iridium center in 1 and 5 plays a major role in the chemistry reported here. The expected deprotonation at the α-carbon atom is competitive with ring opening, but reversible, thereby allowing eventual conversion to acyl products. We are currently examining the scope of this reaction in order to determine if, under the proper conditions, it will prove to be general for other mild nucleophiles and substituted electrophilic carbene ligands.

Acknowledgment. Partial support from the Academic Senate at the University of California, San Diego, is gratefully acknowledged.

Supplementary Material Available: Listings of fractional coordinates, bond distances, bond angles, hydrogen atom coordinates, and thermal parameters and analytical and spectroscopic characterization of all new compounds (10 pages); a table of structure factors (47 pages). Ordering information is given on any current masthead page.

Fundamental Processes at Polynuclear Centers. Kinetic Analysis of the Reaction of a Carbon–Nitrogen Double Bond with the $Rh_2(\mu\text{-}H)_2$ Core of Binuclear Rhodium Hydrides

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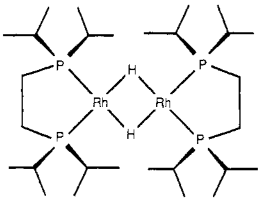
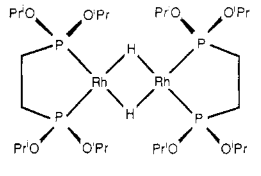
Summary: The binuclear rhodium hydrides $[(R_2PCH_2CH_2PR_2)Rh]_2(\mu\text{-}H)_2$ (R = Pr^i, **1a**; R = OPr^i, **1b**) react with *N*-benzylideneaniline to afford μ-amido hydride complexes in good yield. Spectroscopic monitoring of the reaction at low temperatures revealed that the reaction proceeds through an intermediate stable only below −50 °C; above this temperature, the intermediate decomposes to the amido hydride product. The two steps in this transformation were analyzed kinetically via $^{31}P\{^1H\}$ NMR spectroscopy. The structure of the intermediate is proposed to have a side-on bonded μ-imine ligand which collapses via migratory insertion of the carbon–nitrogen double bond into a terminal hydride bond.

The migratory insertion of unsaturated organic functionalities into metal–carbon and metal–hydride bonds is an important primary reaction in organotransition-metal chemistry. In addition to forming one of the fundamental reaction steps in various homogeneous catalytic hydrogenation[1] and oligomerization cycles,[2] many types of stoichiometric insertions have found wide application in organic synthesis.[3]

Generally, the mechanisms of the migratory insertion process are well understood in those reactions where only one metal center is involved.[4] However, in polynuclear systems, insertion reactions are less common and may be more complex mechanistically. This is not only due to the presence of reactive metal–metal bonds but also because the hydride or alkyl bond that is being formally "inserted into" may be in a bridging mode of ligation. As part of our continuing research in the area of the fundamental reactivity patterns in polynuclear systems,[5] we herein report the apparent "insertion" of an imine carbon–nitrogen double bond into the highly reactive four-center, four-electron $Rh_2(\mu\text{-}H_2)$ core of a family of binuclear rhodium hydrides incorporating chelating phosphine ligands.

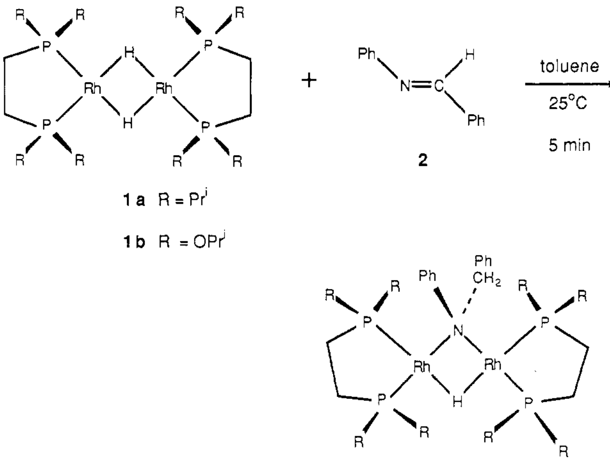


1 a



1 b

The binuclear rhodium hydrides $[(R_2PCH_2CH_2PR_2)Rh]_2(\mu\text{-}H)_2$ (R = Pr^i, **1a**; R = OPr^i, **1b**)[5a,b] react readily with 1 equiv of the *N*-benzylideneaniline, $(C_6H_5)N{=}CH(C_6H_5)$[6] (**2**), to afford the binuclear μ-amido–hydride complexes **3a** and **3b** in 80–85% isolated yields[7] (eq 1). Spectroscopic



2

1 a R = Pr^i

1 b R = OPr^i

(1)

3 a R = Pr^i

3 b R = OPr^i

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(6) *Organic Syntheses*, 2nd ed.; Gilman, H., Blatt, A. H., Eds.; Wiley: New York, 1941; Collect. Vol. 1, p 80.

(7) **Preparation of 3a.** To a stirred solution of **1a** (0.164 g, 0.22 mmol) in toluene (20 mL) was added 0.081 g of *N*-benzylideneaniline (**2**, 2 equiv). Within 5 min, a deep green to orange color change was complete, and the toluene was removed under vacuum. The orange residue was recrystallized from toluene/hexanes, yielding 0.167 g (82%) of orange crystals of **3a** after two recrystallizations. An identical procedure using **1b** was employed to yield **3b** in 84% yield.

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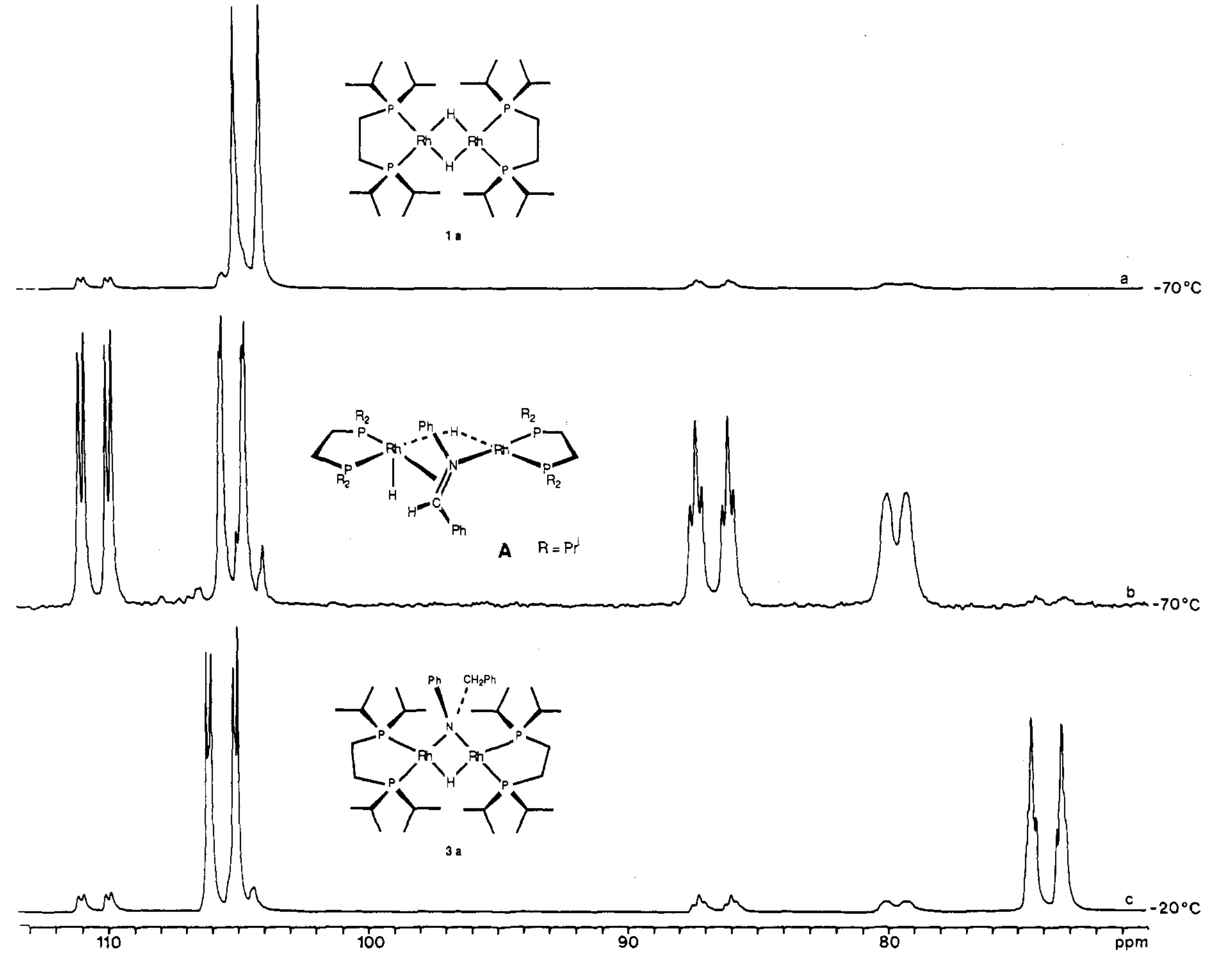

Figure 1. $^{31}P\{^1H\}$ NMR spectra recorded at 162.21 MHz of the proceeding reaction between **1a** and the imine **2** as a function of temperature and time. Spectrum a: initial spectrum recorded at −70 °C and near the beginning of the reaction. The doublet is due to **1a**, while four faint peaks not attributable to **3a** are beginning to grow in. Spectrum b: at time ≈ 1 h (−70 °C), the peaks due to the intermediate (A) have fully appeared. Spectrum c: after warming to −20 °C, A decomposes and the peaks present are due to **3a**.

and analytical data for **3a** are consistent with the structure shown,[8] and the data are also comparable to that obtained for the related, structurally characterized complex $[\{(Pr^iO)_3P\}_2Rh]_2[\mu\text{-}NMe(p\text{-}ClC_6H_4)](\mu\text{-}H)$, recently reported.[9] These bright orange products are very air-sensitive but exhibit high thermal stability; for example, heating a sealed solution of the amido–hydride **3a** in toluene-d_8 at 150 °C for 10 h results in less than 10% decomposition, although deuterium exchange between the solvent and the amido and hydride ligands was observed.[10]

By simple product analysis, the amido–hydrides **3a** and **3b** would appear to have resulted from a direct "insertion" of an imine carbon–nitrogen double bond into a bridging hydride ligand.[11] When the dideuterides **1a**-d_2 or **1b**-d_2 were allowed to react with **2**, the label appeared as one deuterium in the benzylic position of the μ-amido ligand, while one bridging deuterium was retained in the bridging position (i.e. $Rh_2(\mu\text{-}D)$)). However, when the reactions were carried out at low temperature and monitored via NMR spectroscopy, an intermediate was observed, the nature of which provides evidence for a more complex process that involves both metal centers.

Figure 1 shows $^{31}P\{^1H\}$ NMR (162.21 MHz) spectra of the proceeding reaction between **1a** and **2** as a function of temperature and time. At −70 °C, near the beginning of the reaction (Figure 1a), the spectrum consists of the

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(8) **Spectroscopic and Analytical Data for 3a.** ^1H NMR (C_6D_6, ppm): 8.74, ortho C–*H* (d, 2 H, $^3J_{meta}$ = 8.0 Hz); 8.58, ortho C–*H* (d, 1 H, $^3J_{meta}$ = 8.4 Hz); 7.14–7.30, ortho and meta C–*H* (overlapping m, 5 H); 7.0, para C–*H* (t, 1 H, $^3J_{meta}$ = 7.2 Hz); 6.75, para C–*H* (t, 1 H, $^3J_{meta}$ = 7.6 Hz); 5.32, $NCH_2C_6H_5$ (br t, 2 H, $^4J_{P_{trans}} \approx 2.0$ Hz); 2.32, 2.26, 1.78, 1.68, $CH(CH_3)_2$ (d of sp, $^2J_P \approx 3.7\text{–}4.0$ Hz); 1.52, 1.50, 1.13, 1.06, 0.88, 0.85, 0.64, 0.57, $CH(CH_3)_2$ (dd, ^3J_H = 7.2–8.0 Hz, ^3J_P = 12.8–14.4 Hz); CH_2CH_2, (resonances buried underneath signals for the methyl groups); −9.41, Rh–*H*–Rh (ttt, $^2J_{P_{trans}}$ = 56.4 Hz, $^2J_{P_{cis}}$ = 12.8 Hz, $^1J_{Rh}$ = 23.1 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, referenced to internal C_6D_6 at 128.0 ppm): 164.6, $C_{ipso}(N)$; 143.7 $C_{ipso}(C)$; 130.3, 128.8, 127.4, 126.3, 126.1, 124.7, 117.8, 111.3, other aromatic carbons (two signals are obscured by C_6D_6 signal); 66.8 $NCH_2C_6H_5$; 26.8–28.7, $CH(CH_3)_2$ (4 signals); 21.8–22.8, CH_2CH_2 (m); 18.3–22.7 $CH(CH_3)_2$ (8 s). $^{31}P\{^1H\}$ NMR (C_6D_6, referenced to external $P(OMe)_3$ at +141.0 ppm): P_{cisN} = A, P_{transN} = B, Rh = X; δ_A 73.9, δ_B 105.5; $J_{AA'}$ = 33.5 Hz, J_{AB} = 30.3 Hz, $J_{AB'}$ = 2.9 Hz, J_{AX} = 191.3 Hz; $J_{AX'}$ = 5.8 Hz; $J_{BB'}$ = −0.9 Hz; J_{BX} = 166.9 Hz; $J_{BX'}$ = −1.2 Hz; $J_{XX'}$ = 5.6 Hz. Anal. Calcd for $C_{41}H_{75}P_4Rh_2N$: C, 54.01; H, 8.29; N, 1.54. Found: C, 54.30; H, 8.52; N, 1.62.

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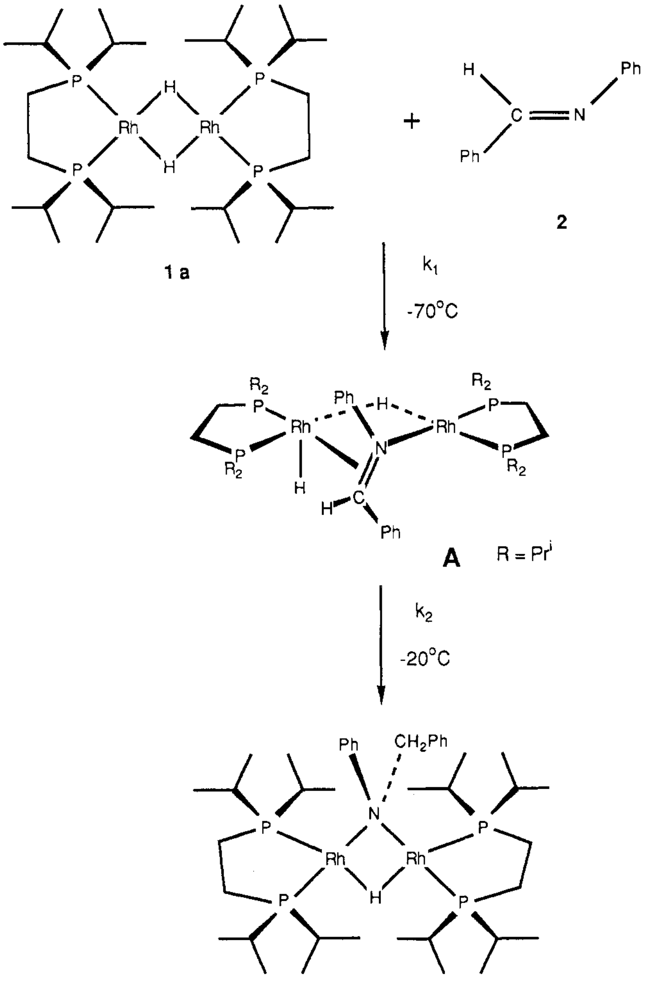
(10) (a) The benzylic protons and the hydride ligand were the first positions to incorporate deuterium in the observed thermally induced H/D exchange with toluene-d_8. Prolonged heating resulted in the incorporation of deuterium into all of the phenyl positions of the amide ligand, with little or no selectivity for the ortho, meta, or para positions. This lack of selectivity is suggestive of an intermolecular or a heterogeneous (i.e., catalyzed by Rh metal perhaps) mechanism of exchange.[10b] (b) Parshall, G. W. *Acc. Chem. Res.* **1975**, *8*, 113.

(11) (a) Though not observed directly, such insertions have been inferred as steps in the catalytic hydrogenation of Schiff bases by rhodium/phosphorus catalyst systems, but mechanistic work suggests that a hydride transfer mechanism is operative rather than the classical four-center insertion mechanism invoked for C═C insertion into a metal hydride bond.[11b,c] (b) Longley, C. J.; Goodwin, T.; Wilkinson, G. *Polyhedron* **1986**, *5*, 1625. (c) Grigg, R.; Mitchell, T. R. B.; Tongpenyai, N. *Synthesis* **1981**, 442.

Scheme I



doublet characteristic of the dihydride **1a** and four faint resonances not attributable to the product **3a**. After approximately 1 h, these signals have grown in almost completely, still with no trace of the peaks due to **3a** (Figure 1b). At temperatures at or below −50 °C, this intermediate is stable in solution but is unstable at higher temperatures, even in the solid state. Thus, when the sample is warmed to −20 °C, the intermediate begins to decompose to **3a**, and after about 45 min, the amido–hydride has formed completely (Figure 1c). A spectroscopically similar reaction course was observed in the analogous reaction involving the rhodium hydride dimer having isopropoxy substituents on the phosphorus donors **1b**.

We have speculatively assigned this intermediate the structure shown in Scheme I (A), based on the available data. The important features to note are the terminal hydride and the π-bound imine C=N unit on the same rhodium center. Both the $^{31}P\{^1H\}$ and $^1H\{^{31}P\}$ NMR spectra indicate such a highly unsymmetrical structure. For example, in addition to four separate phosphorus environments, the proton NMR spectrum shows signals for 16 inequivalent methyl groups on the dippe ligands. The most important structural clue is found in the phosphorus-31-decoupled ^1H NMR spectrum of A in the hydride region, in which signals for one *terminal* hydride ligand (−11.45 ppm (d, $^1J_{Rh}$ = 18.4 Hz)) and one *bridging* hydride (−13.79 ppm (br t, $^1J_{Rh}$ = 19.6–20.4 Hz)) were observed. A broad singlet at 4.90 ppm integrating to one proton is assigned to the imine proton, the resonance shifted significantly upfield due to π-coordination of the C=N bond to rhodium. The $^{13}C\{^1H\}$ NMR of A (formed from **1a** and $(C_6H_5)N{=}^{13}CH(C_6H_5)$ at −70 °C) further suggests π-donation of the imine; a broad signal ($w_{1/2} \approx 20$ Hz) at 62.4 ppm ($^1J_{^{13}C-H}$ = 151.3 Hz) could be assigned to the imino carbon, which resonates at 160.0 ppm in the free imine ($^1J_{^{13}C-H}$ = 158.3 Hz). The structure proposed for A has some analogy to the structure of some μ-η^2-σ-alkenyl–hydride complexes observed upon reaction of **1a** with simple olefins.[5b]

Both steps of this reaction may be conveniently followed kinetically by $^{31}P\{^1H\}$ NMR, and the results of these studies are congruent with the proposed mechanistic pathway shown in the scheme. The first step was found to be cleanly second order ($k_1(-70\ °C) = 3.13\ (8) \times 10^{-3}$ L mol^{-1} s^{-1}), first order in both **1a** and **2**, while the second step was first order in the rate of disappearance of the intermediate A ($k_2(-20\ °C) = 6.92\ (8) \times 10^{-4}$ s^{-1}). Activation parameters were obtained and were not unusual.[12] Kinetic analysis of the reaction of the binuclear dideuteride **1a**-d_2 with **2** revealed a small kinetic isotope effect (k_H/k_D) of 1.41 (5) for step one and a more substantial value of 2.24 (3) for step two. This latter k_H/k_D is within the range of 1.4–2.7 predicted for the primary kinetic isotope effect on the insertion of ethylene into the Nb–H bond of $Cp^*_2Nb(H)(C_2H_4)$.[4b] While the two reactions are quite different, if delivery of the hydride to the imine carbon in A takes place via the four-center transition state commonly invoked for olefin insertion reactions, the kinetic isotope effects should be comparable.

A likely pathway for the production of the intermediate A involves coordination by the lone pair on the nitrogen of the imine to one rhodium center of **1a**, followed by π-donation of the C=N double bond to the adjacent rhodium atom with concomitant rupture[13] of the $Rh_2(\mu\text{-}H_2)$ four-center, four-electron core of the dihydride molecule to form A. The second step can be formally analyzed as an insertion of the C=N double bond into the terminal Rh–H bond, producing **3a**. Although we cannot distinguish unambiguously between migratory insertion of the terminal hydride versus the bridging hydride, the isotope effect is more easily defined by the latter. A migratory insertion of an imine C=N bond and a metal hydride is rarely observed due to the tendency of imines to bond to metals via the lone pair on nitrogen rather than through any bonding through the π-system.[2b] Such π-donation observed here is perhaps induced when another adjacent metal is present to occupy the lone pair.

The importance of these results to the homogeneous hydrogenation of imines by rhodium–phosphine catalysts formed in situ is moot. Reaction of the amido–hydride products **3** with hydrogen does result in formation of *N*-benzylaniline but only after extended reaction times ($t_{1/2} \approx$ 1–2 days). It may well be that the chelating phosphines used in our study change the dynamics of the system in such a way as to render the amido–hydride derivatives kinetically inert "sinks" in the catalytic cycle.

Understanding the primary processes operative at

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(12) For the first step, a ΔH^* of 10.1 (5) kcal mol^{-1} and a ΔS^* of −19.8 (5) eu were obtained. The second step yielded a ΔH^* of 17.5 (3) kcal mol^{-1} and a ΔS^* of −3.6 (3) eu.

(13) The observation of a deuterium isotope effect (k_H/k_D) of 1.41 (5) for the initial coordination of the imine which we propose involves a bridging hydride going to terminal hydride is somewhat counterintuitive for a primary deuterium isotope effect. From zero-point energy arguments, this isotope effect might be predicted to be <1 since putting a deuterium in a terminal position should accelerate the rate if this is rate-determining. We point out however, that the four-center, four-electron $Rh_2(\mu\text{-}H)_2$ core may involve Rh-Rh bond cleavage during this bimolecular step and thus the rate difference observed is a result of a secondary deuterium isotope effect on metal–metal bond disruption.

polynuclear metal centers has been thwarted by the difficulty in kinetically observing individual steps in transformations. Typical thermolysis reactions of polynuclear ruthenium- and osmium-based clusters,[14] for example, are not amenable to detailed study since side reactions can ensue; moreover, analysis of reaction pathways is sometimes based entirely on product identification. The binuclear rhodium hydride systems discussed here on the other hand are very reactive, and many transformations[5] can be followed by spectroscopic means. We are convinced that this system along with a few other selected binuclear[15] and trinuclear[16] complexes are providing fundamental information on the primary processes of polynuclear metal complexes.

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Supplementary Material Available: Tables of raw kinetic data with corresponding graphs (4 pages). Ordering information is given on any current masthead page.

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Synthesis of Binuclear Metal Complexes Incorporating Hydrido and Phosphido Ligands and Structural Characterization of $[Et_4N][(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}(Ph_3PAu)_2)W_2(CO)_8]$

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Summary: The coordinatively unsaturated species $H_2M_2(CO)_8^{2-}$ (M = Mo, W) react with diphenylphosphine to form products incorporating bridging hydrido and phosphido ligands, $(\mu\text{-}H)(\mu\text{-}PPh_2)M_2(CO)_8^{2-}$. A mixed-metal cluster, $(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}(Ph_3PAu)_2)W_2(CO)_8^-$, derived from $(\mu\text{-}H)(\mu\text{-}PPh_2)W_2(CO)^{82-}$, was structurally characterized by X-ray diffraction.

Addition of Ph_2PH to the coordinatively unsaturated species $[Et_4N]_2[H_2M_2(CO)_8]$ (1, M = Mo; 2, M = W) yields $[Et_4N]_2[(\mu\text{-}H)(\mu\text{-}PPh_2)[M_2(CO)_8]$ (3, M = Mo, 51%; 4, M = W, 80%).[1] The infrared spectral pattern of these new complexes in the CO stretching region is very similar to the isoelectronic manganese analogue $(\mu\text{-}H)(\mu\text{-}PPh_2)\text{-}Mn_2(CO)_8$.[2] The ^1H and ^{31}P NMR spectra are also consistent with their formulation: (a) the chemical shifts of the bridging hydrides for 3 and 4 are comparable with those reported in literature,[3-5] (b) the presence of 1:6:1 triplet due to $^{183}W\text{-}H$ coupling in 4 suggests the existence of a symmetrically bridged M–H–M linkage;[6,7] (c) the ^{31}P NMR spectra for 3 and 4 are in agreement with a phosphido group symmetrically bridging a metal–metal bond.[8] While two-bond P–H coupling between the hydrido and the phosphido ligands could be clearly seen in the ^1H and ^{31}P NMR spectra of 3, no such coupling was observed for 4. The chemical behavior of 4 (vide infra) provided further

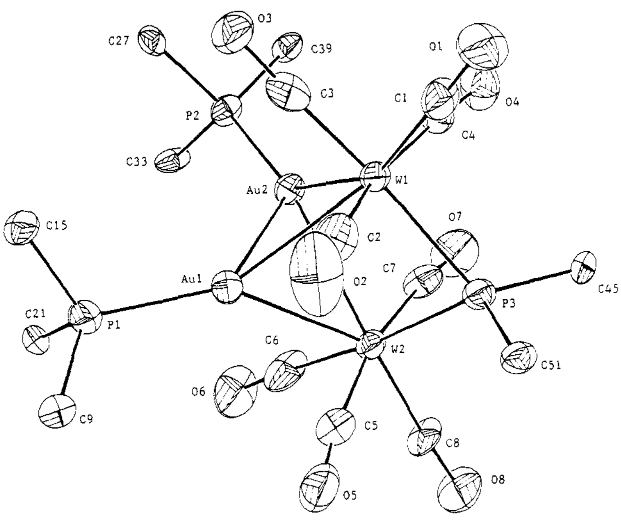

Figure 1. ORTEP drawing of $(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}(Ph_3PAu)_2)W_2(CO)_8^-$. Phenyl groups except ipso carbon atoms are omitted for clarity. The ellipsoids are drawn with 30% probability boundaries.

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(1) A solution of 0.20 g (0.30 mmol) of 1 in acetonitrile (30 mL) was reacted with an excess of Ph_2PH (0.15 mL) at −20 °C for 30 min. The solution was slowly warmed to room temperature (1.5 h) and the solvent removed by evacuation. The resulting orange-yellow precipitate was washed, first with THF until the washings were colorless and then with MeOH (25 mL × 2). The product was then dried in vacuo to provide 0.13 g (51%) of orange-yellow powdery 3. The same procedure was followed for the preparation of 4. Complex 4 was obtained as orange-yellow powders (0.98 g, 80%) from 1.00 g (1.17 mmol) of complex 2. 3: IR (CH_3CN) ν(CO) 1998 mw, 1975 m, 1887 s, 1842 m, 1796 s cm^{-1}; ^1H NMR (CD_3CN) δ 7.7–7.0 (m, 10 H, Ph), 3.14 (q, J_{H-H} = 7.1 Hz, 16 H, CH_2), 1.19 (tt, J_{H-N} = 1.7 Hz, 24 H, CH_3), −10.2 (d, J_{H-P} = 9.8 Hz, 1 H, μ-H); ^{31}P NMR (CD_3CN) δ 92.2 (d). Anal. Calcd for $C_{36}H_{51}N_2O_8PMo_2$: C, 50.12; H, 5.96; N, 3.25. Found: C, 49.92; H, 5.81; N, 3.15. 4: IR (CH_3CN) ν(CO) 1996 mw, 1969 m, 1883 s, 1836 m, 1795 s cm^{-1}; ^1H NMR (CD_3CN) δ 7.8–7.0 (m, 10 H, Ph), 3.14 (q, J_{H-H} = 7.1 Hz, 16 H, CH_2), 1.19 (tt, J_{H-N} = 1.7 Hz, 24 H, CH_3), −12.0 (1:6:1 triplets, J_{H-W} = 42.5 Hz, 1 H, μ-H); ^{31}P NMR (CD_3CN) δ 61.0 (1:6:1 triplets, J_{P-W} = 169 Hz). Anal. Calcd for $C_{36}H_{51}N_2O_8PW_2$: C, 41.64; H, 4.95; N, 2.70. Found: C, 41.55; H, 5.01; N, 2.74.

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