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Reactions of $M(CO)_6$ (M = Mo, W) with PPh_2H and $NaBH_4$

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The reaction of $M(CO)_6$ (M = Mo, W) with PPh_2H and $NaBH_4$ in high-boiling alcohols affords $M(CO)_5PPh_2H$ (1), *cis*-$M(CO)_4(PPh_2H)_2$ (2), *fac*-$M(CO)_3(PPh_2H)_3$ (3), $(OC)_4M(\mu\text{-}PPh_2)_2M(CO)_4$ (4), $(OC)_4M(\mu\text{-}PPh_2)_2M(CO)_3PPh_2H$ (5), *trans*-$HPh_2P(OC)_3M(\mu\text{-}PPh_2)_2M(CO)_3PPh_2H$ (6), and *cis*-$HPh_2P(OC)_3M(\mu\text{-}PPh_2)_2M(CO)_3PPh_2H$ (7). Proper selection of the phosphine/metal carbonyl mole ratio optimizes the formation of 3, 5, or 6, and good yields of these products may be obtained. Complexes 1, 2, 4, and 7 are found as minor products. ^{31}P NMR studies show that 1 and 2 are precursors to the phosphido-bridged complexes. A reaction sequence for the formation of observed products is proposed.

Introduction

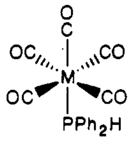
The bright red, phosphido-bridged complexes $(OC)_4M(\mu\text{-}PR_2)_2M(CO)_4$ (M = Cr, Mo, W) were first synthesized in 1964 by reaction of $M(CO)_6$ and R_2PPR_2.[1] The presence of a planar di-μ-phosphido bridge linking the two metal atoms in these compounds was subsequently established by crystallographic studies.[2] More recently, improved syntheses involving thermal or photolytic reactions of $M(CO)_5PPh_2H$ have been reported.[3] In addition, phosphine-substituted derivatives such as *trans*-$R_3P(OC)_3M(\mu\text{-}PR_2)_2M(CO)_3PR_3$ and $R_3P(OC)_3M(\mu\text{-}PR_2)_2M(CO)_4$ have been prepared from PR_3 and $(OC)_4M(\mu\text{-}PR_2)_2M(CO)_4$ by irradiation and by thermolysis.[4]

The purpose of this work has been to explore the potential for producing phosphido-bridged complexes of the group 6 metals by direct reaction of their hexacarbonyls with secondary phosphines. The reaction of $M(CO)_6$ (M = Cr, Mo, W) with tertiary phosphines and sodium borohydride in ethanol has become a standard method for synthesizing monometallic phosphine derivatives of these carbonyls.[5] These borohydride-assisted reactions, which provide facile substitution of tertiary phosphines for carbon monoxide, have not been explored with secondary phosphines. Previous work has shown that secondary phosphines, under vigorous conditions, frequently lose hydrogen to form complexes with bridging phosphido groups.[6] Achieving a similar result for the reactions central to this investigation was one of our principal aims.

We have found that reactions of $M(CO)_6$ with PPh_2H and $NaBH_4$ proceed in ethanol to give the expected monometallic phosphine-substituted derivatives but when the reactions are carried out in a high-boiling alcohol such as 1-butanol, phosphido-bridged products readily form. By using controlled stoichiometric ratios, it is possible to isolate good yields of $HPh_2P(OC)_3M(\mu\text{-}PPh_2)_2M(CO)_4$ and *trans*-$HPh_2P(OC)_3M(\mu\text{-}PPh_2)_2M(CO)_3PPh_2H$. From spectroscopic analysis of product mixtures, conclusions regarding reaction pathways have been drawn.

Results and Discussion

General Features of the Reactions. The reaction of $M(CO)_6$ (M = Mo, W) with PPh_2H and $NaBH_4$ in refluxing ethanol (bp 78 °C), 1-butanol (bp 118 °C), or 1-hexanol (bp 157 °C) proceeds to give some combination of seven products (1–7), the relative amounts of which can be controlled by proper selection of the phosphine/metal carbonyl ratio, solvent, and reaction time.



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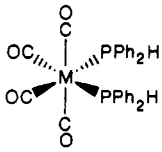

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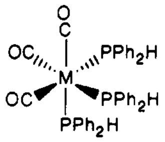

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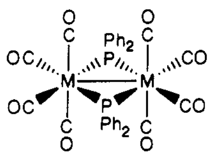

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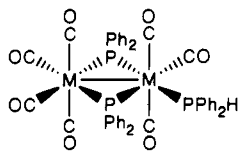

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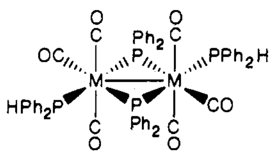

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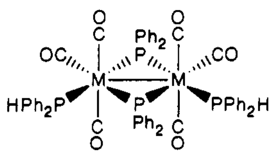

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When the reaction is carried out in refluxing ethanol, only traces of phosphido-bridged products are formed even when the reaction is allowed to proceed for as long as 2 days. In these reactions 3 is the exclusive product if the ratio of phosphine to metal carbonyl is 3.0 or greater. Reducing the ratio to 2.0 gives mixtures of 2 and 3 as principal products and 1 as a minor product.

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[1] (a) Chatt, J.; Thornton, D. A. *J. Chem. Soc.* **1964**, 1005. (b) Hayter, R. G. *Inorg. Chem.* **1964**, *3*, 711. (c) Chatt, J.; Thompson, D. T. *J. Chem. Soc.* **1964**, 2713.

[2] (a) Mais, R. H. B.; Owston, P. G.; Thompson, D. T. *J. Chem. Soc. A* **1967**, 1735. (b) Linck, M. H.; Nassimbeni, L. R. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 1105. (c) Shyu, S.-G.; Callifaris, M.; Nardin, G.; Wojcicki, A. *J. Am. Chem. Soc.* **1987**, *109*, 3617.

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[4] (a) Thompson, D. T. *J. Organomet. Chem.* **1965**, *4*, 74. (b) Basato, M. *J. Chem. Soc., Dalton Trans.* **1976**, 1678. (c) Basato, M. *J. Chem. Soc., Dalton Trans.* **1986**, 217.

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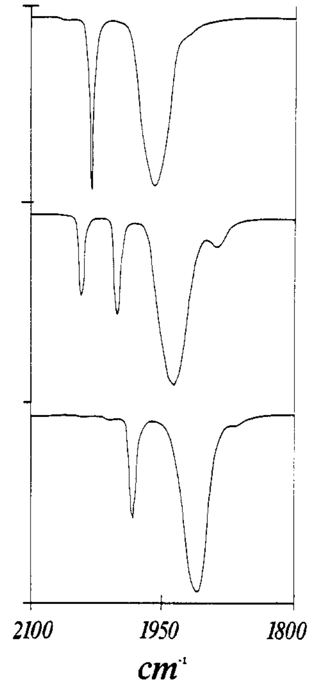

Figure 1. Infrared spectra in the carbonyl region for **4(W)** (top), **5(W)** (middle), and **6(W)** (bottom).

Table I. Infrared Data for Phophido-Bridged Group 6 Carbonyl Complexes ($CHCl_3$)

complex	C–O stretching freq, cm^{-1}	ref
4(W)	1961 (vs), 2032 (s)	1a
5(W)	1890 (w), 1938 (s), 2002 (m), 2043 (m)	3c
6(W)	1910 (vs), 1982 (s)	
4(Mo)	1967 (vs), 2034 (s)	1a
5(Mo)	1903 (w), 1948 (s), 2006 (m), 2044 (m)	
6(Mo)	1920 (s), 1987 (m)	

With 1-butanol as solvent, the reaction results mimic those obtained for ethanol as long as the phosphine to metal carbonyl ratio is 3.0 or greater. However, when the reactant ratio is reduced, bridged bimetallic products predominate. Largest yields of **6(W)** (76%) were obtained at a P/M ratio of 1.8 and a reaction time of 9 h. Small quantities of **2(W)** and **3(W)** also were found in the crude product, and for some trials traces of **7(W)** were detected with ^{31}P NMR. The formation of **5(W)** was apparently optimized (63%) when the ratio was reduced to 1.2. Its production was accompanied by the formation of **4(W)** and **6(W)** as minor products. Reducing the ratio further (as low as 0.5) did not significantly enhance the formation of **4(W)**. Required reaction times for $Mo(CO)_6$, although not studied systematically, were generally shorter than for $W(CO)_6$.

When 1-hexanol is used as the solvent, it is possible to reduce the reaction time to 4 h for reactions involving $W(CO)_6$. This result, in conjunction with the observations made for ethanol and 1-butanol, suggests that lower temperatures favor formation of monometallic complexes as final products whereas higher temperatures promote ultimate formation of phosphido-bridged products.

A series of reactions also were carried out to determine the optimum quantity of $NaBH_4$ required for the formation of **6(W)**. Essentially no reaction occurred in the absence of $NaBH_4$. The maximum yield of **6(W)** was obtained with a $PPh_2H/W(CO)_6/NaBH_4$ ratio of 1.8/1.0/5.0.

Table II. ^{31}P NMR Data for Phosphido-Bridged Group 6 Carbonyl Complexes ($CDCl_3$)

complex	chem shifts, ppm	coupling consts, Hz	
		J_{PP}	J_{WP}
4(W)	180.0		162.0
5(W)	177.0	16.4	150.1
		32.8	184.1
	156.1	16.4	160.2
		34.4	191.4
	-13.1	32.8	245.3
		34.4	
6(W)	155.8	14.2	177.8
		-30.9	
		30.9	
	-10.2	14.2	254.0
		-30.9	
		30.9	
7(W)	176.2	14.9	189.3
		33.2	
	133.2	14.9	168.9
		33.2	
	-10.1	33.2	252.0
		33.2	
4(Mo)	232.9		
5(Mo)	230.5	10.4	
		36.6	
	202.5	10.4	
		36.6	
	20.2	36.6	
		36.6	
6(Mo)	204.2	8.2	
		-33.2	
		33.2	
	23.6	8.2	
		-33.2	
		33.2	

Spectroscopic Properties. Infrared spectra of **4(W)**, **5(W)**, and **6(W)** are shown in Figure 1. Carbonyl stretching frequencies for the molybdenum and tungsten complexes are listed in Table I. As CO groups are sequentially replaced with PPh_2H ligands, the C–O bonds of the remaining carbonyl ligands are observed to weaken, as reflected by the decreasing frequencies of the principal CO absorptions. Furthermore, it is clear that increasing the electron density by phosphine substitution on one metal atom also increases the electron density on the adjacent metal center.

^{31}P NMR data for phosphido-bridged complexes of tungsten and molybdenum are recorded in Table II. The ^{31}P NMR spectrum of **5(W)** shows two doublets of doublets at 177.0 and 156.1 ppm, which are assigned to the bridging PPh_2 ligands supported by a W–W bond.[7] In addition, a triplet (due to overlapping doublets) at -13.1 ppm is assigned to the terminal phosphine. Specific assignments were made for the bridging PPh_2 groups by comparing their chemical shifts to those for **4(W)** and **6(W)**. It is expected that the PPh_2 group of **5(W)** that is trans to two CO groups would be most similar to a PPh_2 group of **4(W)**, which gives an absorption at 180.0 ppm. Therefore the signal at 177.0 ppm for **5(W)** is assigned to the bridging PPh_2 group trans to CO ligands. The PPh_2 group of **5(W)** that is trans to the terminal phosphine ligand should have a chemical shift similar to that of the PPh_2 groups of **6(W)** (155 ppm) and is consistent with the absorption at 156.1 ppm.

Further inspection of the NMR spectrum of **5(W)**, which is first order, allows assignment of coupling constants. A value of 16.4 Hz is ascribed to the phosphorus–phosphorus coupling between bridging phosphido groups. The coupling of the terminal PPh_2H to the bridging PPh_2 groups is particularly interesting because the trans and cis arrangements give values of essentially the same magnitude (32.8 and 34.4 Hz). Analysis of the ^{31}P NMR spectrum of

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[7] (a) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. (b) Carty, A. J. *Adv. Chem. Ser.* **1982**, *No. 196*, 163.

6(W) (vide infra) suggests that these coupling constants are of opposite sign. The tungsten–phosphorus satellite patterns arising from **5(W)** are quite complex because the two nonequivalent tungsten atoms split each doublet of doublets into 16 satellite signals. By comparing the tungsten–phosphorus coupling constants of **4(W)** and **6(W)** with those of **5(W)**, we conclude that the larger of the two tungsten–phosphorus coupling constants associated with each bridging phosphido group of **5(W)** arises from coupling to the tungsten bearing the terminal phosphine. ^{31}P NMR assignments for **5(Mo)** parallel those made for **5(W)**.

The AA′XX′ ^{31}P NMR spectra of **6(W)** and **6(Mo)** were simulated with the program ITRCAL.[8] In each case the value of N ($J_{AX} + J_{AX'}$) is zero within the resolution of the instrument. It is thus apparent that J_{AX} and $J_{AX'}$ are of equal magnitude and opposite sign. Simulated values for these two coupling constants are 30.9 and −30.9 Hz for **6(W)** and 33.2 and −33.2 Hz for **3(Mo)**. The separation of the two outer lines gives directly values of 14.2 and 8.2 Hz for the phosphorus–phosphorus coupling between bridging phosphido groups of **6(W)** and **6(Mo)**, respectively. Since the outer lines are not split, it can be concluded that long-range coupling between the terminal phosphines is essentially zero.

Only trace quantities of **7(W)** were observed by ^{31}P NMR in the course of these studies. We have not found a method of producing it from its trans isomer, **6(W)**, nor have we found a procedure for enhancing its formation in the overall reaction. The ^{31}P NMR spectrum of **7(W)** consists of two doublets of triplets arising from the two nonequivalent bridging PPh_2 groups and a triplet arising from the terminal PPh_2H ligands. The chemical shift at 133.2 ppm can be assigned to the bridging phosphido group that is trans to two terminal PPh_2H ligands whereas the signal at 176.2 ppm is consistent with a bridging phosphido group trans to two CO ligands. For this complex, as with the others in this study, coupling between the bridging and terminal phosphorus moieties is of the same absolute value for both cis and trans arrangements.

Details of the Overall Reaction. In an attempt to elucidate the steps by which the overall reaction proceeds, several trials (with $PPh_2H/W(CO)_6/NaBH_4$ = 1.8/1.0/5.0) were carried out in 1-butanol for varied time periods. In each case the reaction was quenched by removal from heat and, following removal of solvent, a ^{31}P NMR spectrum of the mixture was recorded. After 10 min of reaction time (and maximum temperature = 70 °C) the mixture contained, in addition to unreacted starting material, **1(W)**, **2(W)**, and **3(W)**, with the latter two as the major components. After 80 min of reaction time, all of the PPh_2H had been consumed and traces of **4(W)**, **6(W)**, and **7(W)** were detected along with the three monometallic complexes [**1(W)**/**2(W)**/**3(W)** = 1/5/5] as principal constituents.[9] As the reaction proceeded for longer time periods, the concentration of **6(W)** relative to other components continued to increase with time, and after a total of 6 h **1(W)**, **4(W)**, and **7(W)** were no longer observed. These observations, as well as color changes, suggest that the monometallic compounds form rapidly (and at lower temperatures) whereas the bimetallic complexes form more slowly and require higher temperatures.

In a separate experiment it was established that **3(W)** does not react with $NaBH_4$ under the conditions of the reaction. This strongly implies that the principal origin of the phosphido-bridged complexes is **1(W)** and/or **2(W)** since these are the only reactive phosphorus-bearing species in solution immediately prior to phosphido bridge formation. To test this hypothesis, samples of **1(W)** and **2(W)** were prepared and reactions of each with $NaBH_4$ were carried out. When **1(W)** was refluxed in 1-butanol with $NaBH_4$ for 9 h, conversion to **5(W)** (major product) and **4(W)** (minor product) was observed. When the same

$$\mathbf{1(W)} + NaBH_4 \rightarrow \mathbf{4(W)} + \mathbf{5(W)}$$

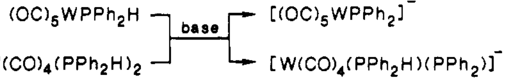
experiment was carried out with **2(W)**, the products observed were **3(W)** and **6(W)** with **3(W)** present in dominant proportions. It is significant that this reaction does

$$\mathbf{2(W)} + NaBH_4 \rightarrow \mathbf{3(W)} + \mathbf{6(W)} + PPh_2H$$

not produce **5(W)** since this implies that **1(W)** is its principal precursor. The appearance of the trisubstituted complex **3(W)** helps to explain why limiting the amount of PPh_2H in the overall reaction fails to prevent the formation of at least some of this product. Its formation is understandable since it would be readily produced by reaction of any labile PPh_2H with **2(W)**. It is also apparent that, in addition to the monosubstituted complex, **4(W)** and **5(W)** are sources of **6(W)** since they can undergo phosphine substitution at the temperature of the reaction.[4]

$$\mathbf{4(W)} \xrightarrow{PPh_2H} \mathbf{5(W)} \xrightarrow{PPh_2H} \mathbf{6(W)}$$

On the basis of the accumulated evidence, a reasonable reaction sequence for the formation of phosphido-bridged complexes such as **4(W)**, **5(W)**, or **6(W)** involves base abstraction of a hydrogen ion from coordinated PPh_2H.



Supporting this view is the fact that reactions leading to phosphido-bridged products proceed best in the presence of excess $NaBH_4$, suggesting that a reasonably basic solution is required. Whether the abstracting base is BH_4^- or an anion generated by reaction of BH_4^- with the solvent, such as BuO^- or $[BH_x(OR)_{4-x}]^-$ (x = 1–4), is open to question. Support for the role of BuO^- in these reactions is provided by a separate experiment in which a 1.8 mole ratio of PPh_2H to $W(CO)_6$ was heated under reflux with NaOBu. The reaction yielded the same major products [**6(W)** and **3(W)**] as were obtained from the borohydride reaction.

In previous work we have shown that $W(CO)_5PPh_2H$ is readily converted by $KOBu^t$ to $[(OC)_4W(\mu\text{-}PPh_2)_2W(CO)_4]^{2-}$ in THF.[3d,e] It is therefore plausible that this anion and/or its phosphine-substituted derivatives may serve as intermediates in this reaction, being generated from the phosphido complexes. Since these dianions are excellent reducing agents, once formed, they would react immediately with solvent to yield the metal–metal bonded complexes.[3a,d,e,12]

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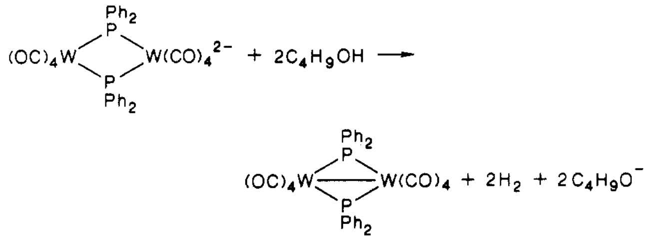
[8] 1180 ITRCAL; Nicolet Instrument Corp.: Madison, WI, 1977.

[9] (a) Ratios are based on ^{31}P NMR signal intensities and are therefore approximate. (b) ^{31}P NMR: $W(CO)_5PPh_2H$, δ −13.7 (J_{WP} = 229.6 Hz); *cis*-$W(CO)_4(PPh_2H)_2$, δ −2.8 (J_{WP} = 224.1 Hz); *fac*-$W(CO)_3(PPh_2H)_3$, δ 6.4 (J_{WP} = 218.5 Hz).[10] (c) Reactions with $Mo(CO)_6$ gave similar results. ^{31}P NMR: $Mo(CO)_5PPh_2H$, δ 7.3; *cis*-$Mo(CO)_4(PPh_2H)_2$, δ 16.9; *fac*-$Mo(CO)_3(PPh_2H)_3$, δ 24.9.[11,2c]

[10] Keiter, R. L.; Sun, Y. Y.; Brodack, J. W.; Cary, L. W. *J. Am. Chem. Soc.* **1979**, *101*, 2638.

[11] (a) Keiter, R. L.; Kaiser, S. L.; Hansen, N. P.; Brodack, J. W.; Cary, L. W. *Inorg. Chem.* **1981**, *20*, 283. (b) Smith, J. G.; Thompson, D. T. *J. Chem. Soc. A* **1967**, 1694.

[12] (a) Dessy, R. E.; Rheingold, A. L.; Howard, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 746. (b) Dessy, R. E.; Kornmann, R.; Smith, C.; Haytor, R. *J. Am. Chem. Soc.* **1968**, *90*, 2001.



Darensbourg has presented evidence that [μ-HW$_2$(CO)$_{10}$]$^-$ is an intermediate in the formation of *cis*-W(CO)$_4$(PR$_3$)$_2$ from the reaction of M(CO)$_6$, PR$_3$, and NaBH$_4$ in THF and in ethanol.[13] In probing the role of the bridging hydride in our reactions, we have shown that it forms when W(CO)$_6$ and NaBH$_4$ are heated in 1-butanol[14] and that it reacts with PPh$_2$H in the presence of NaBH$_4$ to give phosphido-bridged complexes. As in the reactions of W(CO)$_6$ with PPh$_2$H, the products of the reaction depend on the stoichiometric ratio of phosphine to tungsten. Excess PPh$_2$H gave **3(W)** and **6(W)** as principal and minor products, respectively. A phosphine/tungsten ratio of 1.8 gave major quantities of these same two products with traces of **4(W)**. Reducing the ratio to 1.3 also gave these products and in addition traces of **2(W)** and **5(W)**. These results are consistent with the view that the reaction of W(CO)$_6$ with PPh$_2$H and NaBH$_4$ in 1-butanol proceeds by initial formation of [μ-HW$_2$(CO)$_{10}$]$^-$ followed by substitution and decomposition to monometallic species, which then proceed to form phosphido-bridged complexes. We do observe, however, that both **1(W)** and **2(W)** are readily converted to **3(W)** when treated with *excess* PPh$_2$H and NaBH$_4$ but hardly at all in the absence of NaBH$_4$. This outcome is in contrast with the reported observation that Cr(CO)$_5$PPh$_3$ reacts with PPh$_3$ at approximately the same rate with or without NaBH$_4$.[13a] To explain our BH$_4^-$-assisted conversion of **1** to **2** or **2** to **3** requires one to postulate the formation of species such as [μ-HW$_2$(CO)$_8$(PPh$_2$H)$_2$]$^-$ or [μ-HW$_2$(CO)$_6$(PPh$_2$H)$_4$]$^-$ if a bridging hydride intermediate is to be operative.[15]

The reaction of Cr(CO)$_6$ with PPh$_2$H and NaBH$_4$ under the conditions employed for molybdenum and tungsten does not lead to isolable phosphido-bridged products. The reaction, which is much more vigorous initially than that for molybdenum and tungsten, passes through a series of color changes (yellow to red to green), producing *cis*-Cr(CO)$_4$(PPh$_2$H)$_2$ (δ 44.9) with traces of *fac*-Cr(CO)$_3$(PPh$_2$H)$_3$ (δ 52.2) and a dark green insoluble solid which has not been characterized. The appearance of a red color in the course of the reaction suggests that a phosphido-bridged complex forms, but the subsequent color change coupled with the formation of a green solid characteristic of Cr(III) leads us to believe that disproportionation occurs.

Summary

Complexes (OC)$_4\overline{\text{M}(\mu\text{-PPh}_2)_2\text{M}}(CO)_3PPh_2$H **[5(W,Mo)]** and *trans*-HPh$_2$P(OC)$_3\overline{\text{M}(\mu\text{-PPh}_2)_2\text{M}}(CO)_3PPh_2$H **[6(W,Mo)]** can be obtained in good yield directly from the reaction of M(CO)$_6$, PPh$_2$H, and NaBH$_4$ in high boiling alcohols (e.g., 1-butanol). Excess PPh$_2$H leads to the formation of *fac*-M(CO)$_3$(PPh$_2$H)$_3$ **[3(W,Mo)]** as the exclusive product but judicious control of the PPh$_2$H/M(CO)$_6$ stoichiometric ratio allows isolation of **5** or **6** as principal products. By careful monitoring with ^{31}P NMR, it has been shown that the reaction proceeds by initial formation of M(CO)$_5$PPh$_2$H (**1**) and *cis*-M(CO)$_4$(PPh$_2$H)$_2$ (**2**). The former is a principal precursor of **5** whereas the latter serves that function for **6**. In the course of this work we have also observed *cis*-HPh$_2$P(OC)$_3\overline{\text{W}(\mu\text{-PPh}_2)_2\text{W}}(CO)_3PPh_2$H **[7(W)]**, the cis isomer of **6(W)**, a geometry not previously reported for phosphido-bridged complexes.

Other secondary phosphines are currently being tested to explore the generality of this one-step route to bridging phosphido complexes.

Experimental Section

General Data. All reactions were carried out under an atmosphere of dry nitrogen. The phosphines and metal carbonyls were obtained from commercial sources and used without further purification. Commercial 1-butanol was dried with active magnesium and distilled under nitrogen. No qualitative or quantitative difference in reaction products was noted when 1-butanol was used without purification. 1-Hexanol and absolute ethanol were used as obtained from the vendor.

Infrared spectra of chloroform solutions were measured with a Nicolet 20 DXB spectrometer. ^{31}P NMR spectra were recorded at 101.265 MHz on a homebuilt 5.9 T spectrometer. Chemical shifts are relative to 85% H$_3$PO$_4$ with downfield chemical shifts as positive. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN.

Preparation of *trans*-HPh$_2$P(OC)$_3\overline{\text{W}(\mu\text{-PPh}_2)_2\text{W}}(CO)_2PPh_2$H [6(W)]. A slurry of W(CO)$_6$ (3.00 g, 8.52 mmol), PPh$_2$H (2.75 mL, 15.8 mmol), and NaBH$_4$ (1.61 g, 42.5 mmol) in 1-butanol (50 mL) was refluxed vigorously for 9 h. A yellow solution formed within minutes, became orange-yellow within the first hour, and was brownish red for the remainder of the reaction time. The solution was cooled to room temperature and filtered immediately. Failure to filter soon after ambient temperature was reached led to precipitation of *cis*-W(CO)$_4$(PPh$_2$H)$_2$ **[2(W)]**, which made purification more difficult. The substantial quantity of precipitate collected was washed with methanol to remove borate salts. The remaining precipitate consisted of *fac*-W(CO)$_3$(PPh$_2$H)$_3$ **[3(W)]** and **6(W)**. The more dense latter product tended to collect in the bottom of the frit, allowing physical removal of the thin, less highly colored top layer. Recrystallization from a dichloromethane/methanol mixture gave yields of **6(W)** ranging from 2.52 g (54%) to 3.84 g (76%). For cases in which contamination of the product with **3(W)** was substantial, recrystallization was not an effective method of separation. In these instances, excellent separation was achieved by using a 100-cm silica gel (80–200 mesh) column with a 40:60 dichloromethane/hexane solvent mixture as the mobile phase. The bridged product eluted first to give maroon crystals that decomposed above 200 °C with the evolution of PPh$_2$H.

Anal. Calcd for C$_{54}$H$_{42}$O$_6$P$_4$W$_2$: C, 50.73; H, 3.31; P, 9.69. Found: C, 50.46; H, 3.34; P, 9.64.

The reaction for the preparation of **6(W)** also was carried out successfully when scaled up to 15.0 g of W(CO)$_6$. After recrystallization, 15.4 g (61%) of pure product was obtained. Formation of **6(W)** did not appear to be inhibited by greater quantities of NaBH$_4$, but isolation from borate side products was more difficult.

Preparation of *trans*-HPh$_2$P(OC)$_3\overline{\text{Mo}(\mu\text{-PPh}_2)_2\text{Mo}}(CO)_3PPh_2$H [6(Mo)]. A slurry of Mo(CO)$_6$ (3.00 g, 11.4 mmol), PPh$_2$H (3.67 mL, 20.4 mmol), and NaBH$_4$ (2.15 g, 56.9 mmol) in 1-butanol (150 mL) was refluxed for 9 h. Color changes in this reaction paralleled those for the preparation of **6(W)**, and the workup procedure was also the same. The dark maroon crystals, which decomposed at temperatures above 210 °C, were obtained in 80% yield.

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[13] (a) Darensbourg, M. Y.; Walker, N.; Burch, R. R., Jr. *Inorg. Chem.* **1978**, *17*, 52. (b) Darensbourg, M. Y.; Atwood, J. L.; Burch, R. R., Jr.; Hunter, W. E.; Walker, N. *J. Am. Chem. Soc.* **1979**, *101*, 2631. (c) Darensbourg, M. Y.; Atwood, J. L.; Hunter, W. E.; Burch, R. R., Jr., *Ibid.* **1980**, *102*, 3292. (d) Darensbourg, M. Y.; El Mehdawi, R.; Delord, T. J.; Fronczek, F. R.; Watkins, S. F. *Ibid.* **1984**, *106*, 2583. (e) Darensbourg, M. Y.; Deaton, J. C. *Inorg. Chem.* **1981**, *20*, 1644.

[14] The reaction of W(CO)$_6$ with NaBH$_4$ (with Hayter's stoichiometry[1b]) in refluxing 1-butanol for 18 h gave [μ-HW$_2$(CO)$_{10}$]$^-$ as the only product detected by IR.

[15] Lin, J. T.; Shiao, Y. M. *J. Organomet. Chem.* **1987**, *334*, C31.

Anal. Calcd for $C_{54}H_{42}O_6P_4Mo_2$: C, 58.81; H, 3.84; P, 11.23. Found: C, 58.78; H, 3.74; P, 11.21.

Preparation of $(OC)_4\overline{W(\mu\text{-}PPh_2)_2W}(CO)_3PPh_2H$ [5(W)]. A slurry of $W(CO)_6$ (3.00 g, 8.52 mmol), PPh_2H (1.77 mL, 10.2 mmol), and $NaBH_4$ (1.61 g, 42.5 mmol) in 1-butanol (50 mL) was refluxed for 9 h. The bright red precipitate, which formed upon cooling the reaction mixture to room temperature, was filtered and washed with methanol. Recrystallization from a dichloromethane/methanol solution gave 2.39 g (63%) of product. When the product was contaminated with **4(W)** and **6(W)**, a 100-cm silica gel (80–200 mesh) column with 40/60 dichloromethane/hexane as the mobile phase gave effective separation of the three compounds. The order of elution was **4(W)**, **5(W)**, and **6(W)**. Crystals of **5(W)** decomposed above 187 °C.[3c]

Anal. Calcd for $C_{43}H_{31}O_7P_3W_2$: C, 46.09; H, 2.79; P, 8.29. Found: C, 46.26; H, 2.78; P, 8.11.

Preparation of $(OC)_4\overline{Mo(\mu\text{-}PPh_2)_2Mo}(CO)_3PPh_2H$ [5(Mo)]. A slurry of $Mo(CO)_6$ (3.00 g, 11.4 mmol), PPh_2H (2.37 mL, 13.6 mmol), and $NaBH_4$ (2.15 g, 56.8 mmol) in 1-butanol (50 mL) was refluxed for 9 h. The red product was filtered at room temperature and recrystallized from dichloromethane/methanol to give 2.90 g (68%). Contamination of the product with **1(Mo)** was not uncommon but this impurity was removed easily by column chromatography (100-cm column, 80–200 mesh silica gel, 40/60 dichloromethane/hexane) with the contaminant eluting first. The orange-red crystals of **5(Mo)** decomposed above 183 °C.

Anal. Calcd for $C_{43}H_{31}O_7P_3Mo_2$: C, 54.68; H, 3.31; P, 9.84. Found: C, 54.66; H, 3.38; P, 9.84.

Reaction of $(OC)_5WPPh_2H$ with PPh_2H, with and without $NaBH_4$. The preparation of $W(CO)_5PPh_2H$ has been described previously.[10] A mixture of $W(CO)_5PPh_2H$ (0.57 g, 1.2 mmol) and PPh_2H (0.58 mL, 3.3 mmol) in 1-butanol (50 mL) was refluxed for 9 h. After solvent removal, the crude product was examined with IR, which showed unreacted $W(CO)_5PPh_2H$ and a trace of **2(W)**. When the same reaction was carried out with $NaBH_4$ (0.21 g, 5.6 mmol), complete conversion to **3(W)** was observed.

Anal. Calcd for $C_{39}H_{33}P_3O_3W$: C, 56.68; H, 4.02; P, 11.24. Found: C, 56.60; H, 4.22; P, 11.01.

Reaction of $W(CO)_5PPh_2H$ with $NaBH_4$. A mixture of $W(CO)_5PPh_2H$ (1.0 g, 2.3 mmol) and $NaBH_4$ (0.37 g, 9.8 mmol) in 1-butanol (50 mL) was heated under reflux for 7.5 h. The reaction mixture became yellow, changed to orange, and finally became deep red within the first hour after reflux began. Analysis of the product with IR and ^{31}P NMR confirmed the presence of **5(W)** in major proportion and **4(W)** in a minor amount.

Reaction of *cis*-$W(CO)_4(PPh_2H)_2$ with PPh_2H, with and without $NaBH_4$. The starting complex was prepared as described previously.[10] A mixture of *cis*-$W(CO)_4(PPh_2H)_2$ (0.40 g, 0.60 mmol) and PPh_2H (0.42 mL, 2.4 mmol) in 1-butanol (50 mL) was refluxed for 23 h. Examination of the crude product with IR after solvent removal revealed starting material with traces of **3(W)**. When this reaction was carried out in the presence of $NaBH_4$, **3(W)** was the only product obtained.

Reaction of *cis*-$W(CO)_4(PPh_2H)_2$ with $NaBH_4$. A mixture of *cis*-$W(CO)_4(PPh_2H)_2$ (0.79 g, 1.2 mmol) and $NaBH_4$ (0.25 g, 6.6 mmol) in 1-butanol (50 mL) was refluxed for 9 h. A mixture of **3(W)** and **6(W)** was formed as shown by IR and ^{31}P NMR.

Reactions of $[Et_4N][\mu\text{-}HW_2(CO)_{10}]$ with PPh_2H and $NaBH_4$. The Hayter method was used to prepare $[Et_4N][\mu\text{-}HW_2(CO)_{10}]$.[16] A solution of $[Et_4N][\mu\text{-}HW_2(CO)_{10}]$ (0.50 g, 0.64 mmol), PPh_2H (0.56 mL, 3.2 mmol), and $NaBH_4$ (0.12 g, 3.2 mmol) in 1-butanol was refluxed for 9 h. As shown by IR, the major product of the reaction was **3(W)**, which was accompanied by a minor quantity of **6(W)**. When this reaction was performed with 2.3 mmol of PPh_2H, **3(W)** was still dominant but **6(W)** was more prominent; in addition, traces of **4(W)** were present. Reducing the quantity of PPh_2H to 1.7 mmol gave major quantities of **3(W)** and **6(W)** with traces of **2(W)**, **4(W)**, and **5(W)**.

Reaction of $W(CO)_6$ with PPh_2H and NaOBu. A solution of sodium 1-butoxide was prepared by adding 0.5 g of Na to dry 1-butanol (25 mL). This solution was added dropwise to 25 mL of 1-butanol containing $W(CO)_6$ (2.00 g, 5.68 mmol) and PPh_2H (1.80 mL, 10.3 mmol), and the mixture was refluxed for 9 h. Examination of the crude reaction mixture with IR showed two products in roughly equal proportions: **3(W)** and **6(W)**.

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