successful in obtaining analytically pure **12**.

An equilibrium constant for **8** + $H_2 \rightleftarrows$ **11** was determined by allowing a 16 mM C_6D_6 solution of **8** under 59 mm H_2 pressure to reach equilibrium at 22 °C. In less than 18 h equilibrium was established; the equilibrated solution consisted of 63% **11** and 37% **8**. ($K_{eq} = [\mathbf{11}][\mathbf{8}]^{-1}[H_2]^{-1}$ = 37 atm^{-1}). An 8.1 mM C_6D_6 solution of **10** required about 1 week to equilibrate under 60 mm H_2 pressure; the equilibrated solution consisted of 96% **13** and 4% **10** (K_{eq} = 440 atm^{-1}). An attempt was made to determine the equilibrium constant K_{eq} for the **9** + $H_2 \rightleftarrows$ **12** equilibrium, but only a lower limit of K_{eq} = 6500 atm^{-1} was estimated since a 20 mM C_6D_6 solution of **9** reacted completely with 59 mm H_2 pressure, giving **12** as the only product observable by ^1H NMR.

Comparison of the infrared spectra of **11**, **12**, and **13** with the spectra of the dideuterides **11**-d_2, **12**-d_2, and **13**-d_2 allowed unambiguous assignment of M–H and CO vibrations in the 2000 cm^{-1} region since (1) bands due to molybdenum carbonyls are largely unshifted, (2) bands due to M–H are shifted to the 1490-cm^{-1} region upon deuteration, and (3) bands due to Ir–CO trans to Ir–H shift to approximately 25-cm^{-1} higher energy upon deuteration and increase in intensity due to disappearance of a resonance interaction between $\nu_{Ir\text{-}H}$ and $\nu_{Ir\text{-}CO}$ in trans positions. A resonance interaction between vibrations is important when the frequencies of the vibrations are similar and when the interacting groups are trans.[11] This interaction shifts the higher energy

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[8] Roberts, D. A.; Mercer, W. C.; Zahurak, S. M.; Geoffroy, G. L.; DeBrosse, C. W.; Cass, M. E.; Pierpont, C. G. *J. Am. Chem. Soc.* **1982**, *104*, 910.

[9] Klabunde, U.; Forster, D.; Weinreis, W. O. *Inorg. Synth.* **1974**, *15*, 82.

[10] Thomas, K.; Dumler, J. T.; Renoe, B. W.; Nyman, C. J.; Roundhill, D. M. *Inorg. Chem.* **1972**, *11*, 1795.

vibration (ν_{IrH}) to still higher energy and the lower energy vibration (ν_{IrCO}) to still lower energy than expected from force constant considerations only. The resonance interaction disappears for the dideuterides since the frequency difference between the interacting vibrations becomes very large; consequently, the $\nu_{\text{Ir-CO}}$ band shifts to the higher energy position expected from force constants alone upon deuteration. In addition, the intensity of this $\nu_{\text{Ir-CO}}$ band is increased greatly in the deuteride since it no longer "contributes intensity" to an $\nu_{\text{Ir-H}}$ stretch.

In going from **11** to **11**-d_2, the band at 2008 cm^{-1} shifts 21 cm^{-1} to 2029 cm^{-1} and increases in intensity and can therefore be assigned to the CO trans to H. A smaller 12-cm^{-1} shift and little increase in intensity is seen for the band due to Ir–CO trans to phosphorus (2059–2071 cm^{-1}). In addition, the highest energy molybdenum carbonyl band moves 5 cm^{-1} to higher energy upon deuteration. Similarly, in going from **12** to **12**-d_2 and from **13** to **13**-d_2 the stretches assigned to the iridium carbonyls trans to hydrogen shift 25 and 23 cm^{-1} to higher energy.

We have tested all of these new heterobimetallic compounds as possible hydrogenation catalysts, but only small amounts of cyclohexene were hydrogenated, and no CO reduction was observed. For instance, attempted hydrogenation of cyclohexene led to only 0.97 turnover when a 7 mM toluene solution of **5** was heated in the presence of cyclohexene at 140 °C for 12 h under 1000 psi H_2. Moreover we are unable to eliminate the possibility that this very small amount of hydrogenation of cyclohexene to cyclohexane may be due to a decomposition product of **5**. Attempted CO hydrogenation experiments were also unsuccessful; for instance, no CH_4 or CH_3OH was observed when a 15 mM toluene solution of **6** was heated at 120 °C for 17 h under 600 psi CO and 600 psi H_2.

Related Studies. The use of heterodifunctional ligands to link heterobimetallic compounds has been employed frequently. Davison reported the use of $Li^+(C_5H_4PPh_2)^-$ in the preparation of a series of heterobimetallic ferrocene and cobalticenium derivatives.[4d-f] More recently, Rausch has used $Tl^+(C_5H_4PPh_2)^-$ to prepare $C_5H_5(CO)_2Mn[P(C_6H_5)_2C_5H_4]Ti(C_5H_5)(CO)_2$,[12] which does not possess a metal–metal bond. Schore has used a related heterodifunctional ligand in the synthesis of $(C_5H_5)Cl_2Zr[\eta^5\text{-}C_5H_4Si(CH_3)_2CH_2PPh_2]Fe(CO)_4$ and related compounds.[4a-c] Dixneuf reported the preparation of $(CO)_5MoTi(C_5H_5)(\eta^7\text{-}C_7H_6PPh_2)$ from the reaction of $Mo(CO)_6$ with $(C_5H_5)Ti(\eta^7\text{-}C_7H_6PPh_2)$.[4j]

The synthesis of heterobimetallic compounds containing Rh or Ir has recently been reported by several groups. Of particular interest are two iridium dihydrides reported by Geoffroy, $[(CO)_4W(\mu\text{-}PPh_2)_2IrH_2(CO)(PPh_3)]^-K^+$[13] and $(CO)_3(PPh_3)Fe(\mu\text{-}PPh_2)IrH_2(CO)_2(PPh_3)$.[14] Howarth prepared $[(PPh_3)_2Rh(\mu\text{-}H)_2Mo(C_5H_5)_2]^+$ PF_6^- from the reaction of $(C_5H_5)_2MoH_2$ with $[RhH_2(PPh_3)_2(Me_2CO)_2]^+$ PF_6^-.[15] Venanzi reported the preparation of a similar tungsten–iridium compound, $[(C_5H_5)W(\mu\text{-}H)_2(\eta^1\text{-}\eta^5\text{-}C_5H_4)IrH(PEt_3)_2]^+PF_6^-$,[16] in which oxidative addition of a C–H cyclopentadienyl bond has occurred. Balch has used 2-(diphenylphosphino)pyridine as a heterodifunctional ligand to link Rh–Pt[4n] and Rh–Pd[4o] bimetallic compounds. Stone has reported several rhodium-containing heterobimetallic compounds, including A.[17] Other rhodium- or iridium-containing heterobimetallic compounds have been reported by Finke,[18] Green,[19] Shaw,[20] Salzer,[21] Venanzi,[22] Takats,[23] Rauchfuss,[4k] and Collins.[24]

Conclusion

We are still far away from our ultimate goal of synthesizing heterobimetallic dihydrides with one early and one late transition metal linked by a heterodifunctional ligand. Nevertheless, we are making progress in synthesizing heterobimetallic compounds linked by heterodifunctional ligands and have succeeded in adding H_2 to one of the metal centers. We had hoped to observe reductive elimination of a metal hydride from the M′–MH$_2$ species that would have produced a heterobimetallic dihydride. In the cases of the Mo–IrH$_2$ compounds **11**, **12**, and **13**, the failure to see reductive elimination of MoH is probably a thermodynamic problem since this transformation would involve formation of a less stable second-row transition metal hydride (Mo–H) from a more stable third-row metal hydride (Ir–H). In addition, a Mo–Ir bond would be lost in the process. To obtain a system in which reductive elimination of metal hydride will produce a more stable heterobimetallic dihydride, we plan to investigate W–Rh compounds similar to the Mo–Rh compounds reported here. Even though initial H_2 addition to a rhodium center may be thermodynamically unfavorable, the reaction might be driven by subsequent reductive elimination of a more stable third-row tungsten hydride.

In addition to attempting the preparation of Rh–W compounds mentioned above, we are continuing to explore synthetic pathways to "early-late" dihydrides which would have a larger difference in the reactivity of the two hydrides. We recently reported the successful synthesis of heterobimetallic compounds containing Zr–Ru and Zr–Fe bonds,[2] and we are currently involved in preparing Zr–Fe and Zr–Co compounds linked by a heterodifunctional ligand.

Experimental Section

General. All reactions were carried out under nitrogen, using Schlenk glassware or a Vacuum Atmospheres glovebox. Olefin-free hexane, olefin-free pentane, tetrahydrofuran (THF), toluene, diethyl ether, 1,2-dimethoxyethane (DME), and C_6D_6 were distilled from sodium benzophenone ketyl under a nitrogen atmosphere. CH_2Cl_2 was distilled from CaH_2, and CD_2Cl_2 was distilled from P_2O_5. ^{1}H NMR spectra were recorded on a Bruker WH-270 (270 MHz) spectrometer; ^{13}C NMR (50.10 MHz) and ^{31}P NMR (80.76 MHz) 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. All ^{13}C and ^{31}P NMR spectra were broad band proton decoupled. Infrared spectra were recorded on a Beckman 4230 infrared spectrometer. Mass spectra were obtained on a 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. $Li^+[\eta^5\text{-}C_5H_4P(C_6H_4\text{-}p\text{-}CH_3)_2]Mo(CO)_3^-$ was prepared as reported earlier.[3] Gas chromatography was performed on a Hewlett-Packard 5700A instrument with a flame ioni-

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(11) (a) Vaska, L. *J. Am. Chem. Soc.* **1966**, *88*, 4100. (b) King, G. W. "Spectroscopy and Molecular Structure"; Holt, Rinehart and Wilson, Inc.: New York, 1964; pp 348–350. (c) Cotton, F. A. "Chemical Applications of Group Theory", 2nd ed.; Wiley: New York, 1971; pp 330–333.

(12) Rausch, M. D.; Edwards, B. H.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 3882.

(13) Breen, M. J.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 1069.

(14) Breen, M. J.; Duttera, M. R.; Geoffroy, G. L.; Novotnak, G. C.; Roberts, D. A.; Shulman, P. M.; Steinmetz, G. R. *Organometallics* **1982**, *1*, 1008.

(15) (a) Alcock, N. W.; Howarth, O. W.; Moore, P.; Morris, G. E. *J. Chem. Soc., Chem. Commun.* **1979**, 1160. (b) Howarth, O. W.; McAteer, C. H.; Moore, P.; Morris, G. E.; Alcock, N. W. *J. Chem. Soc., Dalton Trans.* **1982**, 541.

(16) Pregosin, P. S.; Togni, A.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 668.

(17) (a) Barr, R. D.; Green, M.; Marsden, K.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 507. (b) Jeffery, J. C.; Sambale, C.; Schmidt, M. F.; Stone, F. G. A. *Organometallics* **1982**, *1*, 1597. (c) Chetcuti, M. J.; Green, M.; Jeffery, J. C.; Stone, F. G. A.; Wilson, A. A. *J. Chem. Soc., Chem. Commun.* **1980**, 948. (d) Jeffery, J. C.; Mead, K. A.; Razay, H.; Stone, F. G. A.; Went, M. J.; Woodward, P. *Ibid.* **1981**, 867.

(18) Finke, R. G.; Gaughan, G.; Pierpont, C.; Cass, M. E. *J. Am. Chem. Soc.* **1981**, *103*, 1394.

(19) Dias, A. R.; Green, M. L. H. *J. Chem. Soc. A* **1971**, 1951.

(20) (a) McEvan, D. M.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1982**, 859. (b) McDonald, W. S.; Pringle, P. G.; Shaw, B. L. *Ibid.* **1982**, 861. (c) Pringle, P. G.; Shaw, B. L. *Ibid.* **1982**, *956*, 1313.

(21) Salzer, A.; Egolf, T.; Von Philipsborn, W. *J. Organomet. Chem.* **1981**, *221*, 351.

(22) (a) Lehner, H.; Musco, A.; Venanzi, L. M.; Albinati, A. *J. Organomet. Chem.* **1981**, *213*, C46. (b) Boron, P.; Musco, A.; Venanzi, L. M. *Inorg. Chem.* **1982**, *21*, 4192. (c) Albinati, A.; Musco, A.; Naegeli, R.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 958.

(23) Bennett, M. J.; Pratt, J. L.; Simpson, K. A.; LiShingman, L. K. K.; Takats, J. *J. Am. Chem. Soc.* **1976**, *98*, 4810.

(24) Audett, J. D.; Collins, T. J.; Santarsiero, B. D.; Spies, G. H. *J. Am. Chem. Soc.* **1982**, *104*, 7352.

zation detector, coupled to a Hewlett-Packard 3380A electronic integrator-recorder; *n*-octane was used as an internal standard.

$[(C_6H_4\text{-}p\text{-}CH_3)_2PCH_2]_2$[25] was prepared by a new procedure that gave purer material. By use of a Schlenk apparatus, a solution of $LiP(C_6H_4\text{-}p\text{-}CH_3)_2$ was prepared by stirring a solution of di-*p*-tolylchlorophosphine (2.36 g, 9.4 mmol) in 50 mL of THF with lithium ribbon (150 mg, 21 mmol) for 20 h. The solution was filtered, and 1,2-dichloroethane (0.375 mL, 0.47 g, 4.7 mmol) in 5 mL of THF was added. The solvent was immediately evaporated and the residue taken up in 1:1 CH_2Cl_2:water. The aqueous solution was extracted with CH_2Cl_2 and the combined CH_2Cl_2 solutions were dried (Na_2SO_4) and evaporated to dryness. The residue was dissolved in toluene, filtered through Celite, and concentrated. Addition of hexane led to the precipitation of a white solid. Evaporation of the mother liquor and addition of hexane gave additional $[(C_6H_4\text{-}p\text{-}CH_3)_2P\text{-}CH_2]_2$ (1.45 g total, 68%): mp 147–148 °C; ^1H NMR (200 MHz, C_6D_6) δ 2.04 (pseudotriplet, CH_2CH_2, $J = 4.0$ Hz), 2.32 (s, CH_3), 7.10 (d, $J = 8$ Hz, meta), 7.21 (m, ortho).

$\{[(C_6H_4\text{-}p\text{-}CH_3)_2PCH_2]_2RhCl\}_2$ (2). An orange-yellow solution of $[(C_2H_4)_2RhCl]_2$[26] (347.7 mg, 0.894 mmol) and $[(C_6H_4\text{-}p\text{-}CH_3)_2PCH_2]_2$ (812.7 mg, 1.788 mmol) in toluene (50 mL) was stirred at room temperature for 12 h. The solution was concentrated to 20 mL, and pentane (30 mL) was added. The resulting precipitate was collected by filtration in a glovebox, washed with hexane, and dried under vacuum to give **2** as a golden-brown solid (871 mg, 82%):[27] mp 152–158 °C dec; ^1H NMR (C_6D_6) δ 7.98 (m, ortho), 6.83 (d, $J_{PH} = 7.7$ Hz, meta), 2.03 (s, CH_3), 1.82 (bd, 18.7 Hz peak separation, CH_2); ^{31}P NMR (acetone-d_6) δ 72.6 (d, $J_{Rh\text{-}P} = 199$ Hz). Anal. Calcd for $C_{74}H_{64}Cl_2P_4Rh_2$: C, 60.77; H, 5.44. Found: C, 60.88; H, 5.63.

$[(C_6H_4\text{-}p\text{-}CH_3)_2PCH_2]_2\overline{RhMo(CO)_3[\eta^5\text{-}C_5H_4P}(C_6H_4\text{-}p\text{-}CH_3)_2]$ (3). A solution of **1**[3] (2.04 mmol) in THF (80 mL) was added by cannula to a solution of **2** (1.20 g, 1.01 mmol) in THF (40 mL) at −78 °C. The solution was stirred at −78 °C for 10 min, warmed to room temperature, and evaporated to dryness on a vacuum line. In a glovebox, the crude product was dissolved in a minimum volume of toluene, filtered through a short column of silica gel, and purified by preparative thin layer chromatography (TLC) (silica gel, toluene, $R_f = 0.4$). Recrystallization from toluene/pentane gave **3** as an orange solid (567 mg, 25%): mp 240–244 °C dec; ^1H NMR (C_6D_6) δ 8.00 (dd, $J_{PH} = 9.6$ Hz, $J_{HH} = 8.1$ Hz, 4 H, ortho), 7.58 (dd, $J_{PH} = 10.7$ Hz, $J_{HH} = 8.1$ Hz, 4 H, ortho), 7.46 (dd, $J_{PH} = 9.9$ Hz, $J_{HH} = 8.1$ Hz, 4 H, ortho), 7.20 (d, $J_{HH} = 6.6$ Hz, 4 H, meta), 6.78 (d, $J_{HH} = 7.3$ Hz, 8 H, meta), 5.04 (m, 2 H, C_5H_4P), 4.62 (pseudoquartet, $J \approx 2$ Hz, 2 H, C_5H_4P), 2.14 (s, CH_3), 2.00 (s, CH_3), 1.99 (s, CH_3), 1.35 (m, CH_2), 0.89 (m, CH_2); partial ^{13}C NMR aromatic carbons omitted (C_6D_6, 0.07 M $Cr(acac)_3$), δ 236.9 (s, Mo(CO)), 229.7 (s, $Mo(CO)_2$); (THF-d_8) 92.9 (d, $J_{PC} = 12.2$ Hz, C_2 of C_5H_4P), 90.5 (d, $J_{PC} = 6.1$ Hz, C_3 of C_5H_4P), 30.0 (m, CH_2), 28.3 (m, CH_2), 21.5 (s, CH_3), 21.4 (s, CH_3), 21.2 (s, CH_3); ^{31}P NMR (C_6D_6, $P_A = PC_5H_4$, P_B cis to P_A, P_C trans to P_A) δ 65.4 (ddd, $J_{P_AP_C} = 345$ Hz, $J_{P_C\text{-}Rh} = 146$ Hz, $J_{P_CP_B} = 32$ Hz, P_C), 54.0 (ddd, $J_{P_B\text{-}Rh} = 183$ Hz, $J_{P_BP_C} = 32$ Hz, $J_{P_BP_A} = 26$ Hz, P_B), 38.6 (ddd, $J_{P_AP_C} = 345$ Hz, $J_{P_A\text{-}Rh} = 129$ Hz, $J_{P_AP_B} = 26$ Hz, P_A); IR (toluene) 1922 (s), 1841 (m), 1801 (m) cm^{-1}. Anal. Calcd for $C_{52}H_{50}MoO_3P_3Rh$: C, 61.55; H, 4.97. Found: C, 61.34; H, 5.25.

$(CO)_2\overline{RhMo(CO)_3[\eta^5\text{-}C_5H_4P}(C_6H_4\text{-}p\text{-}CH_3)_2]$ (4). A solution of **1**[3] (3.10 mmol) in toluene (70 mL) was added by cannula to a stirred suspension of $[(CO)_2RhCl]_2$[7] (0.600 g, 1.54 mmol) in toluene (10 mL) at −72 °C. The black solution was stirred for 10 min at room temperature and concentrated to 10 mL by evaporation. Column chromatography (toluene, alumina) gave a fast moving yellow band which upon concentration and addition of pentane gave olive-green microcrystals of **4** (0.770 g, 41%): mp 168–171 °C dec; ^1H NMR (C_6D_6) δ 7.69 (dd, $J_{PH} = 12.5$ Hz, $J_{HH} = 7.9$ Hz, ortho), 7.94 (dd, $J_{HH} = 8.2$ Hz, $J_{PH} = 1.9$ Hz, meta), 4.79 (pseudoquartet, $J \approx 2$ Hz, 2 H, C_5H_4P), 4.02 (pseudoquartet, $J \approx 2$ Hz, 2 H, C_5H_4P), 1.91 (s, CH_3); ^{13}C NMR (acetone-d_6, 0.07 M $Cr(acac)_3$, 25 °C) δ 235.3 (s, Mo(CO)), 222.4 (s, $Mo(CO)_2$), 184 (br, Rh(CO)), 143.9 (s, para), 134.7 (d, $J_{PC} = 11.0$ Hz, ortho), 130.9 (d, $J_{PC} = 11.0$ Hz, meta), 126.4 (d, $J_{PC} = 51.3$ Hz, ipso), 93.2 (m, C_2 and C_3 of C_5H_4P), 55.0 (d, $J_{PC} = 60.3$ Hz, C_1 of C_5H_4P), 21.5 (s, CH_3); ^{31}P NMR (acetone-d_6, 0.07 M $Cr(acac)_3$) δ 42.7 (d, $J_{Rh\text{-}P} = 118$ Hz); IR (DME) 2062 (s), 1988 (m), 1959 (s), 1884 (m, sh), 1867 (s) cm^{-1}; MS, *m/e* 617.8993 (M^+), calcd for $C_{24}H_{18}MoO_5PRh$ 617.8998. Anal. Calcd for $C_{24}H_{18}MoO_5PRh$: C, 46.78; H, 2.94; P, 5.03. Found: C, 47.05; H, 2.96; P, 5.17. A sample of **4** enriched in ^{13}CO at all carbonyl sites by a combination of heating to 50 °C under ^{13}CO in benzene-d_6 and photolysis showed ^{13}C NMR resonances for $Mo(CO)_3$ but not $Rh(CO)_2$ at room temperature. However, at −70 °C in acetone-d_6, resonances were observed both for molybdenum and rhodium carbonyls at δ 200.8 (dd, $J_{PC} = 108.1$ Hz, $J_{Rh\text{-}C} = 62.3$ Hz, Rh(CO) trans to P) and 183.2 (d, $J_{Rh\text{-}C} = 75.1$ Hz, Rh(CO) trans to Mo).

***trans*-$P(C_6H_4\text{-}p\text{-}CH_3)_3(CO)\overline{RhMo(CO)_3[\eta^5\text{-}C_5H_4P}(C_6H_4\text{-}p\text{-}CH_3)_2]$ (5).** A solution of $P(C_6H_4\text{-}p\text{-}CH_3)_3$ (142.2 mg, 0.468 mmol)[29] and **4** (144 mg, 0.234 mmol) in 10 mL of THF was stirred at room temperature for several minutes. The product was concentrated under vacuum, purified by TLC (silica gel, 1:1 Et_2O:hexane, R_f 0.4) in a glovebox, and crystallized from CH_2Cl_2/hexane to give **5** as a yellow powder (116 mg, 56%): mp 236–242 °C dec; ^1H NMR (C_6D_6) δ 8.08 (m, 10 H, ortho), 7.12 (d, $J_{HH} = 7.1$ Hz, 6 H, meta), 6.92 (d, $J_{HH} = 6.7$ Hz, 4 H, meta), 4.93 (pseudoquartet, $J \approx 2$ Hz, 2 H, C_5H_4P), 4.56 (pseudoquartet, $J \approx 2$ Hz, 2 H, C_5H_4P), 2.05 (s, 9 H, CH_3), 1.99 (s, 6 H, CH_3); ^{13}C NMR (CD_2Cl_2, 0.07 M $Cr(acac)_3$) δ 234.6 (s, Mo(CO)), 225.5 (s, $Mo(CO)_2$), 141.6 (s, 2 C, para), 139.7 (s, 3 C, para), 134.3 (d, $J_{PC} = 10.7$ Hz, 6 C, ortho), 133.4 (d, $J_{PC} = 13.8$ Hz, 4 C, ortho), 130.2 (d, $J_{PC} = 42.8$ Hz, ipso), 129.1 (d, $J_{PC} = 9.2$ Hz, 4 C, meta), 128.4 (d, $J_{PC} = 7.7$ Hz, 6 C, meta), 127.6 (tentatively assigned as one resonance of an ipso tolyl doublet; the other resonance is obscured by the δ 128.4 peak), 93.5 (d, $J_{PC} = 10.7$ Hz, C_2 or C_3 of C_5H_4P), 91.75 (br, s, C_2 or C_3 of C_5H_4P), 60.1 (d, $J_{PC} = 50.5$ Hz, C_1 of C_5H_4P), 20.9 (s, CH_3); ^{31}P NMR (CD_2Cl_2, 0.07 M $Cr(acac)_3$) AB quartet with additional ^{31}P–^{103}Rh coupling δ 47.2 ($J_{PP} = 332$ Hz, $J_{Rh\text{-}P} = 120$ Hz, $(C_6H_4\text{-}p\text{-}CH_3)_2PC_5H_4$), 32.3 ($J_{PP} = 332$ Hz, $J_{Rh\text{-}P} = 130$ Hz, $((C_6H_4\text{-}p\text{-}CH_3)_3P)$; IR (THF) 1966 (m), 1938 (s), 1859 (m), 1832 (s) cm^{-1}. Anal. Calcd for $C_{44}H_{39}MoO_4P_2Rh$: C, 59.21; H, 4.40. Found: C, 58.84; H, 4.41.

***trans*-$P(CH_3)_3(CO)\overline{RhMo(CO)_3[\eta^5\text{-}C_5H_4P}(C_6H_4\text{-}p\text{-}CH_3)_2]$ (6).** On a high vacuum line, $P(CH_3)_3$ (0.30 mmol) was condensed into a flask containing **4** (175 mg, 0.284 mmol) and THF (30 mL). The solution was stirred at room temperature for 20 min and the solvent was evaporated. The crude product was recrystallized from toluene–pentane, washed with pentane, and dried under vacuum to give 6 as a yellow solid (135 mg, 71%): mp 248–257 °C dec; ^1H NMR (C_6D_6) δ 7.95 (dd, $J_{PH} = 11.8$ Hz, $J_{HH} = 8.1$ Hz, ortho), 6.86 (d, $J_{HH} = 7.3$ Hz, meta), 5.01 (pseudoquartet, $J \approx 2$ Hz, 2 H, C_5H_4P), 4.52 (pseudoquartet, $J \approx 2$ Hz, 2 H, C_5H_4P), 1.92 (s, CH_3), 1.48 (dm, $J_{PH} = 8.6$ Hz, $P(CH_3)_3$); ^{13}C NMR (CD_2Cl_2, 0.07 M $Cr(acac)_3$) δ 235.0 (s, Mo(CO)), 225.7 (s, $Mo(CO)_2$), 141.7 (s, para), 133.6 (d, $J_{PC} = 13.8$ Hz, ortho), 129.4 (d, $J_{PC} = 10.7$ Hz, meta), 128.4 (d, $J_{PC} = 42.8$ Hz, ipso), 93.9 (d, $J_{PC} = 10.7$ Hz, C_2 or C_3 of C_5H_4P), 92.1 (br, s, C_2 or C_3 of C_5H_4P), 62.2 (d, $J_{PC} = 45.9$ Hz, C_1 of C_5H_4P), 21.1 (s, CH_3), 16.6 (d, $J_{PC} = 27.5$ Hz, $P(CH_3)_3$); ^{31}P NMR (CD_2Cl_2, 0.07 M $Cr(acac)_3$) 45.4 (dd, $J_{PP} = 348$ Hz, $J_{Rh\text{-}P} = 112$ Hz, $(C_6H_4\text{-}p\text{-}CH_3)_2PC_5H_4$), −1.7 (dd, $J_{PP} = 348$ Hz, $J_{Rh\text{-}P} = 127$ Hz, $P(CH_3)_3$); IR (THF) 1957 (m), 1932 (s), 1851 (m), 1828 (s) cm^{-1}. MS, *m/e* 665.9490 (M^+), calcd for $C_{26}H_{27}MoO_4P_2Rh$: 665.9484. Anal. Calcd for $C_{26}H_{27}MoO_4P_2Rh$: C, 47.01; H, 4.10. Found: C, 46.75; H, 3.85.

Lithium 1-(Di-*p*-tolylphosphino)-2,3,4,5-tetramethylcyclopentadienide. *n*-Butyllithium in hexane (0.63 mL, 1.6 M, 1.01 mmol) was slowly added to freshly distilled 1,2,3,4-tetramethylcyclopentadiene[30] (0.124 g, 1.01 mmol) at −15 °C over 5 min to give a white suspension of lithium tetramethylcyclopentadienide in a pale yellow solution.

Di-*p*-tolylchlorophosphine (0.22 mL, 1.00 mmol) was added to the suspension and stirred for 1 h to give 1-(di-*p*-tolylphosphino)-2,3,4,5-tetramethylcyclopentadiene. Evaporation of solvent from a small aliquot gave a pale yellow oil: ^1H NMR (C_6D_6) δ 1.60 (s, 2 CH_3), 1.81 (s, 2 CH_3), 2.05 (s, 2 CH_3), 3.75 (bs, *CH*–P), 6.95 (d, $J = 8$ Hz, 4 H, meta), 7.50 (t, $J_{HH} = J_{PH} = 8$ Hz, 4 H, ortho).

The solution of 1-(di-*p*-tolylphosphino)-2,3,4,5-tetramethylcyclopentadiene was cooled to −15 °C and *n*-butyllithium (0.63 mL, 1.6 *M*, 1.01 mmol) was slowly added over 5 min to give a red solution. Evaporation of solvent from a small aliquot gave $[(C_6H_4\text{-}p\text{-}CH_3)_2PC_5Me_4]^-Li^+$ as a red foam: ^1H NMR (C_6D_6) δ 2.12 (s, 2 CH_3), 2.22 (s, 2 CH_3), 2.32 (s, 2 CH_3), 7.00 (d, $J = 8$ Hz, 4 H, meta), 7.50 (t, $J_{HH} = J_{PH} = 8$ Hz, 4 H, ortho).

$[(C_6H_4\text{-}p\text{-}CH_3)_2PCH_2]_2\overline{RhMo(CO)_3[\eta^5\text{-}C_5(CH_3)_4P}(C_6H_4\text{-}p\text{-}CH_3)_2]$ (7). $Mo(CO)_6$ (267 mg, 1.0 mmol) was added to the solution of $[(C_6H_4\text{-}p\text{-}CH_3)_2PC_5Me_4]^-Li^+$ prepared above and the mixture was refluxed for 16 h. An IR spectrum of an aliquot of the reaction mixture

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(25) (a) Thornhill, D. J.; Manning, A. R. *J. Chem. Soc., Dalton Trans.* **1973**, 2086. (b) Archer, L. J.; George, T. A. *Inorg. Chem.* **1979**, *18*, 2079.

(26) Cramer, R.; McCleverty, J. A.; Bray, J. *Inorg. Synth.* **1974**, *15*, 14.

(27) The preparation of **2** can also be carried out by using $[RhCl(C_8H_{12})]_2$[28] instead of $[(C_2H_4)_2RhCl]_2$;[26] the isolated yield was 78%.

(28) Giordano, G.; Crabtree, R. H.; Heintz, R. M.; Forster, D.; Morris, D. E. *Inorg. Synth.* **1979**, *19*, 218.

(29) Incomplete reaction was observed when only 1 equiv of $P(C_6H_4\text{-}p\text{-}CH_3)_3$ was used.

(30) Kohler, F. M.; Doll, K. H. *Z. Naturforsch., B* **1982**, *37B*, 144.

showed total disappearance of $Mo(CO)_6$ and appearance of two sets of bands, at 2065 (w), 1983 (s), 1940 (s), 1915 (m) cm^{-1}, that were attributed to $LiC_5(CH_3)_4P(C_6H_4\text{-}p\text{-}CH_3)_2Mo(CO)_5$, and at 1895 (s), 1801 (s), 1782 (s), and 1715 (m) cm^{-1}, that were attributed to $Li(CO)_3MoC_5(CH_3)_4P(C_6H_4\text{-}p\text{-}CH_3)_2$. The ratio was estimated to be 1:1.

The solution was cooled to −78 °C and a solution of **2** (600 mg, 0.5 mmol) in 10 mL of THF was added via syringe over 5 min. The dark brown reaction mixture was stirred for 30 min at room temperature and then evaporated to dryness under vacuum. The resulting oil was purified by column chromatography (silica gel, toluene). After elution of a minor yellow band, a major brown band was collected and evaporated to dryness. This brown material was further purified by preparative thin layer chromatography (silica gel, 3:1 hexane:ether). An orange band (R_f 0.5) was collected and recrystallized from toluene–pentane to give **7** (0.29 g, 27% yield from tetramethylcyclopentadiene) as a yellow-orange solid: mp >260 °C dec. ^1H NMR (C_6D_6) δ 1.44 (s, 2 CH_3), 1.90 (s, 2 CH_3), 1.96 (s, 2 CH_3), 2.01 (s, 2 CH_3), 2.13 (s, 2 CH_3), 6.83 (pseudotriplet, 8 H, meta, $J = 9$ Hz), 7.17 (d, 4 H, meta, $J = 9$ Hz), 7.58 (q, 4 H, ortho, $J_{HH} = 8$ Hz, $J_{PH} = 9.6$ Hz), 7.98 (pseudoquartet, 8 H, ortho, $J_1 = 8$ Hz, $J_2 = 18$ Hz). The $P\text{–}(CH_2)_2P$ resonances were overlapped by the methyl resonances. ^{31}P NMR (C_6D_6, $P_A = PC_5(CH_3)_4$, P_B cis to P_A, P_C trans to P_A), 67.3 (ddd, $J_{P_AP_C} = 351$ Hz, $J_{P_C\text{–}Rh} = 148$ Hz, $J_{P_BP_C} = 32$ Hz, P_C), 51.4 (ddd, $J_{P_B\text{–}Rh} = 185$ Hz, $J_{P_BP_C} = 32$ Hz, $J_{P_AP_B} = 23$ Hz, P_B), 41.2 (ddd, $J_{P_AP_C} = 351$ Hz, $J_{P_A\text{–}Rh} = 130$ Hz, $J_{P_AP_B} = 23$ Hz, P_A); ^{13}C NMR (C_6D_6) δ 11.9, 13.4 (s, α and β CH_3 on Cp ring) 21.0, 21.1, 21.4 (s, CH_3 of *p*-tolyl groups) 104.3 (d, $J_{PC} = 11$ Hz, $C\text{–}CH_3$ on Cp ring), 106.6 (d, $J_{PC} = 5$ Hz, $C\text{–}CH_3$ on Cp ring), 232.1 (s, $Mo(CO)_2$), 238.3 (s, Mo(CO)). The ipso carbon on the Cp ring and the $PCH_2\text{–}CH_2P$ resonances were not detected. The aromatic region was complex and was not assigned. IR (THF) 1915 (s), 1834 (s), 1803 (m) cm^{-1}. Anal. Calcd for $C_{56}H_{58}MoO_3P_3Rh$: C, 62.81; H, 5.46. Found: C, 63.01; H, 5.67.

Attempted Reaction of 7 with Hydrogen. A 10-mg sample of **7** was dissolved in 0.28 mL of C_6D_6 and sealed under 650 mm of H_2 pressure. The ^1H NMR spectrum of this solution did not show any modifications after heating at 72 °C for 60 d.

Attempted Hydrogenation of Cyclohexene by 7. Compound **7** (10 mg, 9.3 μmol), cyclohexene (20 μl, 0.30 mmol) and *n*-octane (20 μl, internal standard for GC) in 5 mL of toluene were heated for 18 h under 1000 psi H_2 pressure in a Parr bomb. All volatile components were then distilled under reduced pressure, collected, and analyzed by GC. At 80 °C and 1000 psi of H_2, less than 2% of cyclohexene had been hydrogenated. At 150 °C under 950 psi of H_2, 30% of cyclohexene had been hydrogenated but some decomposition of **7** had occurred, as evidenced by appearance of several new spots in the TLC of the residue.

$\mathbf{(CO)_2\overline{IrMo(CO)_3[\eta^5\text{-}C_5H_4P}(C_6H_4\text{-}\mathit{p}\text{-}CH_3)_2]}$ (**8**). A solution of **1**,[3] (1.29 mmol) and $(CO)_2Ir(Cl)(H_2NC_6H_4\text{-}p\text{-}CH_3)$[9] (500 mg, 1.28 mmol) in THF (30 mL) was refluxed for 8 h. The solvent was evaporated on the vacuum line, and the resulting solid was purified by column chromatography (alumina, ether) and recrystallization from toluene–pentane to give **8** as an orange microcrystalline solid (250 mg, 28%): mp 178–181 °C dec; ^1H NMR (C_6D_6) 7.70 (dd, $J_{PH} = 12.7$ Hz, $J_{HH} = 8.3$ Hz, ortho), 6.79 (dd, $J_{HH} = 7.7$ Hz, $J_{PH} = 2.2$ Hz, meta), 4.76 (pseudoquartet, $J \approx 2$ Hz, 2 H, C_5H_4P), 4.16 (pseudoquartet, $J = 2.2$ Hz, 2 H, C_5H_4P), 1.91 (s, CH_3); ^{13}C NMR (acetone-d_6, 0.07 M $Cr(acac)_3$) δ 234.2 (s, Mo(CO), 220.7 (s, $Mo(CO)_2$), 144.0 (s, para), 134.5 (d, $J_{PC} = 12.2$ Hz, ortho), 130.9 (d, $J_{PC} = 12.2$ Hz, meta), 125.2 (d, $J_{PC} = 59.7$ Hz, ipso), 94.9 (d, $J_{PC} = 3.0$ Hz, C_2 or C_3 of C_5H_4P), 94.1 (d, $J_{PC} = 9.2$ Hz, C_2 or C_3 of C_5H_4P), 21.6 (s, CH_3), $Ir(CO)_2$, C_1 of C_5H_4P not observed; ^{31}P NMR (acetone-d_6, 0.07 M $Cr(acac)_3$) δ 32.3 (s); IR (THF) 2047 (s), 1971 (s), 1896 (m, sh), 1887 (s). Anal. Calcd for $C_{24}H_{18}IrMoO_5P$: C, 40.86; H, 2.57. Found: C, 40.54; H, 2.71. MS, *m/e* 707.9586 (M^+), calcd for $C_{24}H_{18}IrMoO_5P$ 707.9580.

***trans*-$\mathbf{P(CH_3)_3(CO)\overline{IrMo(CO)_3[\eta^5\text{-}C_5H_4P}(C_6H_4\text{-}\mathit{p}\text{-}CH_3)_2]}$ (9).** On a high vacuum line, $P(CH_3)_3$ (0.18 mmol) was condensed into a flask containing **8** (120 mg, 0.170 mmol) and THF (20 mL). The reaction mixture was warmed to room temperature, evaporated to dryness, and purified by column chromatography (alumina, toluene). Orange crystals of **9** (99 mg, 77%) were obtained by vapor diffusion of hexane into a toluene solution: mp 250–254 °C dec; ^1H NMR (C_6D_6) δ 7.97 (dd, $J_{PH} = 11.9$ Hz, $J_{HH} = 8.1$ Hz, ortho), 6.86 (dm, $J_{HH} = 7.0$ Hz, meta), 4.99 (pseudoquartet, $J \approx 2$ Hz, 2 H, C_5H_4P), 4.68 (pseudoquartet, $J \approx 2$ Hz, 2 H, C_5H_4P), 1.92 (s, CH_3), 1.60 (dd, $^2J_{PC} = 9.5$ Hz, $^4J_{PC} = 2.3$ Hz, $P(CH_3)_3$); ^{13}C NMR (CD_2Cl_2, 0.07 M $Cr(acac)_3$) δ 234.5 (s, Mo(CO)), 224.4 (s, $Mo(CO)_2$), 175.1 (m, Ir(CO)), 141.9 (s, para), 133.6 (d, $J_{PC} = 12.2$ Hz, ortho), 129.4 (d, $J_{PC} = 12.2$ Hz, meta), 127.8 (d, $J_{PC} = 52.0$ Hz, ipso), 94.9 (d, $J_{PC} = 12.2$ Hz, C_2 of C_5H_4P), 93.1 (d, $J_{PC} = 6.1$ Hz, C_3 of C_5H_4P), 65.9 (d, $J_{PC} = 55.1$ Hz, C_1 of C_5H_4P), 21.2 (s, CH_3), 16.9 (d, $J_{PC} = 33.6$ Hz, $P(CH_3)_3$); ^{31}P NMR (CD_2Cl_2, 0.07 M $Cr(acac)_3$) δ 33.2 (d, $J_{PP} = 334$ Hz, $P(C_6H_4\text{-}p\text{-}CH_3)_2$), −14.9 (d, $J_{PP} = 334$ Hz, $P(CH_3)_3$); IR (THF) 1950 (m), 1929 (s), 1854 (m), 1830 (s) cm^{-1}. Anal. Calcd for $C_{26}H_{27}IrMoO_4P_2$: C, 41.44; H, 3.61. Found: C, 41.56; H, 3.64. MS, *m/e* 756.0077, calcd for $C_{26}H_{27}IrMoO_4P_2$ 756.0071.

***trans*-$\mathbf{P(C_6H_5)_3(CO)\overline{IrMo(CO)_3[\eta^5\text{-}C_5H_4P}(C_6H_4\text{-}\mathit{p}\text{-}CH_3)_2]}$ (10).** A solution of $P(C_6H_5)_3$ (55.8 mg, 0.213 mmol) in THF (10 mL) was slowly added to a solution of **8** (100 mg, 0.142 mmol) in THF (15 mL) at −72 °C. After warming to room temperature the solvent was evaporated on a vacuum line, and the residue was purified by preparative TLC (silica gel, 1:1 Et_2O/hexane) in a glovebox. Vapor diffusion of hexane into a toluene solution gave orange crystals of **10** (99 mg, 74%): mp 218–224 °C dec; ^1H NMR (C_6D_6) δ 8.16 (m, ortho protons of $P(C_6H_5)_3$, 8.04 (dd, $J_{PH} = 11.6$ Hz, $J_{HH} = 8.1$ Hz, ortho protons of $P(C_6H_4\text{-}p\text{-}CH_3)_2$), 7.2 (m, meta and para protons of $P(C_6H_5)_3$), 6.90 (dd, $J_{HH} = 7.9$ Hz, $J_{PH} = 1.8$ Hz, meta protons of $P(C_6H_4\text{-}p\text{-}CH_3)_2$), 4.90 (psuedoquartet, $J \approx 2$ Hz, 2 H of C_5H_4P), 4.71 (pseudoquartet, $J \approx 2$ Hz, 2 H of C_5H_4P), 1.98 (s, CH_3); ^{13}C NMR (CD_2Cl_2, 0.07 M $Cr(acac)_3$) δ 233.6 (s, Mo(CO)), 224.1 (s, $Mo(CO)_2$), 141.8 (s, para carbons of $P(C_6H_4\text{-}p\text{-}CH_3)_2$), 134.7 (d, $J_{PC} = 10.7$ Hz, ortho carbons of $P(C_6H_5)_3$), 133.3 (d, $J_{PC} = 12.2$ Hz, ortho carbons of $P(C_6H_4\text{-}p\text{-}CH_3)_2$), 129.9 (s, para carbons of $P(C_6H_5)_3$), 129.2 (d, $J = 10.7$ Hz, meta carbons of $P(C_6H_4\text{-}p\text{-}CH_3)_2$), 127.7 (d, $J_{PC} = 9.2$ Hz, meta carbons of $P(C_6H_5)_3$), 94.6 (d, $J_{PC} = 12.2$ Hz, C_2 of C_5H_4P), 93.8 (d, $J_{PC} = 7.6$ Hz, C_3 of C_5H_4P), 20.9 (s, CH_3) [other resonances observed in THF-d_8 but not in the spectrum taken in CD_2Cl_2: δ 174.4 (s, Ir (CO)), 64.8 (d, $J_{PC} = 54.0$, C_1 of C_5H_4P), ipso carbons not observed]; ^{31}P (C_6D_6) AB quartet: δ 31.0 ($J_{PP} = 336$ Hz, $P(C_6H_4\text{-}p\text{-}CH_3)_2$), 21.1 ($J_{PP} = 336$ Hz, $P(C_6H_5)_3$); IR (THF) 1958 (m), 1938 (s), 1863 (m), 1834 (s) cm^{-1}. Anal. Calcd for $C_{41}H_{33}IrMoO_4P_2$: C, 52.40; H, 3.54. Found: C, 52.68; H, 3.83.

$\mathbf{H_2(CO)_2\overline{IrMo(CO)_3[\eta^5\text{-}C_5H_4P}(C_6H_4\text{-}\mathit{p}\text{-}CH_3)_2]}$ (**11**) formed rapidly at room temperature but was stable only under a H_2 atmosphere. ^1H NMR (C_6D_6, 500 mm H_2) δ 7.66 (dd, $J_{PH} = 13.5$ Hz, $J_{HH} = 8.4$ Hz, ortho), 7.55 (dd, $J_{PH} = 12.7$ Hz, $J_{HH} = 8.0$ Hz, ortho), 6.80 (dd, $J_{HH} = 8.4$ Hz, $J_{PH} = 2.1$ Hz, meta), 6.50 (dd, $J_{HH} = 8.2$ Hz, $J_{PH} = 2.1$ Hz, meta), 4.79, 4.74, 4.0, 3.89 (m, 1 H each, C_5H_4P), 1.91, 1.89 (s, 3 H each, CH_3), −11.37 (dd, $J_{PH} = 14.8$ Hz, $J_{HH} = 2.6$ Hz, 1 H, hydride), −11.58 (dd, $J_{PH} = 17.2$ Hz, $J_{HH} = 2.6$ Hz, 1 H, hydride); ^{13}C NMR (CD_2Cl_2, 35 °C, 0.07 M $Cr(acac)_3$, 500 mm H_2) δ 225 (v br, $Mo(CO)_3$), 172.4 (s, Ir(CO)), 172.1 (s, Ir(CO)), 142.9 (s, para), 142.6 (s, para), 133.4 (d, $J_{PC} = 15.3$ Hz, ortho), 131.9 (d, $J_{PC} = 15.3$ Hz, ortho), 129.7 (d, $J_{PC} = 12.2$ Hz, meta), 129.3 (d, $J_{PC} = 12.2$ Hz, meta), 126.3 (d, $J_{PC} = 55$ Hz, ipso), 126.2 (d, $J_{PC} = 67$ Hz, ipso), 91.0 (d, $J_{PC} = 6.1$ Hz, (1 C, C_5H_4P), 90.2 (m, 3 C, C_5H_4P), 56.5 (d, $J_{PC} = 67.3$ Hz, C_1 of C_5H_4P), 20.9 (s, CH_3), 21.1 (s, CH_3); ^{31}P NMR (CD_2Cl_2, $Cr(acac)_3$) δ 8.5 (s); IR (THF, 1 atm H_2) 2120 (w, $\nu_{Ir\text{–}H}$), 2059 (s), 2008 (m), 1956 (s), 1896 (m), 1877 (s) cm^{-1}. IR (THF, 1 atm D_2) 2071 (s), 2029 (m), 1961 (s), 1897 (m), 1877 (s); $\nu_{Ir\text{–}D}$ not observed, obscured by other bands.

$\mathbf{H_2(CO)P(CH_3)_3\overline{IrMo(CO)_3[\eta^5\text{-}C_5H_4P}(C_6H_4\text{-}\mathit{p}\text{-}CH_3)_2]}$ (**12**). A solution of **9** (50 mg, 6.6×10^{-5} mol) in 3 mL of toluene was stirred under 1 atm H_2 for 10 min. Hydrogen-saturated hexane (30 mL) was added and the mixture was cooled to −30 °C for 12 h to give a yellow precipitate which was collected, washed with hexane, and dried under vacuum to give **9** (25 mg, 50%): mp 246–248 °C dec; ^1H NMR (C_6D_6) δ 7.88 (dd, $J_{PH} = 12.5$ Hz, $J_{HH} = 8.2$ Hz, ortho), 7.82 (dd, $J_{PH} = 12.0$ Hz, $J_{HH} = 8.2$ Hz, ortho), 6.92 (dd, $J_{HH} = 8.2$ Hz, $J_{PH} = 1.7$ Hz, meta), 6.83 (dd, $J_{HH} = 8.4$ Hz, $J_{PH} = 1.9$ Hz, meta), 4.92 (m, 2 H, C_5H_4P), 4.59 (m, 1 H, C_5H_4P), 4.26 (m, 1 H, C_5H_4P), 1.90 (s, CH_3), 1.95 (s, CH_3), 1.60 (dd, $^2J_{PH} = 10.3$ Hz, $^4J_{PH} = 2.6$ Hz, $P(CH_3)_3$), −10.43 (ddd, $J_{PH} = 21.6$ Hz, $J_{PH} = 15.6$ Hz, $J_{HH} = 3.4$ Hz, 1 H, hydride), −13.81 (ddd, $J_{PH} = 14.6$ Hz, $J_{PH} = 11.0$ Hz, $J_{HH} = 3.4$ Hz, 1 H, hydride); ^{13}C NMR (CD_2Cl_2, 0.07 M $Cr(acac)_3$, 30 °C) δ 229 (br s, $Mo(CO)_3$), 177.6 (m, Ir(CO)), 141.8 (br s, para carbons of both $P(C_6H_4\text{-}p\text{-}CH_3)_2$), 133.7 (d, $J_{PC} = 12.2$ Hz, ortho), 133.1 (d, $J_{PC} = 12.2$ Hz, ortho), 130.3 (s, tentatively assigned as one resonance of an ipso tolyl doublet; the other resonance is obscured by the peaks due to the meta carbons), 129.4 (d, $J_{PC} = 12.2$ Hz, meta), 129.0 (d, $J_{PC} = 12.2$ Hz, meta), 127.7 (s, tentatively assigned as one resonance of an ipso tolyl doublet; the other resonance is obscured by the peaks due to the meta carbons), 92.3 (d, $J_{PC} = 12.2$ Hz, 1 C, C_5H_4P), 91.3 (d, $J_{PC} = 9.2$ Hz, 1 C, C_5H_4P), 90.7 (d, $J_{PC} = 6.1$ Hz, 1 C, C_5H_4P), 90.0 (d, $J_{PC} = 6.1$ Hz, 1 C, C_5H_4P), 61.6 (d, $J_{PC} = 41.9$ Hz, C_1 of C_5H_4P), 22.9 (s, CH_3), 22.2 (s, CH_3), 21.1 (d, $J_{PC} = 6.1$ Hz, $P(CH_3)_3$); ^{31}P NMR (CD_2Cl_2, 0.07 M $Cr(acac)_3$) δ 11.6 (d, $J_{PP} = 208$ Hz, $(C_6H_4\text{-}p\text{-}CH_3)_2PC_5H_4$), −48.9 (d, $J_{PP} = 308$ Hz, $P(CH_3)_3$); IR (THF) 2093 (w, $\nu_{Ir\text{–}H}$), 1981 (w), 1938 (s), 1871 (m), 1844 (m) cm^{-1}. Anal. Calcd for $C_{26}H_{29}IrMoO_4P_2$: C, 41.33; H, 3.87. Found: C, 41.55; H, 4.06. MS, *m/e* 758.0232 (M^+), calcd for $C_{26}H_{29}IrMoO_4P_2$ 758.0227.

IR (THF) of $D_2(CO)P(CH_3)_3\overline{IrMo(CO)_3[\eta^5\text{-}C_5H_4P}(C_6H_4\text{-}p\text{-}CH_3)_2]$ 2006 (m), 1943 (s), 1870 (m), 1846 (m), 1492 (w, $\nu_{Ir\text{–}D}$) cm^{-1}.

$\mathbf{H_2(CO)[P(C_6H_5)_3]\overline{IrMo(CO)_3[\eta^5\text{-}C_5H_4P}(C_6H_4\text{-}\mathit{p}\text{-}CH_3)_2]}$ (**13**). A solution of **10** (50 mg, 5.3×10^{-5} mol) in 2 mL of toluene was stirred under 1 atm H_2 at room temperature for 18 h. Hydrogen-saturated hexane (40 mL) was added and the resulting precipitate was collected, washed with hexane, and sucked dry to give **13** as a yellow powder (36 mg, 71%), mp 175–180 °C dec. The ^1H NMR (C_6D_6) of this powder indicated the presence of a 93:7 mixture of **13** and **10**.

For **13**: ^1H NMR (C_6D_6) δ 7.98 (m, 8 H, ortho protons of $P(C_6H_5)_3$ and ortho protons of one $P(C_6H_4\text{-}p\text{-}CH_3)_2$), 7.83 (dd, 2 H, $J_{PH} = 11.2$ Hz, $J_{HH} = 8.2$ Hz, ortho protons of one $P(C_6H_4\text{-}p\text{-}CH_3)_2$), 7.18–7.02 (m, 9 H, meta and para protons of $P(C_6H_5)_3$), 6.84 (d, 4 H, $J_{HH} = 7.7$ Hz, meta protons of $P(C_6H_4\text{-}p\text{-}CH_3)_2$), 4.85 (m, 2 H, C_5H_4P), 4.68 (m, 1 H, C_5H_4P), 4.40 (m, 1 H, C_5H_4P), 1.95 (s, CH_3), 1.93 (s, CH_3), −10.49 (td, $J_{PH} \approx J_{PH} \approx 17.4$ Hz, $J_{HH} = 3.7$ Hz, 1 H, hydride), −12.93 (ddd, $J_{PH} = 15.6$ Hz, $J_{PH} = 11.3$ Hz, $J_{HH} = 3.7$ Hz, 1 H, hydride): ^{13}C NMR (CD_2Cl_2, 0.07 M $Cr(acac)_3$, 30 °C) δ 229.5 (br m, $Mo(CO)_3$), 177.4 (s, Ir(CO)), 141.8 (s, para, $P(C_6H_4\text{-}p\text{-}CH_3)_2$), 141.6 (s, para, $P(C_6H_4\text{-}p\text{-}CH_3)_2$), 135.0 (dd, $^1J_{PC} = 47.4$ Hz, $^3J_{PC} \sim 7$ Hz, ipso, $P(C_6H_5)_3$), 134.0 (d, $J_{PC} = 9.2$ Hz, ortho, $P(C_6H_5)_3$), 133.4 (d, $J_{PC} = 12.2$ Hz, ortho, $P(C_6H_4\text{-}p\text{-}CH_3)_2$), 131.8 (d, $J_{PC} = 12.2$ Hz, ortho, $P(C_6H_4\text{-}p\text{-}CH_3)_2$), 130.0 (s, para, $P(C_6H_5)_3$), 129.3 (d, $J_{PC} = 9.2$ Hz, meta, $P(C_6H_4\text{-}p\text{-}CH_3)_2$), 129.0 (d, $J_{PC} = 9.2$ Hz, meta, $P(C_6H_4\text{-}p\text{-}CH_3)_2$), 127.7 (d, $J_{PC} = 6.1$ Hz, meta, $P(C_6H_5)_3$), 92.1 (d, $J_{PC} = 9.2$ Hz, 1 C, C_5H_4P), 91.8 (d, $J_{PC} = 12.2$ Hz, 1 C, C_5H_4P), 90.7 (d, $J_{PC} = 6.1$ Hz, 1 C, C_5H_4P), 89.6 (d, $J_{PC} = 6.1$ Hz, 1 C, C_5H_4P), 59.6 (d, $J_{PC} = 64.2$ Hz, C_1 of C_5H_4P), 21.0 (s, CH_3), ipso carbons of $P(C_6H_4\text{-}p\text{-}CH_3)_2$ not observed. At −30 °C the Mo carbonyls appeared as three equal intensity singlets at δ 233.9, 227.6, and 224.9 ^{31}P NMR (CD_2Cl_2, 0.07 M $Cr(acac)_3$) AB quartet, δ 14.0 ($J_{PP} = 312$ Hz, $P(C_6H_5)_3$), 9.0 ($J_{PP} = 312$ Hz, $(C_6H_4\text{-}p\text{-}CH_3)_2PC_5H_4$); IR (THF) 2100 (w, ν_{Ir-H}), 1992 (m), 1941 (s), 1874 (m), 1853 (m) cm^{-1}. IR (THF) of $D_2(CO)[P(C_6H_5)_3]IrMo(CO)_3\text{-}[\eta^5\text{-}C_5H_4P(C_6H_4\text{-}p\text{-}CH_3)_2]$ 2015 (m), 1946 (s), 1876 (m), 1852 (m), 1497 (w, ν_{Ir-D}) cm^{-1}.

High-Pressure Reactions. All high-pressure reactions were performed in a 22-mL stainless steel Parr bomb. Solvents, substrates, and organometallic compounds were added to the bomb in an inert atmosphere glovebox. The bomb was surrounded by an aluminum heating block that was maintained at constant temperature by remote control. Samples of the reaction solution were obtained by cooling the bomb to −196 °C (to avoid loss of solvent), releasing the pressure, and taking the bomb into the glovebox where it was opened. Samples of the solution were then removed and analyzed by IR spectroscopy.

Attempted Cyclohexene Hydrogenation. Samples from attempted hydrogenation of cyclohexene were removed from the bomb as described above and bulb-to-bulb distilled on a vacuum line to separate nonvolatile materials. The solution was analyzed by gas chromatography on a 20 ft × $^1/_8$ in 20% UCON-50-HB-280X column at 155 °C.

Attempted CO Reduction Experiments. In order to analyze for formation of methane as a CO reduction product, the outlet of the bomb was connected to an evacuated vacuum line via copper tubing. The bomb was cooled to −78 °C, and the gases in the bomb were allowed to expand into the vacuum line; samples were removed by syringe and analyzed by gas chromatography. A 10 ft × $^1/_8$ in Poropak Q column at room temperature was used for CH_4 analysis. The bomb was then taken into the glovebox, and samples were removed for IR spectroscopy and for analysis for CH_3OH by gas chromatography. A 20 ft × $^1/_8$ in 20% UCON-50-HB-280X column at 135 °C was used for methanol analysis. The sample was bulb-to-bulb distilled on a vacuum line and analyzed by gas chromatography for CH_3OH. When toluene was used as a solvent, it was extracted with 0.20–0.25 mL of H_2O to concentrate any CH_3OH which might have formed, and this aqueous solution was also analyzed for CH_3OH by gas chromatography. Detection limits were 5% for CH_3OH and 1% for CH_4.

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Registry No. 1, 83334-37-6; **2**, 87801-08-9; **3**, 87828-72-6; **4**, 87801-09-0; **5**, 87801-10-3; **6**, 87801-11-4; **7**, 87801-12-5; **8**, 87801-13-6; **9**, 87801-14-7; **10**, 87801-15-8; **11**, 87801-16-9; **11**-d_2, 87801-21-6; **12**, 87801-17-0; **12**-d_2, 87801-22-7; **13**, 87801-18-1; **13**-d_2, 87801-23-8; $[(C_6H_4\text{-}p\text{-}CH_3)_2PCH_2]_2$, 70320-30-8; $LiP(C_6H_4\text{-}p\text{-}CH_3)_2$, 39952-43-7; $[(C_2H_4)_2RhCl]_2$, 12081-16-2; $[(CO)_2RhCl]_2$, 14523-22-9; $Mo(CO)_6$, 13939-06-5; $LiC_5(CH_3)_4P(C_6H_4\text{-}p\text{-}CH_3)_2Mo(CO)_5$, 87801-19-2; $Li(CO)_3MoC_5(CH_3)_4P(C_6H_4\text{-}p\text{-}CH_3)_2$, 87801-20-5; $(CO)_2IrCl(H_2NC_6H_4\text{-}p\text{-}CH_3)$, 14243-22-2; di-*p*-tolylchlorophosphine, 1019-71-2; 1,2-dichloroethane, 107-06-2; lithium 1-(di-*p*-tolylphosphino)-2,3,4,5-tetramethylcyclopentadienide, 87781-75-7; 1,2,3,4-tetramethylcyclopentadiene, 4249-10-9; lithium tetranaphthylcyclopentadienide, 87781-76-8; 1-(di-*p*-tolylphosphino)-2,3,4,5-tetramethylcyclopentadiene, 87781-77-9; cyclohexene, 110-83-8.

A Reversible Chemical Reaction in a Single Crystal. The Dimerization of $(\eta^5\text{-}C_5H_5)Co(S_2C_6H_4)$

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Abstract: A reversible single-crystal chemical reaction was discovered to occur when a crystal of cyclopentadienyl(*o*-dithiobenzene)cobalt, I, converts at room temperature to produce a crystal of the dimer, II. Compound II reverts to I at 150 °C with retention of crystallinity. Dissolution of II in noncomplexing solvents also yields I. The structures of I and II were determined by single-crystal X-ray crystallography. I crystallizes in the space group $P2_1/c$ (No. 14), $a = 15.040$ (2) Å, $b = 9.315$ (1) Å, $c = 16.429$ (3) Å, $\beta = 110.27$ (1)°, $Z = 8$, and $R = 0.060$. Compound II crystallizes in the space group $P2_1/c$, $a = 9.243$ (2) Å, $b = 11.362$ (2) Å, $c = 10.422$ (2) Å, $\beta = 112.51$ (2)°, $Z = 2$, and $R = 0.042$. Covalent Co–S bonds bridge the metal centers in II. However, differential scanning calorimetry measurements reveal that $\Delta H = 18.9$ kJ mol^{-1} for II → I, which suggests that the crystal packing and molecular deformation forces delicately balance the bridging Co–S bond energies in II.

Authentic examples of *reversible* chemical reactions occurring in a single crystal are sublimely rare. Chemical reactions in the solid state almost always consist of irreversible changes, such as polymerization[1–4] or thermal decomposition.[5–8] Another type of solid-state event, the reconstructive solid-phase–solid-phase transformation, generally results from a physical change in the

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(1) Elgavi, A.; Green, B. S.; Schmidt, G. M. J. *J. Am. Chem. Soc.* **1973**, *95*, 2058–9.

(2) Cohen, M. J.; Garito, A. F.; Heeger, A. J.; MacDiarmid, A. G.; Mikulski, C. M.; Saran, M. S.; Kleppinger, J. *J, Am. Chem. Soc.* **1976**, *98*, 3844–48.

(3) Nakaniski, H.; Jones, W.; Thomas, J. M. *Chem. Phys. Lett.* **1980**, *71*, 44–48.

(4) For review, see Gavezzotti, A.; Simonetta, M.; *Chem. Rev.* **1982**, *82*, 1–13.

(5) Paul, I. C.; Curtin, D. Y. *Acc. Chem. Res.* **1973**, *6*, 217–225.

(6) Dubovitskii, F. I.; Korsunskii, B. L. *Russ. Chem. Rev.* (*Engl. Transl.*) **1981**, *50*, 958–978.

0002-7863/83/1505-7580$01.50/0