Chemistry of Hydrido Carbonyl 6B Metalates Substituted by P-Donor Ligands: $HW(CO)_4PR_3^-$ (R = Me, OMe, Ph) and μ-$H[WM(CO)_{10-x}(P(OMe)_3)_x]$ (M = Cr, W; x = 1, 2)[†]

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The synthesis of $PPN^+HW(CO)_4PR_3^-$ (R = Me, OMe, Ph) was accomplished via careful protonation of $W(CO)_4PR_3^{2-}$. The cis orientation of the hydride and P-donor ligands was affirmed by ν(CO) infrared and carbon-13 nuclear magnetic resonance studies. Chemical characterizations included reactions with CO_2, yielding the insertion product $HCOOW(CO)_4P^-$, and with protic, main-group, and transition-metal Lewis acids. With trimethylaluminum the hydride was abstracted and the presumably 5-coordinate $[W(CO)_4P]^0$ resulting therefrom aggregated with unreacted $HW(CO)_4P^-$ to produce μ-$H[W(CO)_4P]_2^-$ (P = $P(OMe)_3$, PMe_3). The latter disubstituted binuclear bridging hydrides were also the products obtained from deliberate thermal or aerobic decomposition of these phosphine hydrides. Aggregation of $HW(CO)_4P(OMe)_3^-$ with photochemically produced $[W(CO)_5]^0$ or $[Cr(CO)_5]^0$ readily occurred, yielding the monosubstituted binuclear bridging hydride anions. Tungsten-183 to proton coupling was interpreted in terms of the electronic and/or steric asymmetry of the hydride in these latter anions.

Introduction

Ligand modifications of homo- and heterogeneous catalysts that serve in processes of activation of carbon monoxide and of dihydrogen frequently affect the outcome of both product distribution and rates of product formation. Whereas studies of the physical and chemical effects of substituent phosphorus-donor ligands on metal carbonyls are legend, relatively few systematic studies of substituent effects on hydride activity exist in the literature.

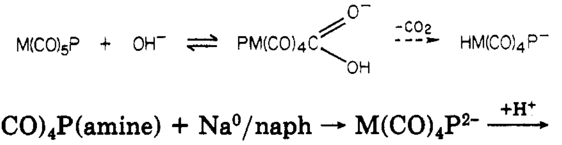
Convenient syntheses of the mononuclear anionic hydrides $HM(CO)_5^-$ (M = Cr, Mo, W) have recently been developed.[1,2] Although the CO groups of $HM(CO)_5^-$ were found to only slowly thermally exchange with carbon-13 labeled CO, the *presumably* 16-electron, coordinatively unsaturated intermediate $[HM(CO)_4^-]$ could not be conveniently trapped by normal excesses of phosphines or phosphites in solution (eq 1).[3] A similar disinclination

$$HM(CO)_5^- + P \rightarrow HM(CO)_4P^- + CO \qquad (1)$$

toward thermal P-ligand substitution has been observed for other carbonyl anions: $V(CO)_6^-$,[4] $CpMo(CO)_3^-$,[5] and $HFe(CO)_4^-$.[6] Hence reaction 1 did not provide a viable route to the phosphine hydrides.

By analogy to known methods of generation of 6B metal carbonyl hydrides, several direct routes to the $HM(CO)_4P^-$ anions are ostensibly possible (eq 2–4) using as starting materials neutral complexes containing the P-donor ligand.

$$M(CO)_4(P)(amine) + PPN^+BH_4^- \rightarrow amine{\rightarrow}BH_3 + HM(CO)_4P^- \qquad (2)$$



$$M(CO)_5P + OH^- \rightleftharpoons PM(CO)_4C(=O^-)OH \xrightarrow{-CO_2} HM(CO)_4P^- \qquad (3)$$

$$M(CO)_4P(amine) + Na^0/naph \rightarrow M(CO)_4P^{2-} \xrightarrow{+H^+} HM(CO)_4P^- \qquad (4)$$

The use of borohydride as a hydride source in a manner similar to reaction 2 is a successful synthetic route to $HCr(CO)_5^-$ and $HW(CO)_5^-$ using $M(CO)_5(NC_5H_{10})$ as a labile ligand complex precursor.[1] For $W(CO)_4^-P(OMe)_3$-(pip) however the mononuclear hydride $HW(CO)_4P(OMe)_3^-$ was formed only very slowly at 50 °C, and an alternate route was sought.

The third route again is a viable route to the all carbonylhydridometalates when the OH^- is highly activated via solubilization techniques[7a,b] and is of import to the mechanism of the water–gas shift reaction.[8] Isotopic labeling studies have clearly shown that the CO groups of $Ph_3PW(CO)_5$ undergo attack by OH^- and subsequent CO oxygen exchange in the (presumed but as yet not detected) carboxylic acid intermediate.[9] Subsequent loss of OH^- in the P-substituted intermediate is evidently a more facile process than is CO_2 loss under the reaction conditions investigated (ambient pressure, concentrations of ca. 0.1 M). Under other experimental conditions (reduced pressures, increased concentrations), the solubilized hydroxide method has been reported to work nicely in the synthesis of $HFe(CO)_3PR_3^-$ from $R_3PFe(CO)_4$.[10]

The fourth possibility (eq 4) takes advantage of the ideas of Ellis[11] and Cooper[12] with regards to the replacement of a labile ligand with two electrons derived from a good electron transfer source. Reaction 4 has been found to be a useful preparation of *cis*-$HW(CO)_4PR_3^-$ and is described in detail below for R = Me, OMe, and Ph. The spectroscopic as well as some chemical characteristics of these activated hydrides are described.

[†] With sincerest respect and admiration, this work is dedicated to Rowland Pettit.

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Table I. Spectroscopic Properties of $PPN^+HW(CO)_4PR_3^-$

	ν(CO) infrared[a]			proton NMR data[b]		
R	A'	A' + A''	A''	δ(W-H)	J_{P-H}, Hz	J_{W-H}, Hz
OCH_3	1986	1856	1822	−4.5	36	54
C_6H_5	1974	1851	1815	−3.0	27	
CH_3	1969	1847 (sh) 1842	1805	−3.6	30	54

[a] Measured in THF solution in cm^{-1}. Assignments based on C_s symmetry. Spectral pattern is medium, strong, medium. [b] Measured in CD_3CN solution at ambient temperature. Hydride resonances in parts per million upfield from Me_4Si standard.

Table II. Spectroscopic Properties of $PPN^+HMW(CO)_{10-x}^-$

M	x	ν(CO) IR[a]	^{1}H NMR[b] (M-H)
Cr	1	2047 (w), 2002 (w), 1931 (s), 1882 (m), 1850 (m)	−14.4 ppm (d, J_{P-H} = 27 Hz, J_{W-H} = 38.4 Hz)
W	1	2054 (w), 2002 (w), 1931 (s), 1879 (m), 1851 (m)	−12.2 ppm (d, J_{P-H} = 25.8 Hz, J_{W_1-H} = 42 Hz, J_{W_2-H} = 45.6 Hz)
W	2	2019 (w), 1997 (w), 1912 (s), 1882 (sh), 1838 (w)	−11.8 ppm (t, J_{P-H} = 21 Hz)

[a] THF solution. [b] CD_3CN solution, Me_4Si reference.

Experimental Section

General Data. An inert-atmospheres glovebox (argon) and Schlenk techniques (hi-dry N_2) were used to render all operations air- and moisture-free. The solvents, tetrahydrofuran and hexane, were distilled from the Na^0/benzophenone scavenger, collected, and transferred under N_2. Acetonitrile (including the NMR solvent CD_3CN) was stirred over CaH_2 and vacuum transferred prior to use. Methanol was dried and distilled from $Mg(OCH_3)_2$ under N_2.

Trimethyl phosphite was distilled from sodium wire under vacuum. Triphenylphosphine and trimethylphosphine were used as received from standard vendors. Phenol was dried by stirring over grade 4A molecular sieves that had been activated by heating under vacuum. Bis(triphenylphosphin)imminium chloride was purchased from Roc/Ric Chemical Corp. and used without further purification. [It is our experience that impurities in this ion-exchange reagent can be detrimental to the isolation of the hydrides in good yields.] Carbon-13 labeled CO (93.3% ^{13}CO) and CO_2 (90.6% $^{13}CO_2$) were obtained from Prochem., B.O.C. Ltd., London.

Infrared spectra were measured of THF solutions in matched, sealed 0.1-mm NaCl cells by using the Perkin-Elmer 283B infrared spectrophotometer that was calibrated below 2000 cm^{-1} on water vapor. The error on the ν(CO) band positions may be assumed to be ±2 cm^{-1}. Proton nuclear magnetic resonance spectra were measured on CD_3CN solutions by using a Varion EM390 spectrometer. Carbon-13 NMR measurements were taken in CD_3CN on a JEOL FX60 instrument.

Preparation of $PPN^+HW(CO)_4PR_3^-$ (R = OCH_3, C_6H_5, and CH_3). A typical preparation is as follows. Aliquots of a 0.2 M solution of sodium naphthalenide were added to a solution of 1.0 g of $W(CO)_4P(OMe)_3(NC_5H_{10})$[13] in 50 mL of THF at −78 °C until the color of the reaction solution went from yellow to dark brown. With the solution still at −78 °C, a solution of 1.2 g of PPN^+Cl^- in 4 mL of MeOH was added. The reaction mixture was warmed to room temperature with subsequent removal of the solvents in vacuo. The solid was extracted with 20 mL of THF and the resulting solution filtered through celite. Upon addition of 50 mL of hexane a yellow oil separated that on further stirring solidified to a yellow solid. The solid was isolated by removing the supernatant and drying in vacuo. The salt could be recrystallized from THF/hexane.

A similar procedure was used for the synthesis of $PPN^+HW(CO)_4PPh_3^-$; however, the PMe_3 product was protonated by MeOH at room temperature. Hence removal of THF and MeOH was carried out at −20 °C to minimize this problem. Isolated yields were on the order of 70%.

Spectroscopic properties for the three new hydrides may be found in Table I. Elemental analyses (Chemical Analytical Services, Berkeley, CA) are as follows. For the PMe_3 derivative, calcd for $C_{43}H_{40}NO_4P_3W$: C, 56.64; H, 4.39; N, 1.54. Found: C, 56.40; H, 4.42; N, 1.52. For the $P(OMe)_3$ derivative, calcd for $C_{43}H_{40}NO_7P_3W$: C, 53.80; H, 4.17; N, 1.46. Found: C, 53.85; H, 4.19; N, 1.49.

Preparation of $PPN^+HW(^{13}CO)_4P(OMe)_3^-$. A THF solution of $PPN^+W(CO)_5Cl^-$ (synthesized by refluxing $W(CO)_6$ together with PPN^+Cl^- in ethylene glycol/dimethyl ether) was stirred under ^{13}CO for 4 h.[14] The enriched chloride was then precipitated by addition of hexane, isolated, and redissolved in MeOH. Under an atmosphere of ^{13}CO over the course of 5 days the chloride was displaced and $W(^{13}CO)_6$ precipitated from solution. It was collected by filtration and purified by sublimation. The enriched $W(^{13}CO)_4(pip)_2$,[13] $W(^{13}CO)_4(pip)(P)OMe)_3)$, and $PPN^+HW(^{13}CO)_4P(OMe)_3^-$ were prepared by the standard methods mentioned above.

Reactions of $HW(CO)_4PR_3^-$. (a) Thermal Stability. The thermal stability studies were carried out in THF solution (ca. 0.01 M) and monitored by ν(CO) IR spectroscopy. The resulting products were dried in vacuo, and ^{1}H NMR spectra were measured on the solids, which were redissolved in CH_3CN. The binuclear bridging hydride products thus obtained were identified by comparison of spectral properties of anions prepared by various routes and of the similar well-characterized derivatives of molybdenum (vide infra).

(b) Trimethylaluminum. Aliquots of neat $[AlMe_3]_2$ were added by microsyringe to 0.10 g of $PPN^+HW(CO)_4PR_3^-$ (R = Me, OMe) dissolved in 10 mL of THF. Progress of the reactions was monitored by ν(CO) infrared spectroscopy, and the disappearance of starting materials corresponded to an (apparently quantitative) appearance of product bands assigned to the dimeric anions: μ-$H[W(CO)_4PR_3]_2^-$ (see Table II).

(c) Phenol. A solution of 0.15 g of phenol in 5 mL of THF was added to 0.30 g of $PPN^+HW(CO)_4P(OMe)_3^-$ dissolved in 30 mL of THF. This reaction was monitored by IR spectroscopy, and over the course of a week the starting hydride was converted to the disubstituted bridging hydride μ-$H[W(CO)_4P(OMe)_3]_2^-$. To this product solution was added 60 mL of hexane, yielding an oil. Removal of the supernatant followed by trituration with hexane produced a waxy solid. The ^{1}H NMR and ν(CO) IR spectra (Table II) are as expected for the formulation given (vide infra).

(d) Transition-Metal Lewis Acids. $[W(CO)_5]^0$ and $[Cr(CO)_5]^0$. A solution of 0.070 g of $Cr(CO)_6$ in 25 mL of THF was placed in a Schlenk tube of approximately 50-mL total capacity. With a purge of N_2 through the solution, it was photolyzed (450-W Hanovia lamp) until all the $Cr(CO)_6$ was converted to $Cr(CO)_5(THF)$ (approximately 30 min). This solution was then transferred to a flask containing 0.35 g of $PPN^+HW(CO)_4P(OMe)_3^-$ in 5 mL of THF. The solution was stirred overnight. After filtration through celite filter aid the product was isolated by the addition of 50 mL of hexane. The oil initially obtained solidified upon stirring. On basis of the ν(CO) IR (Table II) and proton NMR

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(13) Darensbourg, D. J.; Kump, R. L. *Inorg. Chem.* **1978**, *17*, 2680.

(14) Allen, A. D.; Barrett, P. F. *Can. J. Chem.* **1968**, *46*, 1655.

spectra the product was formulated as $PPN^+\mu$-$H[W(CO)_4P(OMe)_3][Cr(CO_5)]^-$. The homonuclear ditungsten analogue was prepared in similar fashion.

(e) Carbon Dioxide. (i) A solution of 0.050 g of $PPN^+HW(CO)_4PR_3^-$ in 5 mL of THF was syringed into a reaction vessel filled with CO_2 at atmospheric pressure. The yellow solution changed to deep yellow immediately upon mixing, and the ν(CO) infrared spectra that were taken as soon as possible showed no starting materials present, but the bands (cm^{-1}) are as follows: for R = OMe, 2006 (w), 1889 (sh), 1874 (s), 1821 (m); for R = Me, 1998 (w), 1875 (sh), 1858 (s), 1805 (m).

(ii) The above **(i)** was repeated in a 10-mm NMR tube by using carbon-13 enriched $PPN^+HW(^{13}CO)_4P(OMe)_3^-$ and $^{13}CO_2$. The following CO carbon resonance positions were observed: for the phosphite formate, δ(downfield from Me_4Si) 204.24 (d, J_{P-C} = 11 Hz), 209.0 (d, J_{P-C} = 7 Hz), 209.55 (d, J_{P-C} = 60 Hz); for the formate carbon, δ 168.0 (J_{P-C} = 3.4 Hz).

(iii) The above (part **i**) was repeated in a 5-mm NMR tube and a ^1H NMR spectrum taken. The resonance of the formate proton was observed at 8.2 ppm.

Results and Discussion

The reduction of $W(CO)_4(PR_3)(NC_5H_{10})$ by sodium naphthalenide at −78 °C was a straightforward reaction.[12] Subsequent protonation by MeOH, in the presence of the ion-exchange agent PPN^+Cl^-, yielded the yellow PPN^+ $HW(CO)_4(PR_3)^-$ salts, soluble in THF and separable from the byproduct NaOMe or excess PPN^+Cl^- by the low solubility of the latter in THF. That the hydridic activity of the phosphorus ligand substituted hydride anions varied with the nature of the P ligand was most clearly shown by the fact that at room temperature MeOH served to further protonate the product containing the most basic P ligand, $HW(CO)_4PMe_3^-$, yielding μ-$H[W(CO)_4PMe_3]_2^-$ (vide infra). This problem was circumvented by isolating the anion at low (−20 °C) temperature. In contrast the trimethyl phosphite and triphenylphosphine derivatives were stable to small excesses of MeOH at room temperature for time periods on the order of hours, and the all carbonyl anion, $HW(CO)_5^-$, was stable to MeOH for extended periods of time (days) at room temperature.

The ν(CO) IR spectra of $HW(CO)_4P^-$ (Table I) showed only three major bands; however, the relative intensity ratios suggested a pseudo C_{2v} structure, i.e., *cis*-$HW(CO)_4P^-$, with two of the expected four IR active bands essentially degenerate. For the $HW(CO)_4PMe_3^-$ derivative the asymmetry of the central intense band is marked (see Figure 1). In view of the very different nature of the two substituent ligands, C_s rather than "pseudo C_{2v}" symmetry is the preferred symmetry designation, and the assignments in Table I are listed accordingly. These phosphine hydride anions are directly analogous to the phosphine halide derivatives, *cis*-$(R_3P)W(CO)_4X^-$ synthesized by Schenk.[15] The *average* CO stretching frequency is higher in the latter, suggesting a greater localization of electron density on the X^- ligand as compared to H^-.

The proton chemical shifts of *H*$W(CO)_4L^-$ vary with the nature of L: L = PPh_3, δ −3.0; PMe_3, −3.6; CO, −4.2; $P(OMe)_3$, −4.5. The significantly lower resonance position of the PPh_3 derivative could be due to some deshielding from the close proximity of the hydride to the ring current of the phenyl rings; however, there is no apparent correlation with electronic properties of the ligands and the hydride chemical shift. On the other hand, the P–H coupling constants (J_{P-H} = 27, 30, and 36 Hz for L = PPh_3, PMe_3, and $P(OMe)_3$, respectively) increase as the W–P bond distances would be expected to decrease as based on the steric requirements of these ligands.[16] [By playing off the π-acceptor and σ-donor ability of the P-donor ligands, electronic arguments can be used equally well to account for variations in the M–P bond distances.]

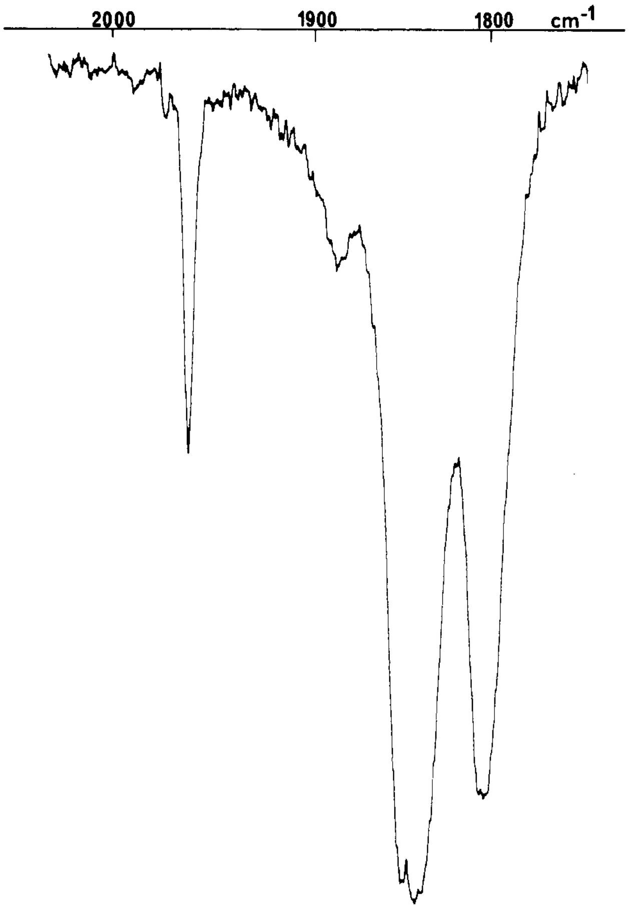
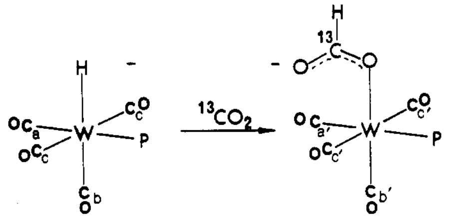


Figure 1. The THF solution infrared spectrum of $PPN^+HW(CO)_4PMe_3^-$ in the ν(CO) stretching region.

The expected carbon-13 NMR spectrum of cis-$HW(CO)_4P(OMe)_3^-$ should show three different electronic environments for the carbonyl carbon nuclei as shown below (eq 5), with a major ^{31}P–^{13}C splitting of that carbon



(5)

which is trans to the $P(OMe)_3$ ligand and smaller P–C splittings of those cis to the phosphorus ligand.[17,18] The proton-decoupled carbon-13 NMR spectrum in Figure 2a is thus interpreted as follows. The doublet ascribed to carbonyl carbon a, centered at 215.6 ppm downfield from Me_4Si, has a J_{P-C} of 41.6 Hz, and the higher field portion of that doublet is degenerate with part of the doublet due to C_b (J_{P-C} = 7 Hz), centered at 214.0 ppm. The two carbons of identical electronic environments, C_c, are split by phosphorus-31 to the extent of 11 Hz and centered at 207.2 ppm. This spectrum was further clarified upon derivatization with $^{13}CO_2$ (eq 5). As shown in Figure 2b,

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(15) Schenk, W. A. *J. Organomet. Chem.* **1979**, *179*, 253.

(16) Tolman, C. *J. Am. Chem. Soc.* **1970**, *92*, 2956.

(17) It should be noted that these expectations for relative couplings hold for the great majority of substituted Mo and W derivatives; however, for Cr a *reversal* in magnitude of the P–C coupling is generally observed.[18]

(18) Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *77*, 1.

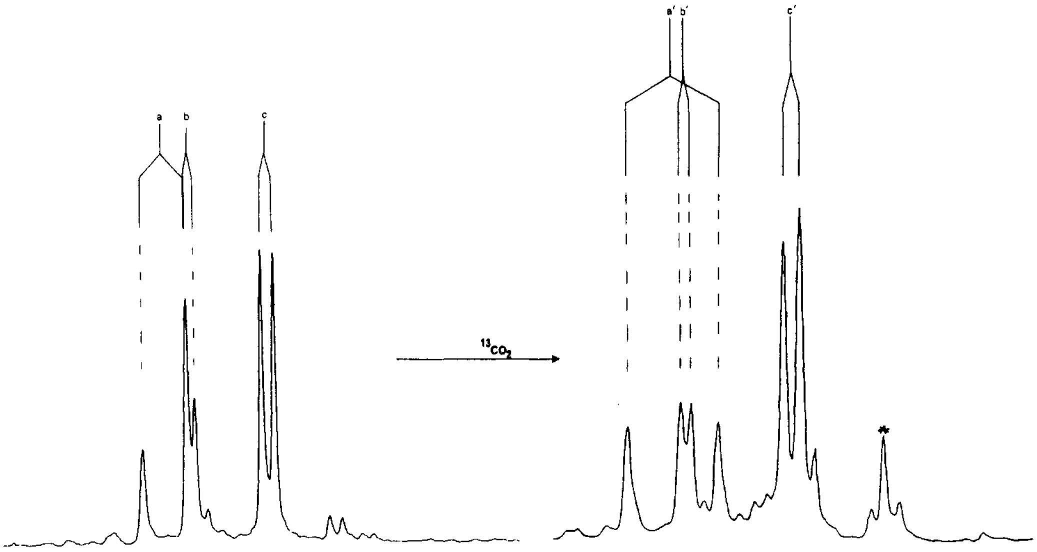

Figure 2. The carbon-13 NMR spectrum of the $PPN^+HW(CO)_4P(OMe)_3^-$ in CD_3CN is shown on the left (a). After reaction of $^{13}CO_2$ the formate, $HCOOW(CO)_4P(OMe)_3^-$, is obtained, spectrum on the right (b). The asterisk denotes the decomposition product, assigned to $W(CO)_5OCHO^-$ as reported in ref 7b.

and analogous to acetate complexes of the type *cis*-$(CH_3COO)W(CO)_4PR_3^-$,[19] the low-field doublet is considerably spread out, removing the degeneracy seen in the previous spectrum. [The additional peaks are assumed to be due to decomposition of the formate, yielding $W(CO)_5(OCHO)^-$ and $W(CO)_5P(OMe)_3$.] The formate carbon resonance is not shown in Figure 2b but is further upfield at 168 ppm with $J_{P-C} = 3.4$ Hz.

All of the phosphine hydrides were highly reactive with CO_2. Reaction was apparently instantaneous and quantitative on basis of spectral analysis. The ν(CO) IR spectral band positions matched very well those of *cis*-$W(CO)_4(PR_3)(OCHO)^-$ prepared by the halide/formate exchange method: *cis*-$W(CO)_4(PR_3)Cl^- + Tl^+OCHO^-$.[20]

Acetic acid and anhydrous HCl reacted with the phosphine hydrides to yield H_2 gas with concurrent replacement of the hydride coordination site with acetate or chloride ligands.

Reactions of the phosphine hydrides with protic acids whose anions were not capable of strong coordination, main-group Lewis acids, and transition-metal Lewis acids led to the production of binuclear anions; i.e., the aggregative nature of hydride-containing anions, well-known for the all CO-containing 6B hydrides (eq 6),[2,21] was not impeded by the presence of the P-donor ligands. Trimethylaluminum was used to abstract a hydride from $HW(CO)_4P(OMe)_3^-$, and the ν(CO) IR indicated the formation of the binuclear μ-$H[W(CO)_4P(OMe)_3]_2^-$ via a process analogous to that of eq 6. In the presence of the aluminum-containing reagent and products however the binuclear salt was difficult to isolate and purify.

$$HM(CO)_5^- + A \rightarrow AH + [M(CO)_5]^0 \xrightarrow{+HM(CO)_5^-} \mu\text{-}H[M(CO)_5]_2^- \quad (6)$$

In the presence of a 5-fold excess of phenol ($pK_a = 9.99$ in H_2O, in contrast to that of MeOH, $pK_a = 16$) the $HW(CO)_4P(OMe)_3^-$ disappeared completely over the course of 24 h and over the course of a week converted quantitatively into the species formulated as μ-$H[W(CO)_4P(OMe)_3]_2^-$. [An assumed intermediate was $(PhO)W(CO)_4P(OMe)_3^-$.][22,23] The formulation of the disubstituted bridging hydride was based on the similarity of the ν(CO) IR spectrum (Table II) to that of the well-characterized μ-$H[Mo(CO)_4PMePh_2]_2^-$,[24] prepared by the thermal substitution of CO groups by phosphine ligands in μ-$H[Mo(CO)_5]_2^-$. Earlier work had suggested that similar thermal P-ligand substitution on the analogous μ-$H[W(CO)_5]_2^-$ anion could not cleanly occur.[25] X-ray crystallographic analysis of the molybdenum dimer mentioned above showed the P ligands to be cis to the hydride bridge, and the molecular framework was of the bent, staggered configuration (with a P_1–Mo_1–Mo_2–P_2 torsion angle averaging 40° for the two crystallographically independent molecular anions in the unit cell).[24]

The chemical shift of the hydride of $PPN^+\mu$-$H[W(CO)_4P(OMe)_3]_2^-$ was found as a triplet centered at −11.8 ppm upfield from Me_4Si with $J_{P-H} = 21$ Hz. Thus the presence of the phosphite ligands as compared to the all-carbonyl dimer, μ-$H[W(CO)_5]_2^-$, δ −12.6,[26] makes only a small difference to the resonance position of the hydride.

Table II also shows the results of the deliberate aggregation of $HW(CO)_4P(OMe)_3^-$ with the transition-metal Lewis acids $[W(CO)_5]^0$ and $[Cr(CO)_5]^0$, in the form of their THF adducts. Again the ν(CO) IR pattern and band positions were highly reminiscent of the well-characterized $Et_4N^+\mu$-$H[Mo(CO)_5][Mo(CO)_4PPh_3]^-$ salt prepared by the direct substitution of PPh_3 onto μ-$H[Mo(CO)_5]_2^-$.[27] The crystal structure of that compound showed a marked asymmetry of the Mo–H–Mo bridge with the hydride being closer to the more electron-deficient $[Mo(CO)_5]^0$ moiety by about 0.5 Å, statistically significant for the structure determination. Due to the presence of the NMR-active tungsten-183 nuclei (natural abundance ca. 16%) in the current compounds under investigation, ^1H NMR data

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[19] Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S.; Kudaroski, R. *Inorg. Chem.* **1982**, *21*, 1656.

[20] Schenk, W. A., personal communication.

[21] Darensbourg, M. Y.; Bau, R.; Marks, M.; Burch, R. R., Jr.; Deaton, J. C.; Slater, S. G. *J. Am. Chem. Soc.*, in press.

[22] The phenoxide intermediate was expected on basis of the successful isolation of $PPN^+W(CO)_5(OPh)^-$ via reaction of $W(CO)_5(pip)$ with PPN^+OPh^-.[23] Typical of O-donor ligands,[19] the phenoxide was found to be quite labile.[23]

[23] Slater, S. G.; Darensbourg, M. Y., unpublished results.

[24] Darensbourg, M. Y.; Atwood, J. L.; Hunter, W. E.; Burch, R. R., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 3290.

[25] Darensbourg, D. J.; Incorvia, M. J. *Inorg. Chem.* **1979**, *18*, 18.

[26] Hayter, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 4376.

[27] Darensbourg, M. Y.; Atwood, J. L.; Burch, R. R., Jr.; Hunter, W. E.; Walker, N. *J. Am. Chem. Soc.* **1979**, *101*, 2631.

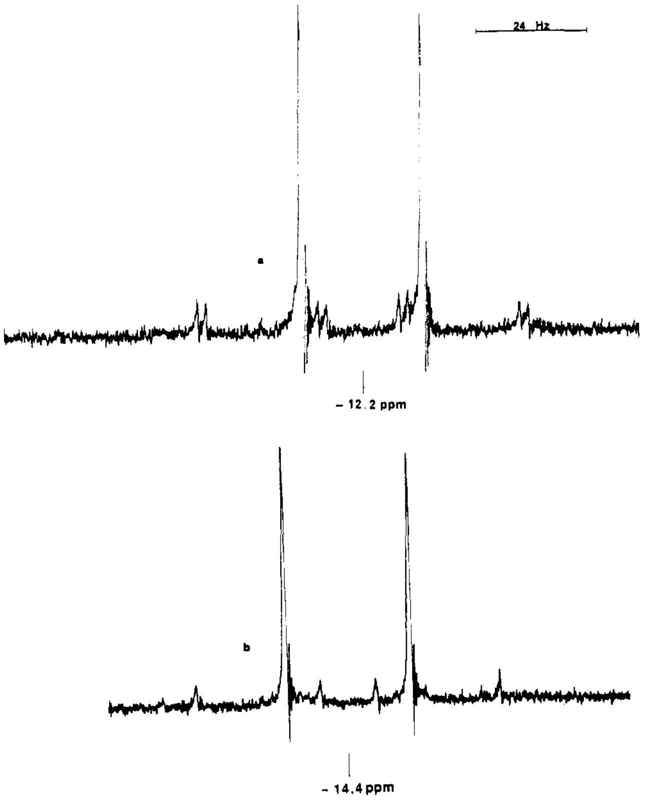

Figure 3. The nuclear magnetic resonance of the hydride in (a) PPN$^+$$\mu$-H[W(CO)$_5$][W(CO)$_4$P(OMe)$_3$]$^-$, measured in CD$_3$CN, and (b) PPN$^+$$\mu$-H[Cr(CO)$_5$][W(CO)$_4$P(OMe)$_3$]$^-$.

may be used to indicate the asymmetry in the μ-H[W(CO)$_5$][W(CO)$_4$P(OMe)$_3$]$^-$ anions. As shown in Figure 3a (and stated in Table II), two different ^{183}W–^{1}H couplings, imposed upon the doublet due to ^{31}P–^{1}H coupling, are readily discernible. For the analogous μ-H[Cr(CO)$_5$][W(CO)$_4$P(OMe)$_3$]$^-$ anion however the larger W–H coupling (45.6 Hz) is lost (Figure 3b), and the smaller coupling decreases from 42 Hz in the homonuclear dimeric anion to 38.4 Hz in the heteronuclear anion. It is tempting to interpret these observations in terms of the expected W–H distances when the tungsten is surrounded by five CO groups as opposed to four CO and one P-donor ligand, analogous to the substituted binuclear molybdenum anion mentioned above. When the short W–H interaction is lost (on substitution by [Cr(CO)$_5$]^0), the larger W–H coupling is lost. Alternatively one might propose an inherent larger difference in coupling of W–H for W in different electronic environments, i.e., [W(CO)$_5$]^0 vs. [W(CO)$_4$P(OMe)$_3$]^0. In the nonsubstituted dimer, μ-H[W(CO)$_5$]$_2^-$ in which the hydride is equally affected by its pendant groups, the $J_{\text{W-H}}$ = 41.9 Hz.[26] Again attempts to explain such differences most likely involve inseparable steric and electronic arguments.

Note the hydride's chemical shift dependence on metal in parts a and b of Figure 3. The presence of the Cr atom has a shielding effect on the hydride. This has been noted for the μ-H[M(CO)$_5$]$_2^-$ anions (for M = Cr, Mo, and W, δ −19.2, −12.2, −12.6, respectively); and on formation of the mixed-metal hydrido carbonylates, an average chemical shift is observed (for example, for μ-[Cr(CO)$_5$][W(CO)$_5$]$^-$, δ −15.4). The higher field chemical shifts do not denote greater hydridic character of the bridging hydride in terms of chemical reactivity. For example, the mononuclear species, HM(CO)$_5^-$ (δ(H) −7.0, −4.0, and −4.2 ppm for M = Cr, Mo, and W, respectively) and our newly synthesized HW(CO)$_4$P$^-$ anions react with acids much more readily. In addition, the latter have been noted to react with alkyl halides, yielding alkanes, whereas the bridging hydrides do not.[28]

The thermal stability of these hydrides presents one of their more interesting properties. When protected from O$_2$ and moisture, the yellow solids appear to be stable indefinitely at room temperature. When allowed to stand in the air, the HW(CO)$_4$P(OMe)$_3^-$ at least very cleanly converts into the μ-H[W(CO)$_4$P(OMe)$_3$]$_2^-$ anion. At 30 °C in THF solution there is very little decomposition of PPN$^+$HW(CO)$_4$P(OMe)$_3^-$ over the course of 1 day; however, at 60 °C under Ar decomposition to μ-H[W(CO)$_4$P(OMe)$_3$]$_2^-$ (spectral properties given in Table II) occurred within 36 h. Under an atmosphere of CO at 60 °C complete conversion of HW(CO)$_4$P(OMe)$_3^-$ to the asymmetric dimer μ-H[W(CO)$_4$P(OMe)$_3$][W(CO)$_5$]$^-$ required approximately the same time period. The same binuclear anion was obtained either upon heating HW(CO)$_4$P(OMe)$_3^-$ and HW(CO)$_5^-$ together in THF to 60 °C, on reacting HW(CO)$_4$P(OMe)$_3^-$ and W(CO)$_6$ under the same conditions, or upon addition of CO to the disubstituted μ-H[W(CO)$_4$P(OMe)$_3$]$_2^-$. The monosubstituted dimeric bridging hydride appeared to be very stable thermally and stable to further substitution by CO.

The point to be made about most of the above reactions is that there is a "lost" hydride. Such a phenomenon is not unprecedented;[29,30] however, it *is* curious in that the solvent is aprotic and very dry, the counterion is *presumably* unreactive with H$^-$, and the reactions appear to be quantitative. We have thus far been unable to account for the disappearance of the missing hydride, but work is continuing in this area.

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Registry No. [HW(CO)$_4$P(OMe)$_3$](PPN), 82963-28-8; [HW(CO)$_4$PPh$_3$](PPN), 82963-30-2; [HW(CO)$_4$(PMe$_3$)](PPN), 82963-32-4; W(CO)$_4$P(OMe)$_3$(NC$_5$H$_{11}$), 82963-33-5; W(CO)$_4$(PPh$_3$)(NC$_5$H$_{11}$), 67010-37-1; W(CO)$_4$(PMe$_3$)(NC$_5$H$_{11}$), 82963-34-6; [HW(^{13}CO)$_4$(POMe)$_3$](PPN), 82963-36-8; [W(CO)$_5$Cl](PPN), 82963-38-0; μ-H[W(CO)$_4$PMe$_3$]$_2^-$, 82963-39-1; [Cr(CO)$_5$], 26319-33-5; W(CO)$_5$, 30395-19-8; μ-H-[W(CO)$_4$P(OMe)$_3$][Cr(CO)$_5$](PPN), 82963-41-5; μ-H[W(CO)$_4$P(OMe)$_3$][W(CO)$_5$](PPN), 82963-43-7; μ-H-[W(CO)$_4$P(OMe)$_3$]$_2$(PPN), 82963-45-9; [HCO$_2$W(CO)$_4$P(OMe)$_3$]$^-$, 82963-46-0; [HCO$_2$W(CO)$_4$PMe$_3$]$^-$, 82963-47-1; W(^{13}CO)$_4$(PIP)P(OMe)$_3$, 82963-48-2; Carbon dioxide, 124-38-9.

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