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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(14) (a) Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1. (b) Lavigne, G.; Kaesz, H. D. In *Metal Clusters in Catalysis*; Gates, B. C., Guczi, L., Knozinger, H., Eds.; Elsevier: New York, 1986; Chapter 4. (c) Adams, R. D.; Babin, J. E.; Kim, H.-S. *J. Am. Chem. Soc.* **1987**, *109*, 1414. (d) Adams, R. D.; Babin, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 6872. (e) Nucciarone, D.; MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J. *Organometallics* **1988**, *7*, 106. (f) Nucciarone, D.; Taylor, N. J.; Carty, A. J.; Tiripicchio, A.; Camellini, M. J.; Sappa, E. *Organometallics* **1988**, *7*, 118. (g) Nucciarone, D.; Taylor, N. J.; Carty, A. J. *Organometallics* **1988**, *7*, 127.

(15) (a) Schore, N. E.; Ilenda, C. S.; White, M. A.; Bryndza, H. E.; Matturo, M. G.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 7451 and references therein. (b) Sivak, A. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1979**, *101*, 4878.

(16) (a) Douglas, G.; Manojlovic-Muir, L.; Muir, K. W.; Rashidi, M.; Anderson, C. M.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 6527. (b) Rashidi, M.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1986**, *108*, 7111. (c) Lloyd, B. R.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 7785.

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.

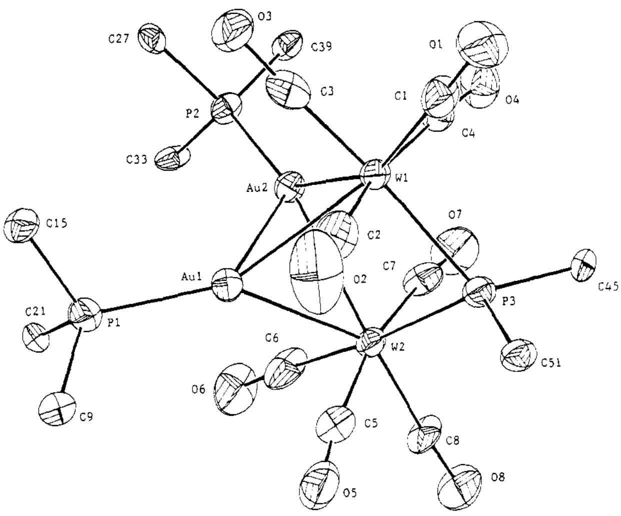

Figure 1. ORTEP drawing of $(\mu\text{-PPh}_2)(\mu\text{-}\eta^2\text{-}(Ph_3PAu)_2)W_2(CO)_8^-$. Phenyl groups except ipso carbon atoms are omitted for clarity. The ellipsoids are drawn with 30% probability boundaries.

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 $(\mu\text{-H})(\mu\text{-PPh}_2)Mn_2(CO)_8$.[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–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

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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.

(2) Iggo, J. Q.; Mays, M. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1983**, 205.

(3) Lin, J. T.; Shiao, Y. M. *J. Organomet. Chem.* **1987**, *334*, C31.

(4) Legzdins, P.; Martin, J. T.; Einstein, F. W. B.; Willis, A. C. *J. Am. Chem. Soc.* **1986**, *108*, 7971.

(5) Darensbourg, M. Y.; Mehdawi, R. El; Delord, T. J.; Fronczek, F. R.; Watkins, S. F. *J. Am. Chem. Soc.* **1984**, *106*, 2583.

(6) Davison, A.; McFarland, W.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 3653.

(7) Hayter, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 4376.

(8) (a) Carty, A. J. *Adv. Chem. Ser.* **1982**, *No. 196*, 163. (b) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. (c) Harley, A. D.; Guskey, G. J.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 53.

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evidence of its correct formulation.

The mechanism of the formation of 3 and 4 is presently unknown. We did observe gas evolution (presumably H_2) during the reactions. It was not possible to resolve whether (a) $M_2(CO)_8(Ph_2PH)_2^{2-}$ formed as in the case of the synthesis of $W_2(CO)_8(PMe_3)_2^{2-}$[9] or (b) $HM_2(CO)_8(Ph_2PH)^-$ formed instead. Oxidative addition of a coordinated secondary phosphine to a metal center with concurrent P–H bond cleavage has ample precedent.[10] Another coordinatively unsaturated complex, $H_2Os_3(CO)_{10}$, was reported to react similarly with Ph_2PH to form $(\mu\text{-H})(\mu\text{-PPh}_2)Os_3(CO)_{10}$.[11]

Complexes 3 and 4 are air-sensitive and are very reactive toward electrophiles. Protonation of 4 with trichloroacetic acid in the presence of Ph_2PH led to the formation of $[Et_4N][(\mu\text{-H})W_2(CO)_8(Ph_2PH)_2]$ (**5**). Complex **5** could be more conveniently prepared[12] by using the strategy developed for the synthesis of $(\mu\text{-})(\mu\text{-Ph}_2PCH_2PPh_2)W_2(CO)_8^-$.[3] A noble mixed-metal cluster, $[Et_4N][(\mu\text{-PPh}_2)(\mu\text{-}\eta^2(Ph_3PAu)_2)W_2(CO)_8]$ (**6**), was obtained in about 70% yield from the reaction of 4 with 2 equiv of Ph_3PAuCl.[13]

The X-ray crystal structure analysis of 6 was undertaken,[14] and the core structure of the anion is shown in Figure 1. Two tungsten and two gold atoms can be regarded as forming a distorted tetrahedron with tungsten atoms bridged by a phosphido ligand and each gold atom containing a coordinated triphenylphosphine. The W–W bond distance of 3.332 (1) Å is longer than the single bond value of 3.0256 (4) Å in $(\mu\text{-PPh}_2)_2W_2(CO)_8$[15] and substantially shorter than the nonbonding value of 4.1018 (4) Å in $[Li(THF)_3^+]_2[(\mu\text{-PPh}_2)_2W_2(CO)_8]$.[15] In comparison, the unsupported W–W single bond in $Cp_2W_2(CO)_6$ is 3.222 (1) Å.[16] The W–P–W bond angle of 83.9 (2)° in 6 also lies within those reported for $(\mu\text{-PPh}_2)_2W_2(CO)_8$ (75.14°) and $(\mu\text{-PPh}_2)_2W_2(CO)_8^{2-}$ (104.20°).[15] The ^{31}P NMR spectra of 6 is consistent with its structure in the solid state. A triplet at 139.2 ppm and a doublet at 73.4 ppm ($^3J_{P-P}$ = 9.7 Hz) were assigned to the bridging phosphido and terminal phosphine ligands, respectively. The small W–P–W bond angle and the downfield shift[8] of the bridging phosphorus atom suggest that there could be some interaction between two tungsten atoms. Alternatively, $(\mu\text{-PPh}_2)(\mu\text{-}\eta^2\text{-}(Ph_3PAu)_2)W_2(CO)_8^-$ can be regarded as consisting of two $W(CO)_4$ units bridged by both PPh_2 and $(Ph_3P)Au\text{–}Au(PPh_3)$ units. The (triphenylphosphine)gold dimer can be considered to be isolobal with hydrogen molecule according to Mingo's principle.[17] Being a bridge between two tungsten atoms, the Au–Au distance of 2.749 (2) Å is well within the range for a Au–Au single bond.[18] Though the mean W–Au distance of 2.915 Å is longer than those in $AuW_2(\mu\text{-CC}_6H_4Me\text{-}4)_2(CO)_4Cp_2^+$ (2.752 Å),[19] $(Ph_2PMe)_2Au_2WS_4$ (2.84 Å),[20] and $CpW(CO)_3AuPPh_3$ (2.698 Å)[21], similar long metal–gold bond lengths were also found in complexes containing bridging gold units such as $Au_3Ru_3(\mu_3\text{-COMe})(CO)_9(PPh_3)_3$[22] and $Os_4H_2(CO)_{12}(AuPPh_3)_2$.[23]

The unusual reactivity of 4 toward Ph_3PAuCl bears a close resemblance to the reaction between $AuPPh_3^+$ and $PtHCl(PEt_3)_2$[24] or $Nb(\eta^5\text{-C}_5H_4SiMe_3)_2H_3$.[25] The chemical properties of 3 and 4 are currently under investigation.

Acknowledgment. We thank Prof. John E. Ellis for helpful discussions. Financial support from the National Science Council is gratefully acknowledged.

Supplementary Material Available: Tables of selected bond distances and angles (Table S1), all bond distances and angles (Table S2), atomic coordinates (Table S3), anisotropic thermal parameters and hydrogen parameters (Table S4) (12 pages); a listing of structure factors (71 pages). Ordering information is given on any current masthead page.

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(9) Lin, J. T.; Hagen, G. P.; Ellis, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2296.

(10) (a) Arif, A. M.; Jones, R. A.; Schwab, S. T. *J. Organomet. Chem.* **1986**, *307*, 219. (b) Rosenberg, S.; Mahoney, W. S.; Hayes, J. M.; Geoffroy, G. L. *Organometallics* **1986**, *5*, 1065. (c) Mercer, W. C.; Geoffroy, G. L. *Organometallics* **1985**, *4*, 1418. (d) Rosenberg, S.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1985**, *4*, 1184. (e) Breen, M. J.; Shulman, P. M.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *Organometallics* **1984**, *3*, 782.

(11) Ebsworth, E. A. V.; McIntosh, A. P.; Schroder, M. *J. Organomet. Chem.* **1986**, *312*, C41.

(12) One equivalent of trichloroacetic acid dissolved in 1 mL of CH_3CN was added dropwise to a vigorously stirred CH_3CN solution of **2** (0.10 g, 0.12 mmol) prechilled to −30 °C, and the color of the solution changed from red to yellow within 30 min. An excess of Ph_2PH (0.30 mL) was then added. After another 30 min at −30 °C, the solution was warmed slowly to room temperature. The solvent was removed and the residue washed with water. Recrystallization from THF/Et_2O provided yellow powdery **5** (0.075 g, 54%): IR (CH_3CN) ν(CO) 2014 m, 1992 mw, 1905 s, 1827 m cm^{-1}; ^1H NMR (CD_3CN) δ 7.6–7.4 (m, 20 H, Ph), 6.78 (dd, J_{H-P} = 335.2 Hz, $^3J_{H-H}$ = 4.26 Hz, 2 H, P–H), 3.14 (q, J_{H-H} = 7.1 Hz, 8 H, CH_2), 1.19 (tt, J_{H-H} = 7.1 Hz, J_{H-N} = 1.7 Hz, 12 H, CH_3), −11.1 (tt with tungsten satellites, J_{H-P} = 17.4 Hz, $^3J_{H-H}$ = 4.2 Hz, J_{H-W} = 44.0 Hz, μ-H); ^{31}P NMR (CD_3CN) δ −2.72 (br d, $^1J_{P-H}$ = 335.2 Hz). Anal. Calcd for $C_{40}H_{43}NO_8P_2W_2$: C, 43.86; H, 3.96; N, 1.28. Found: C, 44.13; H, 4.10; N, 1.18.

(13) A CH_3CN solution of Ph_3PAuCl (0.095 g, 0.19 mmol) prechilled to −30 °C was added dropwise to 50 mL of CH_3CN solution of compound **4** (0.10 g, 0.096 mmol) at −30 °C. The solution was gradually warmed to 0 °C and the color of the solution changed from yellow to red. After 1.5 h, the solvent was removed to give orange powders. Recrystallization from THF/MeOH gave 0.12 g (68%) of **6**: IR (THF) ν(CO) 1984 w, 1954 ms, 1882 s, 1861 s, 1829 s cm^{-1}; ^1H NMR (CD_3CN) δ 7.8–7.0 (m, 40 H, Ph), 3.14 (q, J_{H-H} = 7.1 Hz, 8 H, CH_2), 1.19 (tt, J_{H-H} = 7.1 Hz, J_{H-N} = 1.7 Hz, 12 H, CH_3); ^{31}P NMR (CD_3CN) δ 140 (t with satellites, $^3J_{P-P}$ = 9.7 Hz, J_{P-W} = 172 Hz, 1 P, PPh_2), 73.4 (d, $^3J_{P-P}$ = 9.7 Hz, 2 P, PPh_3). Anal. Calcd for $C_{64}H_{60}NO_8P_3Au_2W_2$: C, 42.10; H, 3.31; N, 0.77. Found: C, 41.59; H, 3.30; N, 0.82.

(14) Suitable single crystals were grown by allowing slow diffusion of Et_2O through a concentrated CH_3CN solution of **6**. Crystal data for $C_{64}H_{60}NO_8P_3Au_2W_2$: space group $P2_1/n$, a = 14.119 (7) Å, b = 27.642 (4) Å, c = 15.892 (2) Å, β = 91.19 (3)°, V = 6200.76 Å^3, d_{calcd} = 1.943 g cm^{-3} for M = 1764.64, Z = 4, μ = 85.8 cm^{-1} for Mo K_α. Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer at room temperature. Absorption corrections according to psi scans of three reflections were made. All the data processing were performed on a PDP 11 and VAX 11 using the NRCC SDP program. The W and Au atoms were determined by Patterson techniques; all other atoms were located by subsequent difference Fourier maps and cycles of least-square refinement. R_F = 0.037 and R_{wF} = 0.037 (722 parameters refined, including the extinction coefficient) for 4437 reflections [$I > 2.5\ \sigma(I)$] of 10 879 unique reflections collected in the range of $0° \le 2\theta \le 50°$.

(15) Shyu, S. G.; Calligaris, M.; Nardin, G.; Wojcicki, A. *J. Am. Chem. Soc.* **1987**, *109*, 3617.

(16) Wilson, F. C.; Shoemaker, D. P. *Naturwissenschaften* **1956**, *43*, 57.

(17) Mingos, D. M. P. *J. Chem. Soc., Dalton Trans* **1974**, 133.

(18) Hall, K. P.; Mingos, D. M. P. *Prog. Inorg. Chem.* **1984**, *32*, 237.

(19) Awang, M. R.; Carriedo, G. A.; Howard, J. A. K.; Mead, K. A.; Moore, I.; Nunn, C. M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1983**, 964.

(20) Huffman, J. C.; Roth, R. S.; Siedle, A. R. *J. Am. Chem. Soc.* **1976**, *98*, 4340.

(21) Wilford, J. B.; Powell, H. M. *J. Chem. Soc. A* **1969**, 8.

(22) Bateman, L. W.; Green, M.; Howard, J. A. K.; Mead, K. A.; Mills, K. M.; Salter, I. D.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1982**, 773.

(23) Handy, L. B.; Ruff, J. K.; Dahl, L. E. *J. Am. Chem. Soc.* **1970**, *92*, 7312.

(24) Braunstein, P.; Lehner, H.; Tiripicchio, D. M. A.; Tiripicchio-Camellini, M. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 304.

(25) Fajardo, M.; Gomez-Sal, M. P.; Royo, P.; Carrera, S. M.; Blanco, S. C. *J. Organomet. Chem.* **1986**, *312*, C44.