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Hydrogen-Bridged Trinuclear Nitrosyl Carbonyl Tungstate: $H_2W_3(CO)_{13}(NO)^-$

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Treatment of $HW_2(CO)_7(THF)_2(NO)$ with P^tBu_3 gives $HW_2(CO)_8(P^tBu_3)(NO)$ (**1**), $[HP^tPBu_3][HW_2(CO)_{10}]$ (**2**), and $[HP^tPBu_3][(\mu\text{-}H)_2W_3(CO)_{13}(NO)]$ (**3**). The anion $(\mu\text{-}H)_2W_3(CO)_{13}(NO)^-$ (**3**$^-$) could be more conveniently prepared and isolated as $[PPN][(\mu\text{-}H)_2W_3(CO)_{13}(NO)]$ (**4**) from the reaction of $HW_2(CO)_9(NO)$ with $[PPN][HW(CO)_5]$ ($PPN^+ = (Ph_3P)_2N^+$). Complex **3** reacts with a nucleophile L to form $[HP^tBu_3][(\mu\text{-}H)_2W_3(CO)_{12}(L)(NO)]$ (**5**, L = PMe_3; **6**, L = PPh_3; **7**, L = $P(OEt)_3$; **8**, L = MeNC). Crystal data for **5**: $C_{27}H_{37}NO_{13}P_2W_3$; *Cc* (monoclinic); $a = 19.275(5)$, $b = 31.730(4)$, $c = 12.948(2)$ Å; $\beta = 91.22(2)°$; $Z = 8$; $R = 0.030$, $R_w = 0.030$.

Introduction

Polynuclear hydrido transition-metal complexes were subjects in several reviews.[1] A three-center, two-electron (3c-2e) metal–hydrogen–metal bond is frequently observed in metal to metal hydrogen transfer in polymetallic hydrides,[2] and complexes containing M–H–M bonds constitute an important class among transition-metal hydrides.[3] Our previous observations that $HW_2(CO)_7(PPh_3)_2(NO)$ readily lost one phosphine ligand in THF[4] and that the substitution of PCy_3 for CO ligands in $HW_2(CO)_9(NO)$ did not proceed beyond $HW_2(CO)_8(PCy_3)(NO)$[5] encouraged us to seek the possibility of synthesizing a coordinatively unsaturated complex, $HW_2(CO)_7(P^tBu_3)(NO)$, by use of a sterically bulkier phosphine, P^tBu_3. Instead of $HW_2(CO)_7(P^tBu_3)(NO)$, a complex $[HP^tBu_3][(\mu\text{-}H)_2W_3(CO)_{13}(NO)]$, was isolated from the reaction of $HW_2(CO)_7(THF)_2(NO)$ with P^tBu_3.

Polynuclear metal complexes with solely M–H–M linkages among metal atoms are very scarce.[6] Although an unsupported M–H–M linkage is fairly common for dimeric group VI metal carbonyls,[7] to our knowledge, $(\mu\text{-}H)_2W_3(CO)_{13}(NO)^-$ is the first tungsten trimer which contains only unsupported M–H–M linkages. In this paper we describe the synthesis and the reactivity of this unusual tungsten trimer.

Experimental Section

General Procedures. All reactions and manipulations were carried out under N_2 with use of standard inert-atmosphere and Schlenk techniques. Solvents were dried by standard procedures. All column chromatography was performed with use of silica gel (230–400 mesh ASTM, Merck) as the stationary phase in a column 35 cm in length and 2.5 cm in diameter. $HW_2(CO)_9(NO)$,[8] $HW_2(CO)_7(THF)_2(NO)$,[4] and $[PPN][HW(CO)_5]$[9] were prepared by published procedures. $HW_2(CO)_9(^{15}NO)$ was prepared in the same way as $HW_2(CO)_9(NO)$, except that $Na^{15}NO_2$ (99% enriched, ICON) instead of $NaNO_2$ was used. Infrared spectra were recorded on a Perkin-Elmer 880 spectrometer. The NMR spectra were obtained by using Bruker AMX500 (^{15}N, ^1H, ^{31}P), AC200 (^1H), and AC300 (^1H, ^{31}P) spectrometers. Elementary analyses were performed on a Perkin-Elmer 2400 CHN analyzer.

Reaction of $HW_2(CO)_7(THF)_2(NO)$ with P^tBu_3. To a solution of $HW_2(CO)_7(THF)_2(NO)$ (2.6 g, 3.52 mmol) in 80 mL of CH_2Cl_2 was added 2.3 mL of THF containing 3.52 mmol of P^tBu_3. After the mixture was stirred for 6 h at room temperature, the solvent was removed in vacuo. The residue was chromatographed on a silica gel column under nitrogen. Elution with hexane gave an orange-yellow band. Further elution with CH_2Cl_2/hexane (1:1) gave the yellow second and the orange-yellow third bands.

$HW_2(CO)_8(P^tBu_3)(NO)$ (**1**) was isolated from the first band in 25% yield. IR (CH_2Cl_2, cm^{-1}): 2085 (w), 2065 (w), 2001 (s), 1931 (vs), ν(CO); 1695 (m), ν(NO). Anal. Calcd for $C_{20}H_{28}NO_9PW_2$: C, 29.11; H, 3.42; N, 1.70. Found: C, 29.07; H, 3.17; N, 1.66.

$[HP^tBu_3][(\mu\text{-}H)W_2(CO)_{10}]$ (**2**) was isolated from the second band in 10% yield. The infrared CO stretching and ^1H NMR of μ-H for **2** are identical to those of $[Et_4N][(\mu\text{-}H)W_2(CO)_{10}]$.

$[HP^tBu_3][(\mu\text{-}H)_2W_3(CO)_{13}(NO)]$ (**3**) was obtained from the third bands in 18.5% yield. IR (CH_2Cl_2, cm^{-1}): 2080 (w), 2060 (m), 2041 (w), 2000 (vs), 1965 (s), 1929 (vs), 1893 (s), ν(CO); 1652 (w), ν(NO). Anal. Calcd for $C_{25}H_{30}NO_{14}PW_3$: C, 26.09; H, 2.63; N, 1.22. Found: C, 26.53; H, 2.52; N, 1.05.

$[PPN][(\mu\text{-}H)_2W_3(CO)_{13}(NO)]$ (4). THF (20 mL) was added to a flask containing $HW_2(CO)_9(NO)$ (226 mg, 34.7 mmol) and $[PPN][HW(CO)_5]$ (300 mg, 34.7 mmol), and the mixture was stirred at room temperature for 1.5 h. After evaporation of the solvent, the residue was washed with hexane. The crude reaction product was then chromatographed. The orange-yellow band eluted with CH_2Cl_2/hexane (1:1 by volume) provided 310 mg (72% yield) of powdery **4**. The IR spectra of **4** in CO and NO stretching region are identical to those of **3**. Anal. Calcd for $C_{49}H_{32}N_2O_{14}P_2W_3$: C, 39.60; H, 2.17; N, 1.88. Found: C, 39.80; H, 2.16; N, 1.84.

$[HP^tBu_3][(\mu\text{-}H)_2W_3(CO)_{12}(PMe_3)(NO)]$ (5). A solution of 0.50 g of **3** (0.43 mmol) in 30 mL of CH_2Cl_2 was stirred with excess PMe_3 (0.23 mL, 2.2 mmol) at room temperature for 18 h. The solvent was removed, and the residue was chromatographed. Elution with hexane gave the yellow first band in a trace amount. Further elution with CH_2Cl_2/hexane (1:1.5 to 1.5:1) resulted in the yellow second band and the orange-yellow

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Table 1. Crystallographic Data for Compound **5**

chem formula	$C_{27}H_{37}NO_{13}P_2W_3$	fw	1197.07
a, Å	19.275(5)	space group	Cc (No. 9)
b, Å	31.730(4)	T, °C	25
c, Å	12.948(2)	λ, Å	0.7093
β, deg	91.22(2)	ρ_{calcd}, g cm^{-3}	1.469
V, Å^3	7917(3)	μ, cm^{-1}	60.4
Z	8	transm coeff	0.63–1.00
R^a	0.030	R_w^b	0.030

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(F_o - F_c)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(F_o) + 0.00005F_o^2]$.

third band. A 14% yield (70 mg) of **3** was recovered from the second fraction. Powdery **5** was obtained from the third band in 41% yield. IR (CH_2Cl_2, cm^{-1}): 2068 (w), 2058 (w), 1998 (ms), 1938 (s), 1909 (sh), ν(CO); 1609 (w), ν(NO). Anal. Calcd for $C_{27}H_{39}NO_{13}P_2W_3$: C, 27.04; H, 3.28; N, 1.17. Found: C, 26.76; H, 2.84; N, 1.15.

The yellow-orange complexes $[HP^tBu_3][(\mu\text{-}H)_2W_3(CO)_{12}(PPh_3)(NO)]$ (**6**), $[HP^tBu_3][(\mu\text{-}H)_2W_3(CO)_{12}(P(OEt)_3)(NO)]$ (**7**), and $[HP^tBu_3][(\mu\text{-}H)_2W_3(CO)_{12}(MeNC)(NO)]$ (**8**) were prepared by essentially the same procedure as for the synthesis of **5**.

Complex **6** had a yield of 45%. IR (CH_2Cl_2, cm^{-1}): 2068 (w), 2060 (w), 2001 (ms), 1933 (s), 1920 (sh), 1885 (sh), ν(CO); 1608 (w), ν(NO). Anal. Calcd for $C_{42}H_{45}NO_{13}P_2W_3$: C, 36.42; H, 3.27; N, 1.01. Found: C, 36.28; H, 2.95; N, 0.96.

Complex **7** had a yield of 55%. IR (CH_2Cl_2, cm^{-1}): 2069 (w), 2059 (w), 2005 (ms), 1943 (s), 1931 (s), 1879 (sh), ν(CO); 1614 (w), ν(NO). Anal. Calcd for $C_{30}H_{45}NO_{16}P_2W_3$: C, 27.95; H, 3.52; N, 1.09. Found: C, 27.73; H, 3.09; N, 1.05.

Complex **8** had a yield of 30%. IR (CH_2Cl_2, cm^{-1}): 2203 (w), ν(CN); 2067 (w), 2058 (w), 2008 (ms), 1970 (sh), 1943 (s), 1885 (sh), ν(CO); 1618 (w) ν(NO). Anal. Calcd for $C_{26}H_{33}N_2O_{13}PW_3$: C, 26.83; H, 2.86; N, 2.41. Found: C, 26.61; H, 2.63; N, 2.24.

All ^{15}N-enriched samples were prepared from $HW_2(CO)_9(^{15}NO)$ according to the procedures described above.

Crystallographic Studies. Crystals of **5** were grown by slow diffusion of hexane into a concentrated solution of complex **5** in CH_2Cl_2. Crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer by using graphite-monochromated Mo Kα radiation (λ = 0.7093 Å) with the θ–2θ scan mode. Unit cells were determined by centering 25 reflections in the suitable 2θ range. Other relevant experimental details are listed in Table 1. Absorption corrections (empirical method) according to ψ scans of three reflections were applied. All data processing was carried out on a MICRO VAX 3600 computer by using the NRCC SDP program.[11] The structures of **5** was solved by direct methods, which located the W atoms. The coordinates of all remaining atoms except hydrogen atoms were obtained from a series of structure factor calculations and Fourier syntheses. The structure was refined by minimizing $\sum w(|F_o|-|F_c|)^2$, where $w = 1/\sigma(F_o)^2$ was calculated from the counting statistics. The atomic scattering factors and anomalous dispersion terms f' and f'' were taken from ref 12. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms except for H–P were included in the structure factor calculation in idealized positions with d_{C-H} = 0.98 Å. The final positional parameters are listed in Table 2, and selected interatomic distances and bond angles are given in Table 3.

Results and Discussion

Equation 1 describes the synthesis of $(\mu\text{-}H)_2W_3(CO)_{13}(NO)^-$ (3^-) in this study. Formation of 3^- from $HW_2(CO)_7(THF)_2(NO)$

$$HW_2(CO)_7(THF)_2(NO) + P^tBu_3 \xrightarrow{CH_2Cl_2} [HP^tBu_3][(\mu\text{-}H)_2W_3(CO)_{13}(NO)] + HW_2(CO)_8(P^tBu_3)(NO) + [HP^tBu_3][HW_2(CO)_{10}] \quad (1)$$

or $HW_2(CO)_9(NO)$ and P^tBu_3 is likely via electron transfer from P^tBu_3 to the tungsten dimer followed by fragmentation of the dimer to $HW(CO)_5^-$. Although there is no direct evidence of

Table 2. Positional Parameters and β_{iso} Values for the Atoms in **5**

atom	x	y	z	B_{iso}, Å^2
W(1A)	0.01332(5)	0.38887(3)	0.30048(7)	3.83(4)
W(2A)	0.06803(5)	0.31736(3)	0.49077(7)	3.90(4)
W(3A)	0.16537(5)	0.43982(3)	0.24949(8)	4.49(4)
P(1A)	−0.0330(3)	0.4386(2)	0.4368(5)	5.4(3)
N(1A)	−0.0230(8)	0.4218(5)	0.2028(13)	5.0(8)
C(1A)	−0.0674(12)	0.3561(6)	0.3081(17)	5.3(11)
C(2A)	0.0561(11)	0.3503(7)	0.2022(15)	5.5(11)
C(3A)	−0.0321(11)	0.3075(7)	0.5221(17)	5.4(12)
C(4A)	0.0766(11)	0.3543(7)	0.6231(16)	5.5(11)
C(5A)	0.0932(12)	0.2692(8)	0.5793(16)	6.0(12)
C(6A)	0.1715(11)	0.3312(6)	0.4693(16)	5.1(11)
C(7A)	0.0593(10)	0.2849(9)	0.3756(18)	7.6(16)
C(8A)	0.2051(15)	0.4457(8)	0.3936(20)	8.6(17)
C(9A)	0.2075(10)	0.3871(8)	0.2390(19)	6.4(13)
C(10A)	0.2498(12)	0.4560(8)	0.1945(18)	6.6(14)
C(11A)	0.1198(11)	0.4342(8)	0.1095(15)	5.5(11)
C(12A)	0.1200(12)	0.4979(8)	0.2716(16)	5.8(12)
C(13A)	0.0318(16)	0.4658(8)	0.5200(21)	8.6(17)
C(14A)	−0.0779(18)	0.4821(10)	0.3835(25)	12.6(24)
C(15A)	−0.0866(16)	0.4192(10)	0.5335(25)	11.2(21)
O(1A)	−0.1209(9)	0.3358(6)	0.3095(15)	9.6(12)
O(2A)	0.0799(9)	0.3287(5)	0.1447(13)	7.9(10)
O(3A)	−0.0881(8)	0.2984(5)	0.5438(12)	7.3(9)
O(4A)	0.0835(9)	0.3754(6)	0.6967(13)	8.3(10)
O(5A)	0.1080(9)	0.2397(6)	0.6286(12)	8.5(10)
O(6A)	0.2276(7)	0.3386(5)	0.4643(14)	7.7(11)
O(7A)	0.0559(9)	0.2568(5)	0.3094(12)	7.6(10)
O(8A)	0.2306(10)	0.4507(6)	0.4776(14)	10.2(12)
O(9A)	0.2347(9)	0.3528(6)	0.2276(13)	8.9(11)
O(10A)	0.2980(8)	0.4781(7)	0.1589(15)	9.9(12)
O(11A)	0.0954(9)	0.4319(7)	0.0308(12)	9.2(12)
O(12A)	0.0958(11)	0.5294(5)	0.2766(14)	10.2(13)
O(13A)	−0.0490(9)	0.4456(5)	0.1341(12)	7.7(10)
W(1B)	0.01585	0.11440(3)	1.04898	3.50(4)
W(2B)	0.07489(5)	0.20547(3)	0.93425(7)	4.43(4)
W(3B)	0.16222(5)	0.05305(3)	1.07299(8)	4.91(5)
P(1B)	−0.0302(4)	0.0808(2)	0.8903(5)	6.0(3)
N(1B)	−0.0648(9)	0.1452(6)	1.0632(14)	5.8(10)
C(1B)	−0.0248(9)	0.0703(6)	1.1301(15)	3.9(10)
C(2B)	0.0553(13)	0.1414(7)	1.1749(16)	6.4(13)
C(3B)	0.0079(11)	0.2285(6)	1.0409(16)	4.8(11)
C(4B)	0.0039(12)	0.2022(7)	0.8274(16)	5.8(13)
C(5B)	0.0920(10)	0.2649(8)	0.8925(17)	6.0(13)
C(6B)	0.1508(13)	0.1828(8)	0.8457(18)	6.7(14)
C(7B)	0.1494(13)	0.2151(8)	1.0492(16)	6.2(13)
C(8B)	0.1939(12)	0.0478(8)	0.9385(23)	7.7(16)
C(9B)	0.2187(11)	0.1077(9)	1.1015(21)	7.7(16)
C(10B)	0.2470(14)	0.0209(9)	1.1261(20)	7.8(16)
C(11B)	0.1338(12)	0.0542(8)	1.2226(18)	6.9(13)
C(12B)	0.1112(13)	−0.0009(8)	1.0631(19)	7.4(15)
C(13B)	0.0228(12)	0.0842(10)	0.7768(18)	8.2(17)
C(14B)	−0.0596(23)	0.0251(9)	0.9003(30)	15.2(29)
C(15B)	−0.1145(15)	0.1009(11)	0.8445(18)	9.9(21)
O(1B)	0.0454(9)	0.0419(6)	1.1815(14)	8.6(11)
O(2B)	0.0828(9)	0.1575(5)	1.2512(11)	6.9(9)
O(3B)	−0.0311(8)	0.2442(5)	1.0981(11)	6.5(9)
O(4B)	−0.0370(9)	0.2008(6)	0.7627(13)	9.2(11)
O(5B)	0.1012(9)	0.2997(6)	0.8640(13)	8.8(11)
O(6B)	0.1905(10)	0.1704(7)	0.7908(15)	11.1(14)
O(7B)	0.1878(10)	0.2246(6)	1.1159(13)	9.3(11)
O(8B)	0.2148(13)	0.0458(8)	0.8517(16)	13.7(17)
O(9B)	0.2517(11)	0.1356(7)	1.1146(21)	13.8(18)
O(10B)	0.2989(8)	0.0061(7)	1.1535(16)	10.5(13)
O(11B)	0.1118(10)	0.0535(7)	1.3082(13)	9.9(13)
O(12B)	0.0832(9)	−0.0338(5)	1.0574(14)	8.5(12)
O(13B)	−0.1202(7)	0.1629(6)	1.0662(13)	7.6(10)
P(1C)	0.8520(3)	0.1450(2)	0.3536(4)	4.3(3)
P(2C)	0.3060(3)	0.1536(2)	0.4056(4)	4.9(3)
C(1C)	0.7862(11)	0.1023(7)	0.3346(14)	5.1(11)
C(2C)	0.7232(14)	0.1093(9)	0.4052(21)	8.2(16)
C(3C)	0.7675(15)	0.0987(8)	0.2239(20)	8.1(16)
C(4C)	0.8117(14)	0.0579(8)	0.3725(22)	8.6(17)
C(5C)	0.9126(12)	0.1373(8)	0.4631(17)	6.3(13)
C(6C)	0.8737(14)	0.1295(11)	0.5624(16)	9.4(19)
C(7C)	0.9609(14)	0.0985(9)	0.4362(21)	8.5(16)
C(8C)	0.9630(14)	0.1776(10)	0.4787(20)	8.9(17)
C(9C)	0.8165(10)	0.1994(7)	0.3409(16)	5.1(11)
C(10C)	0.7594(14)	0.1989(9)	0.2585(21)	8.9(17)
C(11C)	0.7888(17)	0.2145(8)	0.4469(25)	10.9(20)
C(12C)	0.8784(17)	0.2291(10)	0.3103(25)	11.3(21)
C(13C)	0.2616(12)	0.1154(8)	0.4984(21)	7.4(15)
C(14C)	0.1871(13)	0.1300(10)	0.5143(20)	8.2(17)
C(15C)	0.2977(17)	0.1108(10)	0.5935(21)	9.7(19)
C(16C)	0.2613(23)	0.0709(8)	0.4426(32)	14.5(27)
C(17C)	0.4013(12)	0.1406(8)	0.3883(16)	6.2(13)
C(18C)	0.4229(18)	0.1596(11)	0.2876(24)	11.5(23)
C(19C)	0.4451(14)	0.1551(10)	0.4817(22)	9.3(19)
C(20C)	0.4154(15)	0.0910(8)	0.3846(29)	10.4(22)
C(21C)	0.2871(12)	0.2096(7)	0.4295(19)	6.3(13)
C(22C)	0.3311(15)	0.2367(9)	0.3703(30)	12.2(25)
C(23C)	0.2905(16)	0.2188(9)	0.5451(23)	10.3(19)
C(24C)	0.2138(15)	0.2187(10)	0.3855(27)	11.6(22)

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Table 3. Selected Bond Distances (Å) and Angles (deg) for Complexes **5**

Distances			
W(1A)–W(2A)	3.492(2)	W(1B)–W(2B)	3.451(2)
W(1A)–W(3A)	3.422(2)	W(1B)–W(3B)	3.436(2)
W(1A)–C(1A)	1.92(3)	W(1B)–C(1B)	1.91(2)
W(1A)–C(2A)	1.86(3)	W(1B)–C(2B)	1.98(2)
W(1A)–N(1A)	1.76(3)	W(1B)–N(1B)	1.85(2)
W(1A)–P(1A)	2.549(8)	W(1B)–P(1B)	2.483(7)
W(2A)–C(3A)	1.97(3)	W(2B)–C(3B)	2.03(3)
W(2A)–C(4A)	2.06(3)	W(2B)–C(4B)	1.92(3)
W(2A)–C(5A)	1.94(3)	W(2B)–C(5B)	1.90(4)
W(2A)–C(6A)	2.02(3)	W(2B)–C(6B)	1.98(3)
W(2A)–C(7A)	1.82(3)	W(2B)–C(7B)	2.03(3)
W(3A)–C(8A)	1.96(4)	W(3B)–C(8B)	1.72(4)
W(3A)–C(9A)	1.81(3)	W(3B)–C(9B)	1.93(3)
W(3A)–C(10A)	1.96(3)	W(3B)–C(10B)	1.96(4)
W(3A)–C(11A)	1.98(3)	W(3B)–C(11B)	1.98(4)
W(3A)–C(12A)	2.04(3)	W(3B)–C(12B)	1.94(4)
N(1A)–O(13A)	1.27(3)	N(1B)–O(13B)	1.19(3)
C(1A)–O(1A)	1.18(3)	C(1B)–O(1B)	1.18(3)
C(2A)–O(2A)	1.21(4)	C(2B)–O(2B)	1.19(3)
C(3A)–O(3A)	1.22(4)	C(3B)–O(3B)	1.19(3)
C(4A)–O(4A)	1.15(4)	C(4B)–O(4B)	1.16(3)
C(5A)–O(5A)	1.21(3)	C(5B)–O(5B)	1.21(5)
C(6A)–O(6A)	1.11(3)	C(6B)–O(6B)	1.15(3)
C(7A)–O(7A)	1.25(4)	C(7B)–O(7B)	1.17(4)
C(8A)–O(8A)	1.22(4)	C(8B)–O(8B)	1.34(5)
C(9A)–O(9A)	1.28(4)	C(9B)–O(9B)	1.18(4)
C(10A)–O(10A)	1.16(4)	C(10B)–O(10B)	1.18(4)
C(11A)–O(11A)	1.19(3)	C(11B)–O(11B)	1.24(5)
C(12A)–O(12A)	1.12(4)	C(12B)–O(12B)	1.16(5)
P(1C)–HP(1C)	1.08	P(2C)–HP(2C)	1.06
Angles			
W(2A)–W(1A)–W(3A)	101.22(4)	W(2B)–W(1B)–W(3B)	103.68(3)
W(1A)–C(1A)–O(1A)	178(3)	W(1B)–C(1B)–O(1B)	177(2)
W(1A)–C(2A)–O(2A)	176(2)	W(1B)–C(2B)–O(2B)	179(2)
W(1A)–N(1A)–O(13A)	177(2)	W(1B)–N(1B)–O(13B)	178(2)
W(2A)–C(3A)–O(3A)	172(3)	W(2B)–C(3B)–O(3B)	177(2)
W(2A)–C(4A)–O(4A)	176(2)	W(2B)–C(4B)–O(4B)	176(2)
W(2A)–C(5A)–O(5A)	173(2)	W(2B)–C(5B)–O(5B)	177(2)
W(2A)–C(6A)–O(6A)	178(3)	W(2B)–C(6B)–O(6B)	176(3)
W(2A)–C(7A)–O(7A)	175(2)	W(2B)–C(7B)–O(7B)	174(3)
W(3A)–C(8A)–O(*A)	174(3)	W(3B)–C(8B)–O(8B)	176(2)
W(3A)–C(9A)–O(9A)	176(2)	W(3B)–C(9B)–O(9B)	175(2)
W(3A)–C(10A)–O(11A)	173(3)	W(3B)–C(10B)–O(10B)	175(3)
W(3A)–C(11A)–O(11A)	175(2)	W(3B)–C(11B)–O(11B)	173(2)
W(3A)–C(12A)–O(12A)	176(2)	W(3B)–C(12B)–O(12B)	173(3)
P(1A)–W(1A)–N(1A)	90.4(8)	P(1B)–W(1B)–N(1B)	90.6(6)
P(1A)–W(1A)–C(1A)	90(1)	P(1B)–W(1B)–C(1B)	90.1(8)
P(1A)–W(1A)–C(2A)	175.6(9)	P(1B)–W(1B)–C(2B)	177.0(7)
N(1A)–W(1A)–C(1A)	92(1)	N(1B)–W(1B)–C(1B)	89.4(9)
N(1A)–W(1A)–C(2A)	93(1)	N(1B)–W(1B)–C(2B)	92(1)
C(1A)–W(1A)–C(2A)	92(1)	C(1B)–W(1B)–C(2B)	92(1)
C(3A)–W(2A)–C(4A)	89(1)	C(3B)–W(2B)–C(4B)	93(1)
C(3A)–W(2A)–C(5A)	88(1)	C(3B)–W(2B)–C(5B)	88(1)
C(3A)–W(2A)–C(6A)	173(1)	C(3B)–W(2B)–C(6B)	172(1)
C(3A)–W(2A)–C(7A)	90(1)	C(3B)–W(2B)–C(7B)	84(1)
C(4A)–W(2A)–C(5A)	87(1)	C(4B)–W(2B)–C(5B)	88(1)
C(4A)–W(2A)–C(6A)	85(1)	C(4B)–W(2B)–C(6B)	95(1)
C(4A)–W(2A)–C(7A)	177(1)	C(4B)–W(2B)–C(7B)	175(1)
C(5A)–W(2A)–C(6A)	92(1)	C(5B)–W(2B)–C(6B)	92(1)
C(5A)–W(2A)–C(7A)	91(1)	C(5B)–W(2B)–C(7B)	88(1)
C(6A)–W(2A)–C(7A)	97(1)	C(6B)–W(2B)–C(7B)	89(1)
C(8A)–W(3A)–C(9A)	89(2)	C(8B)–W(3B)–C(9B)	94(1)
C(8A)–W(3A)–C(10A)	91(1)	C(8B)–W(3B)–C(10B)	91(1)
C(8A0–W(3A)–C(11A)	179(1)	C(8B)–W(3B)–C(11B)	174(1)
C(8A)–W(3A)–C(12A)	88(1)	C(8B)–W(3B)–C(12B)	91(1)
C(9A)–W(3A)–C(10A)	89(1)	C(9B)–W(3B)–C(10B)	88(1)
C(9A)–W(3A)–C(11A)	92(1)	C(9B)–W(3B)–C(11B)	91(1)
C(9A)–W(3A)–C(12A)	177(1)	C(9B)–W(3B)–C(11B)	175(1)
C(10A)–W(3A)–C(11A)	90(1)	C(10B)–W(3B)–C(11B)	86(1)
C(10A)–W(3A)–C(12A)	90(1)	C(10B)–W(3B)–C(12B)	90(1)
C(11A)–W(3A)–C(12A)	92(1)	C(11B)–W(3B)–C(12B)	84(1)

formation of $HW(CO)_5^-$, bona fide $HW(CO)_5^-$ indeed reacts with $HW_2(CO)_9(NO)$ in THF to provide 3^- in high yield (eq 2).

$$HW_2(CO)_9(NO) + [PPN][HW(CO)_5] \xrightarrow{THF} [PPN][(\mu\text{-}H)_2W_3(CO)_{13}(NO)] \quad (2)$$

It is very common for phosphines to function as electron-transfer reagents toward organometallic complexes.[13] Coordination of P^tBu_3 competes effectively with electron-transfer processes; therefore, complex **1** is the predominant product if more than 1.5 equiv of P^tBu_3 is used. Other reducing agents, such as Na/Ph_2CO, BuLi, and Cp_2Co, also react with $HW_2(CO)_9(NO)$ to form 3^-.[14] Decomposition of both $HW(CO)_5^-$ [15] and 3^- will afford $HW_2(CO)_{10}^-$.

Molecular Structure of $[HP^tBu_3][(\mu\text{-}H)_2W_3(CO)_{12}(PMe_3)(NO)]$ (5). The ORTEP drawing of the anionic unit in **5** (5^-) is shown in Figure 1. The two crystallographically independent molecules of **5** in the unit cell are only slightly different from each other, and only one of them is discussed here. The three tungsten atoms in 5^- reside in approximately octahedral environments. The two hydrides observed in the ^1H NMR spectra (Table 4) should bridge the W(1A)/W(2A) pair and W(1A)/W(3A) pair, respectively, since the W(1A)–W(2A) (3.492(2) Å) and W(1A)–W(3A) (3.422(2) Å) distances fall within the range of a 3c-2e W–H–W bond,[3,4,16] and the W(2A)–W(3A) (5.344(2) Å) distance indicates the absence of any metal–metal interaction. The spectra (vide infra) are also consistent with this assignment. The NO[17] ligand, which is trans to one of the bridging hydrides and cis to the other, is linearly coordinated to the central tungsten atom. The PMe_3 ligand is cis to the NO and both hydride ligands.

The X-ray crystal structure of $[HP^tBu_3][(\mu\text{-}H)_2W_3(CO)_{12}(PMe_3)(NO)]$ (**5**) serves as a complement to elucidate the structure of **3** as $[HP^tBu_3][\{(\mu\text{-}H)W(CO)_5\}_2\{W(CO)_3(NO)\}]$ even though the poor quality of **3**[18] renders differentiation between NO and CO ligands questionable. The structures of $H_2W_3(CO)_{13}(NO)^-$ (3^-) and $H_2W_3(CO)_{12}(PMe_3)(NO)^-$ (5^-) are most similar to that of $HM_2M'(CO)_{14}$ (M = Re, M′ = Mn;[19a] M, M′ = Re;[19b] M = Mn, M′ = Re[19c]), which also has three metal atoms residing in a roughly octahedral environment and is also an open cluster with a bent skeleton. The latter contains a metal–metal bond and only one 3c-2e bond. The complex $Re_3(\mu\text{-}H)_2(CO)_{10}(L)_2^-$ (L = PPh_3,[20a] CO[20b]), on the other hand, has two 3c-2e bonds and one metal–metal bond. It is interesting to note that the cluster skeleton of $W_3(CO)_{14}^{2-}$ was recently reported to be a chain of three tungsten atoms with octahedral coordination.[21]

The spectroscopic data (Table 4) for **3** are fully consistent with its formulation. Though X-ray analysis could not differentiate $[HP^tBu_3]^+$ from P^tBu_3, a characteristic one-bond coupling between P and H (*J* = 444 Hz) in both ^1H and ^{31}P NMR provides solid

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(17) The location of the NO ligand was distinguished from that of the CO ligand by conspicuous discrepancies in the thermal parameters for the N and C atoms when incorrectly assigned. For instance, the reverse of N and C(1) gave the following thermal parameters (B_{iso}, Å^2): N(1A), 7.8(12); C(1A), 3.1(8); N(1B), 5.9(10); C(1B), 4.0(9). The reverse of N and C(2) gave the following thermal parameters (Å^2): N(1A), 8.3(13); C(2A), 3.1(8); N(1B), 9.3(14); C(2B), 3.9(9). Hodgson, D. J.; Ibers, J. A. *Inorg. Chem.* **1968**, *7*, 2345.

(18) Lin, J. T. Unpublished research. Crystals were grown by cooling a solution of **3** in CH_2Cl_2/hexane (1:5) at −5 °C. X-ray crystal data for **3**: $C_{72}H_{60}N_6O_{42}P_3W_9$, fw = 3356.37; triclinic, $P1$; $a = 15.480(4)$, $b = 17.645(3)$, $c = 21.889(8)$ Å; $\alpha = 73.36(2)$, $\beta = 100.68(3)$, $\gamma = 109.23(2)°$; $V = 5382(3)$ Å^3; $Z = 2$; $2\theta_{max} = 45°$, $R = 0.069$, $R_w = 0.066$ for $I > 2\sigma(I)$. The cation $HP^tBu_3^+$ was found to be disordered with a 65% occupancy.

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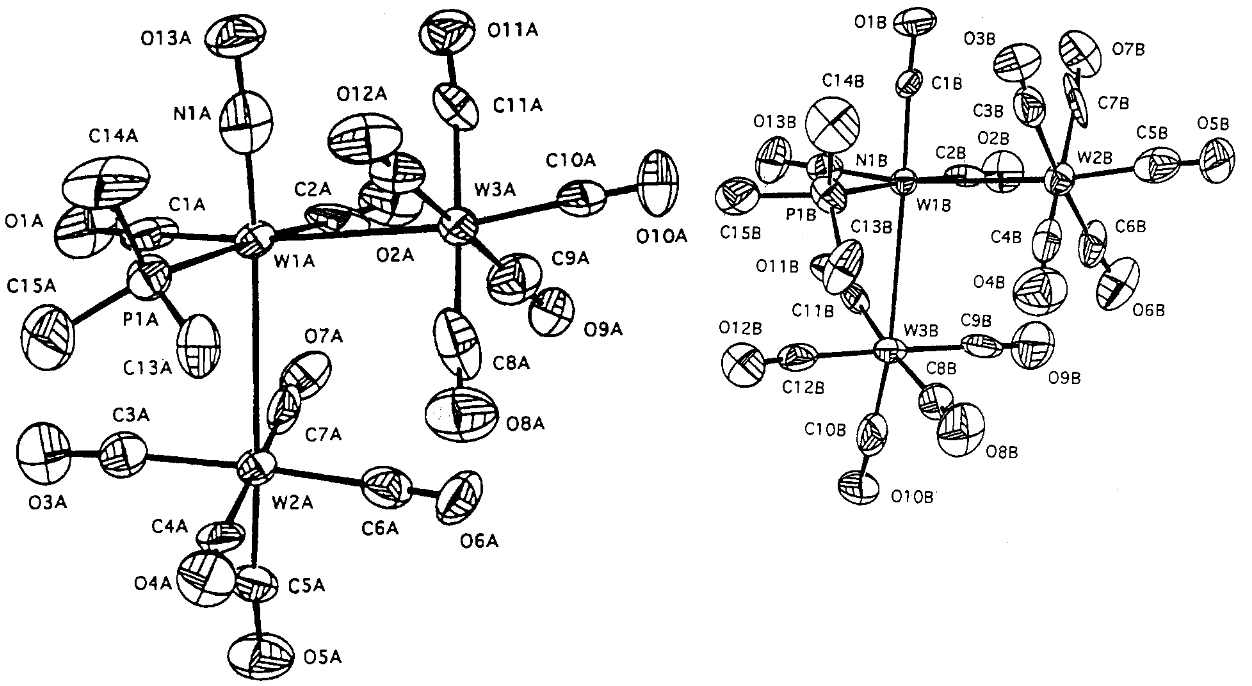

Figure 1. ORTEP drawing of molecules A and B in the anion of $[HP^tBu_3][(\mu\text{-}H)_2W_3(CO)_{12}(PMe_3)(NO)]$ (**5**). Thermal ellipsoids are drawn with 50% probability boundaries.

Table 4. ^1H, $^{31}P\{H\}$, and ^{15}N NMR Data

compd	δ,[a,b] ppm (J, Hz)	δ,[c] ppm (J, Hz)	δ,[d] ppm (J, Hz)
1	1.64 (d, 9 H, $^3J_{P-H} = 12.0$, ^{t}Bu), −11.4 (d, 1 H, $^2J_{P-H} = 8.7$, $^1J_{W-H} = 51.2, 33.4$, μ-H)	87.0 (s, $^1J_{W-P} = 240$)	
3[e]	5.89 (d, 1H, $^1J_{P-H} = 444$, *H*P), 1.75 (d, 9 H, $^3J_{P-H} = 7.7$, ^{t}Bu), −9.88 (dd, 1 H, $^2J_{H-H} = 4.5$, $^2J_{N-H} = 1.16$, $^1J_{W-H} = 48.5, 38.9$, μ-H), −13.0 (dd, 1 H, $^2J_{N-H} = 2.36$, $^1J_{W-H} = 37.7, 27.3$, μ-H)	62.2 (s, H*P*)	−8.86 (dd, $^2J_{N-H} = 2.36, 1.16$, $^1J_{W-N} = 97.7$, *N*O)
4	7.75–7.53 (m, 30 H, Ph), −9.82 (d, 1 H, $^2J_{H-H} = 4.5$, $^1J_{W-H} = 48.5, 38.9$, μ-H), 13.0 (d, 1 H, $^1J_{H-H} = 37.7, 27.3$, μ-H)	26.7 (s, PNP)	
5[e]	5.92 (d, 1 H, $^1J_{P-H} = 447$, *H*P), 1.77 (d, 9 H, $^2J_{P-H} = 15.0$, P*Me*$_3$), 1.76 (d, 9 H, $^3J_{P-H} = 15.0$, ^{t}Bu), −8.99 (ddd, 1 H, $^2J_{P-H} = 17.5$, $^1J_{H-H} = 4.00$, $^2J_{N-H} = 1.08$, $^1J_{W-H} = 52.8, 45.3$, μ-H), −12.4 (ddd, 1 H, $^1J_{P-H} = 17.5$, $^2J_{N-H} = 2.53$, $^1J_{W-H} = 48.2, 32.6$, μ-H)	62.1 (s, 1 P, H*P*), −32.1 (s, 1 P, $^1J_{W-P} = 223$, *P*Me$_3$)	−12.1 (ddd, $^2J_{P-N} = 5.04$, $^2J_{N-H} = 2.47, 1.06$, $^1J_{W-N} = 100$, *N*O)
6[e]	7.63–6.62 (m, 15 H, Ph), 5.86 (d, 1 H, $^1J_{P-H} = 456$, *H*P), 1.76 (d, 9 H, $^3J_{P-H} = 15.9$, ^{t}Bu), −7.97 (ddd, 1 H, $^2J_{P-H} = 16.3$, $^2J_{H-H} = 3.6$, $^2J_{N-H} = 1.02$, $^1J_{W-H} = 54.1, 47.6$, μ-H), −11.3 (ddd, 1 H, $^2J_{P-H} = 14.8$, $^2J_{N-H} = 2.70$, $^1J_{W-H} = 49.8, 42.2$, μ-H)	62.2 (s, 1 P, H*P*), 17.0 (s, 1 P, $^1J_{W-P} = 379$, *P*Ph$_3$)	−12.2 (ddd, $^2J_{P-N} = 4.52$, $^2J_{N-H} = 2.73, 1.08$, $^1J_{W-N} = 99.9$, *N*O)
7	5.85 (d, 1 H, $^1J_{P-H} = 444$, μ-H), 4.16 (m, 6 H, C*H*$_2$), 1.82 (d, 9 H, $^3J_{P-H} = 15.0$, ^{t}Bu), 1.33 (t, 9 H, $^3J_{H-H} = 12.0$, CH$_2$C*H*$_3$), −9.13 (dd, 1 H, $^2J_{P-H} = 21.3$, $^2J_{H-H} = 4.38$, $^1J_{W-H} = 53.1, 45.3$, μ-H), −12.6 (dd, 1 H, $^2J_{P-H} = 21.4$, $^1J_{W-H} = 47.2, 32.9$, μ-H)	62.1 (s, 1 P, H*P*), 130 (s, 1 P, $^1J_{W-P} = 365$, *P*(OEt)$_3$)	
8	5.90 (d, 1 H, $^1J_{P-H} = 447$, *H*P), 3.79 (s, 3 H, *Me*NC), 1.84 (d, 9 H, $^3J_{P-H} = 14.7$, ^{t}Bu), −9.60 (d, 1 H, $^2J_{H-H} = 4.75$, $^1J_{W-H} = 53.6, 44.4$, μ-H), −12.9 (d, 1 H, $^1J_{W-H} = 45.0, 30.0$, μ-H)	62.5 (s, 1 P, H*P*)	

[a] All are measured in acetone-d_6. [b] δ values relative to Me_4Si. [c] δ values relative to 85% H_3PO_4(aq). [d] δ values relative to neat $MeNO_2$: low-field positive, measured at 25 °C. [e] The sample is ^{15}N enriched, and all enriched samples were prepared from $HW_2(CO)_9(^{15}NO)$. Abbreviations: ax = axial, eq = equatorial.

evidence for the ionic nature of **3**. The two hydrides are mutually cis ($^2J_{H-H} = 4.5$ Hz), and both have two sets of tungsten satellites ($J_{W-H} = 38.9, 48.5$ Hz and $27.3, 37.7$ Hz) in the ^1H NMR spectra. The presence of a NO ligand is evident on the basis of a NO stretching at 1652 cm^{-1} in the infrared and one chemical shift at δ_N −8.86 ppm ($J_{N-W} = 97.7$ Hz) in the ^{15}N NMR for ^{15}N-enriched **3**. This NO ligand should be coordinated to the central tungsten atom W(2) since it is coupled to both hydrides. According to our previous studies on a series of dimeric W–H–W complexes containing a NO ligand,[4] we assign the two hydrides in **3** as being cis ($\delta_H = -9.83$ ppm, $J_{H-^{15}N} = 1.16$ Hz) and trans ($\delta_H = -13.0$ ppm, $J_{H-^{15}N} = 2.36$ Hz) to the NO ligand, respectively, on the basis of several observations: (1) the chemical shift of the cis hydride ($\delta = -9.83$ ppm) appears at lower field than that of the trans hydride ($\delta = -13.0$ ppm) by about 3 ppm; (2) the N–H coupling constant of the cis hydride is ca. 1 Hz and that of the trans hydride is ca. 2 Hz; (3) the δ_N value (−8.9 ppm) of **3** appears at lower field than those for complexes which have NO trans to a μ-H ($\delta = -16.0$ to -24.0 ppm) and at higher field than those for complexes which have NO cis to a μ-H ($\delta = 5.5$ to -3.0 ppm).

Chemical Reactivity. Complex **3** was found to be reactive toward nucleophiles such as phosphines and isocyanides (eq 3).

$$(\mu\text{-}H)_2W_3(CO)_{13}(NO)^- + L \xrightarrow{CH_2Cl_2} (\mu\text{-}H)_2W_3(CO)_{12}(L)(NO)^- \quad (3)$$

$$L = PMe_3, PPh_3, P(OEt)_3, MeNC$$

Complexes **5**–**8** were isolated and were found to have the formulation $[W(CO)_2(NO)(L)][(\mu\text{-}H)W(CO)_5]_2$ (vide supra). A large excess of MeNC should be avoided for the synthesis of **8** since it was found that **8** reacted further with MeNC to form

$HW_2(CO)_7(MeNC)_2(NO_{eq})$.[22] It is evident that the NO ligand plays an important role in activating the coordinated CO ligand. Our previous studies on dinuclear M–H–M complexes unanimously have ligand substitution occur at the metal attached to the NO ligand.[4,5,7,23]

The spectroscopic data for complexes **5**–**8** are also consistent with their formulation. The hydride which is cis to the NO ligand appears at lower field ($\delta = -8.0$ to -10.0 ppm) than that which is trans to the NO ligand ($\delta = -11.3$ to -13.0) by ca. 3 ppm in the ^1H NMR spectra. Both hydride ligands are cis to the phosphine ligand for **5**–**7**, and the two-bond phosphorus–hydrogen coupling constants range from 15 to 21 Hz.[24] Each hydride has two sets of tungsten satellites, and the coupling constant, $^1J_{H-W}$, ranges from 30 to 54 Hz. ^{15}N-enriched **5** and **6** have $^2J_{N-H}$(cis) at 1.0 Hz and $^2J_{N-H}$(trans) at 2.5 Hz, respectively. The chemical shift of NO also appears in a reasonable range ($\delta = -12.1$ for **5** and -12.2 for **6**) in the ^{15}N NMR spectra. The one-bond tungsten–phosphorus coupling constants, ranging from 220 to 380 Hz, are consistent with those frequently observed.[25]

Our preliminary results indicated that $HW(CO)_5^-$ reacted with $HW_2(CO)_8(^iPrNC)(NO)$[19] and $HMo_2(CO)_9(NO)$ to form $[W(CO)_2(^iPrNC)(NO)][(\mu\text{-}H)W(CO)_5]^-$ and $(\mu\text{-}H)_2Mo_2W(CO)_{13}(NO)^-$, respectively. The reaction of $HFe(CO)_4^-$ with $HW_2(CO)_9(NO)$, on the other hand, led to the formation of $HFeW(CO)_9^-$ [26] and $Fe(CO)_3(NO)^-$. The mechanistic aspect of the formation of **3**$^-$ as well as the synthesis of related hydrogen-bridged heterobimetallic complexes[27] is currently under investigation.

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Supplementary Material Available: Pluto drawings for $[(\mu\text{-}H)_2W_3(CO)_{13}(NO)]^-$ (**3**$^-$) and the cations, $[HP^tBu_3]^+$, of **5**, listings of crystallographic data, all bond distances and angles, anisotropic thermal parameters and isotropic thermal parameters, and positional parameters for calculated hydrogen atoms for **5**, and listings of positional parameters and B_{iso} values, anisotropic thermal parameters and isotropic thermal parameters, and bond distances for **5** when N(1) and C(1) are reversed and when N(1) and C(2) are reversed (27 pages). Ordering information is given on any current masthead page.

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