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Dinuclear Isocyanide Derivatives of $HW_2(CO)_9(NO)$. Synthesis, Structure, and Mechanistic Studies

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Reactions of $HW_2(CO)_9(NO)$ and $HW_2(CO)_7(THF)_2(NO)$ with excess RNC (R = Me, ^{t}Bu, $PhCH_2$, ^{i}Pr) yields a yellow complex $HW_2(CO)_7(RNC)_2(NO_{ax})$ (ax = axial) and its isomeric reddish complex $HW_2(CO)_7(RNC)_2(NO_{eq})$ (eq = equatorial). Both bent-staggered and bent-eclipsed conformations are found to exist in these isomers. Treatment of complexes $HW_2(CO)_9(NO)$, $HW_2(CO)_8(PPh_3)(NO)$, $HW_2(CO)_7(MeNC)_2(NO_{ax})$, and $HW_2(CO)_7(MeNC)_2(NO_{eq})$ with $Ph_3P{=}NR$ (R = ^{i}Pr, ^{n}Pr, Ph, ^{t}Bu) yields $HW_2(CO)_8(RNC)(NO_{ax})$ (R = ^{i}Pr, Ph, ^{t}Bu), $HW_2(CO)_7(RNC)_2(NO_{ax})$ (R = ^{i}Pr, Ph), $HW_2(CO)_7(PPh_3)(^nPrNC)(NO_{ax})$, $HW_2(CO)_6(PPh_3)(^nPrNC)_2(NO_{ax})$, and $HW_2(CO)_6(MeNC)_2(^nPrNC)(NO_{eq})$. There is no rearrangement, which is found in the reaction of $HW_2(CO)_9(NO)$ with RNC, of ligands during the conversion of coordinated CO ligands to RNC by Ph_3PNR in these reactions. Electronic and steric influences on the sequential conversion of CO to RNC are supported by crystal structures determinations of several new complexes. Crystal data for $HW_2(CO)_8(PhNC)(NO_{ax})$: $C_{15}H_6N_2O_9W_2$; $P2_1/c$ (monoclinic); $a = 10.802(2)$, $b = 11.705(1)$, $c = 16.695(2)$ Å; $\beta = 108.67(1)°$; $Z = 4$; $R = 0.031$, $R_w = 0.032$. $HW_2(CO)_6(PhNC)(^nPrNC)_2(NO_{ax})$: $C_{21}H_{20}N_4O_7W_2$; $P\bar{1}$ (triclinic); $a = 8.718(1)$, $b = 11.135(2)$; $c = 13.832(1)$ Å; $\alpha = 92.24(1)$, $\beta = 79.58(1)$, $\gamma = 91.53(1)°$; $Z = 2$; $R = 0.031$, $R_w = 0.032$. $HW_2(CO)_6(MeNC)_2(^nPrNC)(NO_{eq})$: $C_{14}H_{14}N_4O_7W_2$; $P\bar{1}$ (triclinic); $a = 10.140(2)$; $b = 10.147(2)$; $c = 11.346(2)$ Å; $\alpha = 84.34(2)$, $\beta = 112.86(2)$, $\gamma = 100.92(1)°$; $Z = 2$; $R = 0.033$, $R_w = 0.037$.

Introduction

Ligand substitution reactions of metal carbonyl complexes have been intensively studied over the past two decades.[1] Both associative and dissociative mechanisms have ample precedents in d^6 six-coordinate metal complexes. Ligand rearrangement might occur in an associative substitution due to the facile interconversion among possible seven-coordinate intermediates of different geometries.[2] For the dissociative mechanism, intramolecular ligand rearrangement is also viable and a solid example of vacant-site inversion in a *cis*-$P_2M(CO)_3$ intermediate has been recently reported.[3] Our previous investigation on $HW_2(CO)_9(NO)$ indicated that the "$W(CO)_5$" fragment could be regarded as a template for modifying the heretofore unknown "$HW(CO)_4(NO)$". Although the isolated phosphine derivatives of $HW_2(CO)_9(NO)$ retain their NO ligands at an axial position which is trans to the briding hydrogen ligand,[4] we observed intermediates containing an equatorial NO ligand.[5] The isolation of $HW_2(CO)_7(THF)_2(NO_{eq})$ and $HW_2(CO)_7(RNC)_2(NO_{eq})$ (R = Me, ^{t}Bu, $PHCH_2$), in which NO ligands reside at an equatorial site, have been preliminarily reported.[6] In this paper, we describe these compounds in more detail.

In order to elucidate the mechanistic study on ligand substitution of $HW_2(CO)_9(NO)$ by RNC, we also investigated reactions of $HW_2(CO)_9(NO)$ with various phosphinimines. Being effective reagents for converting a CO ligand to an isocyanide ligand,[7] phosphinimines readily attack $HW_2(CO)_9(NO)$ to afford different isocyanide derivatives of $HW_2(CO)_9(NO)$. The mechanisms for the stepwise conversion of several CO ligands in $HW_2(CO)_9(NO)$ and its derivatives to isocyanide ligands are elucidated on the basis of structural characterization of some representative products as well as spectroscopic studies.

Experimental Section

General Procedure. Infrared measurements were made on a Perkin-Elmer 880 spectrophotometer. The NMR spectra were recorded on a Bruker MSL 200 and AC200 as well as AMX 500 spectrometers. The ^1H and ^{31}P spectra are referenced to TMS and external 85% H_3PO_4, respectively. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer.

All reactions were carried out under a nitrogen atmosphere with use of standard Schlenk techniques or a drybox. All solvents were purified by standard procedures or degassed prior to use. All column chromatography was performed under N_2 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. Phosphin-

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imines,[8] $HW_2(CO)_9(NO)$,[9] and $HW_2(CO)_8(PPh_3)(NO)$[4] were prepared according to the published procedures.

Synthesis of $HW_2(CO)_7(THF)_2(NO_{eq})$ (2). $HW_2(CO)_9(NO)$ (1) (500 mg, 0.768 mmol) was dissolved in 40 mL of THF, and the solution was stirred under N_2 with occasional release of pressure for 2 days. The solvent was removed, and the residue was washed with hexane to provide yellow-orange powdery **2** (482 mg, 85% yield). Anal. Calcd for $C_{15}H_{17}NO_{10}W_2$: C, 24.38; H, 2.32; H, 1.89. Found: C, 23.99; H, 2.07; N, 1.92.

The reactions of $HW_2(CO)_9(NO)$ (1) with RNC (R = Me, ^tBu, $PhCH_2$, ^iPr) provided yellow $HW_2(CO)_7(RNC)_2(NO_{ax})$ and red $HW_2(CO)_7(RNC)_2(NO_{eq})$. Essentially the same procedure was followed, and only the synthesis of $HW_2(CO)_7(MeNC)_2(NO)$ is described below.

Syntheses of $HW_2(CO)_7(MeNC)_2(NO_{ax})$ (3) and $HW_2(CO)_7(MeNC)_2(NO_{eq})$ (4). To 1 (500 mg, 0.768 mmol) in 30 mL of CH_2Cl_2 was added 0.5 mL of MeNC, and the solution was stirred at room temperature with an occasional release of pressure. After 24 h the solvent was removed and the resulting residue was chromatographed. Complex **3** was isolated in 36% yield (187 mg) from the yellow first band using CH_2Cl_2/hexane (1:4) as eluent. Anal. Calcd for $C_{11}H_7N_3O_8W_2$: C, 19.52; H, 1.04; N, 6.21. Found: C, 19.73; H, 1.08; N, 6.01. Complex **4** was isolated from the red second band in less than 1% yield (5 mg). Anal. Calcd for $C_{11}H_7N_3O_8W_2$: C, 19.52; H, 1.04; N, 6.21. Found: C, 19.43; H, 1.04; N, 6.18.

Complex $HW_2(CO)_7(^tBuNC)_2(NO_{ax})$ (5) was obtained in 33% yield. Anal. Calcd for $C_{17}H_139N_3O_8W_2$: C, 26.83; H, 2.52; N, 5.52. Found: C, 27.34; H, 2.58; N, 5.44. Complex $HW_2(CO)_7(^tBuNC)_2(NO_{eq})$ (6) was obtained in 4% yield. Anal. Calcd for $C_{17}H_{19}N_3O_8W_2$: C, 26.83; H, 2.52; N, 5.52. Found: C, 26.77; H, 2.44; N, 5.52. Complex $HW_2(CO)_7(PhCH_2NC)_2(NO_{ax})$ (7) was obtained in 6% yield. Anal. Calcd for $C_{25}H_{15}N_3O_8W_2$: C, 33.32; H, 1.82; N, 5.07. Found: C, 32.95; H, 1.92; N, 5.15. Complex $HW_2(CO)_7(PhCH_2NC)_2(NO_{eq})$ (8) was obtained in <1% yield. Anal. Calcd for $C_{25}H_{15}N_3O_8W_2$: C, 33.32; H, 1.82; N, 5.07. Found: C, 33.59; H, 1.82; N, 5.08. Complex $HW_2(CO)_7(^iPrNC)_2(NO_{ax})$ (9) was obtained in 25% yield. Anal. Calcd for $C_{15}H_{15}N_3O_8W_2$: C, 24.58; H, 2.06; N, 5.73. Found: C, 25.13; H, 2.15; N, 5.22. Complex $HW_2(CO)_7(^iPrNC)_2(NO_{eq})$ (10) was obtained in <1% yield. Anal. Calcd for $C_{15}H_{15}N_3O_8W_2$: C, 24.58; H, 2.06; N, 5.73. Found: C, 24.28; H, 1.77; N, 5.49.

Reactions of $HW_2(CO)_7(THF)_2(NO_{eq})$ (2) with RNC (R = Me, ^tBu, $PhCH_2$, ^iPr) follow the same procedure, and only the reaction of **2** with MeNC is described.

Reaction of 2 with MeNC. A 0.5-mL amount of MeNC was added to a flask containing 500 mg of **2** (0.676 mmol), and the slurry was stirred for 15 min. A 30-mL portion of CH_2Cl_2 was then added, and the solution was stirred for another 3 h. The solvent was removed, and the residue was washed with 15 mL of Et_2O/ hexane (1:14). Recrystallization of the compounds from Et_2O/hexane afforded $HW_2(CO)_7(MeNC)_2(NO_{eq})$ (4) in 88% yield (403 mg).

Yields for **6**, **8**, and **10** are 82, 67, and 49%, respectively.

Reaction of $HW_2(CO)_9(NO)$ (1) with $Ph_3P{=}N^iPr$. Complex 1 (500 mg, 0.768 mmol) and $Ph_3P{=}N^iPr$ (757 mg, 1.54 mmol) in 60 mL of CH_2Cl_2 was stirred at room temperature for 6 h. The solvent was removed, and the residue was chromatographed using CH_2Cl_2/hexane (1:4) as eluent. The yellow complex $HW_2(CO)_8(^iPrNC)(NO_{ax})$ (11) was isolated from the yellow first band in 16% yield (85.0 mg). Anal. Calcd for $C_{12}H_8N_2O_9W_2$: C, 20.97; H, 1.05; N, 3.83. Found: C, 20.82; H, 1.16; N, 4.04. Yellow powdery $HW_2(CO)_7(^iPrNC)_2(NO_{ax})$ (9) was obtained from the second band (264 mg, 47%).

Reaction of 1 with $Ph_3P{=}NPh$. A procedure similar to that for **9** was used. Three yellow products were separated by column chromatography. $HW_2(CO)_8(PhNC)(NO_{ax})$ (12) was eluted first and $HW_2(CO)_7(PhNC)_2(NO_{ax})$ (13) second, using CH_2Cl_2/hexane (1:4) as the eluent. $HW_2(CO)_7(PhNC)(O{=}PPh_3)(NO_{eq})$ (14) was eluted with CH_2Cl_2/hexane (1:2). **12**: yield 45%. Anal. Calcd for $C_{15}H_6N_2O_9W_2$: C, 24.24; H, 0.59; N, 3.81. Found: C, 24.82; H, 0.80; N, 3.86. **13**: yield 5.0%. Anal. Calcd for $C_{21}H_{11}N_3O_8W_2$: C, 25.13; H, 2.15; N, 5.22. Found: C, 24.77; H, 2.21; N, 5.40. **14**: yield 5.0%. Anal. Calcd for $C_{32}H_{21}N_2O_9W_2$: C, 39.23; H, 2.32; N, 2.77. Found: C, 39.37; H, 2.15; N, 2.87.

Reaction of $HW_2(CO)_8(PhNC)(NO)$ (12) with $Ph_3P{=}N^nPr$. A procedure similar to that for **9** was used, and the reaction time was 24 h. $HW_2(CO)_7(^nPrNC)(PhNC)(NO_{ax})$ (15) (15%) was obtained from the yellow first band eluted by CH_2Cl_2/hexane (1:4). $HW_2(CO)_6(^nPrNC)_2(PhNC)(NO_{ax})$ (16) (25%) was obtained from the orange second band eluted by CH_2Cl_2/hexane (1:1). **15**: Anal. Calcd for $C_{18}H_{13}N_3O_8W_2$: C, 28.04; H, 1.61; N, 5.19. Found: C, 28.16; H, 1.62; N, 5.43. **16**: Anal. Calcd for $C_{21}H_{20}N_4O_7W_2$: C, 30.96; H, 2.02; N, 6.85. Found: C, 31.21; H, 2.05; N, 6.93.

Reaction of $HW_2(CO)_8(PPh_3)(NO_{ax})$ (17) with $Ph_3P{=}N^nPr$. The same procedure as for **15** was used. $HW_2(CO)_7(PPh_3)(^nPrNC)(NO_{ax})$ (18) was eluted by CH_2Cl_2/hexane (1:2) as a yellow fraction, but it was not isolated. Further elution with CH_2Cl_2/hexane (1:1) afforded an orange fraction, from which crystalline $HW_2(CO)_6(PPh_3)(^nPrNC)_2(NO_{ax})$ (19) was obtained in 35% yield. **19**: Anal. Calcd for $C_{28}H_{23}N_2O_7PW_2$: C, 39.13; H, 2.17; N, 4.22. Found: C, 38.82; H, 2.52; N, 4.45.

Synthesis of $HW_2(CO)_6(MeNC)_2(^nPrNC)(NO_{ax})$ (20). $HW_2(CO)_7(MeNC)_2(NO_{ax})$ (3; 500 mg, 0.739 mmol) and $Ph_3P{=}N^nPr$ (236 mg, 0.739 mmol) in 60 mL of CH_2Cl_2 was stirred at room temperature for 30 h. The residue was chromatographed after removal of the solvent. Orange crystalline **20** was obtained from the band eluted by CH_2Cl_2/hexane (1:1) in 76% yield (403 mg). MS (EI, W^{183}): *m/e* 716 (M^+). Anal. Calcd for $C_{14}H_{14}N_4O_7W_2$: C, 23.38; H, 1.58; N, 7.67. Found: C, 23.42; H, 1.58; N, 7.80.

Synthesis of $HW_2(CO)_6(MeNC)_2(^nPrNC)(NO_{eq})$ (21). $HW_2(CO)_7(MeNC)_2(NO_{eq})$ (4; 500 mg, 0.739 mmol) and $Ph_3P{=}N^nPr$ (174 mg, 0.739 mmol) in 60 mL of CH_2Cl_2 was stirred at room temperature for 6 days. The solvent was then removed under vacuum, and the residue was chromatographed. A 15% yield (75 mg) of **4** was recovered from the first fraction eluted by CH_2Cl_2/hexane (1:2). Complex **21** was obtained as red crystals in 15% yield from the fraction eluted by CH_2Cl_2 (1:1). Anal. Calcd for $C_{14}H_{14}N_4O_7W_2$: C, 23.42; H, 1.97; N, 7.80. Found: C, 23.70; H, 1.93; N, 7.66.

X-ray Structural Determination of 12, 16, and 21. All crystals were grown by cooling a concentrated solution of the complex in CH_2Cl_2/hexane ((1:2)–(1:5) by volume) at −5 °C for several days. Crystals were mounted in thin-walled glass capillary tubes. 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 the data processing was carried out on a MICRO VAX 3600 computer by using the NRCC SDP program.[10] The coordinates of tungsten atoms were obtained from Patterson syntheses. The coordinates of all the 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 f_0 and anomalous dispersion terms f' and f'' were taken from ref 11. The position of the bridging hydrogen atom for **12** was located from the difference Fourier maps and then refined. Other hydrogen atoms were included in the structure factor calculation

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Table I. Crystal Data for Compounds 12, 16, and 21

	12	16	21
formula	$C_{15}H_6N_2O_9W_2$	$C_{21}H_{20}N_4O_7W_2$	$C_{14}H_{14}N_4O_7W_2$
fw	725.92	808.11	717.99
a, Å	10.802(2)	8.718(1)	10.140(2)
b, Å	11.705(1)	11.135(2)	10.147(2)
c, Å	16.695(2)	13.832(1)	11.346(2)
α, deg		92.24(1)	84.34(2)
β, deg	108.67(1)	79.58(1)	112.86(2)
γ, deg		91.53(1)	100.92(1)
cryst syst	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Z	4	2	2
V, Å^3	1999.8(5)	1319.4(3)	1055.8
d_{calc}, g/cm^3	2.411	2.034	2.259
cryst size, mm	0.31 × 0.18 × 0.25	0.38 × 0.30 × 0.18	0.39 × 0.25 × 0.48
radiation		Mo Kα (λ = 0.7107 Å)	
μ, cm^{-1}	117.9	89.4	111.6
transmissn factors (max; min)	1.00; 0.33	1.00; 0.58	1.00; 0.58
2θ range, deg	0–45	0–50	0–50
octants	±*h* (−11 to +11), +*k* +(0–12), +*l* (0–17)	±*h* (−10 to +10), +*k* (0–13), ±*l* (−16 to +16)	±*h* (−12 to +11), +*k* (0–12), ±*l* (−13 to +13)
no. of unique rflns	2598	4633	3694
no. of rflns with *I* > *n*σ	1791 (*n* = 2)	3059 (*n* = 2)	2839 (*n* = 2)
no. of variables	257	307	248
R, R_w	0.031; 0.032	0.031; 0.032	0.033; 0.037
GOF	1.37	1.36	1.85
max Δ/σ	0.037	0.008	0.202

in idealized positions with d_{C-H} = 0.98 Å. The final positional parameters for the atoms in **12**, **16**, and **21** are given in Table II.

Results and Discussion

$HW_2(CO)_9(NO)$ (**1**) appears to be rather reactive among metal nitrosyl complexes.[12] The reactions of **1** with isocyanides are particularly interesting, since products of various structures are isolated (vide infra). The ^{1}H NMR monitoring of the reaction (Figure 1) between **1** and ^{i}PrNC indicated that both $HW_2(CO)_8(^iPrNC)(NO_{eq})$ and $HW_2(CO)_8(^iPrNC)(NO_{ax})$ (**11**) formed initially and were gradually converted to $HW_2(CO)_7(^iPrNC)_2(NO_{eq})$ (**10**) and $HW_2(CO)_7(^iPrNC)_2(NO_{ax})$ (**9**). The formulation of $HW_2(CO)_8(^iPrNC)(NO_{eq})$ was based on our previous spectroscopic data on analogous complexes.[5] Complex **11** could be synthesized via alternative synthetic pathway (vide infra), and its reaction with ^{i}PrNC yields both **9** and **10** (Figure 2). There was no interconversion between $HW_2(CO)_8(^iPrNC)(NO_{eq})$ and $HW_2(CO)_8(^iPrNC)(NO_{ax})$ (**11**) or between **10** and **9** under the reaction conditions. However, we found that $HW_2(CO)_7(RNC)_2(NO_{eq})$ could be converted completely to $HW_2(CO)_7(RNC)_2(NO_{ax})$ in CH_3CN at 60 °C or higher temperature (R = Me, 60 °C, 5 h; R = ^{t}Bu, 82 °C, 10 h; R = ^{i}Pr, 82 °C 8 h; R = $PhCH_2$, 82 °C, 8 h). No intermediate was detected during the conversion, and no new compounds were detected if a different isocyanide ligand was added during thermolysis. Therefore, the transformation of $HW_2(CO)_7(RNC)_2(NO_{eq})$ to $HW_2(CO)_7(RNC)_2(NO_{ax})$ is likely via an intramolecular process such as trigonal twist. Although $HW_2(CO)_7(RNC)_2(NO_{eq})$ was isolated only in very low yields from reactions of **1** with RNC, they could be conveniently synthesized in good yields from reactions of $HW_2(CO)_7(THF)_2(NO_{eq})$ (**2**) with RNC. Scheme I depicts the overall reactions described above as well as the production of $HW_2(CO)_7(RNC)_2(NO_{ax})$ from **1** with Ph_3PNR (vide infra). Mechanistically, the reaction of **1** with RNC is different from that with phosphines, although rearrangement of the NO ligand from the axial to the equatorial position occurs in both cases. In the latter, $HW_2(CO)_7(PPh_3)_2(NO_{ax})$ is derived from $HW_2(CO)_8(PPh_3)(NO_{eq})$ instead of $HW_2(CO)_8(PPh_3)(NO_{ax})$.[6]

Four distinct structures are found among the complexes $HW_2(CO)_7(RNC)_2(NO)$: (a) eclipsed with an equatorial NO, $HW_2(CO)_7(MeNC)_2(NO_{eq})$ (**4**); (b) staggered with an equatorial NO, $HW_2(CO)_7(RNC)_2(NO_{eq})$ (**6**, R = ^{t}Bu; **8**, R = $PhCH_2$); (c) eclipsed with an axial NO, $HW_2(CO)_7(PhCH_2NC)_2(NO_{ax})$ (**7**); (d) staggered with an axial NO, $HW_2(CO)_7(RNC)_2(NO_{ax})$ (**3**, R = Me; **5**, R = ^{t}Bu). The structures of **3** and **4** have been reported,[6] and the relevant data for **5**–**8** are provided as supplementary material. The corresponding W–W distances are listed: **3**, 3.389(1) Å; **4**, 3.4798(9) Å; **5**, 3.444(1) Å; **6**, 3.3995(8) Å; **7**, 3.5727(8) Å; **8**, 3.370(1) Å. The steric contacts between equatorial ligands undoubtedly play a decisive role in the structural variation of these complexes on the basis of the following reasons: (i) complexes with an eclipsed conformation, **4** and **7**, appear to have the longest W–W distances among all species; (ii) for sterically more congested ^{t}BuNC, $HW_2(CO)_7(RNC)_2(NO)$ complexes adopt a staggered conformation no matter whether NO is equatorial or axial; (iii) for the structurally analogous isomers $HW_2(CO)_7(RNC)_2(NO)$ (R = ^{t}Bu, ^{i}Pr), placement of the sterically less hindered NO ligand in the equatorial site reduces the W–W distances (**6** vs **5**). Since an unsupported M–H–M linkage is very flexible in nature,[13] it is not clear whether the structural variation in **3**/**4** and **7**/**8** is due to the delicate balance between steric and electronic factors or solely due to crystal-packing forces.

Similar to the case for many metal nitrosyl complexes,[14] carbonyl ligands of **1** should be susceptible to nucleophilic

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Table II. Positional Parameters and B_{iso} Values for the Atoms in Compounds 12, 16, and 21

atom	*x*	*y*	*z*	B_{iso}, Å^2	atom	*x*	*y*	*z*	B_{iso}, Å^2
Compound **12**									
W1	0.14179(6)	0.37106(5)	0.25251(3)	4.06(3)	C3	0.0364(17)	0.4770(14)	0.1572(10)	6.0(9)
W2	0.25385(6)	0.21065(5)	0.12165(3)	3.97(3)	C4	0.2568(17)	0.2673(13)	0.3437(9)	5.0(8)
N1	0.3410(12)	0.1270(10)	0.0649(7)	5.2(7)	C5	0.1111(15)	0.4707(12)	0.3380(10)	5.1(9)
N2	0.2914(11)	0.4627(10)	0.0448(7)	4.4(6)	C6	0.2267(18)	0.0650(16)	0.1831(10)	6.6(10)
O1	−0.1106(11)	0.2327(10)	0.2576(7)	6.7(7)	C7	0.4234(19)	0.2445(13)	0.2176(11)	5.4(10)
O2	0.3911(13)	0.5229(10)	0.2687(7)	7.8(8)	C8	0.0795(16)	0.1891(13)	0.0238(9)	4.9(9)
O3	−0.0196(15)	0.5338(12)	0.1054(9)	10.4(9)	C10	0.2770(15)	0.3730(13)	0.0704(8)	4.7(8)
O4	0.3179(13)	0.2082(10)	0.3951(6)	7.8(8)	C11	0.3091(14)	0.5686(12)	0.0127(8)	4.5(7)
O5	0.0929(13)	0.5330(10)	0.3885(8)	8.1(8)	C12	0.3447(17)	0.5763(13)	−0.0586(10)	5.9(10)
O6	0.2146(15)	−0.0119(11)	0.2183(8)	9.7(9)	C13	0.3612(19)	0.6866(19)	−0.0883(11)	7.5(11)
O7	0.5205(13)	0.2655(11)	0.2702(7)	7.7(8)	C14	0.3410(19)	0.7791(15)	−0.0463(14)	7.2(11)
O8	−0.0153(12)	0.1780(11)	−0.0299(7)	7.3(8)	C15	0.3092(19)	0.7690(14)	0.0231(12)	6.8(11)
O9	0.3914(12)	0.0672(9)	0.0253(7)	7.3(7)	C16	0.2912(17)	0.6667(13)	0.0544(9)	5.6(9)
C1	−0.0219(17)	0.2797(13)	0.2535(9)	5.1(9)	H	0.120(21)	0.262(16)	0.168(12)	18.2(74)
C2	0.3027(17)	0.4657(12)	0.2619(8)	4.9(9)					
Compound **16**									
W1	0.95953(5)	0.87822(4)	0.17715(3)	3.96(2)	C5	1.1468(14)	0.9763(10)	0.1285(9)	6.0(6)
W2	0.67748(4)	0.66545(3)	0.26543(3)	3.57(2)	C6	0.8348(14)	0.5573(10)	0.1768(8)	5.1(6)
N1	0.5542(9)	0.5423(7)	0.3116(6)	4.3(4)	C7	0.5668(11)	0.6977(9)	0.1437(7)	4.2(5)
N2	0.5131(10)	0.7196(8)	0.0780(7)	5.3(5)	C8	0.5204(11)	0.7959(9)	0.3449(7)	4.2(5)
N3	0.4330(10)	0.8636(8)	0.3780(7)	5.4(5)	C10	0.8102(11)	0.6626(8)	0.3789(7)	4.1(5)
N4	0.8826(9)	0.6605(7)	0.4401(7)	4.6(4)	C11	0.4443(14)	0.7455(13)	−0.0047(10)	7.3(7)
O1	1.1806(9)	0.6795(8)	0.2279(7)	7.6(5)	C12	0.4754(18)	0.6498(13)	−0.0854(10)	7.6(8)
O2	0.9670(12)	0.7523(8)	−0.0332(7)	8.4(6)	C13	0.6371(18)	0.6226(14)	−0.1207(11)	8.8(9)
O3	0.7409(12)	1.0821(10)	0.1288(7)	10.3(6)	C21	0.3137(15)	0.9488(14)	0.4103(12)	9.0(9)
O4	0.9354(12)	0.9928(11)	0.3909(7)	9.8(7)	C22	0.3478(25)	1.0621(16)	0.3878(23)	18.4(21)
O5	1.2548(11)	1.0323(8)	0.0996(7)	8.8(6)	C23	0.4526(22)	1.1271(14)	0.3480(17)	13.7(14)
O6	0.9174(10)	0.4957(7)	0.1271(6)	7.4(5)	C31	0.9780(12)	0.6598(8)	0.5103(8)	4.4(5)
O9	0.4738(8)	0.4575(7)	0.3427(6)	6.4(4)	C32	1.1371(13)	0.6492(10)	0.4802(8)	5.1(5)
C1	1.0978(13)	0.7485(11)	0.2101(8)	5.5(6)	C33	1.2315(12)	0.6514(10)	0.5491(10)	5.8(6)
C2	0.9640(13)	0.7961(10)	0.0430(9)	5.4(6)	C34	1.1707(14)	0.6648(10)	0.6463(9)	5.8(6)
C3	0.8209(15)	1.0095(11)	0.1449(9)	6.1(6)	C35	1.0104(15)	0.6727(11)	0.6756(8)	6.3(6)
C4	0.9454(14)	0.9523(13)	0.3147(10)	6.5(7)	C36	0.9139(12)	0.6728(10)	0.6083(8)	5.1(6)
Compound **21**									
W1	0.28371(4)	0.85570(4)	0.07342(4)	3.42(2)	C2	0.1069(13)	0.7322(12)	−0.0320(11)	5.0(6)
W2	0.31866(4)	0.69095(4)	0.35666(4)	3.47(2)	C3	0.1539(11)	0.9403(10)	0.1329(10)	4.2(5)
N1	0.3177(9)	0.8584(9)	0.4065(8)	4.3(5)	C4	0.4637(11)	0.9769(10)	0.1904(10)	4.0(5)
N2	−0.0345(9)	0.6172(10)	0.2169(10)	5.3(5)	C5	0.2568(12)	0.9923(13)	−0.0680(11)	5.1(6)
N3	0.3364(9)	0.3929(9)	0.2720(8)	4.6(5)	C6	0.3206(11)	0.6105(11)	0.5183(10)	4.5(6)
N4	0.6683(10)	0.7565(9)	0.4325(9)	5.0(5)	C8	0.0898(13)	0.6416(10)	0.2690(10)	4.5(6)
O1	0.4748(11)	0.7094(10)	−0.0207(10)	8.5(7)	C9	−0.1869(13)	0.5836(15)	0.1488(14)	7.4(8)
O2	0.0003(10)	0.6640(11)	−0.0905(10)	8.7(6)	C10	0.3288(10)	0.4951(10)	0.3006(9)	3.6(5)
O3	0.0801(8)	0.9881(9)	0.1616(8)	6.2(5)	C11	0.3501(15)	0.2671(11)	0.2385(12)	6.2(8)
O4	0.5609(8)	1.0467(8)	0.2549(8)	5.5(4)	C12	0.5482(12)	0.7316(10)	0.4080(10)	4.2(5)
O5	0.2402(9)	1.0725(9)	−0.1478(8)	6.8(5)	C13	0.8193(14)	0.7933(19)	0.4599(16)	10.3(11)
O6	0.3154(10)	0.5638(9)	0.6146(8)	6.8(5)	C14	0.9153(16)	0.7561(22)	0.5728(18)	11.7(13)
O7	0.3180(9)	0.9655(8)	0.4395(8)	6.0(5)	C15	1.0725(14)	0.7876(19)	0.5993(17)	10.4(12)
C1	0.4081(12)	0.7625(12)	0.0133(11)	5.2(6)					

attack in view of the high CO stretching frequencies.[15] Indeed, phosphinimine $Ph_3P{=}NR$ reacts with 1 in CH_2Cl_2 at room temperature to give $HW_2(CO)_8(RNC)(NO)$, $HW_2(CO)_7(RNC)_2(NO)$, and $HW_2(CO)_6(RNC)_3(NO)$. The number of CO ligands converted depends upon the identity and the quantity of phosphinimines used. Although ^{1}H NMR monitoring of the reaction of $HW_2(CO)_9(NO)$ (1) with RNC indicated that replacement of two CO ligands proceeded in a stepwise manner in forming $HW_2(CO)_7(RNC)_2(NO)$, our early attempt in isolating $HW_2(CO)_8(RNC)(NO)$ from the reaction of $HW_2(CO)_9(NO)$ (1) was hampered due to the difficulty in handling notoriously toxic RNC in a stoichiometric quantity. However, use of phosphinimines allows us to successfully isolate the desired product. Moreover, in sharp contrast to the reaction of 1 with isocyanides, in no case did we observe the rearrangement of the ligands (vide infra). This also provides us with an opportunity to trace the conversion of several reactive CO ligands of 1 to isocyanides.

The slower reaction of $HW_2(CO)_9(NO)$ (1) with $Ph_3P{=}N^tBu$ and the inability of $Ph_3P{=}N^tBu$ to react with $HW_2(CO)_8(^tBuNC)(NO_{ax})$ apparently are steric in origin. Analysis of the coordination sites of $HW_2(CO)_9(NO_{ax})$ (1)[9] indicates a decreasing order of steric crowdedness: exo (8), exo (9), endo (6), or endo (7). The PhNC ligand of $HW_2(CO)_8(PhNC)(NO_{ax})$ (**12**) was found to reside at site exo (8) (vide infra). Reaction of **12** with $Ph_3P{=}N^nPr$ would introduce ^{n}PrNC ligand at site exo (9) on the grounds of steric constraint. Results of Fenske–Hall calculations[16] on $HW_2(CO)_8(PhNC)(NO)$ (**12**) suggest that attack of a nucleophile at the endo (7) CO is electronically favored over the endo (6) CO or endo (7) CO. The structural characterization of $HW_2(CO)_7(^iPrNC)_2(NO_{ax})$ (**9**), which was synthesized from 1 with $Ph_3P{=}N^iPr$, further substantiates the argument that sites exo (8) and exo (9) are preferentially occupied by RNC ligands in the reaction of 1 with $Ph_3P{=}NR$.

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(15) (a) Darensbourg, D. J.; Darensbourg, M. Y. *Inorg. Chem.* **1970**, *9*, 1691. (b) Angelici, R. J. *Acc. Chem. Res.* **1972**, *5*, 335.

(16) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768. The Mulliken atomic charges for carbon atoms at sites exo (9), endo (7), and endo (6) are 0.055, 0.045, and 0.020, respectively.

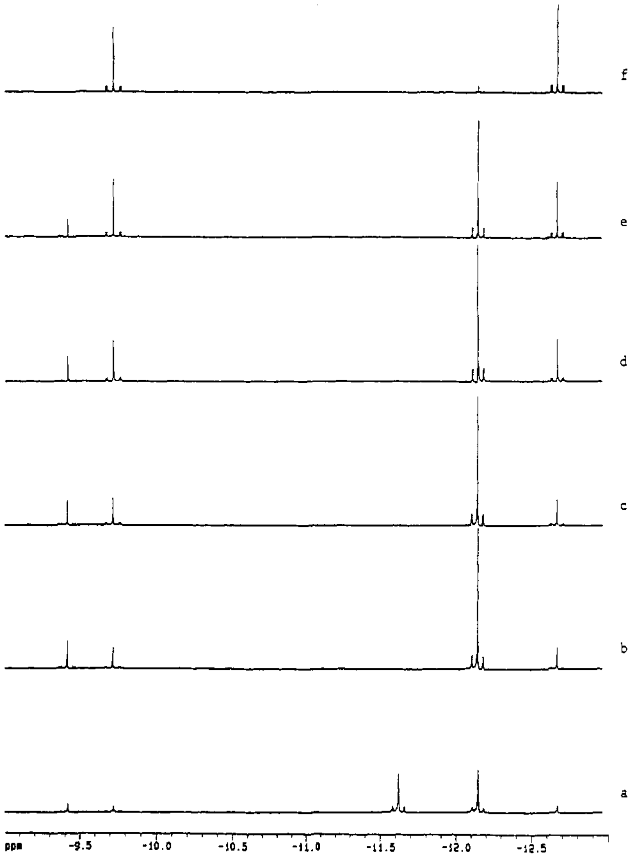

Figure 1. ^1H NMR monitoring of the reaction of $HW_2(CO)_9(NO)$ with ^iPrNC in the hydride region (solvent CD_2Cl_2): (a) 5 min; (b) 15 min; (c) 1 h; (d) 3 h; (e) 6 h; (f) 23 h. The chemical shifts of $HW_2(CO)_8(^iPrNC)(NO_{eq})$, $HW_2(CO)_7(^iPrNC)_2(NO_{eq})$, $HW_2(CO)_9(NO)$, $HW_2(CO)_8(^iPrNC)(NO_{ax})$, and $HW_2(CO)_7(^iPrNC)_2(NO_{ax})$ appear at δ −9.42, −9.72, −11.62, −12.15, and −12.67 ppm, respectively.

From the reaction of $HW_2(CO)_9(NO)$ with $Ph_3P{=}NPh$, we isolated the complexes $HW_2(CO)_8(PhNC)(NO_{ax})$ (**12**) and $HW_2(CO)_7(PhNC)_2(NO_{ax})$ (**13**), and the interesting product $HW_2(CO)_7(PhNC)(O{=}PPh_3)(NO_{ax})$ (**14**) as well. The ^1H NMR monitoring of the reaction clearly indicated that **14** was formed from **12** instead of **13**. Complex **14** has its PhNC, $O{=}PPh_3$, and NO ligands occupying sites exo (9), exo (8), and endo (7), respectively.[17] Although complexes containing coordinated $O{=}PR_3$ have frequently been proposed,[18] to our knowledge, there has only been one other structurally characterized tungsten(0) complex that contained $O{=}PR_3$.[19] The most unusual feature of **14** is that NO resides in an equatorial site trans to $O{=}PPh_3$. It seems to be energetically favored to have the NO ligand reside in an equatorial position trans to a good σ-donor ligands such as THF ($HW_2(CO)_7(THF)_2(NO_{eq})$ (**2**), pyridine ($HW_2(CO)_7(py)_2(NO_{eq})$[5]), or $O{=}PPh_3$ (**14**). $HW_2(CO)_7(O{=}PPh_3)_2(NO_{eq})$ (**22**) could also be easily synthesized from $HW_2(CO)_9(NO)$ and $O{=}PPh_3$.[20] The $O{=}PPh_3$ ligand in **14** and **22** is labile and could be readily displaced with other ligands.

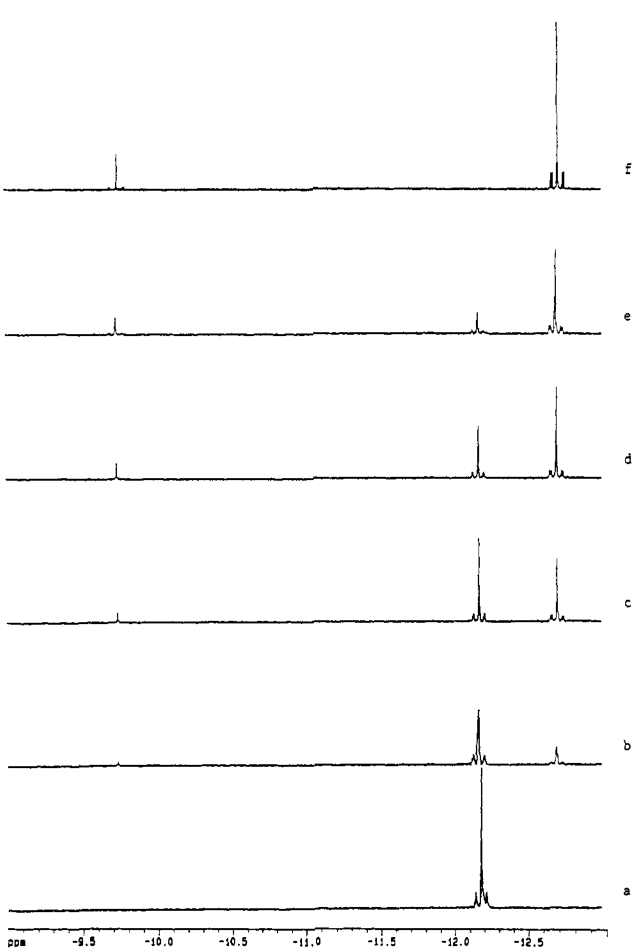

Figure 2. ^1H NMR monitoring of the reaction of $HW_2(CO)_8(^iPrNC)(NO_{ax})$ with ^iPrNC in the hydride region (solvent CD_2Cl_2): (a) 5 min; (b) 50 min; (c) 2 h; (d) 3 h; (e) 4 h; (f) 21 h.

Under vigorous conditions, up to four CO ligands in $W(CO)_4(NO)I$ could be displaced by ^tBuNC,[21] whereas direct ligand substitution of $HW_2(CO)_9(NO)$ (**1**) with various ligands does not proceed beyond $HW_2(CO)_7(L)_2(NO)$.[4-6] Use of phosphinimines results in the formation of several trisubstituted derivatives of **1** which have a substituent at an endo site. These include $HW_2(CO)_6(PPh_3)(^nPrNC)_2(NO_{ax})$ (**19**), $HW_2(CO)_6(PhNC)(^nPrNC)_2(NO_{ax})$ (**16**), $HW_2(CO)_6(MeNC)_2(^nPrNC)(NO_{ax})$ (**20**), and $HW_2(CO)_6(MeNC)_2(^nPrNC)(NO_{eq})$ (**21**). Electronic factors play a decisive role in synthesizing these trisubstituted derivatives of $HW_2(CO)_9(NO)$. Scheme II depicts the stepwise synthesis of complexes **16** and **19**. Complexes **12**, **16**, **17**,[4] and **19**[22] in Scheme II have been structurally characterized. In complex **15**, the CO ligand at site endo (6) should be more susceptible to nucleophilic attack than the CO ligand at endo (7), since the former is trans to a better π-acceptor, i.e., PhNC.[23] In contrast, the better π-accepting ability of ^nPrNC compared to PPh_3

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[17] Crystal data for **14**: $C_{32}H_{21}N_2O_9W_2$, M_r = 976.2, monoclinic, space group $P2_1/a$, a = 17.600(8) Å, b = 10.919(2) Å, c = 18.584(4) Å, β = 91.45(1)°, V = 3426(2) Å^3, Z = 4, D_c = 1.892 g cm^{-3}, $F(000)$ = 1848, μ(Mo Kα) = 69.5 mm^{-1}, R = 0.089 for 3450 unique, observed reflections ($I > 2.0\sigma(I)$), $0 < 2\theta < 50°$.

[18] (a) Darensbourg, D. J.; Walker, N.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1980**, *102*, 1213. (b) Darensbourg, D. J.; Darensbourg, M. Y.; Walker, N. *Inorg. Chem.* **1981**, *20*, 1918. (c) Webb, S. L.; Giandomenico, C. M.; Halpern, J. *J. Am. Chem. Soc.* **1986**, *108*, 345.

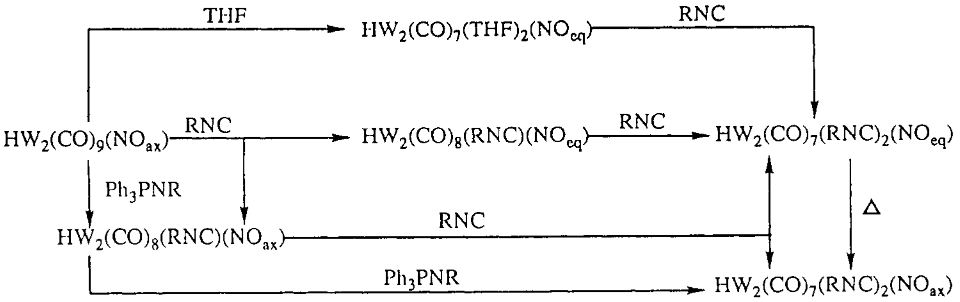
[19] Goldberg, S. Z.; Raymond, K. N. *Inorg. Chem.* **1973**, *12*, 2923.

[20] Complex **22** was obtained in 47% yield. Anal. Calcd for $C_{43}H_{31}NO_{10}P_2W_2$: C, 44.86; H, 2.71; N, 1.22. Found: C, 44.50; H, 2.71; N, 1.35. ν(CO) (in CH_2Cl_2): 2061 w, 1995 m, 1968 w, 1919 vs, 1891 sh cm^{-1}. ν(NO): 1623 m cm^{-1}. ^1H NMR: δ 7.72–7.27 (m, 30 H), −5.06 (dd with satellites, J(H–P) = 2.0, 1.0 Hz; J(H–W) = 54, 51 Hz, 1H).

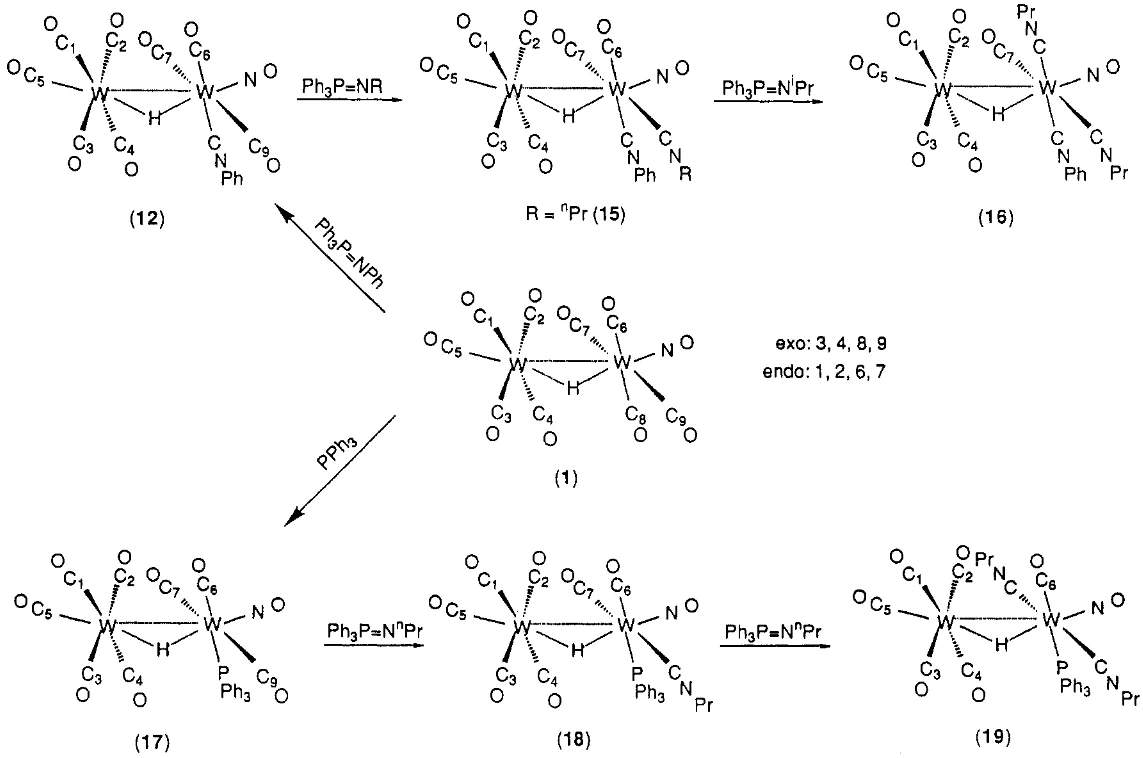
[21] King, R. B.; Saran, M. S.; Anand, S. P. *Inorg. Chem.* **1974**, *13*, 3038.

[22] Crystal data for **19**: $C_{32}H_{30}N_3O_7PW_2$, M_r = 967.3, triclinic, space group $P1$, a = 9.464(2) Å, b = 11.726(3) Å, c = 17.556(4) Å, α = 97.05(2)°, β = 91.45(1)°, γ = 109.43(2)°, V = 1753.2(6) Å^3, Z = 2, D_c = 1.832 g cm^{-3}, $F(000)$ = 812, μ(Mo Kα) = 67.9 mm^{-1}, R = 0.039 for 6161 unique, observed reflections ($I > 2.0\sigma(I)$), $0 < 2\theta < 50°$.

Scheme I



Scheme II



should render the endo (7) CO to be more electrophilic than the endo (6) CO for complex **18**. Indeed, complex **19** was found to have site (7) occupied by ⁿPrNC. The reaction between $HW_2(CO)_7(RNC)_2(NO_{eq})$ and $Ph_3P{=}NR'$ was very slow, and even after 6 days substantial amounts of $HW_2(CO)_7(RNC)_2(NO_{eq})$ still remained unreacted. The lower reactivity of $HW_2(CO)_7(MeNC)_2(NO_{eq})$ (**4**), compared to that of $HW_2(CO)_7(MeNC)_2(NO_{ax})$ (**3**), toward $Ph_3P{=}NR$ is attributable to electronic effects, as the former has CO stretching frequencies relatively lower than the latter. The ⁿPrNC ligand was found to be in the endo (7) site for **21**. The occupancy of endo (7) in **21** by the NO ligand provides a solid evidence for the argument that no rearrangement of ligands occurs during the reaction of $HW_2(CO)_9(NO)$ and analogues with phosphinimines.

Molecular structure of $HW_2(CO)_8(PhNC)(NO_{ax})$ (12), $HW_2(CO)_6(PhNC)(^nPrNC)_2(NO_{ax})$ (16), and $HW_2(CO)_6(MeNC)_2(^nPrNC)(NO_{eq})$ (21). The ORTEP drawings of **12**, **16** and **21** are shown in Figures 3–5, respectively. Selective interatomic distances and angles are listed in Table III. In all of the complexes the tungsten atoms reside in roughly octahedral environments. These complexes have a bent, staggered configuration, similar to dinuclear metal complexes reported by us[4–6,24] and others.[25] Complexes **12** and **16** have their NO ligand in the axial site, whereas **21** has its NO ligands in the equatorial site.[26]

The nitrosyl (**12**, 176(1)°; **16**, 178.5(7)°; **21**, 179.3(8)°) and carbonyl ligands (**12**, 178(1)°; **16**, 178 (1)°; **21**, 178(1)°) are linearly coordinated to W. The W–N distances (**12**, 1.82(1) Å; **16**, 1.785 (8) Å; **21**, 2.01(5) Å) are shorter than the average W–C distances (**12**, 2.04(4) Å; **16**, 2.02(3) Å; **21**, 2.01(5) Å) by about 0.1–0.2 Å. These distances are similar to those found for *mer*-$W(\eta^1\text{-}FSbF_5)(CO)_3(NO)(PMe_2Ph)$ (W–N = 1.836(2) Å; W–C = 2.09(2), 2.09(2), 2.05(2) Å),[27] $HW(CO)_2(NO)(PR_3)_2$ (R = Me, Ph, MeO) (W–N = 1.83(1), 1.842(5), 1.846(2) Å; W–C = 2.01(2)/2.05(1), 2.033(8)/2.038(6), 2.021(8) Å,[28] *trans,trans*-$W[(\eta^1\text{-}OPO(OH)_2](CO)_2(NO)(PPh_3)_2$ (W–N = 1.79(1) Å; W–C = 2.08(2), 2.06(2) Å),[29] and *trans*-$W(\eta^2\text{-}O_2CCH_3)$-

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[23] Malatesta, L.; Bonati, F. *Isonitrile Complexes of Metals*; Wiley: New York, 1969.

[24] Lin, J. T.; Chang, K. Y.; Wang, S. Y.; Wen, Y. S.; Tseng, L. H.; Chang, C. C.; Peng, S. M.; Wang, Y.; Lee, G. H. *Organometallics* **1991**, *10*, 2377.

[25] Hart, D. W.; Bau, R.; Koetzle, T. F. *Organometallics* **1985**, *4*, 1590.

[26] The location of the NO ligand was distinguished from the CO ligands by conspicuous discrepancies in the thermal parameters for the N and C atoms when incorrectly assigned.

Table III. Selected Bond Distances (Å) and Angles (deg) for Complexes 12, 16, and 21

	12	16	21
	Distances		
W1–W2	3.3848(8)	3.4610(7)	3.3952(9)
W1–C1	2.07(2)	2.02(1)	2.05(1)
W1–C2	2.02(2)	2.03(1)	2.00(1)
W1–C3	2.05(2)	2.03(1)	2.04(1)
W1–C4	2.03(2)	2.03(1)	2.05(1)
W1–C5	1.95(2)	1.97(1)	1.98(1)
W2–C6	2.06(2)	2.05(1)	1.93(1)
W2–C7	2.05(2)	2.13(1)	
W2–C8	2.08(2)	2.15(1)	2.12(1)
W2–C9			
W2–C10	2.13(2)	2.11(1)	2.18(1)
W2–N1	1.82(1)	1.785(8)	1.846(9)
W1–H	1.9(2)		1.9
W2–H	2.0(2)		1.9
C1–O1	1.13(2)	1.13(2)	1.13(1)
C2–O2	1.14(2)	1.14(2)	1.16(2)
C3–O3	1.10(2)	1.14(2)	1.12(1)
C4–O4	1.14(2)	1.12(2)	1.13(1)
C5–O5	1.18(2)	1.13(1)	1.14(1)
C6–O6	1.10(2)	1.13(2)	1.16(1)
C7–O7	1.16(2)		
C8–O8	1.13(2)		
N1–O7			1.18(1)
N1–O9	1.21(2)	1.21(1)	
C7–N2		1.13(1)	
C8–N2			1.15(2)
C8–N3		1.11(1)	
C9–N2			1.42(2)
C10–N2	1.16(2)		
C10–N3			1.14(1)
C10–N4		1.14(4)	
C11–N3			1.41(1)
C12–N4			1.12(1)
C13–N3			1.12(1)
C13–N4			1.42(2)
	Angles		
W1–C1–O1	177(1)	176.9(9)	179(1)
W1–C2–O2	177(1)	178(1)	176(1)
W1–C3–O3	179(2)	178(1)	177.7(9)
W1–C4–O4	178(1)	179(1)	178.9(8)
W1–C5–O5	178(1)	179(1)	178(1)
W2–C6–O6	178(2)	178(1)	176.7(9)
W2–C7–O7	178(1)		
W2–C8–O8	180(1)		
W2–N1–O6		175(2)	
W2–N1–O7			179.4(8)
W2–N1–O9		178.5(7)	
W2–C7–N2		176.6(9)	
W2–C8–N2			177.3(9)
W2–C8–N3		173.2(9)	
W2–C10–N2	178(1)		
W2–C10–N3			179.0(8)
W2–C10–N4		179.5(9)	
W2–C12–N4			177.8(9)
C1–W1–C2	174.9(5)	89.1(5)	89.6(4)
C1–W1–C3	93.2(6)	179.6(5)	177.4(4)
C1–W1–C4	90.3(6)	90.1(5)	91.5(4)
C1–W1–C5	87.6(6)	89.4(5)	92.4(5)
C2–W1–C3	88.8(6)	91.3(5)	88.2(4)
C2–W1–C4	88.0(6)	176.4(5)	176.8(4)
C2–W1–C5	87.6(6)	92.1(5)	91.9(5)
C3–W1–C4	176.0(6)	89.5(5)	90.6(4)
C3–W1–C5	91.4(6)	90.5(5)	89.1(4)
C4–W1–C5	90.6(6)	91.4(5)	91.1(4)
C6–W2–C7	90.3(6)	90.0(4)	
C6–W2–C8	93.1(6)	172.8(4)	92.4(4)
C6–W2–C10	172.8(6)	90.7(4)	88.6(4)
C6–W2–C12			96.9(4)
C7–W2–C8	175.8(6)	85.7(4)	
C7–W2–C10	87.2(6)	169.6(4)	
C8–W2–C10	89.2(6)	92.5(4)	87.3(4)
C8–W2–C12			168.4(4)
C10–W2–C12			86.0(4)
N1–W2–C6	89.6(6)	93.6(4)	91.5(4)
N1–W2–C7	91.7(6)	96.6(4)	
N1–W2–C8	90.9(6)	92.6(4)	94.9(4)
N1–W2–C10	97.1(5)	93.7(3)	177.8(4)
N1–W2–C12			91.9(4)
W1–H–W2	125(11)		126

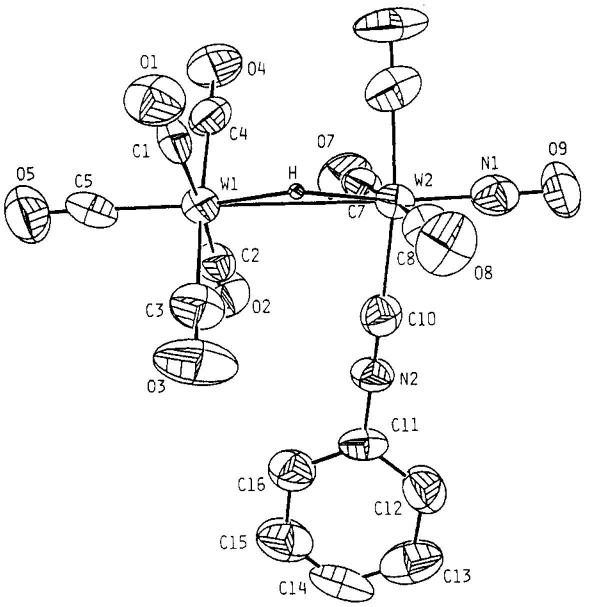

Figure 3. ORTEP drawing of $HW_2(CO)_8(PhNC)(NO_{ax})$. Thermal ellipsoids are drawn with 50% probability boundaries.

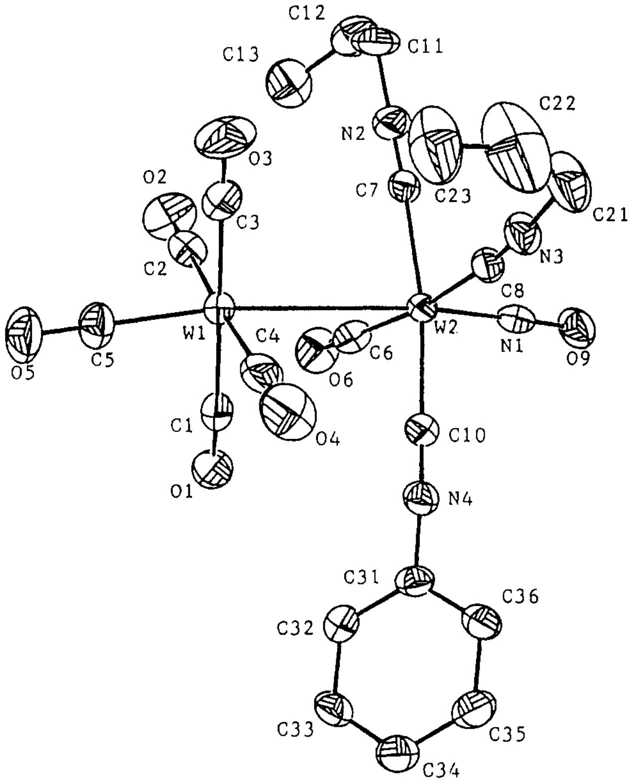

Figure 4. ORTEP drawing of $HW_2(CO)_6(PhNC)(^nPrNC)_2(NO_{ax})$. Thermal ellipsoids are drawn with 50% probability boundaries.

$(CO)(NO)(PP_3)_2$ (W–N = 1.836(7) Å; W–C = 1.914(8) Å).[29] In general, the W–C bonds of carbonyl groups trans to the bridging hydride (1.93–1.98 Å) are shorter than the others (1.94–2.08 Å). Isocyanide ligands in these complexes also coordinate linearly to the tungsten atom, indicating

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Table IV. IR and ^{1}H and ^{31}P{^{1}H} NMR Spectra

compd	ν(*CN*), ν(CO), ν(NO)[a] (cm^{-1})	^{1}H δ (ppm)[b,c] (*J* (Hz))
2	2064 w, 2002 m, 1969 w, 1928 vs. 1904 m^{-s}, **1662** m	4.61–4.23 (m, 4 H), 4.05–3.92 (m, 4 H), 2.20–2.10 (m, 4H), 2.08–1.96 (m, 4 H), –5.21 (s, 1 H, J_{H-W} = 60, 50, μ-H)
3	*2220* w, *2201* w, 2067 w, 2033 s, 1980 s, 1926 vs. **1651** m	3.88 (s, 6 H, Me), –12.6 (s, 1 H, J_{H-W} = 43, 32, μ-H)
4	*2230* w, *2210* w, 2064 w, 2022 s, 1947 s, 1921 vs. 1892 sh, **1688** m	3.88 (s, 3 H, Me), 3.78 (s, 3 H, Me), –9.49 (s, 1 H, J_{H-W} = 53, 44, μ-H)
5	*2190* w, *2170* w, 2065 w, 2028 s, 1977 s, 1925 vs. **1648** m	1.86 (s, 18 H, Me), –12.6 (s, 1 H, J_{H-W} = 43, 32, μ-H)
6	*2202* w, *2179* w, 2063 w, 2019 s, 1949 s, 1925 vs. 1896 sh, **1682** m	1.78 (s, 9 H, Me), 1.69 (s, 9 H, Me), –9.56 (s, 1 H, J_{H-W} = 50, 42, μ-H)
7	*2204* w, *2183* w, 2066 w, 2032 s, 1982 s, 1925 vs. **1655** m	7.63–7.54 (m, 10 H, Ph), 5.55 (s, 4 H, CH_2), –12.3 (s, 1 H, J_{H-W} = 43, 34, μ-H)
8	*2217* w, *2188* w, 2064 w, 2021 s, 1951 s, 1924 vs. 1900 sh, **1685** m	7.44–7.24 (m, 10 H, Ph), 5.11 (s, 2 H, CH_2), 4.86 (s, 2 H, CH_2), –9.46 (s, 1 H, J_{H-W} = 54, 41, μ-H)
9	*2198* w, *2179* w, 2066 w, 2030 s, 1978 s, 1924 vs. **1647** m	4.54 (hept, 2 H, $^3J_{H-H}$ = 6.5, CH), 1.56 (d, 12 H, Me), –12.7 (s, 1 H, J_{H-W} = 43, 32, μ-H)
10	*2209* w, *2186* w, 2064 w, 2020 s, 1948 s, 1922 vs, 1900 sh, **1680** m	4.52 (hept, 1 H, $^3J_{H-H}$ = 6.5, CH), 4.33 (hept, 1 H, $^3J_{H-H}$ = 6.5, CH), 1.55 (d, 6 H, Me), 1.45 (d, 6 H, Me), –9.72 (s, 1 H, J_{H-W} = 50, 42, μ-H)
11	*2199* w, 2095 m, 2064 m, 2018 vs. 1980 sh, 1934 vs. **1700** m	4.60 (hept, 1 H, $^3J_{H-H}$ = 6.5, CH), 1.54 (d, 6 H, Me), –12.2 (s, 1 H, J_{H-W} = 42, 36, μ-H)
12	*2208* w, 2095 m, 2065 m, 2020 vs. 1983 sh, 1933 vs. **1701** m	4.16 (t, 2 H, $^3J_{H-H}$ = 6.4, CH_2), 1.93 (m, 2 H, CH_2), 1.17 (t, 3 H, $^3J_{H-H}$ = 7.4, Me), –12.2 (s, 1 H, J_{H-W} = 41, 34, μ-H)
13	*2205* w, *2185* w, 2066 m, 2031 s, 1976 s, 1924 vs. **1650** m	4.15 (t, 4 H, $^3J_{H-H}$ = 6.4, CH_2), 1.92 (m, 4 H, CH_2), 1.17 (t, 6 H, $^3J_{H-H}$ = 7.3, Me), –12.6 (s, 1 H, J_{H-W} = 43, 35, μ-H)
14	*2172* w, 2093 m, 2064 m, 2018 vs. 1980 sh, 1931 vs. **1700** m	7.76–7.60 (m, 5 H, Ph), –12.0 (s, 1 H, J_{H-W} = 41, 35, μ-H)
15	*2201* w, *2154* w, 2065 m, 2032 s, 1982 s, 1927 vs. **1653** m	7.71–7.61 (m, 5 H, Ph), 4.14 (t, 2 H, $^3J_{H-H}$ = 6.5, CH_2), 1.90 (m, 2 H, CH_2), 1.12 (t, 3 H, $^3J_{H-H}$ = 7.3, CH_2), –12.4 (s, 1 H, J_{H-W} = 43, 33, μ-H)
16	*2193* w, *2165* w, *2100* w-m, 2067 m, 1972 s, 1918 vs	7.59–7.47 (m, 5 H, Ph), 4.08 (t, 4 H, $^3J_{H-H}$ = 6.5, CH_2), 1.87 (m, 4 H, CH_2), 1.121 (t, 3 H, $^3J_{H-H}$ = 7.3, Me), 1.119 (t, 3 H, $^3J_{H-H}$ = 7.3, Me), –12.8 (s, 1 H, J_{H-W} = 45, 29, μ-H)
18	*2191* w, 2067 m, 2021 s, 1964 s, 1922 vs. 1885 sh, **1660** m	7.62–7.48 (m, 15 H, Ph), 3.81 (t, 2 H, $^3J_{H-H}$ = 6.6, CH_2), 1.63 (m, 2 H, CH_2), 0.86 (t, 3 H, $^3J_{H-H}$ = 7.3, Me), –11.0 (d, 1 H, $^2J_{H-P}$ = 16, J_{H-W} = 48; 38, μ-H)
19	*2144* s, 2064 w, 1956 s, 1924 s, 1896 sh, **1630** m	7.60–7.48 (m, 15 H, Ph), 3.80 (t, 4 H, $^3J_{H-H}$ = 6.6, CH_2), 1.60 (m, 4 H, CH_2), 0.87 (t, 6 H, $^3J_{H-H}$ = 7.3, Me), –11.2 (d, 1 H, $^2J_{H-P}$ = 15, J_{H-W} = 51, 33, μ-H)
20	*2208* w, *2157* s, 2061 w, 1962 s, 1916 vs. 1843 sh, **1608** m	4.03 (t, 2 H, $^3J_{H-H}$ = 6.5, CH_2), 3.802 (s, 3 H, Me), 3.798 (s, 3 H, Me), 1.85 (m, 2 H, CH_2), 1.09 (t, 3 H, $^3J_{H-H}$ = 7.3, Me),–13.1 (s, 1 H, J_{H-W} = 46, 28, μ-H)
21	*2223* w, *2156* s, 2059 w, 1960 sh, 1921 vs. 1908 sh, **1642** m	4.02 (t, 2 H, $^3J_{H-H}$ = 6.6, CH_2), 3.79 (s, 3 H, Me), 3.60 (s, 3 H, Me), 1.84 (m, 2H, CH_2), 1.09 (t, 3 H, $^3J_{H-H}$ = 7.4, Me), –9.88 (s, 1 H, J_{H-W} = 45, 45, μ-H)

[a] Measured in CH_2Cl_2 solution except for **2**. [b] Measured in acetone-d_6 except for **2** and **16**, which were measured in CD_2Cl_2. All are relative to δ(Me_4Si) 0 ppm. [c] The ^{31}P{^{1}H} values are as follows and are relative to δ(85% H_3PO_4) 0 ppm: **22**, 15.9 (s, J_{P-W} = 236); **23**, 11.7 (s, J_{P-W} = 226); **25**, –10.4 (s, J_{P-W} = 222); **26**, –7.2 (s, J_{P-W} = 211); **27**, 17.2 (s, J_{P-W} = 235). Abbreviations: s = singlet, d = doublet, t = triplet, hept = heptet, m = multiplet. These abbreviations do not include the satellites.

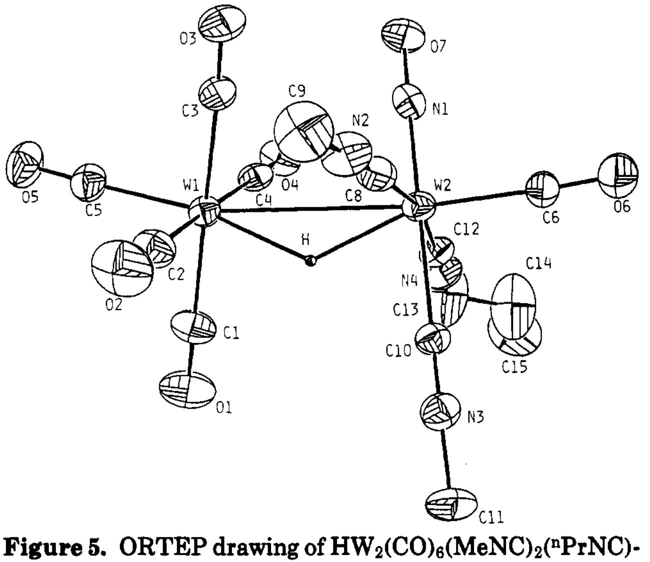

Figure 5. ORTEP drawing of $HW_2(CO)_6(MeNC)_2(^nPrNC)(NO_{eq})$. Thermal ellipsoids are drawn with 50% probability boundaries.

equivalent retrodative π bonding to both π orbitals. The W–C–N and C–N–C′ angles for the isocyanide ligands range from 173 to 180° and from 173 to 179°, respectively. The W–C and C–N distances range from 2.07 to 2.18 Å and from 1.11 to 1.20 Å, respectively.

As more CO ligands in $HW_2(CO)_9(NO)$ are displaced, the interligand repulsive interaction will increase, and longer W–W distances are expected. For instance, $HW_2(CO)_8(PhNC)(NO)$ (**14**) has a shorter W–W distance (3.3848(8) Å) than $HW_2(CO)_7(PhNC)(^iPrNC)(NO)$ (**20**) (3.443(1) Å), and this is also the case for $HW_2(CO)_8(^iPrNC)(NO)$ (**11**) (3.420(1) Å) compared to $HW_2(CO)_7(^iPrNC)_2(NO_{ax})$ (**9**) (3.475 Å). As expected, the W–W distance in $HW_2(CO)_6(MeNC)_2(^nPrNC)(NO_{ax})$ (**20**) (3.441 Å) is longer than that in $HW_2(CO)_7(MeNC)_2(NO_{ax})$ (**3**) (3.389(1) Å). In contrast, contraction of the W–W distance occurs in going from $HW_2(CO)_7(MeNC)_2(NO_{eq})$ (**4**) (3.4800(9) Å) to $HW_2(CO)_6(MeNC)_2(^nPrNC)(NO_{eq})$ (**21**) (3.3953(9) Å), possibly due to the eclipsed conformation of the former.

The spectroscopic properties (Table IV) of the aforementioned new complexes are consistent with their formulation. One ν(CN) stretching is observed for $HW_2(CO)_8(RNC)(NO_{ax})$ (**11**, R = ^{i}Pr; **12**, R = Ph) and $HW_2(CO)_7(PPh_3)(^nPrNC)(NO_{ax})$ (**18**). Two ν(CN) stretchings of similar intensity are found in $HW_2(CO)_7(RNC)_2(NO_{ax})$ (**3**, R = Me; **5**, R = ^{t}Bu; **7**, R = $PhCH_2$; **9**, R = ^{i}Pr; **13**, R = Ph), $HW_2(CO)_7(RNC)_2(NO_{eq})$ (**4**, R = Me; **6**, R = ^{t}Bu; **8**, R = $PhCH_2$; **10**, R = ^{i}Pr), and $HW_2(CO)_7(RNC)(R'NC)(NO_{ax})$ (**15**, R = Ph, R′ = ^{n}Pr), which have two isocyanides cis to each other. $HW_2(CO)_6(PhNC)(^nPrNC)_2(NO_{ax})$ (**16**) has three meridional isocyanides and exhibits three ν(CN) stretchings, whereas only two ν(CN) stretchings are resolved for the meridional isocyanide derivatives

$HW_2(CO)_6(MeNC)_2(^nPrNC)(NO)$ (**20, 21**). As the degree of substitution increases, the enhanced $d\pi \rightarrow p\pi$ backbonding causes a decrease in $\nu(NO_{ax})$. The $\nu(NO_{ax})$ values for the mono-, di-, and trisubstituted (the substituents including phosphines) derivatives of $HW_2(CO)_9(NO)$ are at ca. 1700, 1650, and 1610 cm^{-1}, respectively. Being trans to a strong σ-donor, hydride, the axial NO ligand is expected to have a lower stretching frequency than the equatorial NO ligand which is trans to a π acceptor, RNC or CO. For comparison, $HW_2(CO)_7(RNC)_2(NO_{eq})$ and $HW_2(CO)_6(RNC)_2(R'NC)(NO_{eq})$ have $\nu(NO)$ at about 1685 and 1645 cm^{-1}, respectively.

The ^1H NMR spectra of the hydrides in the complexes are consistent with the presence of a W–H–W linkage:[30] δ-9 to -12 ppm (except for **14**), and two sets of tungsten satellites ($^1J_{W-H}$ = ca. 30–50 Hz). The hydrides for the complexes with an equatorial NO always appear at lower field by ca. 3 ppm than the corresponding complexes with an axial NO. The coupling constant between the hydride and phosphorus atom of $O{=}PPh_3$ in $HW_2(CO)_7(PhNC)(O{=}PPh_3)(NO)$ (**14**) is 1.29 Hz. Selective decoupling of the phosphorus nucleus in $O{=}PPh_3$ simplifies the spectrum of the hydride to a singlet. $^{31}P\{^1H\}$ spectra also indicate that the phosphorus atom of $O{=}PPh_3$ is not directly bonded to the tungsten atom, since no tungsten satellites are observed. The very low field shift of the hydride (δ −7.27 ppm) for **14** is similar to those reported for $HW_2(CO)_7(py)_2(NO_{eq})$ (δ −7.10 ppm)[5] and $HW_2(CO)_7(THF)_2(NO_{eq})$ (δ −5.21 ppm),[6] which contain both a hard σ-donor ligand and NO ligands in the equatorial plane.

Conclusion

The ligand rearrangement of $HW_2(CO)_9(NO)$ is found in its reaction with RNC. On the other hand, substitution of RNC for THF of $HW_2(CO)_7(THF)_2(NO_{eq})$ does not perturb the positions of other ligands. Conversion of coordinated CO, in $HW_2(CO)_9(NO_{ax})$ and its derivatives, to RNC also proceeds without any ligand rearrangement.

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Supplementary Material Available: Listings of all bond distances and angles, anisotropic thermal parameters and isotropic thermal parameters, and positional parameters for calculated hydrogen atoms for complounds **12, 16,** and **21** and listings of crystal data, bond distances and angles, thermal parameters, and positional parameters and ORTEP drawings for **5–8** (29 pages). Ordering information is given on any current masthead page.

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