Organometallics **2008,** *27,* 3901–3906

Synthesis and Structure of Molybdenum and Tungsten Bisphosphine Carbonyl Dimers

Daniel F. Brayton and D. Michael Heinekey*

Department of Chemistry, University of Washington, Seattle, Washington 98195

Received March 27, 2008

The synthesis of two bisphosphine ligands $(R_2P)_2C_6H_4$ with a para-disubstituted phenyl moiety is described (R = Cy (**3**), *i*-Pr (**4**)). Solutions of $M(CO)_3(C_7H_8)$ ($C_7H_8 = \eta^6$-cycloheptatriene, M = Mo and W) and **3** or **4** were reacted under CO affording dimeric compounds of the general formula $[M_2(CO)_8((R_2P)_2C_6H_4)_2]$ (M = W, R = Cy (**5**); M = Mo, R = Cy (**6**); and M = W, R = *i*-Pr (**7**)). When the same reactions are carried out in the presence of H_2, similar $W-H_2$ analogues of the general formula $[W_2(CO)_6((R_2P)_2C_6H_4)_2(H_2)_2]$, R = Cy (**8**), R = *i*-Pr (**9**), can be observed by ^1H and ^{31}P NMR spectroscopy. Compounds **8** and **9** are not isolable, due to facile ligand redistribution forming **5** and **7**, respectively.

Introduction

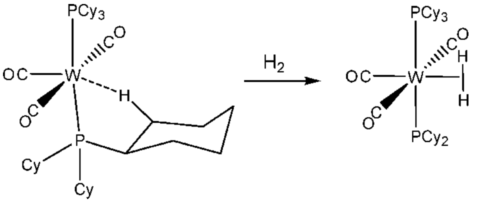
Transition-metal dihydrogen complexes have emerged as a fascinating area of research in coordination chemistry. The first of these complexes were characterized by Kubas and co-workers using a $W(CO)_3(PCy_3)_2$ moiety.[1] This nominally 16-electron fragment is stabilized by an agostic interaction with a C−H bond, which is displaced by hydrogen, Scheme 1. The developments leading up to the discovery of hydrogen complexes have been recently reviewed.[1] A large number of hydrogen complexes are now known, involving a wide range of metal and ligand combinations.[2]

The unsaturated tungsten fragment exhibits a versatile coordination chemistry, binding many other donors, including SO_2, H_2O, N_2, and the Si−H bonds of silanes, among others.[2] Related complexes of chromium and molybdenum exhibit similar chemistry, but have been less studied.

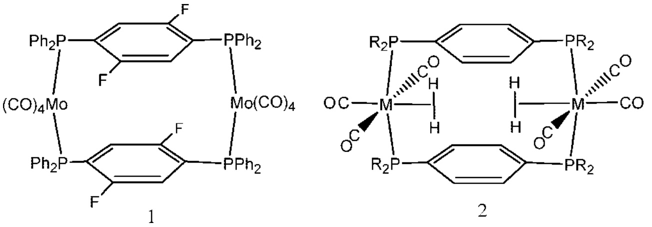
Since hydrogen complexation is now well established, the coordination of σ-bonds such as the C−H bonds of alkanes has become a target for investigation. In contrast to the large number of agostic species,[3] with *intramolecular* complexation of C−H bonds, the *intermolecular* complexation of alkanes is much more difficult to observe.[4] Only recently has the complexation of alkanes been directly detected by NMR spectroscopy.[5]

We sought to explore this novel coordination chemistry environment by the synthesis of a bimetallic complex with two adjacent vacant sites for ligand binding. We anticipated that the existence of two adjacent binding sites could lead to enhanced binding of weak σ bond donors. A literature search revealed that a molybdenum dimer had been prepared using a spanning bidentate phosphine ligand with a difluoro-substituted phenyl linker **1** as shown in Scheme 2.[6] Based on this architecture, we envisaged the preparation of bimetallic complexes which would bind two donor molecules such as hydrogen. Depicted above as complex **2** is one of the targets of our investigation. We now report the synthesis of new spanning bisphosphine ligands and our attempts to prepare molecules such as complex **2**.

Scheme 1

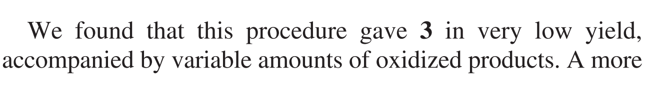


Scheme 2



Results and Discussion

Phosphine Ligand Synthesis. Generation of a para-dilithiated benzene followed by reaction with the chlorophosphine Cy_2PCl is reported to afford the bisphosphine **3**, albeit in only modest yield (22%), eq 1.[7]



(1)

R = Cy(3), *i*Pr(4)

We found that this procedure gave **3** in very low yield, accompanied by variable amounts of oxidized products. A more

---

* To whom correspondence should be addressed. E-mail: heinekey@chem.washington.edu.

(1) Kubas, G. J. *Chem. Rev.* **2007**, *107*, 4152.

(2) Kubas, G. J., *Metal Dihydrogen and σ-Bond Complexes: Structure, Theory and Reactivity*; Kluwer Academic/Plenum Publishers: New York, 2001.

(3) Brookhart, M.; Green, M. L. H.; Parkin, G. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 6908.

(4) Perutz, R. N.; Hall, C. *Chem. Rev.* **1996**, *96*, 3125.

(5) Geftakis, S.; Ball, G. E. *J. Am. Chem. Soc.* **1998**, *120*, 9953. See also: Ball, G. E.; Brookes, C. M.; Cowan, A. J.; Darwish, T. A.; George, M. W.; Kawanami, H. K.; Portius, P.; Rourke, J. P. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 6927, and references therein.

(6) Hogarth, G.; Norman, T. *J. Chem. Soc., Dalton Trans.* **1996**, 1077.

(7) Imhof, D.; Burckhardt, U.; Dahmen, K. H.; Joho, F.; Nesper, R. *Inorg. Chem.* **1997**, *36*, 1812.

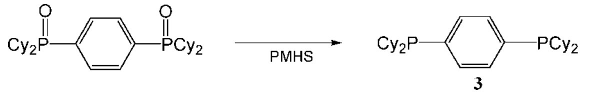
10.1021/om800273t CCC: $40.75

Table 1. Crystallographic Data for 3, 4, 6, and 7

	3 $(Cy_2P)_2C_6H_4$	**4** $(i\text{-}Pr_2P)_2C_6H_4$	**6** $[Mo_2(CO)_8((Cy_2P)_2PC_6H_4)_2]$	**7** $[W_2(CO)_8((i\text{-}Pr_2P)_2PC_6H_4)_2]$
empirical formula	$C_{30}H_{48}P_2$	$C_{18}H_{32}P_2$	$C_{68}H_{96}Mo_2O_8P_4$, CH_2Cl_2	$C_{44}H_{64}O_8P_4W_2$, C_7H_{16}
FW	470.62	310.38	1442.14	1312.73
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	9.4004(5)	10.2911(5)	19.6088(4)	14.3209(2)
b (Å)	13.1537(9)	8.0562(5)	14.9522(3)	15.2303(2)
c (Å)	10.8292(8)	23.5323(14)	23.7674(5)	15.9883(2)
α (deg)	90.00	90.00	90.00	110.8158(6)
β (deg)	97.526(3)	99.591(3)	94.8711(11)	108.9489(7)
γ (deg)	90.00	90.00	90.00	105.0426(7)
vol (Å^3)	1327.34(15)	1923.64(19)	6943.3(2)	2791.99(7)
Z	2	4	4	2
D_{calc} (g cm^{-3})	1.177	1.072	1.380	1.561
T (K)	140(2)	140(2)	130(2)	140(2)
θ range (deg)	2.19−28.36	2.68−26.42	2.08−27.40	2.27−28.43
goodness-of-fit on F^2	0.934	0.994	0.971	1.042
$R(F)^a$ (%)	6.02	5.89	6.19	3.93
$R_w(F^2)^b$(%)	11.85	13.36	16.99	9.18
λ (Å)	0.71073	0.71073	0.71073	0.71073

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

reliable procedure was developed in which the reaction was quenched with water and the product collected in the air, allowing oxidation. The oxidized product was sequentially washed with water, MeOH, pentane, and Et_2O. The phosphine oxide was then reduced with a polymeric silane compound, polymethylhydrosiloxane (PMHS), using a previously reported method, eq 2.[8] This procedure affords bisphosphine **3** in an improved yield of 69%.



(2)

While bisphosphine **3** has been previously described, we report here additional characterization data including the molecular structure as determined by X-ray crystallography (see Table 1 and Supporting Information). In the ^1H NMR spectrum, the cyclohexyl resonances were broad and uninformative, but the aromatic region exhibits a characteristic multiplet centered at $\delta = 7.40$ ppm which proved to be diagnostic. The ^{13}C NMR spectrum displayed a lower than expected symmetry, resulting from the diastereotopic carbon atoms in the cyclohexyl rings. Previous literature reports have noted that phosphines such as $(Cy)_2(Ph)P$ exhibit six separate resonances in the ^{13}C NMR spectrum for the cyclohexyl rings.[9,10] Bisphosphine **3** exhibits a ^{13}C NMR spectrum analogous to that reported for $(Cy)_2(Ph)P$, Figure 1.[9] As with $(Cy)_2(Ph)P$, the shielding of the ^{13}C shifts for **3** follow the expected trend, moving upfield with increasing separation from the phosphorus atom; however, the attenuation of the J_{CP} couplings does not follow a similar trend (see the Experimental Section).

The previously unknown isopropyl-containing bisphosphine ligand **4** was prepared by a procedure similar to that employed for **3**, but without air oxidation. Monitoring the progress of the reaction by ^{31}P NMR allowed for optimization of the product yield after ~10 h. An anaerobic aqueous workup was performed by transfer of the entire reaction mixture into a round-bottom flask with a degassed 1:1 mixture of water/Et_2O. The biphasic solution was vigorously stirred for 20 min. The organic layer was separated and then slowly evaporated with a flow of N_2 overnight yielding colorless crystals, which were collected after evacuation under high vacuum for 2 h.

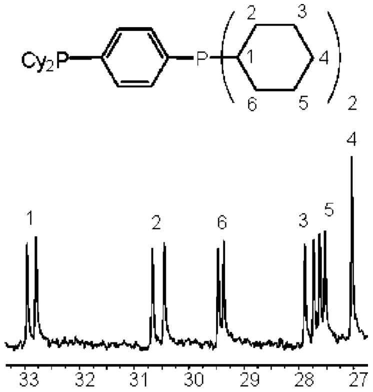


Figure 1. Partial (cyclohexyl region) ^{13}C NMR spectrum of **3** (75 MHz, 298 K, CD_2Cl_2).

The aryl region of the ^1H NMR spectrum for **4** is analogous to **3**, displaying the same characteristic multiplet centered at $\delta = 7.43$ ppm. One signal (a septet of doublets) is observed for the P-CH protons and two resonances (doublet of doublets) for the methyl groups. Similar features have been reported for related *i*-Pr phosphines.[11] A single resonance was observed at $\delta = 10.5$ ppm in the ^{31}P NMR spectrum.

Solid-State Structure of $(i\text{-}Pr_2P)_2C_6H_4$ (4). The bisphosphine ligand **4** was crystallized by slow evaporation from a concentrated Et_2O solution, affording large platelike crystals suitable for X-ray diffraction, Figure 2 (see Table 1; details of the X-ray structure determination are given in the Experimental Section and in the Supporting Information).

Synthesis of Dimeric Metal Complexes. The procedure developed by Kubas and co-workers for the preparation of nominally 16 electron complexes of Mo and W uses the reaction of $M(CO)_3(C_7H_8)$ ($C_7H_8 = \eta^6$-cycloheptatriene; M = Mo, W) with a sterically demanding alkylphosphine. To date, successful synthesis of $M(CO)_3(PR_3)_2$ complexes has been limited to R = Cy, *i*-Pr, or cyclopentyl. Smaller phosphine ligands, such as PPh_3 afford unreactive trisphosphine adducts $M(CO)_3(PPh_3)_3$. The occurrence of a ligand redistribution reaction affording

---

[8] Briggs, J. C.; McAuliffe, C. A.; Hill, W. E.; Minahan, D. M.; Taylor, J. G.; Dyer, G. *Inorg. Chem.* **1982**, *21*, 4204.

[9] Schraml, J.; Capka, M.; Blechta, V. *Magn. Reson. Chem.* **1992**, *30*, 544.

[10] Benn, R. *Org. Magn. Reson.* **1983**, *21*, 60.

[11] Jia, G. C.; Puddephatt, R. J.; Scott, J. D.; Vittal, J. J. *Organometallics* **1993**, *12*, 3565.

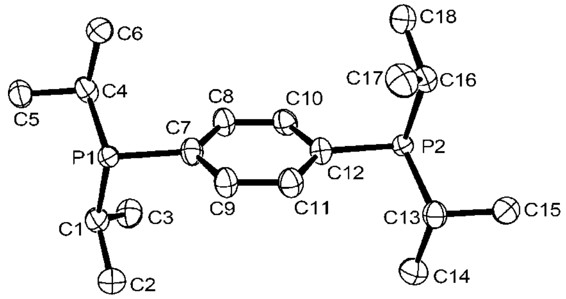
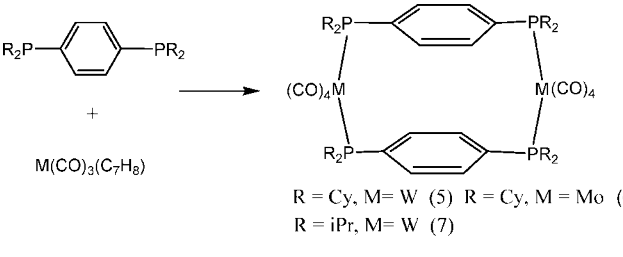


Figure 2. ORTEP diagram of bisphosphine compound **4**. Hydrogen atoms are omitted for clarity. 50% thermal ellipsoids are shown. The P1−P2 distance is 6.50 Å.

$M(CO)_4(PR_3)_2$ is a side reaction reported by Kubas, particularly in aromatic solvents upon heating.[12]

In a typical procedure, we attempted the reaction of bisphosphine **3** with a deep red solution of $W(CO)_3(C_7H_8)$ in alkane solvent at room temperature. [13] At room temperature, no reaction was observed over 24 h. The reaction mixture was heated to 50 °C for 10−12 h, upon which a lightening of the solution was observed. The solution was filtered, leaving behind small amounts of an unidentified dark solid. The solvent was removed in vacuo, leaving a solid which was washed with hexanes to remove unreacted $W(CO)_3(C_7H_8)$. The product was obtained as a deep yellow solid. Similar results were obtained with the Mo analogues and with the isopropyl bisphosphine ligand **4**, eq 3.

Compounds **5**, **6**, and **7** all exhibited similar infrared spectra in the carbonyl stretching region, featuring a strong, broad band at 1865−1875 cm^{-1} and a weaker, sharp absorption above 2000 cm^{-1}. The broad band appeared at 1872, 1865, and 1875 cm^{-1} and the sharper band at 2004, 2009, and 2007 for **5**, **6**, and **7**, respectively. These infrared features closely resemble previously reported spectra for *cis*-$M(CO)_4(PCy_3)_2$ compounds, [14] which led us to suspect that a ligand redistribution reaction had occurred, eq 3. This hypothesis was verified by the lack of reactivity of these complexes with added CO. Consistent with this formulation, we found that the yields of complexes **5** and **6** and particularly complex **7** were improved when the reactions were conducted under an atmosphere of CO.



(3)

In the ^1H NMR spectrum, formation of **5**, **6**, and **7** is indicated by an upfield shift of the aryl protons, from δ 7.4 ppm for the free bisphosphine to δ 6.9 ppm for **5**, **6**, and **7**. In the ^{31}P NMR spectrum, a typical downfield shift is observed from 2 and 10.5 ppm for the free phosphines to 20.6, 37.0, and 29.1 ppm for the corresponding complexes **5**, **6**, and **7**. The ~17 ppm difference in ^{31}P chemical shifts between Mo and W adducts is commonly observed for similar carbonyl compounds of group VI. [15] Tungsten satellites ($J = 228$ Hz for **5** and 227 Hz for **7**) are also observed and are comparable to literature values. [16] The ^{13}C NMR spectra of **5** and **6** each exhibit six different peaks for the cyclohexyl groups, indicating the diastereotopic effects observed in **3** (described above) are carried through to the metal analogues. The resonance due to carbon C1 is shifted 7 ppm farther downfield, a trend which has also been reported for $M(CO)_4(PCy_3)_2$ compounds.[14] Similarly, the tertiary carbon attached directly to phosphorus in **7** is shifted ~7 ppm downfield. Two signals were observed in the aromatic region of **5**, **6**, and **7** at ~132 and ~133 ppm. The signal at 133 ppm displays a triplet-like feature with $J_{CP} = 10$ Hz and is assigned to the apical quaternary carbon bound directly to the phosphorus. The larger broad signal at 132 ppm is assigned to the four aryl ring carbons, for which the coupling to ^{31}P was too small to resolve.

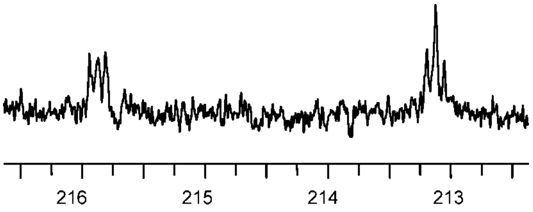


Figure 3. Partial (carbonyl region) ^{13}C NMR spectrum of **6** *cis*-$[Mo_2(CO)_8((Cy_2P)_2C_6H_4)_2]$ (125 MHz, 298 K, CD_2Cl_2).

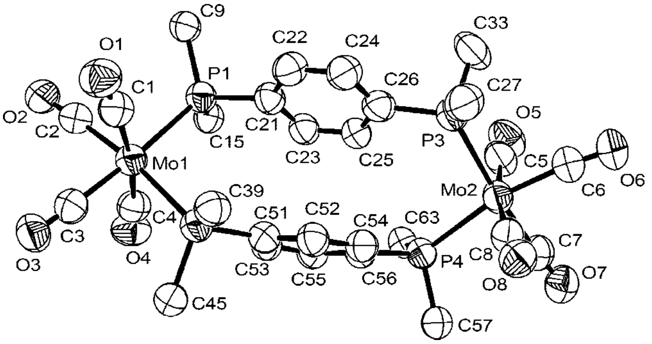


Figure 4. ORTEP diagram for compound **6**. Hydrogen atoms and cyclohexyl carbon atoms (except carbon atoms adjacent to phosphorus) are omitted for clarity. 50% thermal ellipsoids are shown.

The carbonyl region of the ^{13}C NMR spectrum for the Mo complex **6** exhibits a virtual triplet ($J \approx 8$ Hz) at δ 215.9 ppm corresponding to the equatorial carbonyls and a triplet at δ 213.1 ppm ($J = 9$ Hz) corresponding to the axial carbonyls, Figure 3. These shifts, splitting patterns, and couplings are similar to those previously reported for *cis*-$Mo(CO)_4(Cy_3P)_2$.[17] This data indicates a cis arrangement of the phosphine ligands for complex **6**, which is confirmed by a solid-state structure determination, Figure 4.

The carbonyl region for compounds of the general formula *cis*-$W(CO)_4(PR_3)_2$ is not as definitive as two resonances are reported with very similar chemical shifts, causing significant overlap.[15] Complexes **5** and **7** both exhibit this type of overlap with at resonances at 205.7 and 215.9 ppm, respectively. This data implies but does not confirm that complex **5** also has a cis arrangement of the phosphine ligands around the W center.

---

(12) Wasserman, J. H.; Kubas, J. K.; Ryan, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2295.

(13) Kubas, G. J. *J. Chem. Soc., Chem. Commun.* **1980**, 61.

(14) Demircan, O.; Ozkar, S.; Ulku, D.; Yildirim, L. T. *J. Organomet. Chem.* **2003**, *688*, 68.

(15) Bodner, G. M. *Inorg. Chem.* **1975**, *14*, 2694.

(16) Grim., S. O.; McAllister, P. R.; Singer, M. R. *J. Chem. Soc., Chem. Commun.* **1969**, 2–38.

(17) Watson, M.; Woodward, S.; Conole, G.; Kessler, M.; Sykara, G. *Polyhedron* **1994**, *13*, 2455.

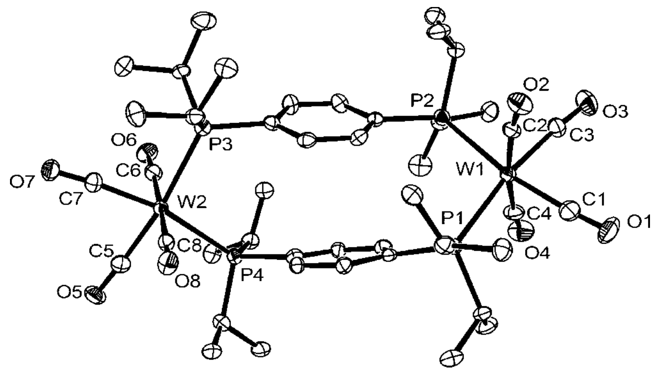
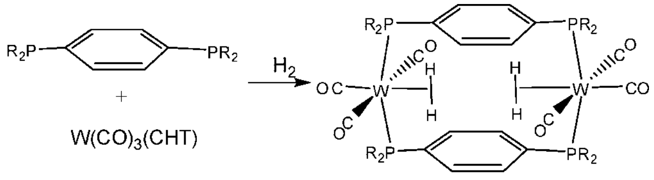


Figure 5. ORTEP diagram for compound **7**. Hydrogen atoms and phosphine carbon labels are omitted for clarity. 30% thermal ellipsoids are shown.

Solid-State Structure of Complex 6. The dimeric tetracarbonyl formulation was confirmed by the determination of the structure of complex **6** by X-ray crystallography (Figure 4). Clear crystals of complex **6** suitable for X-ray diffraction were recovered from a methylene chloride solution. (See Table 1, the Experimental Section, and the Supporting Information for details). The cis geometry of the phosphine ligands about the Mo center is confirmed. A Mo−Mo distance of 9.34 Å is observed. The axial carbonyls have shorter Mo−C bonds (1.97 Å) compared to the equatorial carbonyls (2.02 Å). The phosphorus bite angles at the metal center are 100.0 and 105.1°, significantly greater than the ideal 90° for an octahedral geometry. The bond angles at phosphorus range from 116.7 to 120.7°. The deviation from ideal bond angles in **6** suggests that this compound has a significant amount of strain. Consistent with this, one of the phosphorus atoms (P4) is perturbed out the plane of the aryl linker by 0.231 Å, this is significantly strained when compared to the 0.084 Å in the free ligand. Similar angles were observed for the previously reported compound **1**.[6] The aryl rings have a staggered arrangement and a distance between centroids of 3.66 Å. Although this distance could suggest weak π-stacking, as was previously proposed for **1**, the aryl planes deviate from an ideal parallel stacking orientation with a dihedral angle of 26.4° (Table 1), in contrast to the corresponding angle of 0.8° previously reported for **1**.[6]

Solid-State Structure of Complex 7. The structure of complex **7** was determined by X-ray crystallography (Figure 5). Yellow crystals of complex **7** suitable for X-ray diffraction were recovered from a heptane solution. A summary of the structure determination is in Table 1. The details of the data collection and refinement are given in the Experimental Section and in the Supporting Information. The cis geometry of the phosphine ligands about the W center is confirmed. A W−W distance of 9.31 Å is observed. The axial carbonyls have shorter W−C bonds (1.97 Å) compared to the equatorial carbonyls (2.02 Å). The coordination geometry around each tungsten center closely resembles that previously reported for *cis*-$(PCy_3)_2W(CO)_4$.[17] As noted above for **6**, many of the bond angles in **7** deviate from ideal values, suggesting a strained structure. The dihedral angle between aryl planes is 21.4°, similar to compound **6**, but very different from **1**.

Complexation of Hydrogen. When $W(CO)_3(C_7H_8)$ and bisphosphine **4** were allowed to react under a hydrogen atmosphere, a new H_2-containing tungsten species formulated as $[W_2(CO)_6(H_2)_2(i\text{-}Pr_2P)_2C_6H_4)_2]$ (**8**) was observed. In contrast to the upfield shift of the aryl protons observed for compounds **5**−**7**, the ^1H NMR spectrum of compound **8** exhibits a downfield shift to 7.9 ppm. The bound H_2 appears as a broad resonance centered at −4.2 ppm. As expected, when the preparative reaction is carried out with HD gas, this resonance is replaced by a broad 1:1:1 triplet (J_{HD} = 33 Hz). Integration of the hydride resonance versus the aryl protons is consistent with the presence of one H_2 molecule per metal center. Monitoring of the reaction by ^{31}P NMR spectroscopy showed a resonance for **8** at 47.2 ppm (J_{PW} = 280 Hz) and unreacted phosphine **4** at 2 ppm. Formation of **8** was slow, reaching a maximum yield of ca. 80% only after 5−6 days. At this time, a competing ligand redistribution reaction begins to occur, leading to precipitation of compound **7**. Attempts to isolate compound **8** under various conditions were unsuccessful, always leading to compound **7** and unidentified products. Dihydrogen complex **8** was rapidly converted to **7** by treatment with CO gas.



8, R = *i*Pr; 9, R = Cy

Under the same conditions, reaction of **3** with $W(CO)_3(C_7H_8)$ under an atmosphere of H_2 slowly affords a similar hydrogen complex, formulated as $[W_2(CO)_6(H_2)_2(Cy_2P)_2C_6H_4)_2]$ (**9**). The bound H_2 ligand exhibits a broad signal at −3.75 ppm. When compound **9** was prepared using HD gas, this resonance was replaced by a broad 1:1:1 triplet with J_{HD} = 33 Hz. As with compound **8**, attempts to isolate **9** under a variety of conditions were not successful, with ligand redistribution leading to formation of tetracarbonyl compound **5** and unidentified products. In the case of **9**, ligand redistribution occurs more rapidly than for **8**.

Similar reaction conditions were explored with $Mo(CO)_3(C_7H_8)$ and bisphosphines **3** and **4**. No evidence for hydrogen complexation was obtained. All molybdenum reactions regardless of solvent choice, temperature, hydrogen pressure or reaction time showed varying amounts of dimeric tetracarbonyl adducts, starting material, and unknown decomposition products. We conclude that the ligand redistribution occurs more rapidly for the molybdenum complexes than the corresponding tungsten complexes.

Reactivity of Complexes 5−7. Removal of a CO ligand from the tetracarbonyl complexes **5**−**7** was explored with the intention of generating coordinatively unsaturated metal centers. Photolysis of these complexes under conditions similar to those previously employed for related tetracarbonyl species[18] gave primarily dissociation of the phosphine ligand, as shown by ^{31}P NMR spectroscopy. Similarly, reaction of the tetracarbonyl complexes with Me_3NO did not afford oxidative removal of CO; rather, phosphine ligand oxidation was observed.

Conclusion

In contrast to the monomeric complexes reported by Kubas, the dimeric complexes described here do not afford an observable coordinatively unsaturated, formally 16-electron species. Instead, facile ligand redistribution reactions afford the corresponding tetracarbonyl analogues and unidentified decomposition products. Although H_2 complexes were observed in solution, the synthetis reactions did not go to completion, and ultimately,

---

[18] Heinekey, D. M.; Law, J. K.; Schultz, S. M. *J. Am. Chem. Soc.* **2001**, *123*, 12728.

these efforts suffered from competing ligand redistribution. Higher temperature conditions accelerated the ligand redistribution regardless of metal or phosphine employed. Although Kubas has reported decreased stability when moving up the triad, Cr and Mo adducts could be prepared.[19] In contrast, we were unable to observe complexation of H_2 to molybdenum centers due to very rapid ligand redistribution reactions.

Experimental Section

General Procedures. All solvents used were reagent grade, and anhydrous solvents were distilled from calcium hydride. Chlorodicyclohexylphosphine was supplied by Strem Chemicals, Inc. $W(CO)_3(C_7H_8)$[20] and $Mo(CO)_3(C_7H_8)$[21] were prepared as described in the literature. All other chemicals were purchased from Aldrich and used as received. Where anaerobic techniques were required, glovebox and standard Schlenk techniques were used. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded at ambient temperatures with chemical shifts specified in ppm relative to the specified solvent. Elemental analyses were performed by Desert Analytics, Phoenix, AZ.

Preparation of $(Cy_2P)_2C_6H_4$ (3). *p*-Dibromobenzene (1.202 g, 5.09 mmol) was dissolved in Et_2O (20 mL). A solution of 2.5 M *n*-BuLi in hexane (8.15 mL, 20.4 mmol) was slowly added at 0 °C. The resulting solution was vigorously stirred for 2.5 h at 50 °C. After the solution was cooled to 0 °C, chlorodicyclohexylphosphine (2.5 mL, 11.3 mmol) was added dropwise, and the resulting solution was heated (50 °C) for 12 h. After the solution was cooled to room temperature, the reaction was quenched with a 1:1 mixture of $MeOH/H_2O$ (20 mL). The white precipitate was collected in the air and washed with water, MeOH, pentane, and cold Et_2O. The solid was dried under vacuum and then placed in an oven-dried H-tube. Benzene (20 mL) was transferred to the vessel, and PMHS (1 mL) was syringed into the reaction. The solution was cooled to ~6 °C and filtered, yielding 1.651 g (69%) of a white solid. ^1H NMR (500 MHz, $CDCl_3$): 7.40 (m, 4 H, Ar-H); 2.2 −1.0 (m, 44 H). ^{13}C NMR: δ 135.5 (d, $J = 19$ Hz), 133.7 (dd, $J = 19, 7$ Hz), 32.3 (d, $J = 13$ Hz), 30.0 (d, $J = 19$ Hz), 28.9 (d, $J = 7$ Hz), 27.3 (d, $J = 13$ Hz), 27.0 (d, $J = 7$ Hz), 26.5 (s). ^{31}P: δ 2.0 (s).

Synthesis of $(i\text{-}Pr_2P)_2C_6H_4$ (4). *p*-Dibromobenzene (3.547 g, 15.0 mmol) was dissolved in Et_2O (20 mL). A 2.5 M solution of *n*-BuLi in hexane (24.0 mL, 60.2 mmol) was slowly added at 0 °C causing the solution to turn greenish yellow. The resulting solution was vigorously stirred for 2.5 h at 50 °C. After the solution was cooled to 0 °C, chlorodiisopropylphosphine (5.0 mL, 31.5 mmol) was added dropwise, and the resulting solution was heated at 45 °C for 10 h, after which time the reaction mixture was heterogeneous with a fine colorless precipitate. The reaction mixture was cannula transferred into a degassed 1:1 mixture of water and Et_2O (100 mL). After 20 min of vigorous stirring, the organic layer was cannula transferred into another Schlenk flask and the solvent volume reduced to 15 mL. After slow evaporation of the solvent in a stream of N_2, large colorless crystals of compound **4** were obtained. After pumping off residual volatiles, 2.85 g of **4** was collected (61%). ^1H NMR (500 MHz, CD_2Cl_2): 7.43 (m, 4 H, Ar-H); 2.10 (septet of doublets, 4 H, −CH−, $J_{HH} = 7$ Hz, $J_{HP} = 1.7$ Hz); 1.07 (dd, 12 H, $-CH_3$, $J = 15, 7$ Hz); 0.90 (m, 12 H, $-CH_3$, $J = 12, 7$ Hz). ^{13}C: δ 136.2 (d, 2C, $J = 20$ Hz); 134.2 (dd, 4C, $J = 19, 7$ Hz), 23.2 (d, 4C, $J = 13$ Hz), 20.2 (d, 4C, $J = 18$ Hz), 19.1 (d, 4C, $J = 9$ Hz). ^{31}P: δ 10.5 (s). Anal. Calcd for $C_{18}H_{32}P_2$: C, 69.65; H, 10.39. Found: C, 69.59; H, 10.44.

Synthesis of $[W_2(CO)_8((Cy_2P)_2C_6H_4)_2]$ (5). A CH_2Cl_2 solution (20 mL) of bisphosphine **3** (0.305 g, 0.648 mmol) and $W(CO)_3(C_7H_8)$ (0.237 g, 0.660 mmol) was stirred overnight (10−12 h) under an atmosphere of CO gas. After removal of solvent, pentane (~15 mL) was vacuum transferred into the vessel producing a yellowish precipitate and pinkish red solution. The pentane solution was filtered, washing away excess $W(CO)_3(C_7H_8)$, to afford 0.210 g (42%) of a light yellow solid. ^1H NMR (500 MHz, CD_2Cl_2): 6.90 (br s, 4 H, Ar-H); 2.2−1.0 (m, 44 H). $^{13}C\{^1H\}$ NMR (125.70 MHz): δ 205.69 (m, 8 C, CO); 132.67 (t, 4 C, P-C_{Ar}, $J_{PC} = 11$ Hz); 132.10, (br s, 8 C, C-Ar); 39.03 (br s, 8 C, P-C_{Cy}); 29.51 (s, 8 C, C_{Cy}); 29.40 (s, 8 C, C_{Cy}); 28.07 (t, 8C, C_{Cy}, $J_{PC} = 5$ Hz); 27.92 (t, 8C, C_{Cy}, $J_{PC} = 5$ Hz); 26.85 (t, 8C, C_{Cy}). ^{31}P: δ 20.6 (s, $J_{PW} = 228$ Hz). IR (cm^{-1}): 2004, br 1872. Anal. Calcd for $W_2P_4O_8C_{68}H_{96}$: C, 53.27; H, 6.31. Found: C, 52.37; H, 6.36.

Synthesis of $[Mo_2(CO)_8((Cy_2P)_2C_6H_4)_2]$ (6). A CH_2Cl_2 solution (20 mL) of **3** (0.139 g, 0.295 mmol) and $Mo(CO)_3(C_7H_8)$ (0.083 g, 0.305 mmol) was stirred overnight (10−12 h) under an atmosphere of CO gas. The solvent was then stripped, and pentane (~15 mL) was vacuum transferred into the vessel producing a yellowish precipitate and light reddish orange solution. The pentane solution was filtered, washing away excess $Mo(CO)_3(C_7H_8)$ and leaving behind 0.090 g (45.9%) of a faint yellow solid. ^1H NMR (500 MHz, CD_2Cl_2: 6.89 (br s, 4 H, Ar-H); 2.2−1.0 (m, 44 H). $^{13}C\{^1H\}$-NMR (125.70 MHz): δ 215.9 (t, 4 C, CO, $J_{PC} = 8$ Hz); 213.1 (t, 4 C, CO, $J_{PC} = 9$ Hz); 133.10 (t, 4 C, P-C_{Ar}, $J_{PC} = 11$ Hz); 132.10, (br s, 8 C, C-Ar); 37.80 (br s, 8 C, P-C_{Cy}); 29.28 (s, 8 C, C_{Cy}); 29.13 (s, 8 C, C_{Cy}); 28.12 (t, 8C, C_{Cy}, $J_{PC} = 5$ Hz); 27.94 (t, 8C, C_{Cy}, $J_{PC} = 5$ Hz); 26.83 (t, 8C, C_{Cy}). ^{31}P: δ 37.0 (s). IR (cm^{-1}): 2009, br 1865. Anal. Calcd for $Mo_2P_4O_8C_{68}H_{96}$: C, 60.17; H, 7.13. Found: C, 59.17; H, 7.06.

Synthesis of $[W_2(CO)_8((iPr_2P)_2C_6H_4)_2]$ (7). A CH_2Cl_2 solution (20 mL) of ligand **4** (0.142 g, 0.458 mmol) and $W(CO)_3(C_7H_8)$ (0.165 g, 0.458 mmol) was stirred overnight (10−12 h) under an atmosphere of CO gas. After removal of solvent, pentane (~15 mL) was vacuum transferred into the vessel, producing a yellowish precipitate and pinkish red solution. The pentane solution was filtered, washing away excess $W(CO)_3C_7H_8$, and yielding 0.160 g (58%) of a light yellow solid. ^1H NMR (500 MHz, CD_2Cl_2): δ 6.97 (br s, 4 H, Ar−H); 2.54 (br s, 4 H, −CH−); 1.26−1.15 (m, 24 H, $-CH_3$). $^{13}C\{^1H\}$ NMR (125.70 MHz): δ 215.9 (m, 8 C, CO, $J_{PC} = 8$ Hz); 133.10 (t, 4 C, P-C_{Ar}, $J_{PC} = 11$ Hz); 132.10, (br s, 8 C, C-Ar); 28.92 (br s, 8 C, P-CH−); 19.55 (s, 8 C, $-CH_3$); 19.42 (s, 8 C, $-CH_3$). ^{31}P: δ 29.1 (s, J_{PW} 227 Hz). IR (cm^{-1}): 2007, br 1875. Anal. Calcd for $W_2P_4O_8C_{44}H_{64}$: C, 43.58; H, 5.32. Found: C, 43.72; H, 5.43.

Observation of $[W_2(CO)_6(H_2)_2(Cy_2P)_2C_6H_4)_2]$ (8). Fluorobenzene-d_5 (1 mL) was transferred into a J. Young NMR tube charged with **3** (6 mg, 0.0127 mmol) and $W(CO)_3(C_7H_8)$ (5 mg, 0.0134 mmol). While the solvent was still frozen, the tube was backfilled with an atmosphere of H_2 (or HD) gas. The mixture was left to react at room temperature for several days over which time the solution turned from a deep red to an orange color. ^1H NMR (500 MHz, fluorobenzene-d_5): 8.1−7.9 (br s, 4 H, Ar-H); 2.2 −1.0 (m, 44 H); −3.75 (br s, H_2). ^{31}P: δ 37.4 (s). Complex **8**-d_1 was prepared similarly with HD gas: $\delta = -3.81$ (br t, $J_{HD} \approx 33$ Hz).

Observation of $[W_2(CO)_6(H_2)_2(iPr_2P)_2C_6H_4)_2]$ (9). An NMR tube fitted with a high-vacuum Kontes valve was charged with $(i\text{-}Pr_2P)_2C_6H_4$ (8 mg, 0.0258 mmol) and $W(CO)_3C_7H_8$ (9 mg, 0.0250 mmol). Toluene-d_8 (1 mL) was vacuum transferred, and while the solvent was still frozen the vessel was backfilled with an atmosphere of H_2 (or HD) gas. The tube was allowed to stir at room temperature for 5 days over which time the solution turned from a deep red to an orange-yellow color. ^1H NMR (500 MHz, toluene-d_8): 8.0−7.8 (br s, 4 H, Ar-H); 2.10 (septet, 4 H, −CH−); 1.1 (m, 12 H, $-CH_3$); 1.06 (m, 12 H, $-CH_3$); −4.10 (b s, H_2). ^{31}P: $\delta = 47.2$ (s, J_{PW} 280 Hz). Complex **9**-d_1 was prepared similarly with HD gas: δ −4.21 (br t, $J_{HD} \approx 33$ Hz).

---

(19) Gonzalez, A. A.; Mukerjee, S. L.; Chou, S. J.; Kai, Z.; Hoff, C. D. *J. Am. Chem. Soc.* **1988**, *110*, 4419.

(20) Kubas, G. J. *Inorg. Chem.* **1983**, *22*, 692.

(21) Cotton, F. A.; McCleverty, J. A.; White, J. E. *Inorg. Synth.* **1990**, *28*, 45.

Crystallographic Studies. [$(Cy_2P)_2C_6H_4$] (3), [$(iPr_2P)_2C_6H_4$] (4), [$Mo_2(CO)_8((Cy_2P)_2C_6H_4)_2$] (6), and [$(W_2(CO)_8((iPr_2P)_2PC_6H_4)_2$] (7). Single crystals of **3**, **4**, and **6** were grown from the slow evaporation of methylene chloride. Single crystals of **7** were grown over ~3 weeks from a heptane solution. Diffraction measurements were obtained in a nitrogen stream at 130 K on a Nonius Kappa CCD diffractometer using graphite-monochromated radiation (λ= 0.71073 Å). The data was integrated and scaled using *hkl*-SCALEPACK. This program applies a multiplicative correction factor (S) to the observed intensities (I) and has the following form: $S = \exp(2B(\sin q/\lambda)^2)/\text{scale}$. S is calculated from the scale, and the B factor is determined for each frame and is then applied to I to give the corrected intensity (I_{corr}). Solution by direct methods (SHELXS97) produced a complete heavy atom phasing model consistent with the proposed structure. All hydrogen atoms were located using a riding model. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods.

Acknowledgment. This work was supported by the National Science Foundation.

Supporting Information Available: Crystallographic data and other relevant data including CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800273T