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Articles

Structural and Mechanistic Investigation Probing Ligand Substitution of $HW_2(CO)_9(NO)$

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Syntheses of $HW_2(CO)_8(P(p\text{-}C_6H_4X)_3)(NO)$ (**1**, X = Me; **3**, X = OMe; **5**, X = F), $HW_2(CO)_7(P(p\text{-}C_6H_4X)_3)_2(NO)$ (**2**, X = Me; **4**, X = OMe; **6**, X = F), $HW_2(CO)_8(AsPh_3)(NO)$ (**7**), $[NMe_4][HW_2(CO)_7(\eta^2\text{-}S_2CR_2)(NO)]$ (**8**, $R_2 = Et_2$; **9**, $R_2 = -CH_2(CH_2)_2CH_2$), and $HW_2(CO)_7(L)_2(NO)$ (**10** (isomers I and II), L = py (pyridine); **11** (isomers I and II), L = bipy (2,2′-bipyridine)) from either $HW_2(CO)_9(NO)$ or $HW_2(CO)_7(THF)_2(NO)$ are reported. IR and ^1H, ^{31}P, and ^{15}N NMR spectral studies are used as probes for mechanistic insight into the reactions with phosphines. Both $HW_2(CO)_9(NO)$ and $HW_2(CO)_7(THF)_2(NO)$ follow mainly a dissociative pathway with subsequent rearrangement of the NO ligand. X-ray crystal structural analyses for **5**, **6**, **10** (isomer I), and **11** (isomer I) were carried out, yielding the following data. **5**: triclinic; $P\bar{1}$; $Z = 2$; $a = 9.1656$ (7), $b = 10.791$ (1), $c = 15.442$ (1) Å; $\alpha = 97.73$ (1), $\beta = 76.21$ (1), $\gamma = 104.290$ (6)°; $V = 1432.8$ (2) Å^3; $R = 0.021$; $R_w = 0.026$. **6**: triclinic; $P\bar{1}$; $Z = 2$; $a = 10.116$ (1), $b = 11.387$ (1), $c = 19.342$ (2) Å; $\alpha = 95.91$ (1), $\beta = 98.53$ (1), $\gamma = 106.70$ (1)°; $V = 2085.5$ (3) Å^3; $R = 0.023$; $R_w = 0.026$. **10** (isomer I): monoclinic; $P2_1/c$; $Z = 4$; $a = 9.865$ (1), $b = 10.6616$ (8), $c = 20.610$ (1) Å; $\beta = 90.744$ (7)°; $V = 2167.5$ (3) Å^3; $R = 0.025$; $R_w = 0.029$. **11** (isomer I): monoclinic; $C2/c$; $Z = 8$; $a = 20.872$ (2), $b = 10.5217$ (9), $c = 19.095$ (3) Å; $\beta = 100.12$ (1)°; $V = 4128.2$ (8) Å^3; $R = 0.025$; $R_w = 0.028$.

Introduction

We recently reported the substitution of phosphine for CO ligands in $HW_2(CO)_9(NO)$ and characterized several derivatives with novel structures.[1] For the three monodentate phosphines (L) used, the relative yield of disubstituted products vs monosubstituted product increases (35:15 for L = Ph_2PH; 12:55 for L = PPh_3; 0:40 for L = PCy_3) as the cone angle of the phosphines (Ph_2PH, 126°; PPh_3, 145°; PCy_3, 170°)[2] decreases. In an effort to improve the yields of the disubstituted products, we set out to investigate the mechanism of these reactions, and we were surprised by the presence of two monosubstituted derivatives prior to the formation of the disubstituted product. Meanwhile, our successful characterization of complexes containing an equatorial NO ligand, $HW_2(CO)_7(THF)_2(NO)$ and $HW_2(CO)_7(MeNC)_2(NO)$,[3] suggested that the mechanism of ligand substitution of $HW_2(CO)_9(NO)$ could be more complex than we initially thought. In this paper, we will describe reactions of $P(p\text{-}C_6H_4X)_3$ (X = F, Me, OMe), $AsPh_3$, $R_2NCS_2^-$ ($R_2 = Et_2$, $-CH_2(CH_2)_2CH_2$), pyridine (py), and 2,2′-bipyridine (bipy) with $HW_2(CO)_9(NO)$ or $HW_2(CO)_7(THF)_2(NO)$. Structural characterizations for several products as well as mechanistic investigations by IR, ^1H NMR, and ^{15}N NMR techniques are also included.

Experimental Section

General Procedures. All reactions and manipulations were carried out under N_2 with use of standard inert-atmosphere and Schlenk techniques.[4] 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. $HW_2(CO)_9(NO)$[5] and $HW_2(CO)_7(THF)_2(NO)$[3] were prepared by published procedures. Infrared measurements were made on a Perkin-Elmer 880 spectrometer. The NMR spectra were measured by using Bruker AMX500 (^{15}N, ^1H, ^{31}P), AC200 (^1H), and MSL200 (^1H, ^{31}P) spectrometers. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer.

For the reactions of $HW_2(CO)_9(NO)$ or $HW_2(CO)_7(THF)_2(NO)$ with $P(p\text{-}C_6H_4X)_3$ (X = F, Me, OMe) essentially the same procedures were followed, and thus only the reactions of $HW_2(CO)_9(NO)$ and $HW_2(CO)_7(THF)_2(NO)$ with $P(p\text{-}C_6H_4F)_3$ will be described in detail.

Reaction of $HW_2(CO)_9(NO)$ with $P(p\text{-}C_6H_4Me)_3$. A mixture of $HW_2(CO)_9(NO)$ (300 mg, 0.46 mmol) and $P(p\text{-}C_6H_4Me)_3$ (280 mg, 0.92 mmol) in 30 mL of CH_2Cl_2 was stirred under nitrogen for 72 h, and the solution was soaked with 2 g of silica gel and pumped dry. It was then carefully placed on the top of the column packed with silica gel/hexane and chromatographed under nitrogen. Careful elution with CH_2Cl_2/hexane (1:4) gave first an orange band and then a yellow band. The solvent was removed from the fractions.

$HW_2(CO)_8(P(p\text{-}C_6H_4Me)_3)(NO)$ (**1**) was isolated from the first band in a yield of 56%. IR (CH_2Cl_2, cm^{-1}): 2090 (w), 2062 (w), 2008 (s), 1934 (vs), ν(CO); 1700 (m, br), ν(NO). Anal. Calcd for $C_{29}H_{22}NO_9PW_2$: C, 37.55; H, 2.37; N, 1.50. Found: C, 37.47; H, 1.91; N, 1.43.

$HW_2(CO)_7(P(p\text{-}C_6H_4Me)_3)_2(NO)$ (**2**) was isolated from the second band in 21% yield. IR (CH_2Cl_2, cm^{-1}): 2068 (m), 2015 (m), 1950 (vs), 1926 (s), ν(CO); 1662 (m, br), ν(NO). Anal. Calcd for $C_{49}H_{43}NO_8P_2W_2$: C, 48.88; H, 3.57; N, 1.16. Found: C, 48.84; H, 3.48; N, 1.08.

Reaction of $HW_2(CO)_9(NO)$ with $P(p\text{-}C_6H_4OMe)_3$. Column chromatography gave two bands with the use of CH_2Cl_2/hexane (1:4) as eluent.

$HW_2(CO)_8(P(p\text{-}C_6H_4OMe)_3)(NO)$ (**3**) was isolated from the orange first band in 30% yield. IR (CH_2Cl_2, cm^{-1}): 2090 (w), 2062 (w), 2008

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Table I. Crystal Data for Compounds **5**, **6**, **10(I)**, and **11(I)**

	5	**6**	**10(I)**	**11(I)**
chem formula	$C_{26}H_{13}F_3NO_9PW_2$	$C_{43}H_{25}F_6NO_8P_2W_2$	$C_{17}H_{11}N_3O_8W_2$	$C_{17}H_9N_3O_8W_2$
fw	939.05	1227.3	752.99	750.97
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$C2/c$
a, Å	9.1656 (7)	10.116 (1)	9.865 (1)	20.872 (2)
b, Å	10.791 (1)	11.387 (1)	10.6616 (8)	10.5217 (9)
c, Å	15.442 (1)	19.342 (2)	20.610 (1)	19.095 (3)
α, deg	97.73 (1)	95.91 (1)		
β, deg	76.21 (1)	98.53 (1)	90.744 (7)	100.12 (1)
γ, deg	104.29 (1)	106.70 (1)		
V, Å^3	1432.8 (2)	2085.5 (3)	2167.5 (3)	4128.2 (8)
Z	2	2	4	8
T, °C	+25	+25	+25	+25
λ(Mo Kα), Å	0.7101	0.7101	0.7101	0.7101
ρ_{calcd}, g cm^{-3}	2.177	1.954	2.308	2.417
μ(Mo Kα), cm^{-1}	8.32	5.78	10.88	11.43
transm coeff	0.99–0.62	1.00–0.88	1.00–0.34	1.00–0.67
R^a	0.021	0.023	0.025	0.025
$R_w{}^b$	0.026	0.026	0.029	0.028

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

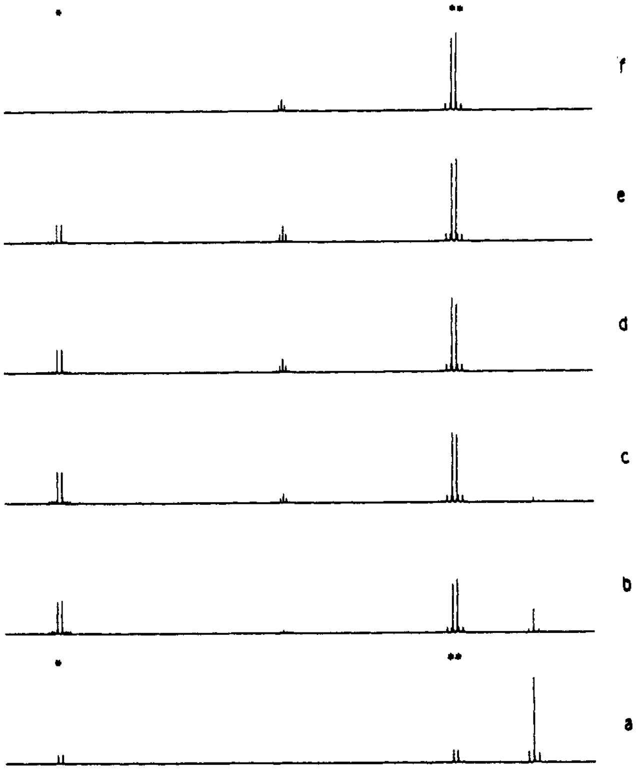


Figure 1. ^1H NMR monitoring of the reaction of $HW_2(CO)_9(NO)$ with PPh_3 in the hydride region (solvent CD_2Cl_2): (a) 1 h; (b) 6 h; (c) 15 h; (d) 22 h; (e) 32 h; (f) 72 h. Peaks marked with * and ** are from $HW_2(CO)_8(PPh_3)(NO)$ (isomer I) and $HW_2(CO)_8(PPh_3)(NO)$ (isomer II), respectively.

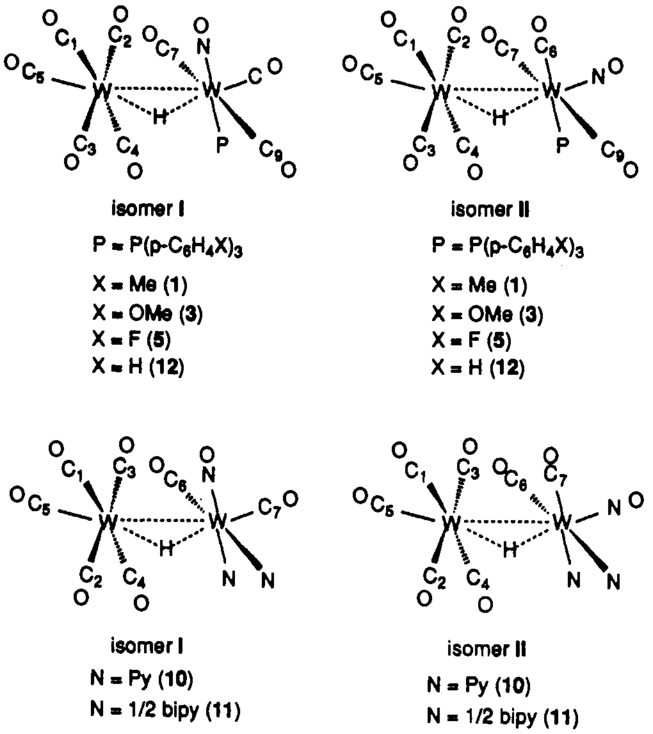
(s), 1934 (vs), ν(CO); 1700 (m, br), ν(NO). Anal. Calcd for $C_{29}H_{22}NO_{10}PW_2$: C, 35.70; H, 2.20; N, 1.44. Found: C, 36.18; H, 2.10; N, 1.24.

$HW_2(CO)_7(P(p\text{-}C_6H_4OMe)_3)_2(NO)$ (**4**) was isolated from the yellow second band in 15% yield. IR (CH_2Cl_2, cm^{-1}): 2068 (m), 2015 (m), 1952 (vs), 1923 (s), ν(CO); 1665 (m, br). Anal. Calcd for $C_{49}H_{43}NO_{10}P_2W_2$: C, 45.28; H, 3.30; N, 1.08. Found: C, 45.55; H, 2.90; N, 0.95.

Reaction of $HW_2(CO)_9(NO)$ with $P(p\text{-}C_6H_4F)_3$. Column chromatography gave two bands with CH_2Cl_2/hexane (1:4) as eluent.

$HW_2(CO)_8(P(p\text{-}C_6H_4F)_3)(NO)$ (**5**) was isolated from the orange first band in a yield of 55%. IR (CH_2Cl_2, cm^{-1}): 2090 (w), 2063 (w), 2011 (s), 1935 (vs), ν(CO); 1701 (m, br), ν(NO). Anal. Calcd for $C_{26}H_{13}F_3NO_9PW_2$: C, 33.23; H, 1.38; N, 1.49. Found: C, 33.14; H, 1.27; N, 1.50.

Chart I



isomer I

P = P(p-C6H4X)3

X = Me (1)
X = OMe (3)
X = F (5)
X = H (12)

isomer II

P = P(p-C6H4X)3

X = Me (1)
X = OMe (3)
X = F (5)
X = H (12)

isomer I

N = Py (10)
N = 1/2 bipy (11)

isomer II

N = Py (10)
N = 1/2 bipy (11)

$HW_2(CO)_7(P(p\text{-}C_6H_4F)_3)_2(NO)$ (**6**) was isolated from the yellow second band in only a trace amount.

Reaction of $HW_2(CO)_7(THF)_2(NO)$ with $P(p\text{-}C_6H_4X)_3$. The procedure followed was the same as that for the synthesis of **1**–**6** from $HW_2(CO)_9(NO)$, except that the reaction period was 1 day instead of 3 days.

Complexes **1** (or **3** or **5**) and **2** (or **4** or **6**) were isolated from the orange first band and the yellow second band, respectively. Yields: **1**, 25%; **2**, 40%; **3**, 24%; **4**, 65%; **5**, 20%; **6**, 25%.

$HW_2(CO)_7(P(p\text{-}C_6H_4F)_3)_2(NO)$ (6). IR (CH_2Cl_2, cm^{-1}): 2069 (m), 2021 (m), 1961 (vs), 1927 (s), ν(CO); 1662 (m, br), ν(NO). Anal. Calcd for $C_{43}H_{25}F_6NO_8P_2W_2$: C, 42.06; H, 2.04; N, 1.14. Found: C, 41.81; H, 1.76; N, 1.11.

$HW_2(CO)_8(AsPh_3)(NO)$ (7). The procedure for the synthesis of **1** from $HW_2(CO)_9(NO)$ was followed, except that the reaction time was 48 h. Only one orange band was eluted by column chromatography with CH_2Cl_2/hexane (1:4). The solvent was removed to give orange powdery **7**. IR (CH_2Cl_2, cm^{-1}): 2092 (w), 2063 (w), 2011 (s), 1930 (vs), ν(CO); 1700 (m, br), ν(NO). Anal. Calcd for $AsC_{26}H_{16}NO_9W_2$: C, 33.60; H, 1.72; N, 1.51. Found: C, 33.54; H, 1.46; N, 1.46.

$[NMe_4][HW_2(CO)_7(\eta^2\text{-}S_2CNEt_2)(NO)]$ (8). To a flask containing 500 mg (0.66 mmol) of $HW_2(CO)_7(THF)_2(NO)$ and 150 mg of $NaS_2CNEt_2\cdot 3H_2O$ (0.66 mmol) was added 20 mL of THF. The reaction

Table II. Positional Parameters and B_{iso} Values for the Atoms in Compounds **5**, **6**, **10(I)**, and **11(I)**

atom	x	y	z	B_{iso}, Å^2	atom	x	y	z	B_{iso}, Å^2
Compound **5**									
W1	0.53064 (3)	0.11925 (2)	0.74090 (2)	2.92 (1)	C7	0.2726 (7)	0.0583 (7)	0.9487 (4)	3.3 (3)
W(2)	0.22052 (3)	−0.08848 (2)	0.85532 (1)	2.45 (1)	C8	0.0674 (9)	0.0023 (7)	0.8241 (4)	4.0 94)
P	0.14096 (18)	−0.27943 (15)	0.74589 (10)	2.49 (7)	C11	0.0814 (6)	0.2510 (6)	0.6476 (3)	2.5 (3)
N	0.0781 (6)	−0.1707 (5)	0.9458 (3)	3.3 (3)	C12	0.1336 (8)	−0.1329 (6)	0.6115 (4)	3.2 (3)
F1	−0.0312 (5)	−0.1897 (4)	0.4179 (2)	5.1 (2)	C13	0.1004 (8)	−0.1124 (7)	0.5330 (4)	3.8 (3)
F2	0.6073 (5)	−0.5789 (4)	0.5669 (3)	5.7 (2)	C14	0.0074 (8)	−0.2106 (7)	0.4935 (4)	3.4 (3)
F3	−0.3937 (6)	−0.6013 (4)	0.9715 (3)	7.2 (3)	C15	−0.0484 (8)	−0.3292 (7)	0.5260 (4)	3.4 (3)
O1	0.3362 (8)	0.3260 (6)	0.8328 (4)	6.8 (4)	C16	−0.0110 (7)	−0.3497 (6)	0.6029 (4)	2.9 (3)
O2	0.6604 (6)	0.1231 (5)	0.9135 (4)	5.5 (3)	C21	0.2789 (7)	−0.3785 (5)	0.6957 (4)	2.5 (3)
O3	0.4484 (7)	0.1216 (5)	0.5525 (4)	6.0 (3)	C22	0.2388 (8)	−0.5082 (6)	0.6700 (4)	3.4 (3)
O4	0.7483 (7)	−0.0717 (5)	0.6573 (4)	6.2 (3)	C23	0.3478 (9)	−0.5756 (8)	0.6280 (5)	3.9 (4)
O5	0.8104 (7)	0.3478 (5)	0.6849 (3)	5.6 (3)	C24	0.4978 (8)	−0.5128 (7)	0.6102 (4)	3.9 (4)
O6	0.4860 (7)	−0.2158 (5)	0.8810 (4)	5.4 (3)	C25	0.5429 (9)	−0.3848 (8)	0.6325 (5)	4.5 (4)
O7	0.2933 (6)	0.1355 (5)	1.0053 (3)	5.2 (3)	C26	0.4344 (8)	−0.3169 (7)	0.6742 (5)	3.9 (3)
O8	−0.0158 (8)	0.0501 (7)	0.8071 (4)	7.6 (4)	C31	−0.0234 (7)	−0.3868 (6)	0.8085 (4)	2.8 (3)
O9	−0.0102 (6)	−0.2221 (5)	1.0058 (3)	4.6 (3)	C32	−0.1727 (8)	−0.3678 (6)	0.8173 (4)	3.4 (3)
C1	0.4000 (9)	0.2519 (7)	0.8010 (4)	4.0 (4)	C33	−0.2967 (9)	−0.4405 (7)	0.8727 (5)	4.3 (4)
C2	0.6065 (8)	0.1205 (6)	0.8540 (5)	3.5 (3)	C34	−0.2699 (9)	−0.5290 (7)	0.9178 (5)	4.3 (4)
C3	0.4726 (8)	0.1195 (6)	0.6213 (5)	3.7 (4)	C35	−0.1285 (10)	−0.5055 (7)	0.9117 (5)	4.3 (4)
C4	0.6665 (8)	−0.0048 (7)	0.6863 (5)	4.1 (4)	C36	−0.0025 (8)	−0.4777 (6)	0.8571 (4)	3.6 (3)
C5	0.7072 (9)	0.2628 (7)	0.7055 (4)	3.9 (4)	H	0.352 (7)	−0.018 (5)	0.748 (4)	4.0 (14)
C6	0.3914 (8)	−0.1704 (6)	0.8731 (4)	3.5 (3)					
Compound **6**									
W1	0.23793 (3)	0.52263 (2)	0.77518 (1)	3.25 (1)	C21	−0.1132 (6)	0.2615 (5)	0.6125 (3)	3.0 (3)
W2	−0.11214 (2)	0.40560 (2)	0.80063 (1)	2.47 (1)	C22	−0.0109 (7)	0.2123 (6)	0.6393 (3)	3.5 (3)
P1	−0.22537 (17)	0.29675 (15)	0.67265 (8)	2.87 (7)	C23	0.0695 (7)	0.1711 (6)	0.5957 (4)	4.2 (4)
P2	−0.11965 (16)	0.20594 (14)	0.85752 (8)	2.62 (7)	C24	0.0464 (8)	0.1841 (7)	0.5261 (4)	5.0 (4)
N	−0.2818 (5)	0.4090 (4)	0.8185 (3)	3.4 (2)	C25	−0.0534 (8)	0.2342 (7)	0.4981 (3)	5.0 (4)
F1	−0.5085 (6)	0.6448 (4)	0.5597 (3)	8.3 (3)	C26	−0.1351 (7)	0.2734 (6)	0.5416 (3)	4.1 (4)
F2	0.1256 (5)	0.1444 (4)	0.4829 (2)	7.2 (3)	C31	−0.3651 (6)	0.1485 (5)	0.6599 (3)	3.0 (3)
F3	−0.6730 (5)	−0.1865 (4)	0.6382 (3)	7.1 (3)	C32	−0.4535 (6)	0.1250 (6)	0.7090 (3)	3.6 (3)
F4	0.2847 (5)	0.2692 (4)	1.1245 (2)	7.2 (3)	C33	−0.5570 (6)	0.0128 (6)	0.7010 (4)	4.6 (4)
F5	−0.6727 (4)	−0.0011 (5)	0.9397 (2)	8.0 (3)	C34	−0.5733 (7)	−0.0759 (6)	0.6441 (4)	4.8 (4)
F6	0.0383 (6)	−0.1588 (4)	0.6722 (2)	7.4 (3)	C35	−0.4888 (7)	−0.0570 (6)	0.5949 (4)	5.0 (4)
O1	0.1289 (6)	0.5377 (5)	0.6145 (3)	6.6 (3)	C36	−0.3851 (7)	0.0552 (6)	0.6027 (3)	4.1 (3)
O2	0.1893 (7)	0.7764 (5)	0.8260 (4)	9.6 (4)	C41	0.0008 (6)	0.2274 (5)	0.9417 (3)	2.8 (3)
O3	0.3175 (5)	0.2751 (4)	0.7430 (3)	5.9 (3)	C42	0.1357 (6)	0.3112 (6)	0.9514 (3)	3.5 (3)
O4	0.4002 (6)	0.5572 (6)	0.9320 (3)	7.7 (3)	C43	0.2313 (7)	0.3282 (6)	1.0144 (4)	4.5 (4)
O5	0.5220 (5)	0.6848 (5)	0.7434 (3)	6.8 (3)	C44	0.1909 (8)	0.2550 (6)	1.0636 (3)	4.8 (4)
O6	0.0527 (5)	0.5723 (4)	0.9456 (2)	4.8 (2)	C45	0.0611 (8)	0.1718 (6)	1.0568 (4)	4.8 (4)
O7	−0.1099 (6)	0.6598 (4)	0.7512 (3)	5.6 (3)	C46	−0.0338 (7)	0.1570 (5)	0.9945 (3)	3.7 (3)
O8	−0.3915 (5)	0.4194 (5)	0.8298 (3)	5.6 (3)	C51	−0.2882 (6)	0.1350 (6)	0.8827 (3)	3.1 (3)
C1	0.1622 (7)	0.5286 (6)	0.6720 (4)	4.4 (3)	C52	−0.3563 (7)	0.0082 (6)	0.8714 (3)	3.9 (3)
C2	0.2013 (7)	0.6840 (6)	0.8058 (5)	5.7 (4)	C53	−0.4873 (7)	−0.0387 (6)	0.8916 (4)	4.7 (4)
C3	0.2878 (7)	0.3648 (6)	0.7527 (4)	4.2 (4)	C54	−0.5436 (7)	0.0435 (7)	0.9215 (4)	5.3 (4)
C4	0.3373 (7)	0.5393 (7)	0.8763 (4)	4.6 (4)	C55	−0.4791 (7)	0.1677 (7)	0.9358 (4)	5.0 (4)
C5	0.4181 (7)	0.6235 (7)	0.7559 (3)	4.5 (3)	C56	−0.3492 (7)	0.2144 (6)	0.9167 (3)	4.1 (3)
C6	−0.0074 (6)	0.5102 (5)	0.8944 (3)	3.2 (3)	C61	−0.0775 (6)	0.0832 (5)	0.8052 (3)	3.0 (3)
C7	−0.1050 (7)	0.5669 (6)	0.7655 (3)	3.8 (3)	C62	−0.1753 (7)	0.0004 (6)	0.7500 (3)	3.6 (3)
C11	−0.3168 (7)	0.3953 (5)	0.6287 (3)	3.3 (3)	C63	−0.1395 (8)	−0.0841 (6)	0.7049 (3)	4.6 (4)
C12	−0.4589 (7)	0.3739 (6)	0.6273 (4)	4.3 (4)	C64	0.0006 (8)	−0.0789 (6)	0.7167 (4)	4.8 (4)
C13	−0.5233 (8)	0.4587 (8)	0.6035 (4)	5.7 (5)	C65	0.0986 (8)	−0.0004 (7)	0.7692 (4)	5.0 (4)
C14	−0.4462 (9)	0.5597 (7)	0.5814 (4)	5.8 (5)	C66	0.0592 (7)	0.0803 (6)	0.8139 (4)	4.0 (4)
C15	−0.3056 (9)	0.5863 (6)	0.5825 (4)	5.4 (4)	H	0.076 (7)	0.398 (6)	0.775 (3)	6.8 (18)
C16	−0.2407 (8)	0.5010 (6)	0.6055 (4)	5.0 (4)					
Compound **10(I)**									
W1	0.51598 (4)	0.75667 (4)	0.10880 (2)	3.19 (2)	C4	0.4525 (12)	0.6605 (10)	0.1864 (6)	4.0 (6)
W2	0.84022 (4)	0.76140 (4)	0.16928 (2)	3.10 (2)	C5	0.3423 (12)	0.7306 (11)	0.0642 (6)	4.8 (6)
N	0.8804 (10)	0.7018 (9)	0.0846 (6)	5.1 (5)	C6	0.8026 (10)	0.5908 (9)	0.1941 (6)	3.5 (5)
N11	0.7932 (9)	0.8355 (7)	0.2703 (4)	3.0 (4)	C7	1.0320 (12)	0.7461 (10)	0.1958 (5)	4.0 (5)
N21	0.8756 (9)	0.9629 (8)	0.1398 (5)	3.7 (4)	C12	0.6846 (13)	0.7947 (10)	0.3024 (6)	4.8 (6)
O1	0.6437 (11)	0.9014 (9)	−0.0100 (5)	8.6 (6)	C13	0.6593 (14)	0.8293 (13)	0.3644 (7)	5.6 (7)
O2	0.3733 (11)	1.0040 (9)	0.1578 (5)	8.0 (6)	C14	0.7413 (15)	0.9114 (11)	0.3954 (6)	4.8 (7)
O3	0.6201 (9)	0.4936 (7)	0.0569 (5)	6.0 (5)	C15	0.8524 (14)	0.9538 (10)	0.3628 (6)	5.0 (7)
O4	0.4197 (9)	0.6022 (9)	0.2306 (5)	6.4 (5)	C16	0.8751 (12)	0.9152 (10)	0.3012 (6)	4.3 (6)
O5	0.2371 (10)	0.7149 (9)	0.0387 (5)	7.6 (6)	C22	0.9861 (14)	0.9943 (12)	0.1056 (7)	6.1 (8)
O6	0.7831 (9)	0.4882 (7)	0.2066 (5)	6.6 (6)	C23	1.0080 (17)	1.1128 (14)	0.0837 (8)	7.5 (9)
O7	1.1443 (9)	0.7366 (8)	0.2104 (5)	6.3 (5)	C24	0.9134 (19)	1.2025 (12)	0.0927 (7)	6.5 (8)
O8	0.9070 (10)	0.6615 (9)	0.0330 (5)	6.5 (5)	C25	0.8022 (16)	1.1747 (11)	0.1267 (7)	6.5 (8)
C1	0.5971 (15)	0.8496 (11)	0.0330 (6)	5.1 (7)	C26	0.7828 (13)	1.0524 (11)	0.1498 (6)	5.3 (6)
C2	0.4307 (12)	0.9178 (11)	0.1416 (6)	4.3 (6)	H	0.649 (8)	0.812 (7)	0.161 (4)	3.5 (21)
C3	0.5892 (11)	0.5885 (10)	0.0752 (6)	3.8 (6)					

Table II (Continued)

atom	*x*	*y*	*z*	B_{iso}, Å^2	atom	*x*	*y*	*z*	B_{iso}, Å^2
				Compound **11**(I)					
W1	0.07726 (2)	0.24328 (4)	0.11077 (2)	3.98 (2)	C4	0.0713 (6)	0.2656 (11)	0.0042 (6)	6.0 (6)
W2	0.21298 (2)	0.06027 (4)	0.14610 (2)	3.52 (2)	C5	0.0119 (5)	0.3732 (10)	0.1132 (7)	6.3 (6)
N	0.2264 (4)	0.1574 (8)	0.2306 (4)	2.8 (4)	C6	0.2581 (5)	0.1889 (11)	0.1007 (5)	7.0 (6)
N11	0.1884 (4)	−0.0751 (7)	0.0569 (4)	3.9 (4)	C7	0.2966 (4)	−0.0163 (8)	0.1784 (4)	3.2 (4)
N21	0.1552 (3)	−0.0914 (6)	0.1837 (4)	3.5 (3)	C12	0.1508 (5)	−0.1748 (10)	0.0653 (5)	4.3 (5)
O1	0.0784 (4)	0.1967 (8)	0.2740 (4)	6.2 (4)	C13	0.1315 (5)	−0.2633 (10)	0.0117 (7)	6.1 (6)
O2	−0.0265 (4)	0.0230 (8)	0.0847 (6)	9.2 (6)	C14	0.1520 (7)	−0.2452 (13)	−0.0524 (7)	7.4 (7)
O3	0.1867 (4)	0.4554 (7)	0.1376 (5)	7.9 (5)	C15	0.1909 (6)	−0.1438 (14)	−0.0618 (6)	6.9 (7)
O4	0.0658 (5)	0.2770 (9)	−0.0556 (5)	9.4 (6)	C16	0.2073 (5)	−0.0621 (10)	−0.0072 (5)	5.3 (5)
O5	−0.0268 (4)	0.4558 (7)	0.1136 (6)	10.1 (7)	C22	0.1320 (4)	−0.1856 (9)	0.1363 (5)	4.6 (5)
O6	0.2871 (4)	0.2713 (8)	0.0750 (4)	7.4 (4)	C23	0.0938 (5)	−0.2840 (9)	0.1554 (6)	5.2 (6)
O7	0.3502 (3)	−0.0508 (6)	0.1985 (4)	5.7 (4)	C24	0.0811 (6)	−0.2880 (11)	0.2232 (8)	6.4 (7)
O8	0.2364 (3)	0.2127 (6)	0.2849 (4)	5.2 (3)	C25	0.1038 (6)	−0.1958 (13)	0.2704 (6)	6.4 (6)
C1	0.0801 (5)	0.2140 (10)	0.2163 (6)	5.0 (5)	C26	0.1407 (5)	−0.0997 (9)	0.2495 (5)	4.7 (5)
C2	0.0101 (6)	0.1024 (10)	0.0933 (7)	6.0 (6)	H	0.124 (4)	0.128 (7)	0.091 (4)	5.7 (21)
C3	0.1476 (6)	0.3808 (10)	0.1291 (6)	5.6 (6)					

Scheme I

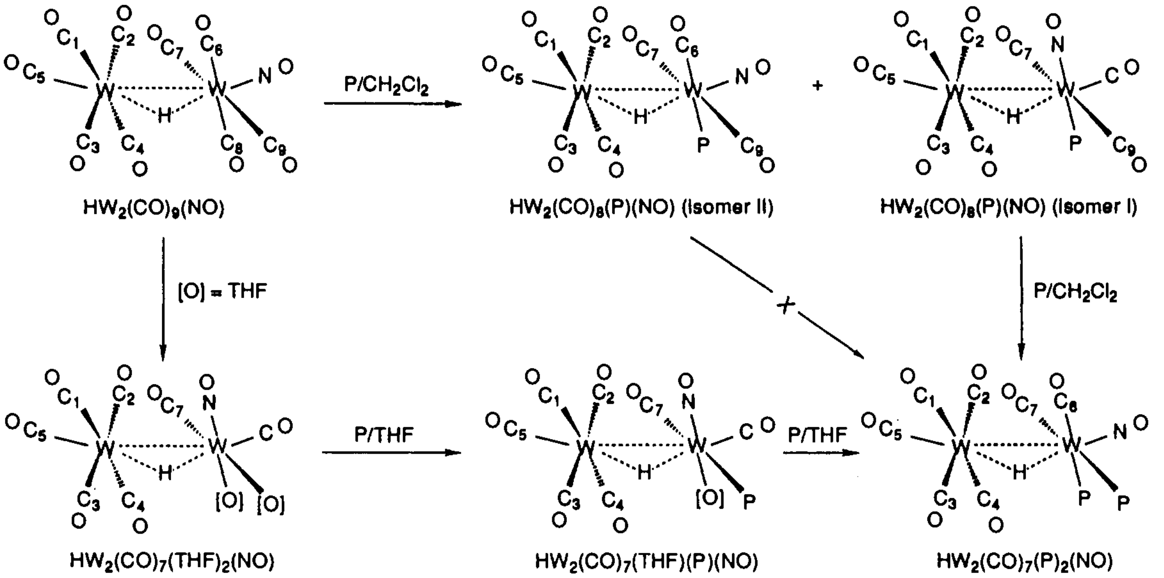
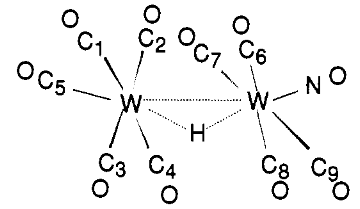


Chart II



exo: 3, 4, 8, 9

endo: 1, 2, 6, 7

mixture was stirred for 1 h at room temperature, and then the solution was concentrated to ca. 3 mL under reduced pressure. Addition of 300 mL of aqueous solution of $Me_4N^+Cl^-$ (72 mg, 0.66 mmol) to the solution produced a yellow suspension. The solution was set in a refrigerator (ca. 5 °C) overnight, after which the yellow solid was collected on a filter frit, washed with H_2O, and dried under vacuum. The compound was further washed with hexane and dried. Yield: 404 mg, 75%. IR (CH_2Cl_2, cm^{-1}): 2059 (m), 2041 (w), 1984 (s), 1924 (vs), 1885 (s), ν(CO); 1609 (m), ν(NO). Anal. Calcd for $C_{16}H_{23}N_3O_8S_2W_2$: C, 23.51; H, 2.82; N, 5.14. Found: C, 23.10; H, 2.53; N, 4.97.

[NMe_4][$HW_2(CO)_7(\eta^2\text{-}S_2CN(CH_2)_3CH_2)(NO)$] (9). This compound was prepared in the same way as **7**. Yield: 63%. IR (CH_2Cl_2, cm^{-1}): 2058 (m), 2041 (m), 1987 (s), 1931 (vs), 1887 (s), ν(CO); 1609 (m), ν(NO). Anal. Calcd for $C_{16}H_{21}N_3O_8S_2W_2$: C, 23.57; H, 2.58; N, 5.16. Found: C, 23.26; H, 2.38; N, 4.95.

$HW_2(CO)_7(py)_2(NO)$ (10). Method A. To a flask containing 500 mg (0.77 mmol) of $HW_2(CO)_9(NO)$ was added 50 mL of pyridine (py). The solution was stirred for 1 day at room temperature, and the solvent was then evaporated under vacuum. Column chromatography gave three removable bands, which were eluted with CH_2Cl_2/hexane (1:6). The yellow first band gave $W(CO)_5(py)$ in a trace amount. Compound **10** was isolated from the orange second band in 40% yield. There were two isomers, I and II, which could not be separated completely from each other, isomer II existing in only a very small amount (less than 5%). Single crystals of isomer I were used for IR and elemental analyses. IR (CH_2Cl_2, cm^{-1}): 2065 (m), 2007 (s), 1973 (m), 1928 (vs), ν(CO); 1659 (m), ν(NO). Anal. Calcd for $C_{17}H_{11}N_3O_8W_2$: C, 27.10; H, 1.46; N, 5.58. Found: C, 27.05; H, 1.34; N, 5.34. The deep orange third band remained uncharacterized.

Method B. The procedure followed was the same as for method A, except that $HW_2(CO)_7(THF)_2(NO)$ was used instead of $HW_2(CO)_9(NO)$. The yellow first band was $W(CO)_5(py)$. Compound **10** was obtained from the orange third band in a yield of 52%.

$HW_2(CO)_7(bipy)(NO)$ (11). Method A. Essentially the same procedure as that for the synthesis of **10** from $HW_2(CO)_9(NO)$ was followed. Dark red **11** was obtained from the first major band in 35% yield. There were two isomers, I and II, which could not be separated completely from each other, isomer II existing in only a very small amount (less than 5%). Single crystals of isomer I were used for IR and elemental analyses. IR (CH_2Cl_2, cm^{-1}): 2064 (m), 2006 (s), 1971 (m), 1934 (vs), ν(CO); 1649 (m), ν(NO). Anal. Calcd for $C_{17}H_9N_3O_8W_2$: C, 27.17; H, 1.20; N, 5.60. Found: C, 27.62; H, 1.55; N, 7.24.

Method B. The same procedure as that for the synthesis of **10** from $HW_2(CO)_7(THF)_2(NO)$ was followed. Compound **11** was obtained from the dark red second band in 50% yield.

Crystallographic Studies. Crystals of $HW_2(CO)_8(P(p\text{-}C_6H_4F)_3)(NO)$ (**5**), $HW_2(CO)_7(P(p\text{-}C_6H_4F)_3)_2(NO)$ (**6**), $HW_2(CO)_7(py)_2(NO)$ (**10**), and $HW_2(CO)_7(bipy)(NO)$ (**11**) were grow by cooling a concentrated

Table III. Selected Bond Distances (Å) and Angles (deg) for Compounds **5**, **6**, **10**(I), and **11**(I)

	5	**6**	**10(I)**	**11(I)**
W1–W2	2.4281 (5)	3.5354 (5)	3.4182 (7)	3.3937 (6)
W1–C1	2.074 (8)	2.045 (7)	2.02 (1)	2.03 (1)
W1–C2	2.025 (7)	2.024 (7)	2.03 (1)	2.03 (1)
W1–C3	2.041 (7)	2.025 (7)	2.06 (1)	2.05 (1)
W1–C4	2.018 (8)	2.025 (7)	2.01 (1)	2.03 (1)
W1–C5	1.971 (7)	1.967 (7)	1.95 (1)	1.94 (1)
W2–C6	2.066 (8)	2.023 (6)	1.93 (1)	1.94 (1)
W2–C7	2.039 (7)	2.009 (6)	1.97 91)	1.923 (9)
W2–C8	2.071 (8)			
W2–P1		2.586 (2)		
W2–P2		2.613 (2)		
W2–P	2.558 (2)			
W2–N	1.827 (5)	1.810 (5)	1.90 (1)	1.888 (8)
W2–N11			2.279 (8)	2.211 (7)
W2–N21			2.261 (8)	2.195 (7)
C1–O1	1.10 (1)	1.137 (8)	1.15 (2)	1.12 (1)
C2–O2	1.136 (9)	1.130 (9)	1.13 (2)	1.12 (1)
C3–O3	1.140 (9)	1.150 (8)	1.12 (1)	1.22 (1)
C4–O4	1.14 (1)	1.133 (8)	1.15 (2)	1.14 (1)
C5–O5	1.159 (9)	1.156 (8)	1.17 (2)	1.19 (1)
C6–O6	1.132 (9)	1.132 (7)	1.14 (1)	1.21 (1)
C7–O7	1.140 (8)	1.133 (7)	1.15 (2)	1.17 (1)
C8–O8	1.12 (1)			
N–O8		1.198 (7)	1.18 (2)	1.18 (1)
N–O9	1.174 (7)			
W1–H	1.91 (6)	1.84 (6)	1.79 (8)	1.64 (8)
W2–H	1.92 (5)	2.06 (6)	1.97 (8)	2.10 (8)
W1–C1–O1	177.1 (7)	175.2 (6)	179 (1)	176.4 (9)
W1–C2–O2	174.7 (6)	175.3 (6)	174 (1)	179 (1)
W1–C3–O3	176.3 (6)	177.1 (6)	175 (1)	178 (1)
W1–C4–O4	177.0 (6)	174.5 (6)	178 (1)	178 (1)
W1–C5–O5	179.6 (6)	178.0 (6)	178 (1)	178 (1)
W2–C6–O6	178.6 (5)	177.5 (5)	177 (1)	177.4 (8)
W2–C7–O7	175.1 (6)	172.2 (6)	179 (1)	173.2 (7)
W2–C8–O8	179.4			
W2–N–O8		175.6 (5)	177.9 (9)	176.6 (7)
W2–N–O9	177.8 (5)			
C1–W1–C2	91.6 (3)	90.4 (3)	90.7 (5)	87.2 (5)
C1–W1–C3	91.6 (3)	94.3 (3)	91.3 (5)	92.4 (4)
C1–W1–C4	176.8 (3)	171.3 (3)	174.9 (5)	177.3 (4)
C1–W1–C5	88.8 (3)	84.6 (3)	93.4 (5)	89.0 (4)
C2–W1–C3	175.3 (3)	174.8 (3)	176.1 (4)	178.0 (4)
C2–W1–C4	85.8 (3)	86.4 (3)	91.8 (5)	90.1 (5)
C2–W1–C5	88.0 (3)	87.2 (3)	85.0 (5)	92.9 (4)
C3–W1–C4	90.8 (3)	83.6 (3)	86.4 (4)	90.3 (4)
C3–W1–C5	88.6 (3)	91.1 (3)	91.6 (5)	89.1 (4)
C4–W1–C5	89.3 (3)	87.2 (3)	91.3 (5)	91.3 (5)
C6–W2–C7	91.1 (2)	86.1 (2)	92.1 (4)	87.2 (4)
C6–W2–C8	173.2 (3)			
C6–W2–N	92.8 (2)	93.3 (2)	88.3 (4)	89.6 (4)
C6–W2–N11			92.5 (4)	99.8 (3)
C6–W2–N21			177.8 (4)	172.6 (3)
C7–W2–N	87.1 (2)	84.0 (2)	90.9 (4)	87.8 (3)
C8–W2–N	93.9 (3)			
C7–W2–N11			89.0 (4)	93.0 (3)
C7–W2–N21			90.1 (4)	96.3 (3)
N–W2–N11			179.2 (4)	170.6 (3)
N–W2–N21			92.1 (4)	97.0 (3)
N11–W2–N21			87.1 (3)	73.6 (3)
C6–W2–P1		171.9 (2)		
C6–W2–P2		89.3 (2)		
C6–W2–P	89.5 (2)			
C7–W2–P1		87.3 (2)		
C7–W2–P2		175.0 (2)		
C7–W2–P	176.3 (2)			
C8–W2–P	89.8 (2)			
N–W2–P1		90.6 (2)		
N–W2–P2		94.1 (2)		
P1–W2–P2		97.43 (5)		
W1–H–W2	126 (3)	130 (3)	130 (5)	130 (4)

solution of the relevant compound in CH_2Cl_2/hexane (1:5) at −5 °C for several days. 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 = 0.7107 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 I. Absorption corrections 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.[6] The coordinates of tungsten atoms were obtained from Patterson syntheses. The coordinates of all remaining atoms except hydrogen atoms were obtained from a series of structure factor calculations and Fourier syntheses. The structures were 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 7. All non-hydrogen atoms were refined anisotropically. The positions of the bridging hydrogen atoms were located from the final difference Fourier maps and then refined. Other hydrogen atoms 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 II,'and selected interatomic distances and bond angles are given in Table III.

Results and Discussion

Mechanism of Ligand Substitution of $HW_2(CO)_9(NO)$ and $HW_2(CO)_7(THF)_2(NO)$ by Group 15 Donor Ligands. $HW_2(CO)_{10}^-$ was proposed to fragment into $W(CO)_5$ and $HW(CO)_5^-$ during its catalytic hydrogenation of aldehydes.[8] $W(CO)_5$ was also reported to form via metal–metal bond cleavage of $[(L)(CO)_4MW(CO)_5]^-$ (M = Mn, Re; L = CO, PR_3).[9] Our previous detection of $W(CO)_6$ from the decomposition of $HW_2(CO)_9(NO)$ in common noncoordinating solvents poses the possibility of similar fragmentation of $HW_2(CO)_9(NO)$ in forming $HW_2(CO)_7(L)_2$ (L = phosphine).[1] The reactions of $HW_2(CO)_9(NO)$ with four different monodentate phosphine ligands, PPh_3, $P(p\text{-}C_6H_4Me)_3$, $P(p\text{-}C_6H_4OMe)_3$, and $P(p\text{-}C_6H_4F)_3$, were thus followed by ^1H NMR spectroscopy (vide infra). In no case did we find absorption assignable to a terminal hydride, suggesting that the 3c–2e W–H–W bond remained intact during the reaction. The following infrared studies further disprove the cleavage of the dimer as a viable pathway in forming $HW_2(CO)_7(\text{phosphine})_2(NO)$. The equilibrium constant for eq 1, K_1, should be negligible,

$$HW_2(CO)_9(NO) \overset{K_1}{\rightleftharpoons} W(CO)_5 + HW(CO)_4(NO) \tag{1}$$

since the formation of $W(CO)_6$ was completely suppressed if the CH_2Cl_2 solution of $HW_2(CO)_9(NO)$ was saturated with atmospheric pressure CO in a closed system.

Another observation of ours, that addition of an equimolar amount of H_2O to a CH_2Cl_2 solution of $HW_2(CO)_9(NO)$ did not lead to the formation of $HW_2(CO)_{10}^-$,[10] argues against the existence of an alternative equilibrium shown in eq 2.

$$HW_2(CO)_9(NO) \overset{K_2}{\rightleftharpoons} HW(CO)_5^- + W(CO)_4(NO)^+ \tag{2}$$

The ^1H NMR monitoring (Figure 1) of the reaction of $HW_2(CO)_9(NO)$ with PPh_3 showed that there exist two isomeric monosubstituted complexes, formulated as $HW_2(CO)_8(PPh_3)(NO)$, prior to the formation of the disubstituted complex, $HW_2(CO)_7(PPh_3)_2(NO)$. As the reaction proceeded, $HW_2(CO)_7(PPh_3)_2(NO)$ appeared at the expense of isomer I of $HW_2(CO)_8(PPh_3)(NO)$ (see Chart I). Furthermore, isomer II of $HW_2(CO)_8(PPh_3)(NO)$ was isolated and was found to be unreactive toward substitution by PPh_3, resulting in no formation of $HW_2(CO)_7(PPh_3)_2(NO)$. It is important to note that the

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

compd	δ,$^{a-c}$ ppm (J, Hz)	δ,^{a,d} ppm (J, Hz)
1	7.50–7.34 (m, 12 H, Ph), 2.40 (s, 9 H, Me), –11.0 (d, 1 H, ${}^2J_{P-H}$ = 16.9, ${}^1J_{W-H}$ = 45.2, 40.4, μ-H, isomer II), –7.93 (d, ${}^2J_{P-H}$ = 17.9, ${}^1J_{W-H}$ = 61.0, 44.9, μ-H, isomer I)	13.1 (s, 1 P, ${}^1J_{W-P}$ = 244)
2	7.43–7.00 (m, 24 H, Ph), 2.34 (s, 18 H, Me), –9.66 (t, 1 H, ${}^2J_{P-H}$ = 11.4, ${}^1J_{W-H}$ = 50.6, 39.8, μ-H)	15.2 (s, 1 P, ${}^1J_{W-P}$ = 245)
3	7.52–7.05 (m, 12 H, Ph), 3.86 (s, 9 H, OMe), –11.0 (d, 1 H, ${}^2J_{P-H}$ = 17.2, ${}^1J_{W-H}$ = 44.6, 40.3, μ-H, isomer II), –7.92 (d, ${}^2J_{P-H}$ = 18.0, ${}^1J_{W-H}$ = 62.4, 42.0, μ-H, isomer I)	10.8 (s, 1 P, ${}^1J_{W-P}$ = 245)
4	7.32–6.88 (m, 24 H, Ph), 3.87 (s, 18 H, OMe), –9.59 (t, 1 H, ${}^2J_{P-H}$ = 11.4, ${}^1J_{W-H}$ = 50.4, 39.8, μ-H)	13.5 (s, 1 P, ${}^1J_{W-P}$ = 246)
5	7.70–7.36 (m, 12 H, Ph), –11.0 (d, 1 H, ${}^2J_{P-H}$ = 17.6, ${}^1J_{W-H}$ = 44.6, 40.5, μ-H, isomer II), –7.99 (d, ${}^2J_{P-H}$ = 17.9, ${}^1J_{W-H}$ = 62.0, 41.3, μ-H, isomer I)	13.6 (s, 1 P, ${}^1J_{W-P}$ = 246)
6	7.42–7.12 (m, 24 H, Ph), –9.74 (t, 1 H, ${}^2J_{P-H}$ = 17.6, ${}^1J_{W-H}$ = 49.8, 40.2, μ-H)	15.3 (s, 1 P, ${}^1J_{W-P}$ = 245)
7	7.72–7.50 (m, 15 H, Ph), –11.0 (s, 1 H, ${}^1J_{W-H}$ = 44.6, 40.7, μ-H)	
8	3.73 (q, 4 H, ${}^2J_{H-H}$ = 7.0, $\mathit{CH_2}CH_3$), 2.95 (s, 12 H, NMe_4), 1.25 (t, 6 H, $CH_2\mathit{CH_3}$), –9.69 (s, 1 H, ${}^1J_{W-H}$ = 48.7, 30.3, μ-H)	
9	3.80–3.31 (m, 4 H, NCH_2), 2.95 (s, 12 H, NMe_4), 2.10 (m, 4 H, CH_2), –9.62 (s, 1 H, ${}^1J_{W-H}$ = 48.9, 30.2, μ-H)	
10	9.20–7.12 (m, 12 H, py), –5.12 (s, ${}^1J_{W-H}$ = 57.1, 50.0, μ-H, isomer I), –7.10 (s, ${}^1J_{W-H}$ = 52.0, 42.1, μ-H, isomer II)	
11	9.50–8.52 (m, 8 H, bipy), –7.10 (s, ${}^1J_{W-H}$ = 53.4, 46.3, μ-H, isomer I), –9.45 (s, ${}^1J_{W-H}$ = 47.7, 36.2, μ-H, isomer II)	
12	7.54–7.22 (m, 15 H, Ph), –7.90 (d, ${}^2J_{P-H}$ = 20, ${}^1J_{W-H}$ = 50.0, 45.0, μ-H, isomer I), –10.99 (d, ${}^2J_{P-H}$ = 17, ${}^1J_{W-H}$ = 45.0, 40.6, μ-H, isomer II)	

[a] All are measured in acetone-d_6. [b] δ values relative to Me_4Si. [c] The spectra of isomer II for **1**, **3**, and **5** were obtained from the monitoring reaction in CD_2Cl_2, and only δ values of the hydrides are reported. [d] δ values relative to 85% H_3PO_4 (aq).

Table V. ${}^1H$ NMR Data for the Hydrides and ${}^{15}N\{H\}$ NMR Data for NO of ${}^{15}NO$-Enriched Complexes

compd^a	δ, ppm (J, Hz)	δ,^{b} ppm (J, Hz)
1 (isomer I)	–7.93 (${}^2J_{N-H}$ = 1.27)	
1 (isomer II)	–10.9 (${}^2J_{N-H}$ = 2.54)	
2 (isomer II)	–9.66 (${}^2J_{N-H}$ = 2.54)	
3 (isomer I)	–7.92 (${}^2J_{N-H}$ = 1.27)	
3 (isomer II)	–11.0 (${}^2J_{N-H}$ = 2.54)	
4	–9.59 (${}^2J_{N-H}$ = 2.54)	
5 (isomer I)	–7.99 (${}^2J_{N-H}$ = 1.27)	
5 (isomer II)	–11.0 (${}^2J_{N-H}$ = 2.54)	
6	–9.74 (${}^2J_{N-H}$ = 2.54)	–16.0
$HW_2(CO)_8(PPh_3)$ (isomer I)	–7.90 (${}^2J_{N-H}$ = 1.20)	5.46 (d, ${}^2J_{N-P}$ = 19.2)
$HW_2(CO)_8(PPh_3)$ (isomer II)	–11.0 (${}^2J_{N-H}$ = 2.68)	–23.9
$HW_2(CO)_7(PPh_3)_2(NO)$	–9.57 (${}^2J_{N-H}$ = 2.68)	–17.1
$HW_2(CO)_7(THF)_2(NO_{eq})$	–5.21 (${}^2J_{N-H}$ = 0.50)	2.0 (${}^1J_{W-N}$ = 98)
$HW_2(CO)_7(MeNC)_2(NO_{eq})$	–9.49 (${}^2J_{N-H}$ = 1.27)	–3.0 (${}^1J_{W-N}$ = 96)
$HW_2(CO)_7)MeNC)_2(NO_{ax})$	–12.6 (${}^2J_{N-H}$ = 1.91)	–19.4 (${}^1J_{W-N}$ = 96)
$HW_2(CO)_2({}^tBuNC)_2(NO_{eq})$	–9.56 (${}^2J_{N-H}$ = 1.28)	–2.0
$HW_2(CO)_7({}^tBuNC)_2(NO_{ax})$	–12.6 (${}^2J_{N-H}$ = 2.20)	–18.7 (${}^1J_{W-N}$ = 115)
$HW_2(CO)_8(MeNC)(NO_{ax})$		–19.2 (${}^1J_{W-N}$ = 103)
$HW_2(CO)_8(BuNC)(NO_{ax})$		–19.6 (${}^1J_{W-N}$ = 103)

[a] All are measured in acetone-d_6 except for **1** (isomer I), **3** (isomer I), **5** (isomer I), and $HW_2(CO)_9({}^{15}NO)$ (in CD_2Cl_2) and $HW_2(CO)_7(THF)_2({}^{15}NO)$ (in THF-d_8). Abbreviations: ax = axial, eq = equatorial. [b] δ values relative to neat $MeNO_2$: low-field positive, measured at 25 °C.

reaction of $HW_2(CO)_9(NO)$ with $P(p\text{-}C_6H_4X)_3$ (X = OMe, Me, F) behaves similarly to that with PPh_3 on the basis of our ${}^1H$ NMR study. Scheme I summarizes the reaction of $HW_2(CO)_9(NO)$ with $P(p\text{-}C_6H_4X)_3$ (X = H, Me, OMe, F) as well as the reaction of $HW_2(CO)_7(THF)_2(NO)$ with $P(p\text{-}C_6H_4X)_3$ (vide infra). At present, we are not certain whether $HW_2(CO)_9(NO)$ undergoes both dissociative and associative CO substitution, similar to that found in $W(CO)_4(NO)X$ (X = Cl, Br, I)[11] and several other metal nitrosyl carbonyls.[12]

The structures for isomers II of $HW_2(CO)_8(P(p\text{-}C_6H_4X)_3)(NO)$ (**12**, X = H; **1**, X = Me; **3**, X = OMe; **5**, X = F) and $HW_2(CO)_7(P(p\text{-}C_4H_4F)_3)_2(NO)$ (**6**) have been determined (vide infra). Of the coordination sites in $HW_2(CO)_9(NO)$ (see Chart II), the phosphorus atoms prefer the least hindered exo[13] position 8 in complexes **1**, **3**, **5**, and **12**. In complex **2**, both exo positions 8 and 9 are occupied by phosphine ligands. We suggest that isomer I of $HW_2(CO)_8(P(p\text{-}C_6H_4X)_3)(NO)$ has the structure depicted in Scheme I; i.e., the phosphine ligand resides at exo position 8 and the nitrosyl ligand is at an endo position trans to the phosphine ligand, on the basis of several observations: (1) the coupling constant (${}^2J_{P-H} \sim 18$ Hz, Table IV) between the hydride and the phosphine implies that the two ligands are mutually cis; (2) the chemical shift of the hydride in isomer I appears at lower field than that of the hydride in isomer II by ca. 3 ppm in the ${}^1H$ NMR spectra. This is consistent with our findings for the isomeric pairs of $HW_2(CO)_7(RNC)_2(NO)$[3] and $HW_2(CO)_7(py)_2(NO)$. That is, the complex with an equatorial NO ligand seems to have its hydride at lower field by ca. 3 ppm than the isomer with an axial NO ligand; (3) in ${}^{15}N$ NMR spectra (Table V) of several derivatives of $HW_2(CO)_9({}^{15}NO)$, the δ values of ${}^{15}NO$ in the complexes containing an equatorial NO ligand shift to lower field by ca. 20 ppm than those for complexes with an axial NO ligand. Similarly, the chemical shift of ${}^{15}NO$ in isomer I appears at lower field than that for isomer II; (4) a cis

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(11) Sulfab, Y.; Basolo, F.; Rheingold, A. L. *Organometallics* **1989**, *8*, 2139.

(12) (a) Thorsteinson, E. M.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 3929. (b) Morris, D. E.; Basolo, F. *J. Am. Chem. Soc.* **1968**, *90*, 2531, 2536. (c) Shi, O. Z.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *Inorg. Chem.* **1984**, *23*, 957.

(13) The exo (endo) positions refer to those coordination sites exo (endo) to the bent molecular framework and hydride bridge.

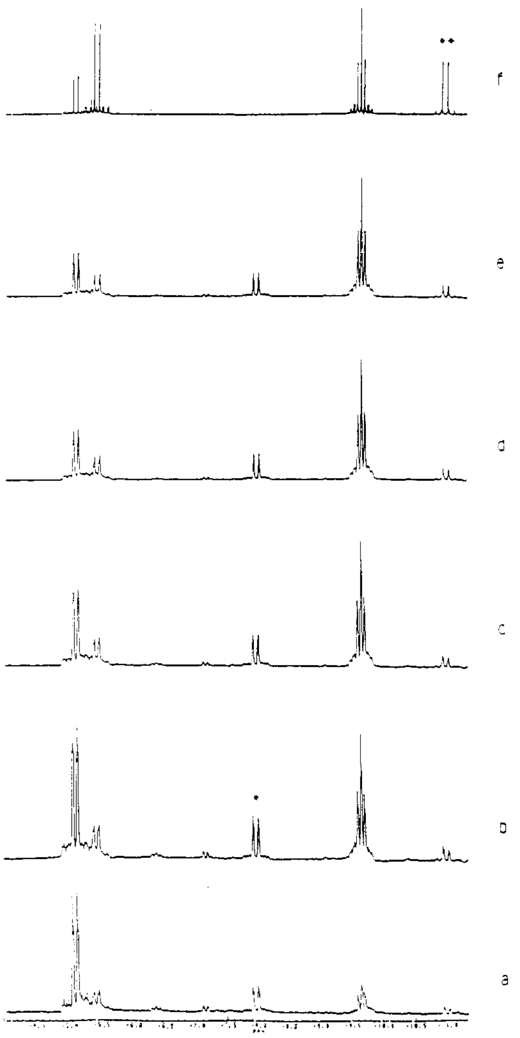

Figure 2. ^{1}H NMR monitoring of the reaction of HW$_2$(CO)$_7$(THF)$_2$(NO) with PPh$_3$ in the hydride region (solvent is THF-d_8): (a) 1 h; (b) 5 h; (c) 10 h; (d) 20 h; (e) 30 h; (f) 40 h. Peaks marked with ✱ and ✱✱ are from HW$_2$(CO)$_8$(PPh$_3$)(NO) (isomer I) and HW$_2$(CO)$_8$(PPh$_3$)(NO) (isomer II), respectively. They stem from decomposition of HW$_2$(CO)$_7$(THF)$_2$(NO).

$^2J_{\text{N-H}}$ is generally smaller than a trans $^2J_{\text{N-H}}$, although the difference between the two is small (Table V). The value of $^2J_{\text{N-H}}$, which is smaller for isomer I (^{15}N enriched) than for isomer II, is not inconsistent with this trend; (5) isomer II has a two-bond ^{15}N–W–^{31}P coupling constant of 18.9 Hz, which is much larger than those for complexes where nitrogen and phosphorus atoms are mutually cis.[14] A trans ^2J(^{15}N–W–^{31}P) of 20.0 Hz was also found for HW$_2$(CO)$_7$(η^2-dppe)(NO$_{\text{eq}}$) (vide infra).

Clearly, after the dissociation of the first CO from HW$_2$(CO)$_9$(NO), the newly-formed HW$_2$(CO)$_8$(NO) could pick up an incoming PPh$_3$ to form isomer I. Alternatively, rearrangement of NO from an axial to an equatorial position could occur before the incorporation of PPh$_3$. The mechanism for the formation of HW$_2$(CO)$_7$(PPh$_3$)$_2$(NO) from isomer I of HW$_2$(CO)$_8$(PPh$_3$)(NO) is less obvious. Due to the steric crowdedness in isomer I, we feel that the reaction of isomer I with PPh$_3$ to form HW$_2$(CO)$_7$(PPh$_3$)$_2$(NO) is rather unlikely to be associative. The very sterically congested complexes HW$_2$(CO)$_7$(L)$_2$(NO) (L = P(p-C$_6$H$_4$X)$_3$; X = H, Me, OMe, F), were found to readily lose one phosphine ligand in tetrahydrofuran to form HW$_2$(CO)$_7$(THF)(L)(NO), and an equilibrium was eventually established between HW$_2$(CO)$_7$(L)$_2$(NO) and HW$_2$(CO)$_7$(THF)(L)(NO). Dissociation of a phosphine ligand from sterically congested metal complexes is fairly common, and a similar phenomenon was observed in a related dinuclear tungsten complex, (μ-H)(μ-Ph$_2$PCH$_2$PPh$_2$)W$_2$(CO)$_6$(PhPH$_2$)(NO).[15] On the contrary, no dissociation of phosphine was found in HW$_2$(CO)$_7$(Ph$_2$PH)$_2$(NO), wherein the phosphine has a smaller cone angle, or in HW$_2$(CO)$_7$(Ph$_2$PCH$_2$PPh$_2$)(NO).

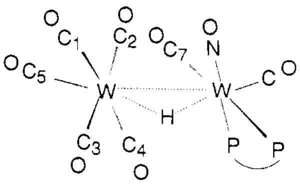

Figure 3. Structure of HW$_2$(CO)$_7$(η^2-dppe)(NO$_{\text{eq}}$).

The coordinated THF ligands in HW$_2$(CO)$_7$(THF)$_2$(NO) are labile and readily exchange with THF-d_8. A better yield of HW$_2$(CO)$_7$(L)$_2$(NO) (L = triarylphosphine) could be obtained from HW$_2$(CO)$_7$(THF)$_2$(NO) than from HW$_2$(CO)$_9$(NO) (see Experimental Section). The rearrangement of NO from an equatorial to an axial position occurs during successive displacement of the two ligated THF's by two phosphine ligands. Due to the instability of HW$_2$(CO)$_7$(THF)$_2$(NO), a certain degree of decomposition results in formation of HW$_2$(CO)$_8$(L)(NO). ^{1}H NMR monitoring of the reaction of HW$_2$(CO)$_7$(THF)$_2$(NO) with PPh$_3$ in THF-d_8 was undertaken (Figure 2). There was immediate formation of an intermediate containing only one PPh$_3$, HW$_2$(CO)$_7$(THF)(PPh$_3$)(NO) ($\delta(\mu\text{-H}) = -5.0$ ppm), the structure of which is likely to be that depicted in Scheme I on the basis of spectroscopic data: ^1J(W–H) = 62.9, 49.2 Hz for a bridging hydride; ^2J(P–H) = 15.0 Hz for a cis H–W–P; δ(^{15}NO) = −1.38 ppm and ^2J(^{15}N–H) = 0.90 Hz for an equatorial NO; ^2J(^{15}N–P) < 0.95 Hz for a cis N–W–P. On the contrary, HW$_2$(CO)$_7$(THF)$_2$(NO) reacts with dppe to form initially HW$_2$(CO)$_7$(η^2-dppe)(NO$_{\text{eq}}$), where both dppe and NO reside on the equatorial sites, which then isomerizes to the previously synthesized HW$_2$(CO)$_7$(η^2-dppe)(NO$_{\text{ax}}$).[1] The ^{1}H NMR (pseudotriplet with $\delta = -7.62$ ppm; ^2J(P–H) = 14.6 Hz; ^2J(^{15}N–H) = 1.10 Hz for ^{15}NO-enriched sample) and ^{31}P{H} NMR spectra (δ(P$_1$) = 37.3 ppm; δ(P$_2$) = 25.0 ppm; ^2J(^{15}N–P$_2$) = 20.0 Hz for ^{15}NO-enriched sample) of HW$_2$(CO)$_7$(η^2-dppe)(NO$_{\text{eq}}$) are consistent with its proposed structure in Figure 3.

The compound HW$_2$(CO)$_7$(THF)$_2$(NO) seems to be synthetically useful. Better yields of HW$_2$(CO)$_7$(py)$_2$(NO) (**10**) and HW$_2$(CO)$_7$(bipy)(NO) (**11**) could also be obtained by using HW$_2$(CO)$_7$(THF)$_2$(NO) as the starting material. The slightly air-sensitive complexes [NMe$_4$][HW$_2$(CO)$_7$(η^2-S$_2$CNR$_2$)(NO)] (**8** and **9**) could only be obtained from HW$_2$(CO)$_7$(THF)$_2$(NO), not from HW$_2$(CO)$_9$(NO). The isolated major and minor products for **10** and **11** are isomeric and cannot be completely separated (see Experimental Section). The major product (isomer I) for **10** or **11** has its NO in an equatorial position (vide supra). Similar to that of HW$_2$(CO)$_7$(L)$_2$(NO) (L = isocyanide), the chemical shift of the hydride in isomer I of **10** or **11** moves to a lower field position relative to that of isomer II containing an axial NO.

Apparently, rearrangement of NO also occurs in going from HW$_2$(CO)$_9$(NO) or HW$_2$(CO)$_7$(THF)$_2$(NO) to **10** or **11**. In following the reaction of HW$_2$(CO)$_9$(NO) with THF-d_8, we observed transient intermediates which might have their NO in axial positions. In phosphine-substituted derivatives of HW$_2$(CO)$_9$(NO), NO always moves to an axial position regardless of whether one starts from HW$_2$(CO)$_9$(NO) or HW$_2$(CO)$_7$(THF)$_2$(NO). Theoretical calculations on these complexes to investigate their relative stabilities are currently underway.

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(15) Lin, J. T.; Chang, K. Y.; Gong, M. L.; Chang, C. C.; Gau, H. M.; Tsen, L. H.; Wen, Y. S. *J. Organomet. Chem.* **1992**, *431*, 65.

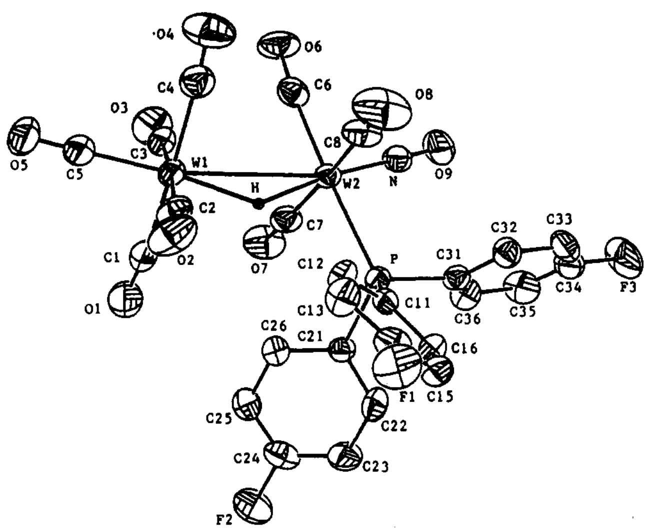

Figure 4. ORTEP drawing of $HW_2(CO)_8(P(p\text{-}C_6H_4F)_3)(NO)$. Thermal ellipsoids are drawn with 50% probability boundaries.

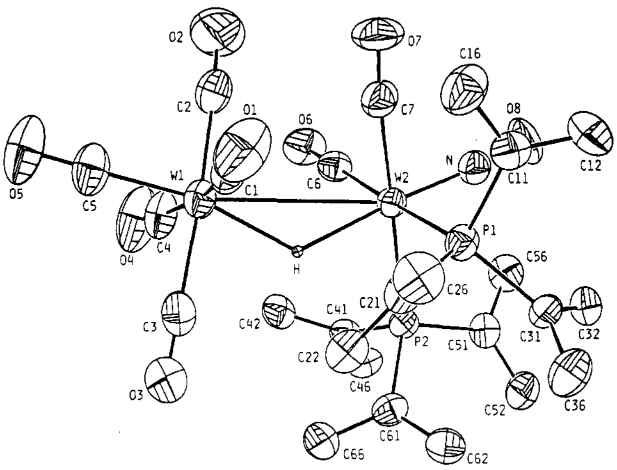

Figure 5. ORTEP drawing of $HW_2(CO)_7(P(p\text{-}C_6H_4F)_3)_2(NO)$. Thermal ellipsoids are drawn with 50% probability boundaries.

Although the coordinative unsaturation of the intermediates involved in the syntheses of complexes **1–11** might not be the sole driving force for NO rearrangement, it seems to be a necessary condition. It is interesting to note that the monomeric six-coordinate tungsten complexes *trans*-$W(CO)_4(NO)X$ undergo CO substitution by phosphines without rearrangement of NO relative to X in the final products,[16] whereas NO in $W(CO)_2(CH_3CN)_2(NO)(SnPh_3)$ changes its position relative to $SnPh_3$ during CH_3CN substitution by phosphines,[17] similar to the reactions observed in this research.

Molecular Structures of $HW_2(CO)_8(P(p\text{-}C_6H_4F)_3)(NO)$ (5), $HW_2(CO)_7(P(p\text{-}C_6H_4F)_3)_2(NO)$ (6), $HW_2(CO)_7(py)_2(NO)$ (10, Isomer I), and $HW_2(CO)_7(bipy)(NO)$ (11, Isomer I). The ORTEP drawings of **5**, **6**, **10(I)**, and **11(I)** are shown in Figures 4–7, respectively. The structures of $HW_2(CO)_8(P(p\text{-}C_6H_4X)_3)(NO)$ (**1**, X = Me; **3**, X = OMe; **12**, X = H) and **10** (isomer II)[18] were also determined and will be published elsewhere; only relevant data are cited below.

We were able to locate the position of μ-H in the final difference Fourier maps for most of the compounds. The observed W–H distances (**1**, 1.75/1.97 Å; **5**, 1.91/1.92 Å; **6**, 1.84/2.06 Å; **10(I)**, 1.79/1.97 Å; **10(II)**, 1.81/1.90 Å; **11**, 1.64/2.10 Å; **12**, 1.9/2.2 Å) and the W–H–W angles (**1**, 132°; **5**, 126°; **6**, 130°; **10(I)**, 130°; **10(II)**, 137°; **11**, 130°; **12**, 112°) are in agreement with the reported values (W–H, 1.8–1.9 Å; W–H–W, 115–135°).[19] In general, μ-H is closer to the tungsten atom with five coordinated carbonyls, possibly due to the steric crowdedness of the other tungsten atom.

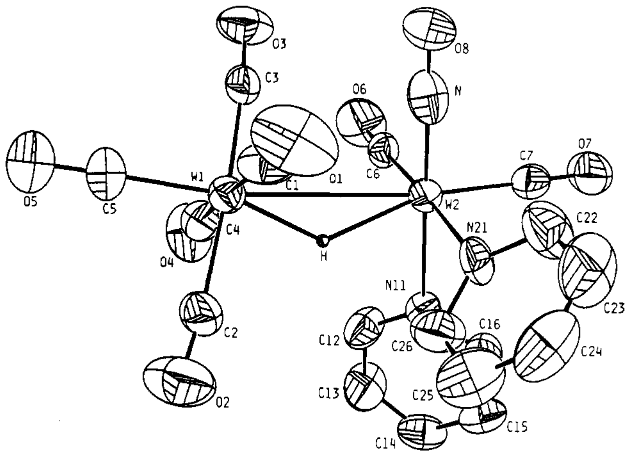

Figure 6. ORTEP drawing of $HW_2(CO)_7(py)_2(NO)$ (isomer I). Thermal ellipsoids are drawn with 50% probability boundaries.

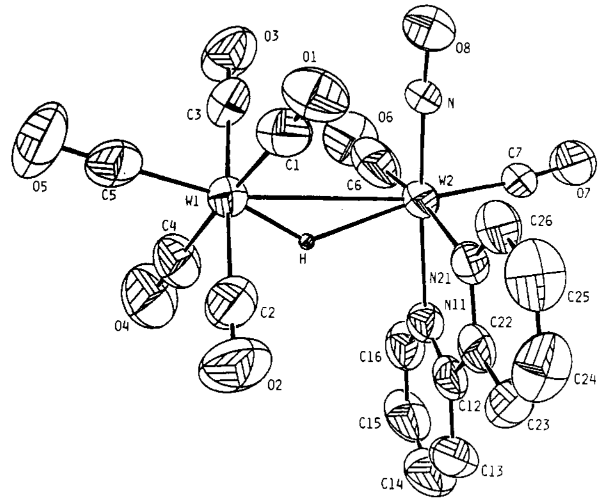

Figure 7. ORTEP drawing of $HW_2(CO)_7(bipy)(NO)$ (isomer I). Thermal ellipsoids are drawn with 50% probability boundaries.

The steric influence of the substituent on the structure is evident. The overall structure in these complexes is bent, and the equatorial groups are staggered. Furthermore, the W–W distances in **6** are longer than those in **1**, **3**, **5**, and **12**. Compound **6** has the longest W–W distance (3.5345 (5) Å) among structurally characterized complexes derived from $HW_2(CO)_9(NO)$, and virtually no metal–metal interaction is considered in the 3c–2e W–H–W unit of **6**. Compound **11** has a much shorter W–W distance (3.3937 (6) Å) than those in **10** (isomer I, 3.4182 (7) Å; isomer II, 3.4515 (7) Å) due to the planar nature of bipy in the former and the mutually perpendicular py molecules in the latter.

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[16] (a) Bond, A. M.; Colton, R.; Panagiotidou, P. *Organometallics* **1988**, *7*, 1774. (b) Sulfab, Y.; Basolo, F.; Rheingold, A. L. *Organometallics* **1989**, *8*, 2139.

[17] (a) Liu, L. K.; Lin, J. T.; Fang, D. C. *Inorg. Chim. Acta* **1989**, *161*, 239. (b) Lin, J. T.; Shan, C. H.; Fang, D. C. *Inorg. Chim. Acta* **1989**, *161*, 239.

[18] Crystal data: for **1**, $C_{29}H_{22}NO_9PW_2$, monoclinic, space group $P2_1/c$, a = 16.9343 (15) Å, b = 8.3226 (8) Å, c = 22.617 (17) Å, β = 92.527 (7)°, V = 3184.5 (5) Å^3, Z = 4, R = 0.024, R_w = 0.029; for **3**, $C_{29}H_{23}NO_{12}PW_2$, monoclinic, space group $C2/c$, a = 20.898 (4) Å, b = 12.3827 (13) Å, c = 26.443 (6) Å, β = 103.641 (17)°, V = 6649.7 (20) Å^3, Z = 8, R = 0.031, R_w = 0.039; for **12**, $C_{26}H_{16}NO_9PW_2$, monoclinic, space group $C2/c$, a = 22.787 (6) Å, b = 14.120 (1) Å, c = 18.835 (6) Å, β = 113.53 (2)°, V = 5556 (2) Å^3, Z = 8, R = 0.046, R_w = 0.048; for **10(II)**, $C_{17}H_{11}N_3O_8W_2$, triclinic, space group $P\bar{1}$, a = 8.4402 (8) Å, b = 9.2951 (14) Å, c = 15.3426 (13) Å, α = 93.414 (11)°, β = 105.138 (8)°, γ = 113.754 (10)°, V = 1044.81 (21) Å^3, Z = 2, R = 0.031, R_w = 0.034.

[19] Bau, R.; Teller, R. G.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, *12*, 176.

The NO ligand[20] in **10**(I) or **11** occupies the same equatorial position as that in $HW_2(CO)_7(THF)_2(NO)$.[3] Other relevant crystal data appear to be normal. The W–C–O and W–N–O linkages can be regarded as linear. The W–N(NO) distances are shorter than those of W–C by 0.1–0.6 Å. The W–C bonds of carbonyl groups trans to the bridging hydride or N-donor ligands (py, bipy) are shorter than those trans to each other.

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Supplementary Material Available: For the structures of **5**, **6**, **10**(I), and **11**(I), a full table of crystal data, listings of all bond distances and angles, tables of anisotropic thermal parameters and isotropic thermal parameters, and tables of positional parameters for calculated hydrogen atoms (14 pages). Ordering information is given on any current masthead page.

Registry No. **1** (isomer I), 143173-03-9; **1** (isomer II), 143235-77-2; **2**, 143173-04-0; **3** (isomer I), 143173-05-1; **3** (isomer II), 143290-23-7; **4**, 143173-06-2; **5** (isomer I), 143173-07-3; **5** (isomer II), 143235-78-3; **6**, 143173-08-4; **7**, 143173-09-5; **8**, 143173-11-9; **9**, 143173-13-1; **10**, 143173-14-2; **11**, 143173-15-3; **12** (isomer I), 143173-17-5; **12** (isomer II), 129493-82-9; $HW_2(CO)_7(PPh_3)_2(NO)$, 143173-16-4; $HW_2(CO)_7(THF)_2(NO_{eq})$, 143173-18-6; $HW_2(CO)_7(MeNC)_2(NO_{eq})$, 143173-19-7; $HW_2(CO)_7(MeNC)_2(NO_{ax})$, 143235-79-4; $HW_2(CO)_7(^tBuNC)_2(NO_{eq})$, 143173-20-0; $HW_2(CO)_7(^tBuNC)_2(NO_{ax})$, 143235-80-7; $HW_2(CO)_8(MeNC)(NO_{ax})$, 143173-21-1; $HW_2(CO)_8(BuNC)(NO_{ax})$, 143173-22-2; $HW_2(CO)_9(NO)$, 143173-23-3.

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(20) The location of the NO ligand in all complexes was distinguished from the CO ligand by conspicuous discrepancies in the thermal parameters for the N and C atoms when incorrectly assigned: Hodgson, D. J.; Ibers, J. A. *Inorg. Chem.* **1968**, *11*, 2345.