

# Heterobimetallic Compounds Linked by Heterodifunctional Ligands

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The chill of the oil crisis in the mid-1970s brought about renewed interest in the Fischer-Tropsch process for converting coal via CO and H<sub>2</sub> into chemicals and hydrocarbon fuels. The organometallic community responded with fundamental studies of postulated intermediates in metal-catalyzed CO reduction. Syntheses of metal-formyl complexes (M-CO-H), of hydroxymethyl-metal compounds (M-CH<sub>2</sub>OH), and of di- and polynuclear compounds with bridging hydrocarbon ligands gave new insight into the basic chemistry involved in CO reduction. Reinvestigations of homogeneous and heterogeneous CO hydrogenation catalysts also provided better understanding of these CO reduction processes. Yet the basic problem of finding an efficient and selective CO hydrogenation catalyst remained. It was becoming clear that totally new kinds of catalysts would be required for a significant breakthrough.

We felt that heterobimetallic complexes offered a unique opportunity for development of powerful new catalysts for CO reduction. Therefore, several years ago we set as one of our long-range goals the synthesis of a heterobimetallic dihydride with one hydridic M-H bond to an early transition metal (Ti, Zr, Nb, etc.), one acidic M-H bond to a late transition metal (Co, Ru, Rh, etc.), and a heterodifunctional ligand joining the two metals. We believe that such compounds will be powerful reducing agents for polar molecules, including CO.

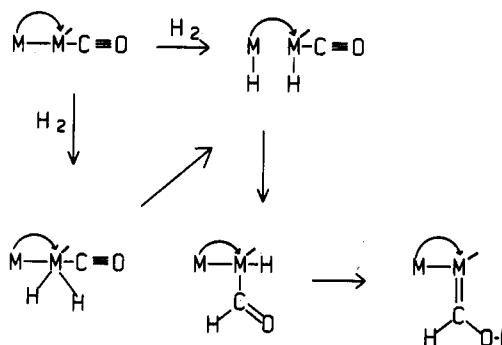
Early transition metal hydrides are known to be good donors of hydride anion to coordinated CO. For example, Labinger has demonstrated that (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>NbH<sub>3</sub> reacts with Fe(CO)<sub>5</sub> to produce an unstable formyl complex,<sup>1</sup> and Bercaw has shown that (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ZrH<sub>2</sub> reacts with metal carbonyls such as (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>WCO to produce formyl compounds with zirconium bonded to the formyl oxygen.<sup>2</sup>

Hydride donation is a necessary but not sufficient condition to reduce coordinated CO because the anionic formyl complexes generated by hydride addition are resistant to further reduction by hydride anion sources. To continue the reduction of the formyl ligand, an acid

source is required. For example, addition of acid to the iron-formyl complex [(RO)<sub>3</sub>P](CO)<sub>3</sub>Fe(CHO)<sup>-</sup> results in methanol formation.<sup>3</sup> Apparently, protonation of the formyl oxygen produces a hydroxy-carbene complex that is easily reduced by the much less potent hydride donor—a second molecule of the formyl complex. Late transition metal hydrides are moderately acidic (the pK<sub>a</sub> of (CO)<sub>4</sub>CoH is 8.3 and of (CO)<sub>5</sub>MnH is 15.1 in acetonitrile)<sup>4</sup> and are targeted as proton donors necessary for multiple hydride donation to coordinated CO.

The role envisioned for the heterodifunctional ligand joining the two metals is twofold. First, the heterodifunctional ligand can be independently optimized for the early and late transition metal centers. Second, linking the two metal centers through a bridging ligand system maximizes the opportunity for the resulting metal hydrides to act cooperatively to reduce polar molecules.

We hoped to obtain heterobimetallic hydrides by addition of H<sub>2</sub> to a metal-metal bonded system. The



compatibility of a hydridic and an acidic metal hydride is a potential problem since H<sub>2</sub> evolution might be expected; optimistically, this can be viewed as the microscopic reverse of the desired reaction of H<sub>2</sub> with a metal-metal bond. It is more important that this reaction be facile than that the equilibrium lie far on the side of the heterobimetallic dihydride. Two possible routes from a metal-metal bonded heterobimetallic compound to the related dihydride are (1) direct cleavage of the metal-metal bond by H<sub>2</sub> and (2) oxidative addition of H<sub>2</sub> to one metal center followed by

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(2) Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* 1979, 101, 218-220.

(3) Casey, C. P.; Neumann, S. M. *Adv. Chem. Ser.* 1979, No. 173, 131-139.

(4) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* 1986, 108, 2257-2263.

R. Morris Bullock was born in Greensboro, NC, in 1957. After receiving his B.S. from the University of North Carolina at Chapel Hill in 1979, he joined C. P. Casey's group at the University of Wisconsin and completed his Ph.D. in 1984. After time as a postdoc with J. R. Norton at Colorado State University, he joined the scientific staff at Brookhaven National Laboratory in 1985 where his research involves reactions of metal hydrides with unsaturated substrates.

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metal hydride elimination.

We have taken a two-pronged approach to the synthesis of early-late heterobimetallic dihydrides linked by a heterodifunctional ligand. Since synthetic methods for the preparation of the desired precursors with directly bonded early and late transition metals are just beginning to be developed, our initial approach has centered on making bimetallic compounds linked by a heterodifunctional ligand but having directly bonded metals with smaller electronegativity differences. This Account describes our synthesis of some complexes of this type and their reactions with  $H_2$ . In a second line of research, which will be touched on only briefly in this Account, we have developed routes into bimetallic compounds with directly bonded early and late transition metals. Initially, no effort was made to link these metals by a heterodifunctional ligand.

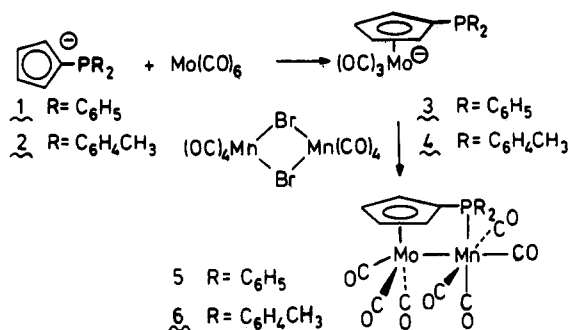
### Mo-Mn Complexes Linked by a (Diarylphosphino)cyclopentadienyl Ligand

A heterodifunctional ligand is one in which two different ligands ( $\eta^5$ -cyclopentadienyl,  $\eta^6$ -arene, phosphine, arsine, nitrogen ligand, sulfur ligand) are joined together to form a new ligand capable of simultaneously bonding to two metals. Part of the reason for the difficulty in designing successful syntheses of these heterobimetallic complexes is the problem of attaching the first metal to one site of the heterodifunctional ligand while keeping the other site of the ligand inert to complexation until the second metal is introduced.

Our work has centered upon the use of a heterodifunctional ligand containing a cyclopentadienyl anion bonded to a diarylphosphine. The cyclopentadienyl group is an excellent ligand for an early transition metal, while the phosphine is an excellent ligand for a late transition metal. Deprotonation of 1-(diphenylphosphino)cyclopentadiene with *n*-butyllithium gave lithium (diphenylphosphino)cyclopentadienide, **1**, which can be isolated and stored indefinitely in the absence of air and moisture.<sup>5</sup> We used **1** in our initial studies but later turned to the use of the analogous *p*-tolyl compound **2** which offers the advantage of simplified  $^1H$  NMR spectra. The methyl group of the *p*-tolyl unit serves as a useful marker, and the aromatic resonances appear as a resolved pattern.

In our synthetic scheme, we initially attached the cyclopentadienyl ligand to a metal center and then introduced the second metal. Reaction of **1** with  $Mo(CO)_6$  in refluxing THF produced the cyclopentadienyl-molybdenum compound **3** as the predominant product.<sup>5</sup> We were unable to obtain completely pure samples of **3**; spectroscopic evidence indicated that **3** was typically 85–90% pure. The major impurity appeared to be  $(CO)_5MoPPh_2(C_5H_4)^-$ , with the phosphine portion (instead of the cyclopentadienyl) of **1** bonded to molybdenum.

Molybdenum anion **3** can be viewed as a difunctional chelate ligand, with phosphine and metal anion donor groups. We anticipated that the reaction of **3** with halogen-bridged metal dimers would provide a versatile synthetic route to a variety of heterobimetallic compounds linked by the (diarylphosphino)cyclopentadienyl ligand. The reaction of **3** with  $[(CO)_4Mn-$



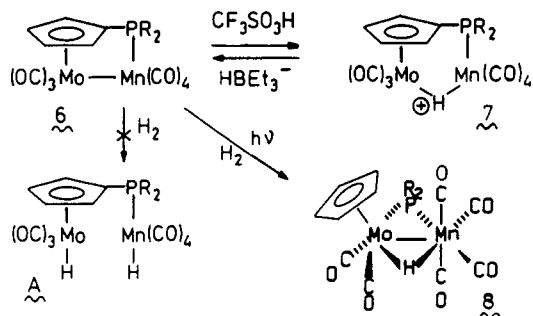
$Br]_2$  gave the Mo-Mn complex **5**.<sup>1</sup> The  $^{13}C$  NMR spectrum of **5** was particularly useful in structure elucidation. As expected, the molybdenum carbonyls appeared as two singlets in a 1:2 ratio in the  $^{13}C$  NMR at room temperature, whereas the manganese carbonyls gave rise to a  $^{55}Mn$  quadrupole broadened resonance. In the  $^{13}C$  NMR of **5** at  $-40^\circ C$ , "thermal decoupling" of the  $^{55}Mn$  quadrupole resulted in the appearance of three peaks in a 1:1:2 intensity ratio, in agreement with the proposed structure. An unusual feature of the  $^{13}C$  NMR spectrum was that the cyclopentadienyl carbon atom bonded to phosphorus appeared as a doublet ( $J = 51.3$  Hz) at  $\delta$  57.8. The normal position for the resonance of a cyclopentadienyl ring bonded to a transition metal is about  $\delta$  90; the dramatic upfield shift observed is probably related to the fact that this carbon is held directly above the Mo-Mn bond. While the spectroscopic data established the overall structure, the crystal structure of **5** was determined in collaboration with Rheingold and Fultz at the University of Delaware to examine distortions caused by the heterodifunctional ligand.<sup>5</sup> The ring system consisting of the two metals and the heterodifunctional ligand is somewhat strained. The most notable distortion is that the phosphorus atom is bent down 0.42 Å from the plane of the cyclopentadienyl ring toward manganese. Additionally, the P-Mn-Mo angle is contracted to  $77.3^\circ$  from the  $90^\circ$  expected for idealized octahedral geometry at manganese.

In an effort to observe formation of a heterobimetallic dihydride, molybdenum-manganese compound **5** was placed under high pressures of hydrogen. Initial experiments were carried out by heating solutions of **5** under hydrogen to successively higher temperatures, cooling the solutions under hydrogen, and examining the IR spectra at room temperature. No evidence for any reaction with  $H_2$  was detected. However, since it was possible that any dihydride such as **A** which was formed under high pressure might reductively eliminate hydrogen when the pressure was lowered, the behavior of **5** under high pressure of  $H_2$  was examined directly by high-pressure IR spectroscopy with the help of Stan Polichnowski and Norma Lafferty at Tennessee Eastman. No change in the IR spectrum of **5** was observed upon heating at  $145^\circ C$  under 1200 psi of  $H_2$ , and higher temperatures caused slow decomposition.<sup>5</sup>

Since we were unable to prepare the desired heterobimetallic dihydride **A** by reaction with  $H_2$ , we next attempted to synthesize it by treatment of the *p*-tolyl substituted molybdenum-manganese compound **6** with acid, followed by a hydride donor.<sup>6</sup> Addition of  $CF_3SO_3H$  to a solution of **6** resulted in the appearance of

(5) Casey, C. P.; Bullock, R. M.; Fultz, W. C.; Rheingold, A. L. *Organometallics* 1982, 1, 1591–1596.

(6) Casey, C. P.; Bullock, R. M. *J. Organomet. Chem.* 1983, 251, 245–248.



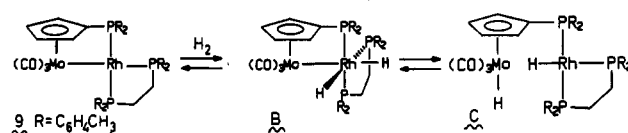
a peak at  $\delta -19.2$  in the  $^1\text{H}$  NMR spectrum, characteristic of a bridging metal hydride. Further evidence for formation of the cationic bridging hydride complex 7 was the observation that the metal carbonyl stretching frequencies moved to higher energy. The position of the  $^{13}\text{C}$  NMR resonance for the cyclopentadienyl carbon bonded to phosphorus moved downfield by over 20 ppm when 6 was protonated to form the cationic monohydride 7. This may reflect a relief of strain in the heterodifunctional ligand connecting the two metals upon protonation of 6. Reactions of the cationic monohydride 7 with hydride donors such as  $\text{HBEt}_3^-$  failed to produce the neutral heterobimetallic dihydride A by addition of  $\text{H}^-$ . Instead, 7 was simply deprotonated to regenerate 6.

In another attempt to prepare molybdenum–manganese dihydride A, 6 was photolyzed under an atmosphere of  $\text{H}_2$ . No evidence for the formation of dihydride A was seen. Instead, a novel reaction occurred in which the phosphorus–cyclopentadienyl bond of 6 was cleaved and the molybdenum–manganese bridging hydride complex 8 was formed.<sup>7</sup> The X-ray crystal structure of 5 indicated that the bridging heterodifunctional ligand system was somewhat strained, and it is this strained system that is broken up in the photochemical reaction. If such cleavage reactions turn out to be facile, then the use of bimetallic complexes possessing the  $\text{C}_5\text{H}_4\text{PR}_2$  ligand in catalysis may be limited. Mays<sup>8</sup> subsequently reported the X-ray structure of a closely related compound which was obtained from photolysis of  $\text{HPPH}_2$  and  $(\text{C}_5\text{H}_5)(\text{CO})_3\text{MoMn}(\text{CO})_5$ .

### Rh–Mo Complexes Linked by a (Diarylphosphino)cyclopentadienyl Ligand

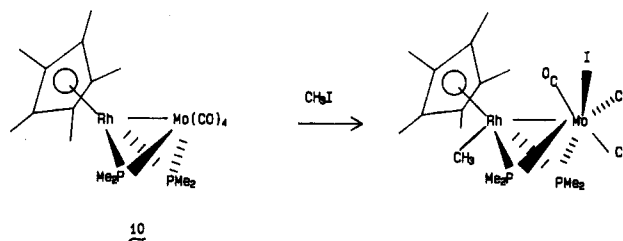
The failure of manganese–molybdenum compound 5 to react with  $\text{H}_2$  is probably traceable to the fact that it is coordinatively saturated; it would have to undergo ligand loss or metal–metal bond rupture in order to react with hydrogen. We therefore directed our efforts toward the preparation of new compounds containing a metal capable of undergoing facile oxidative addition of  $\text{H}_2$  without prior ligand loss. A Rh(I) derivative was chosen as the initial candidate for this purpose, since there are numerous examples of Rh(I) compounds that oxidatively add  $\text{H}_2$ . As shown below, our intent was to form a dihydride such as B by oxidative addition of  $\text{H}_2$  to Rh(I), followed by elimination of a molybdenum hydride to yield a compound such as C in which a rhodium hydride and a molybdenum hydride were linked solely by the heterodifunctional ligand.

Reaction of the molybdenum–phosphine anion 4 with the chlorine-bridged rhodium dimer  $\{[(\text{C}_6\text{H}_4\text{-p-}$

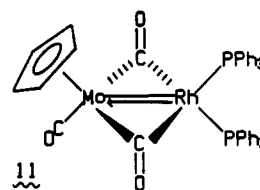


$\text{CH}_3)_2\text{PCH}_2)_2\text{RhCl}]_2$  gave Rh–Mo compound 9.<sup>9</sup> The IR spectrum of 9 exhibited metal carbonyl bands at 1922, 1841, and 1801  $\text{cm}^{-1}$ . The band at 1801  $\text{cm}^{-1}$  is surprisingly low in energy for a terminal carbonyl and is of similar energy so that observed for bridging carbonyls. However, in the  $^{13}\text{C}$  NMR spectrum of 8, the resonances of the molybdenum carbonyls are similar to those observed in 5, for which the X-ray crystal structure conclusively indicates that no bridging carbonyls are present. Furthermore, the absence of coupling between the  $^{103}\text{Rh}$  and  $^{13}\text{C}$  demonstrates that the molybdenum carbonyls do not interact appreciably with rhodium. The low-energy IR carbonyl stretches of 9 are probably a result of a highly polarized  $\delta^+\text{Rh}-\text{Mo}^\delta-$  bond. As better electron donors are placed on Rh, the metal–metal bond becomes more polarized, and the  $\text{Mo}(\text{C}-\text{O})_3$  stretches move to lower energy.

Finke prepared compound 10, which also has a polar Rh–Mo bond.<sup>10</sup>  $\text{CH}_3\text{I}$  adds across the polar Rh–Mo bond of 10 to produce an addition compound.<sup>11</sup>



Another heterobimetallic compound with a polar Rh–Mo bond was reported by Carlton.<sup>12</sup> In the absence of a heterodifunctional ligand linking Mo and Rh, the reaction of  $\text{Na}^+(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3^-$  with  $\text{RhCl}(\text{PPh}_3)_3$  produced compound 11, which has a metal–metal dou-



ble bond and two bridging carbonyl ligands. The formation of 11 might have resulted from loss of  $\text{PPh}_3$  from an initially formed  $(\text{C}_5\text{H}_5)(\text{CO})_3\text{Mo}-\text{Rh}(\text{PPh}_3)_3$  intermediate. The main difference between this proposed intermediate and our Mo–Rh compound 9 is that all of the phosphines in 9 are part of a chelating ligand arrangement which would be expected to retard loss of a phosphine. Examination of the X-ray crystal structure of 11 indicates it would be impossible to form a similar compound with a heterodifunctional cyclopentadienylphosphine ligand joining Mo and Rh. A

(9) Casey, C. P.; Bullock, R. M.; Nief, F. J. *Am. Chem. Soc.* **1983**, *105*, 7574–7580.

(10) Finke, R. G.; Gaughan, G.; Pierpont, C.; Cass, M. E. *J. Am. Chem. Soc.* **1981**, *103*, 1394–1399.

(11) Finke, R. G.; Gaughan, G.; Pierpont, C.; Noordik, J. H. *Organometallics* **1983**, *2*, 1481–1483.

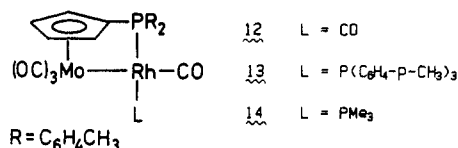
(12) Carlton, L.; Lindsell, W. E.; McCullough, K. J.; Preston, P. N. *J. Chem. Soc., Chem. Commun.* **1982**, 1001–1003.

(7) Casey, C. P.; Bullock, R. M. *Organometallics* **1984**, *3*, 1100–1104.

(8) Horton, A. D.; Mays, M. J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1985**, 247–250.

structure similar to 11 in which the cyclopentadienylphosphine is bonded only to Mo is possible, but it appears that the tendency of the cyclopentadienylphosphine ligand to bridge the two metals is greater than the tendency to form structures such as 11.

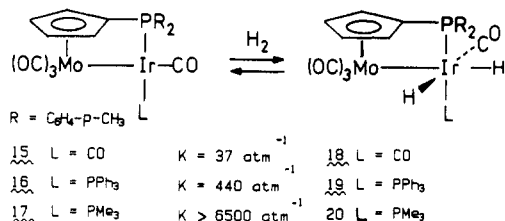
Reaction of molybdenum anion 4 with  $[(\text{CO})_2\text{RhCl}]_2$  produced compound 12 with two carbonyl ligands on rhodium; the carbonyl trans to the phosphine of the cyclopentadienylphosphine was readily displaced by  $\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-CH}_3)_3$  or  $\text{P}(\text{CH}_3)_3$  to give 13 and 14, respectively.<sup>9</sup> None of these four Rh–Mo compounds (9, 12,



13, 14) reacted with  $\text{H}_2$  to form observable dihydrides, even under forcing conditions of high pressures and temperatures. It is not clear whether kinetic or thermodynamic factors are responsible for the failure to observe oxidative addition of  $\text{H}_2$  to the 16-electron Rh(I) centers in these compounds. They may be reacting rapidly and reversibly with  $\text{H}_2$  to form thermodynamically unstable dihydrides. Molybdenum is apparently acting as a strong electron-withdrawing group which inhibits oxidative addition to Rh(I).

#### Ir–Mo Complexes Linked by a (Diarylphosphino)cyclopentadienyl Ligand

Since third-row transition metals usually form stronger bonds to hydrogen than their second-row counterparts and since oxidative addition of  $\text{H}_2$  to Ir(I) is more favorable than to Rh(I),<sup>13</sup> we decided to prepare Ir–Mo compounds and investigate their reactivity with  $\text{H}_2$ . Attempted syntheses of Ir–Mo compounds from chlorine-bridged iridium dimers were unsuccessful. However, we found that a mononuclear iridium precursor,  $(\text{CO})_2\text{IrCl}(\text{H}_2\text{NC}_6\text{H}_4\text{-}p\text{-CH}_3)$ , reacted with molybdenum–phosphine anion 4 to generate Ir–Mo compound 15.<sup>9</sup> The iridium carbonyl trans to the phosphine of the heterodifunctional ligand was readily replaced by  $\text{P}(\text{C}_6\text{H}_5)_3$  or  $\text{P}(\text{CH}_3)_3$  to give the phosphine substitution products 16 and 17.



In contrast to the forcing conditions used in the attempted addition of  $\text{H}_2$  to the Rh–Mo compounds, all three Ir–Mo compounds reacted with  $\text{H}_2$  to form dihydrides 18, 19, and 20.<sup>9</sup> Although all three of the iridium dihydrides were formed under mild conditions (1 atm of  $\text{H}_2$ , room temperature), their rates of formation differed significantly. The dicarbonyliridium compound 15 and the trimethylphosphine substituted compound 17 were converted to dihydrides 18 and 20 within minutes at room temperature. In contrast, the

triphenylphosphine substituted compound 16 reacted slowly with  $\text{H}_2$  (400-mm pressure) to form dihydride 19 with a half-life of about 30 min. The slower rate of reaction of triphenylphosphine substituted 16 with  $\text{H}_2$  must be due to steric retardation since the rate is substantially slower than that of either 17, which has a better electron donor  $\text{P}(\text{CH}_3)_3$  ligand on Ir, or 15, which has a better acceptor CO ligand in place of  $\text{P}(\text{C}_6\text{H}_5)_3$ .

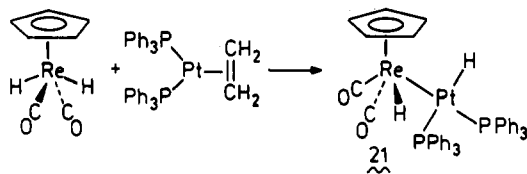
In contrast to steric control of the rates of formation of the dihydrides, electronic effects have a dominant influence on the equilibrium constants for formation of the dihydrides. Better donor ligands on iridium stabilized the products of oxidative addition of  $\text{H}_2$ .<sup>9</sup> A lower limit of  $K_{\text{eq}} > 6500 \text{ atm}^{-1}$  was determined for the addition of  $\text{H}_2$  to the  $\text{PMe}_3$  substituted iridium complex 17. Smaller equilibrium constants were seen for addition of  $\text{H}_2$  to complexes with weaker donor ligands:  $K_{\text{eq}} = 440 \text{ atm}^{-1}$  for the  $\text{PPh}_3$  substituted complex 16 and  $K_{\text{eq}} = 37 \text{ atm}^{-1}$  for the CO substituted complex 15. The high thermodynamic stability of the  $\text{PMe}_3$  substituted dihydride 20 allowed its isolation as an analytically pure solid. The somewhat less stable  $\text{PPh}_3$  substituted dihydride 19 could only be obtained as a mixture contaminated with starting material 16. The addition of  $\text{H}_2$  to CO substituted complex 15 was so readily reversible that attempted isolation of dihydride adduct 18 led only to reisolation of starting material 15.

While we have succeeded in adding  $\text{H}_2$  to one of the metal centers of a heterobimetallic compound linked by a heterodifunctional ligand, we failed to observe reductive elimination of a metal hydride from the  $\text{M}'\text{-MH}_2$  species which would have produced two metal hydrides linked by a heterodifunctional ligand. In the cases of the Mo–IrH<sub>2</sub> compounds 18, 19, and 20, the failure to see reductive elimination of MoH might be due to 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 a metal hydride would produce a more stable heterobimetallic dihydride, we plan to investigate W–Rh and W–Ir compounds similar to the Mo–Ir compounds discussed here. Even though initial  $\text{H}_2$  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. The net reaction would be cleavage of a metal–metal bond and formation of a third-row and a second-row metal hydride. An even more favorable net reaction would involve cleavage of a W–Ir bond to form two strong third-row metal–hydrogen bonds.

A more fundamental question is whether the elimination of a metal hydride from a  $\text{M}'\text{-MH}_2$  system is thermodynamically feasible since this transformation always involves a net loss of the  $\text{M-M}'$  bond. In an attempt to probe this question, we have begun studies of the reactions of metal hydrides with coordinatively unsaturated metals. Recently, we succeeded in adding  $(\text{C}_5\text{H}_5)(\text{CO})_2\text{ReH}_2$  to  $\text{Pt}(\text{PPh}_3)_2(\text{CH}_2=\text{CH}_2)$  to produce the heterobimetallic dihydride 21.<sup>14</sup> Earlier, Janowicz at du Pont discovered a similar addition of  $(\text{C}_5\text{H}_5)(\text{CO})_3\text{MoH}$  to  $\text{Pt}(\text{PPh}_3)_2(\text{CH}_2=\text{CH}_2)$ .<sup>15</sup>

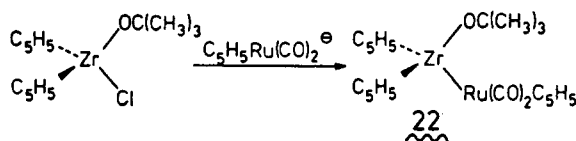
(13) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980; pp 210–212.

(14) Casey, C. P.; Rutter, E. W., unpublished results.



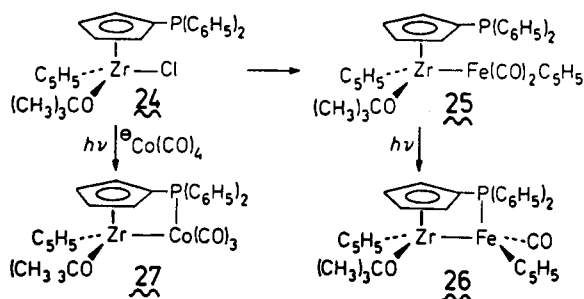
### Early-Late Complexes Linked by a (Diarylphosphino)cyclopentadienyl Ligand

Having established the use of the (diarylphosphino)cyclopentadienyl ligand in the synthesis of the Mo-Mn, Mo-Rh, and Mo-Ir compounds, we were ready to use the ligand to join early and late transition metals in the same molecule. This became possible because Richard Jordan in our group had discovered that stable metal-metal bonded Zr-Fe and Zr-Ru compounds could be readily synthesized.<sup>16</sup> For example, reaction of  $(C_5H_5)_2Zr(OCMe_3)Cl$  with  $K^+(C_5H_5)(CO)_2Ru^-$  produced  $(C_5H_5)_2(Me_3CO)Zr-Ru(CO)_2(C_5H_5)$ , **22**.



Francois Nief in our group combined the use of the heterodifunctional  $C_5H_4PPh_2$  ligand and the Zr-Fe bond-forming chemistry in the synthesis of Zr-Fe and Zr-Co compounds linked by a heterodifunctional ligand and by an early-late transition metal bond.<sup>17</sup>

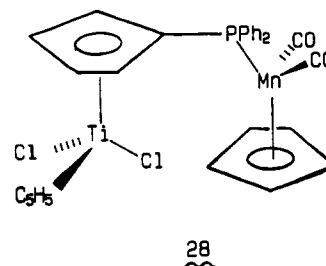
Reaction of (diphenylphosphino)cyclopentadienide **1** with  $(C_5H_5)ZrCl_2 \cdot 2THF$  gave  $(\eta^5-C_5H_4PPh_2)(C_5H_5)ZrCl_2$ , **23**. Potassium *tert*-butoxide was employed to displace one chloride from zirconium to produce  $(\eta^5-C_5H_4PPh_2)(C_5H_5)Zr(OCMe_3)Cl$ , **24**.<sup>17</sup> Reaction of **24**



with  $K^+(C_5H_5)Fe(CO)_2^-$  gave compound **25**, which has a Zr-Fe bond but no bond between the phosphine and Fe. Photolysis of **25** led to expulsion of one carbonyl and bonding of the phosphine to Fe in **26**. Both Zr and Fe are stereocenters in **26**, and separate resonances were seen for all four protons on the  $C_5H_4PPh_2$  ligand. Although there are two possible diastereomers for **26**, only a single isomer was observed, and molecular models suggest the configuration drawn for **26** would be less crowded.

No reaction was observed between **24** and  $Na^+Co(CO)_4^-$  until the solution was photolyzed; this led to loss of one CO from cobalt and formation of Zr-Co bonded compound **27**.<sup>17</sup> Compounds **26** and **27** are the first examples of bimetallic compounds in which a group 4

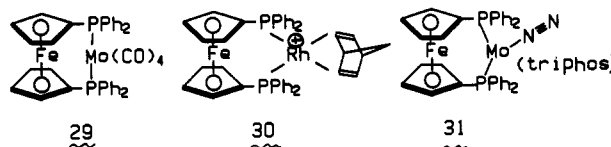
metal and a late transition metal are joined by both a direct metal-metal bond and a heterodifunctional ligand. Earlier, Rausch had reported the synthesis of the Ti-Mn compound **28** in which the early and late transition metal were linked only by the (diphenylphosphino)cyclopentadienyl ligand and not by a metal-metal bond.<sup>18</sup>



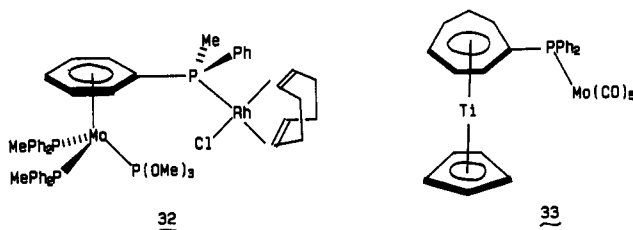
### Related Work on Heterodifunctional Ligands

Many other research groups are also actively pursuing the synthesis of heterobimetallic compounds linked by heterodifunctional ligands. Some of their fascinating new systems will be mentioned here to put our own work into perspective.

Early work involved compounds in which the metal centers were linked by one or more heterodifunctional ligands but not by a metal-metal bond. Davison pioneered work on the use of (diphenylphosphino)cyclopentadienyl ligands and synthesized 1,1'-bis(diphenylphosphino)ferrocene as a bidentate chelating ligand for preparing heterobimetallic complexes such as Fe-Mo compounds **29**.<sup>19</sup> Subsequently, Cullen employed 1,1'-bis(diphenylphosphino)ferrocene as a chelating ligand to make the Fe-Rh compound **30**, which acts as a hydrogenation catalyst.<sup>20</sup> George and Tisdale found that use of 1,1'-bis(diphenylphosphino)ferrocene as a chelating ligand on molybdenum-dinitrogen complex **31** led to improved yields of  $NH_3$  upon treatment with  $HBr$ .<sup>21</sup>



Heterodifunctional ligands in which phosphorus is directly attached to six- and seven-membered aromatic rings were used by Luck and Morris<sup>22</sup> to link Mo and Rh in **32** and by Dixneuf<sup>23</sup> to link Ti and Mo in **33**.



(18) Rausch, M. D.; Edwards, B. H.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 3882-3886.

(19) Rudie, A. W.; Lichtenberg, D. W.; Katcher, M. L.; Davison, A. *Inorg. Chem.* **1978**, *17*, 2859-2863.

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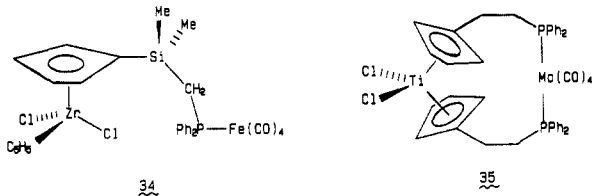
(22) Luck, R.; Morris, R. H. *J. Organomet. Chem.* **1983**, *255*, 221-230.

(15) Janowicz, A., private communication.

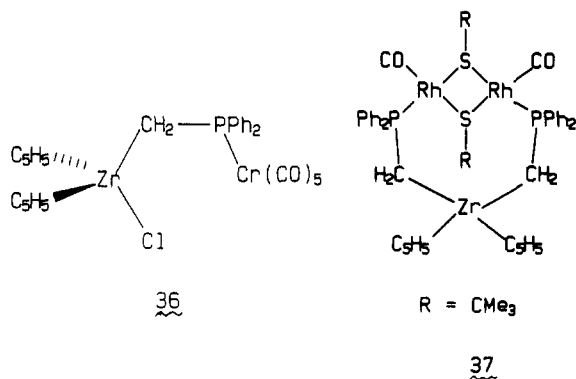
(16) Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 665-667; *Organometallics* **1984**, *3*, 504-506.

(17) Casey, C. P.; Nief, F. *Organometallics* **1985**, *4*, 1218-1220.

Several groups have synthesized heterodifunctional ligands in which a phosphine and a cyclopentadiene ligand are separated by two intervening atoms. For example, Schore<sup>24</sup> used this strategy for making the Zr-Fe bimetallic complex **34** and Leblanc<sup>25</sup> employed a similar approach in designing the Ti-Mo complex **35**.

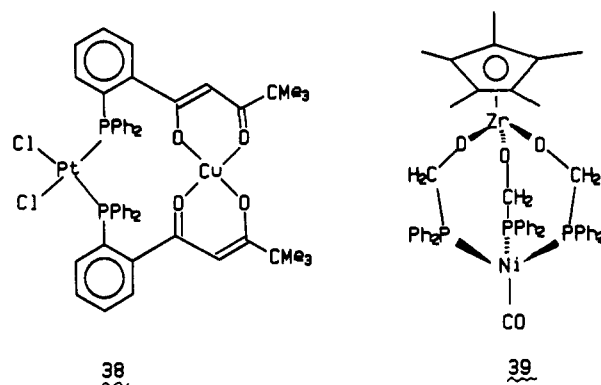


The (diphenylphosphino)methyl ligand has been used to prepare several early-late heterobimetallic compounds. Schore<sup>26</sup> reported the synthesis of **36** from the reaction of  $(\text{CO})_5\text{Cr}(\text{THF})$  with  $(\text{C}_5\text{H}_5)_2\text{ClZrCH}_2\text{PPh}_2$ . Gervais used this ligand in the synthesis of several compounds containing early and late transition metals.<sup>27</sup> Their  $\text{Rh}_2\text{Zr}$  compound **37** is a catalyst for hydroformylation of 1-hexene at low pressure.<sup>27a</sup>

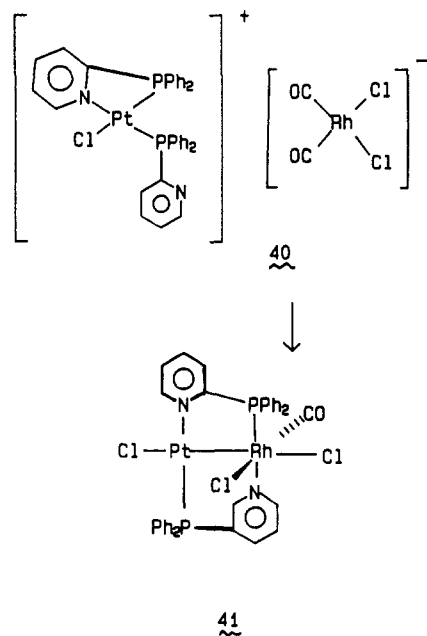


More recently, heterodifunctional ligands with hard and soft donor groups have begun to receive attention. Rauchfuss<sup>28</sup> synthesized Pt-Cu compound **38** and several other heterobimetallic compounds bridged by a heterodifunctional ligand containing phosphine and  $\beta$ -diketonate donor groups; this ligand was designed with the idea that it would be able to bond to "hard" and "soft" metals. A related approach has been utilized by Wolczanski,<sup>29</sup> who described the use of an alkoxyalkylphosphine bridging ligand in the synthesis of a series of Zr-Ni compounds such as  $(\text{C}_5\text{Me}_5)_2\text{Zr}(\mu\text{-OCH}_2\text{PPh}_2)_3\text{Ni}(\text{CO})$ , **39**.

Balch has used the heterodifunctional 2-(diphenylphosphino)pyridine ligand in the synthesis of a series of metal-metal bonded Rh-Pt, Rh-Pd, Mo-Pt, W-Pt,



Ru-Pd, and Pt-Pd complexes.<sup>30</sup> One of their most interesting observations involved the reaction of  $[(\text{C}-\text{O})_2\text{RhCl}]_2$  with  $\text{cis-Cl}_2\text{Pt}(\text{PPh}_2)_2$ , which initially produced the ionic complex **40**. The formation of **40** involves transfer of chloride from Pt to Rh and formation of a phosphine-pyridine chelate at Pt. Upon heating, **40** is converted to the metal-metal bonded Pt-Rh complex **41** in which each metal is bonded to the phosphorus of one ligand and the nitrogen of the other.



The conversion of the heterodifunctional ligand from phosphorus to nitrogen binding at platinum is readily understood in terms of the chelated intermediate **40**. Oxidative addition of  $\text{Cl}_2$  to **41** does not disrupt the Rh-Pt bond but rather adds to the 16-electron Pt center; this is similar to the oxidative addition of  $\text{H}_2$  to the 16-electron Ir center observed for Ir-Mo complexes **15**, **16**, and **17**.

### Concluding Remarks

The variety of compounds with heterodifunctional ligands linking two different metal centers is nearly limitless. In the last several years, such rapid progress has been made in the preparation and characterization

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of these new materials that it is now possible to synthesize bimetallic complexes designed to take advantage of the properties of two different metal centers acting cooperatively. However, achieving the desired chemical reactivity from the bimetallic complexes has proven extremely difficult. These difficulties highlight our need to learn much more about the properties and reactions of metal-metal bonds. Our own goals of cleaving M-M' bonds with H<sub>2</sub> and of reducing CO with the resultant metal hydrides are unfulfilled. Nevertheless, our studies turned up new and interesting

chemistry of heterobimetallic complexes that have pointed the way to designing new molecules that may eventually lead to the desired reactivity.

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## Study of the Genesis, Structure, and Reactions of Small Metal Clusters Using a Rotating Cryostat<sup>1</sup>

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Investigations of metal clusters, both naked and ligated, are in vogue for two main reasons. First, they are now both theoretically and experimentally accessible, and second, they not only have an intrinsic scientific interest but also may have commercial applications in catalysis, material science, and electronics. The theorist has often led and spurred the experimentalist in this field as his ability to calculate and predict the geometries and electronic structures of such complex multielectron ensembles has grown.<sup>2</sup> Metal clusters are intermediate between the single-atom and the "infinite"-atom arrays of the bulk metal state and hence invoke questions about the number of atoms needed to produce the delocalized continuum electronic state of a metal. They are also probably the nuclei for phase changes, and silver clusters are the latent image of the silver halide photographic process.<sup>3,4</sup> They are neither "fish nor fowl", and in many ways it is their dissimilarity to both the extreme atomic and metallic states that provides their fascination for the chemist and is the reason for their importance in so many physicochemical processes.

In this review we shall deal only with naked neutral metal clusters, since several reviews on carbonyl and other clusters are already available.<sup>5</sup> Ligand-free metal clusters have also been recently reviewed by Ozin and Mitchell,<sup>6</sup> Weltner and Van Zee,<sup>7</sup> and Morse.<sup>8</sup>

Two experimental methods have been used to prepare naked metal clusters:

(I) Pulsed laser ablation of bulk metal and expansion cooling has been used to produce gaseous clusters whose structures and reactions are studied by multiphoton laser mass spectroscopy and other techniques.<sup>9-12</sup>

(II) Matrix isolation methods in conjunction with high-temperature sources of metal atoms and clusters is a further extension of the isolation methods used so successfully to study transient free-radical species.<sup>13-15</sup>

The laser ablation method has recently provided penetrating insight into metal clusters and their reactions, but in this review we will concentrate on results from matrix isolation methods, especially on our own work using the rotating cryostat variant of the technique.

**Matrix Isolation.** Active species of interest are kept in isolation by being trapped in substitutional and interstitial sites in a solid matrix, usually at low temperatures. The low diffusion rate in the solid effectively

(1) Issued as NRCC No. 27344.

(2) See for example: (a) *J. Phys. Chem.* **1985**, *89*, 2121-2235. (b) Messmer, R. P. *Surf. Sci.* **1981**, *106*, 225-238.

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