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# Substitution of phosphine for CO ligand in $HW_2(CO)_9(NO)$. The structures of $HW_2(CO)_8(NO)(\eta^1$-$(\eta^5$-$C_5H_4PPh_2)_2Fe)$, $HW_2(CO)_7(NO)(Ph_2PH)_2$, $HW_2(CO)_7(NO)$-$(\eta^2$-$Ph_2PCH_2PPh_2)$, and $[HW_2(CO)_8(NO)]_2$-$(\mu$-$Ph_2PCH_2CH_2PPh_2)$

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## Abstract

Several binuclear tungsten complexes containing a three-center, two-electron (3c-2e) metal–hydrogen–metal bond, $HW_2(CO)_8(NO)(L)$ (L = $Ph_2PH$ (**1**), $PPh_3$ (**2**), $PCy_3$ (**3**), $\eta^1$ – $(\eta^5$-$C_5H_4PPh_2)_2Fe$ (**4**)), $HW_2(CO)_7(NO)(L')_2$ (L′ = $Ph_2PH$ (**5**), $PPh_3$ (**6**), $Ph_2PCH_2PPh_2/2$ (**7**), $Ph_2PCH_2CH_2PPh_2/2$ (**8**)), $[HW_2(CO)_8(NO)[_2(\mu$-L ~ L) (L ~ L = $Ph_2PCH_2CH_2PPh_2$ (**9**), $(\eta^5$-$C_5H_4PPh_2)_2Fe$ (**10**)), are obtained by treatment of $HW_2(CO)_9(NO)$ with phosphine ligands. X-ray diffraction studies of **4**, **5**, **7**, **9** were carried out to give the data as follows. **4**: $P\bar{1}$, $Z = 2$, $a = 9.602(3)$, $b = 11.467(2)$, $c = 22.824(3)$ Å, $\alpha = 107.1(1)$, $\beta = 76.37(2)$, $\gamma = 109.23(2)°$, $V = 2240.43$ Å$^3$, $R = 0.037$, $R_w = 0.041$. **5**: $P2_1/c$, $Z = 4$, $a = 9.344(2)$, $b = 16.514(5)$, $c = 21.525(9)$ Å, $\beta = 92.52(3)°$, $V = 3318.41$ Å$^3$, $R = 0.028$, $R_w = 0.031$. **7**: $P2_1/n$, $Z = 4$, $a = 16.372(6)$, $b = 12.868(6)$, $c = 16.654(11)$ Å, $\beta = 107.52(4)°$, $V = 3346.01$ Å$^3$, $R = 0.023$, $R_w = 0.032$. **9**: $P\bar{1}$, $Z = 2$, $a = 10.024(6)$, $b = 10.516(2)$, $c = 12.614(1)$ Å, $\alpha = 78.67(1)°$, $\beta = 73.74(2)°$, $\gamma = 81.05(3)°$, $V = 1244.39$ Å$^3$, $R = 0.023$, $R_w = 0.030$.

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## Introduction

Transition-metal hydrides are of fundamental importance, because they are central to several catalytic process and they effect many useful stoichiometric organic reactions [1]. Complexes with three-center, two-electron (3c-2e) metal–hydrogen–metal bonds constitute an important class [2] among transition-metal hydrides of versatile structures [3]. Our interest in bridged binuclear metal complexes [4] led us to investigate the reactions of $HW_2(CO)_9(NO)$ [5] toward various ligands.

Only two reports [6] describe the reactions of $HW_2(CO)_9(NO)$ since its discovery; furthermore, one describes the rupture of the dimer [6a]. Here we describe the synthesis and characterization of several phosphine-substituted derivatives of $HW_2(CO)_9(NO)$. In accord with Bau's observation [6b], we found that these derivatives of $HW_2(CO)_9(NO)$ still retain the W–H–W linkage. Although the positions of the bridging hydride ligands were not directly located from our X-ray diffraction measurements, they were readily inferred by the proton magnetic resonance spectroscopy. We also located precisely the position of the nitrosyl ligands in these complexes.

## Experimental

*Materials and apparatus.* $^1H$ and $^{31}P$ NMR spectra were recorded on Bruker MSL 200 spectrometers. IR spectra were measured with a Perkin–Elmer 880 spectrometer. Elemental analyses were carried out by use of a Perkin–Elmer 2400 CHN Elemental Analyzer.

All preparations were carried out under dry nitrogen. Solvents were dried by standard procedures. All the column chromatography was performed by use of silica gel (230–400 mesh ASTM, Merck) as the stationary phase in columns 35 cm long and 2.5 cm in diameter. $HW_2(CO)_9(NO)$ [5] and $(\eta^5\text{-}C_5H_4PPh_2)_2Fe$ [7] were prepared by published procedures.

Reactions of $HW_2(CO)_9(NO)$ with $Ph_2PH$, $PPh_3$, $PCy_3$, $Ph_2CH_2PPh_2$ (DPPM), $Ph_2PCH_2CH_2PPh_2$ (DPPE), and $(\eta^5\text{-}C_5H_4PPh_2)_2Fe$ (dppf) all follow essentially the same procedure except that only one equivalent of phosphine ligands was used in the cases of DPPM, DPPE, and dppf. Only the reaction of $HW_2(CO)_9(NO)$ with $Ph_2PH$ will be described in more detail.

*Reaction of $HW_2(CO)_9(NO)$ with $Ph_2PH$.* $HW_2(CO)_9(NO)$ (1.0 g, 1.54 mmol) and $Ph_2PH$ (0.54 ml, 3.08 mmol) in 60 ml of $CH_2Cl_2$ was stirred under nitrogen for 48 h and the solvent was removed under vacuum. The crude reaction mixture was dissolved in a minimum volume of $CH_2Cl$ and separated by column chromatography. Three bands were developed with $CH_2Cl_2$/hexane (1 : 4) as eluent: first an orange band, then a yellow band, and finally an unremovable dark orange band. The solvent was removed from the fractions.

$HW_2(CO)_8(NO)(Ph_2PH)$ (186 mg, 15% yield) was isolated from the first band. IR($CH_2Cl_2$, $cm^{-1}$): $\nu$(CO) 2093 (w), 2062 (w), 2014 (s), 1981 (w), 1937 (vs); $\nu$(NO) 1701 (m, br). Anal. Found: C, 30.54; H, 1.60; N, 1.73. $C_{20}H_{12}NO_9PW_2$ calcd.: C, 30.69; H, 1.50; N, 1.73%.

$HW_2(CO)_7(NO)(Ph_2PH)_2$ (521 mg, 35% yield) was isolated from the second band. IR($CH_2Cl_2$, $cm^{-1}$): $\nu$(CO) 2068 (m), 2025 (m), 1968 (s), 1929 (vs); $\nu$(NO) 1676 (m, br). Anal. Found: C, 38.50; H, 2.39; N, 1.06. $C_{31}H_{23}NO_8P_2W_2$ calcd.: C, 38.50; H, 2.40; N, 1.45%.

*Reaction of $HW_2(CO)_9(NO)$ with $PPh_3$.* Column chromatography, gave three bands with $CH_2Cl_2$/hexane (1 : 4) as eluent.

$HW_2(CO)_8(NO)(PPh_3)$ (55% yield) was isolated from the orange, first band. IR($CH_2Cl_2$, $cm^{-1}$): $\nu$(CO) 2093 (w), 2062 (w), 2010 (s), 1977 (w), 1934 (vs); $\nu$(NO) 1707 (m, br). Anal. Found: C, 35.24; H, 1.96; N, 1.62. $C_{26}H_{16}NO_9PW_2$ calcd.:, C, 35.28; H, 1.82; N, 1.58%.

$HW_2(CO)_7(NO)(PPh_3)_2$ (12% yield) was isolated from the yellow second band. IR($CH_2Cl_2$, $cm^{-1}$): $\nu$ (CO) 2068 (m), 2018 (m), 1957 (vs), 1927 (s), 1906 (sh); $\nu$ (NO) 1672 (m, br). Anal. Found: C, 46.48; H, 2.91; N, 1.28. $C_{43}H_{31}NO_8P_2W_2$ calcd.: C, 46.14; H, 2.79; N, 1.25%.

*Reaction of $HW_2(CO)_9(NO)$ with $PCy_3$.* Column chromatography gave two removable bands that were eluted with $CH_2Cl_2$/hexane (1:6). The yellow, first band gave $HW_2(CO)_8(NO)(PCy_3)$ (40% yield). IR($CH_2Cl_2$, $cm^{-1}$) $\nu$ (CO): 2085 (w), 2060 (w), 2000 9s), 1980 (w), 1930 (vs); $\nu$ (NO) 1698 (m, br). Anal. Found: C, 34.53; H, 3.44; N, 1.48. $C_{26}H_{34}NO_9PW_2$ calcd.: C, 34.57; H, 3.79; N, 1.55%. The compound (trace) from the second, an orange-yellow band was not identified.

*Reaction of $HW_2(CO)_9(NO)$ with $Ph_2PCH_2PPh_2$ (DPPM).* From column chromatography, two removable bands were eluted with $CH_2Cl_2$/hexane (1:4). The yellow, first major band remained uncharacterized. $HW_2(CO)_7(NO)(\eta^2\text{-DPPM})$ (17% yield) was isolated from the orange-yellow, second band. IR($CH_2Cl_2$, $cm^{-1}$): $\nu$ (CO) 2067 (m), 2016 (m). 1959 (vs), 1924 (s), 1910 (sh); $\nu$(NO) 1685 (m, br). Anal. Found: C, 39.10; H, 2.14; N, 1.36. $C_{32}H_{23}NO_8P_2W_2$ calcd.: C, 39.25; H, 2.37; N, 2.43%.

*Reaction of $HW_2(CO)_9(NO)$ with $Ph_2PCH_2CH_2PPh_2$ (DPPE).* Two removable bands were eluted with $CH_2Cl_2$/hexane (1:4). The yellow, first band remained uncharacterized. The orange-yellow, second band gave $[HW_2(CO)_9(NO)]_2(\mu\text{-DPPE})$ (7.3% yield). IR($CH_2Cl_2$, $cm^{-1}$): $\nu$ (CO) 2090 (w); 2063 (w), 2013 (s), 1935 (vs); $\nu$ (NO) 1692 (m, br). Anal. Found: C, 30.58; H, 1.70; N, 1.66. $C_{42}H_{26}N_2O_{18}P_2W_4$ calcd.: C, 30.68; H, 1.59; N, 1.70%.

$HW_2(CO)_7(NO)(\eta^2\text{-DPPE})$ (28% yield) was isolated from the yellow, third band. IR($CH_2Cl_2$, $cm^{-1}$): $\nu$ (CO) 2066 (m), 2011 (m), 1956 (vs), 1924 (s), 1904 (sh); $\nu$ (NO) 1680 (m, br). Anal. Found: C, 39.57; H, 2.14; N, 1.32. $C_{33}H_{24}NO_8P_2W_2$ calcd.: C, 39.91; H, 2.54; N, 1.41%.

*Reaction of $HW_2(CO)_9(NO)$ with $(\eta^5\text{-}C_5H_4PPh_2)_2Fe$(dppf).* From column chromatography, four removable bands were eluted with $CH_2Cl_2$/hexane (1:9). The compound (trace) from the pale-yellow, first band remained uncharacterized. The orange-yellow, second band gave $HW_2(CO)_8(NO)(\eta^1\text{-dppf})$ (18% yield). IR($CH_2Cl_2$, $cm^{-1}$): $\nu$ (CO) 2090 (w), 2063 (w), 2010 (s), 1932 (vs); $\nu$ (NO) 1701 (m, br). Anal. Found: C, 42.44; H, 2.40; N, 1.11. $C_{42}H_{29}NO_9P_2FeW_2$ calcd.: C, 42.85; H, 2.48; N, 1.19%. The orange-yellow, third band contained $HW_2(CO)_7(NO)(\eta^2\text{-dppf})$, the formulation of which was based on $^1H$ and $^{31}P$ NMR spectra. However, we could not isolate it pure.

$[HW_2(CO)_8(NO)]_2(\mu\text{-dppf})$ (estimated 10% yield) was isolated from the orange, fourth band. The $^{31}P$ NMR spectra indicated that the complex was contaminated with small amounts of $HW_2(CO)_8(NO)(\eta^1\text{-dppf})$ and other impurities. IR($CH_2Cl_2$, $cm^{-1}$): $\nu$ (CO) 2090 (w), 2063 (w), 2010 (s), 1980 (sh), 1932 (vs); $\nu$ (NO) 1701 (m, br). Anal. Found: C, 34.52; H, 3.21; N, 1.03. $C_{50}H_{30}N_2O_{18}P_2FeW_4$ calcd.: C, 33.36; H, 1.68; N, 1.56%.

*Crystallographic studies.* Crystals of each complex, $HW_2(CO)_8(NO)(\eta^1\text{-dppf})$ (**4**), $HW_2(CO)_7(NO)(Ph_2PH)_2$ (**5**), $HW_2(CO)_7(NO)(\eta^2\text{-DPPM})$ (**7**), and $[HW_2(CO)_8(NO)]_2(\mu\text{-DPPE})$ (**9**), suitable for X-ray diffraction measurements were grown by cooling a concentrated solution of the relevant complex in $CH_2Cl_2$/hexane (1:5) at −5°C for several days. Complex **4** was found to crystallize with one molecule of $CH_2Cl_2$. Crystals were mounted in thin-walled glass capillaries. Diffrac-

*(continued on p. 158)*

Table 1

Crystal data for complexes **4**, **5**, **7**, and **9**.

| | **4**·$CH_2Cl_2$ | **5** | **7** | **9** |
|---|---|---|---|---|
| Formula | $C_{43}H_{31}Cl_2FeNO_9P_2W_2$ | $C_{31}H_{22}NO_8P_2W_2$ | $C_{32}H_{22}NO_8P_2W_2$ | $C_{34}H_{25}NO_9P_2W_2$ |
| Formula weight | 1261.69 | 966.17 | 978.18 | 1021.23 |
| a, Å | 9.602(3) | 9.344(2) | 16.372(6) | 10.024(6) |
| $b$, Å | 11.467(2) | 16.514(5) | 12.868(6) | 10.516(2) |
| $c$, Å | 22.824(3) | 21.525(9) | 16.654(11) | 12.614(1) |
| $\alpha$, deg | 107.15(1) | 90 | 90 | 78.67(1) |
| $\beta$, deg | 76.37(2) | 92.52(3) | 107.52(4) | 73.74(2) |
| $\gamma$, deg | 109.23(2) | 90 | 90 | 81.05(3) |
| Crystal system | triclinic | monoclinic monoclinic | triclinic | |
| Space group | $P\bar{1}$ | $P2_1/c$ | $P2_1/n$ | $P\bar{1}$ |
| $Z$ | 2 | 4 | 4 | 2 |
| $V$, Å$^3$ | 2240.43 | 3318.41 | 3346.01 | 1244.39 |
| $D$calc, g/cm$^3$ | 1.87 | 1.93 | 1.94 | 2.73 |
| Cryst size, mm | 0.46×0.20×0.13 | 0.47×0.63×0.75 | 0.34×0.38×0.43 | 0.50×0.17×0.13 |
| Radiation | Mo-$K_\alpha$ | Mo-$K_\alpha$ | Mo-$K_\alpha$ | Mo-$K_\alpha$ |
| $\mu$ (cm$^{-1}$) | 58.0 | 72.2 | 71.6 | 96.4 |
| Transmission factors (max; min) | 0.999650; 0.624710 | 0.997470; 0.622830 | 0.999360; 0.489800 | 0.997230; 0.577930 |
| $2\theta$ range | 0–50 | 0–50 | 0–50 | 0–50 |
| Octants | $\pm h, +k, \pm l$<br>$-11 \sim 10, 0 \sim 13, -27 \sim 25$ | $\pm h, +k, +l$<br>$-11 \sim 11, 0 \sim 19, 0 \sim 25$ | $\pm h, +k, +l$<br>$-19 \sim 18, 0 \sim 15, 0 \sim 19$ | $\pm h, +k, \pm l$<br>$-11 \sim 11, 0 \sim 12, -14 \sim 14$ |
| No. of unique reflections | 7862 | 5832 | 5883 | 4380 |
| Reflections with $I > 2.5\sigma(T)$ | 5549 | 4428 | 4839 | 3684 |
| No. of variables | 542 | 398 | 407 | 308 |
| $R$; $R_w$ | 0.037; 0.041 | 0.028; 0.031 | 0.023; 0.032 | 0.023; 0.030 |
| GOF | 1.710 | 1.61 | 1.620 | 1.287 |
| max $\Delta/\sigma$ | 0.421 | 0.005 | 0.018 | 0.004 |

Table 2

Positional parameters and $B_{iso}$ for the atoms in complexes **4**, **5**, **7**, and **9**.

*Complex **4***

| Atom | $x$ | $y$ | $z$ | $B_{iso}$ |
|---|---|---|---|---|
| W1 | 0.29662(5) | 0.46174(4) | 0.12930(2) | 3.96(2) |
| W2 | 0.04675(4) | 0.62537(3) | 0.14909(2) | 3.23(2) |
| Fe | 0.10939(14) | 0.99508(12) | 0.32986(5) | 3.40(7) |
| P1 | 0.19615(25) | 0.86001(20) | 0.17127(10) | 2.89(10) |
| P2 | 0.28276(32) | 1.24101(25) | 0.44443(12) | 4.59(14) |
| N | −0.1117(9) | 0.6780(8) | 0.1451(4) | 4.9(5) |
| O1 | 0.0450(10) | 0.2834(8) | 0.2056(4) | 8.2(6) |
| O2 | 0.4740(14) | 0.5727(9) | 0.2426(5) | 11.0(8) |
| O3 | 0.1427(9) | 0.3097(7) | 0.0094(3) | 6.2(5) |
| O4 | 0.5251(10) | 0.6579(9) | 0.0549(4) | 7.8(5) |
| O5 | 0.4910(10) | 0.2710(8) | 0.0863(5) | 8.7(6) |
| O6 | 0.1646(8) | 0.5973(6) | 0.0039(3) | 5.6(4) |
| O7 | −0.1578(9) | 0.3422(7) | 0.1203(4) | 6.6(5) |
| O8 | −0.0596(10) | 0.6097(7) | 0.2896(3) | 7.5(5) |
| O9 | −0.2124(9) | 0.7090(9) | 0.1414(4) | 7.9(6) |
| C1 | 0.1414(15) | 0.3501(10) | 0.1787(5) | 5.8(7) |
| C2 | 0.4101(15) | 0.5374(11) | 0.2025(5) | 6.4(8) |
| C3 | 0.1959(12) | 0.3661(9) | 0.0513(5) | 4.7(6) |
| C4 | 0.4445(13) | 0.5854(11) | 0.0823(5) | 5.4(7) |
| C5 | 0.4182(13) | 0.3390(11) | 0.1013(5) | 6.0(7) |
| C6 | 0.1254(11) | 0.6109(8) | 0.0560(5) | 4.1(5) |
| C7 | −0.0763(12) | 0.4410(10) | 0.1296(5) | 4.7(6) |
| C8 | −0.0180(11) | 0.6205(9) | 0.2398(5) | 4.8(5) |
| C11 | 0.2002(9) | 0.9240(7) | 0.1066(4) | 3.1(4) |
| C12 | 0.2968(10) | 0.8985(8) | 0.0519(4) | 3.7(5) |
| C13 | 0.3002(11) | 0.9441(9) | 0.0026(4) | 4.4(5) |
| C14 | 0.2096(13) | 1.0176(10) | 0.0062(5) | 5.0(6) |
| C15 | 0.1124(12) | 1.0453(9) | 0.0606(5) | 4.8(6) |
| C16 | 0.1075(10) | 0.9974(8) | 0.1107(4) | 3.7(5) |
| C21 | 0.3929(9) | 0.9150(7) | 0.1822(4) | 3.1(4) |
| C22 | 0.4443(10) | 0.8496(8) | 0.2110(4) | 3.7(5) |
| C23 | 0.5902(11) | 0.8948(10) | 0.2228(5) | 4.5(6) |
| C24 | 0.6822(11) | 1.0037(10) | 0.2055(5) | 4.9(6) |
| C25 | 0.6342(11) | 1.0680(9) | 0.1767(5) | 4.9(5) |
| C26 | 0.4873(10) | 1.0246(9) | 0.1647(4) | 3.9(5) |
| C31 | 0.0692(12) | 1.1412(9) | 0.3072(4) | 4.5(5) |
| C32 | −0.0625(11) | 1.0413(10) | 0.3122(4) | 4.6(6) |
| C33 | −0.0393(10) | 0.9273(8) | 0.2685(4) | 3.6(5) |
| C34 | 0.1101(10) | 0.9598(8) | 0.2366(4) | 3.3(4) |
| C35 | 0.1765(11) | 1.0912(8) | 0.2612(4) | 3.8(5) |
| C41 | 0.1873(11) | 0.8670(8) | 0.3507(4) | 4.0(5) |
| C42 | 0.2896(10) | 0.9912(9) | 0.3617(4) | 3.8(5) |
| C43 | 0.2122(10) | 1.0743(9) | 0.4071(4) | 4.0(5) |
| C44 | 0.0627(11) | 1.0002(10) | 0.4224(4) | 4.3(5) |
| C45 | 0.0498(11) | 0.8748(9) | 0.3882(4) | 4.4(5) |
| C51 | 0.3344(11) | 1.2243(9) | 0.5132(4) | 4.3(5) |
| C52 | 0.3509(11) | 1.1129(10) | 0.5187(4) | 4.9(6) |
| C53 | 0.3920(13) | 1.1039(12) | 0.5714(5) | 5.9(7) |
| C54 | 0.4165(15) | 1.2097(14) | 0.6191(6) | 7.0(8) |
| C55 | 0.4013(15) | 1.3215(13) | 0.6156(5) | 7.3(8) |
| C56 | 0.3592(13) | 1.3291(11) | 0.5632(5) | 6.4(7) |
| C61 | 0.4636(12) | 1.2812(9) | 0.3953(5) | 5.1(6) |
| C62 | 0.4681(15) | 1.3233(10) | 0.3437(5) | 6.5(7) |

*(continued)*

Table 2 (continued)

| *Complex 4* | | | | |
|---|---|---|---|---|
| Atom | $x$ | $y$ | $z$ | $B_{\text{iso}}$ |
| C63 | 0.5954(21) | 1.3473(14) | 0.3027(7) | 8.9(10) |
| C64 | 0.7255(20) | 1.3353(13) | 0.3135(9) | 9.7(11) |
| C65 | 0.7250(16) | 1.2980(13) | 0.3652(9) | 9.5(11) |
| C66 | 0.5930(14) | 1.2693(11) | 0.4060(6) | 6.8(8) |
| Cl1 | 0.1496(9) | 0.5238(6) | 0.3716(4) | 20.6(7) |
| Cl2 | 0.1123(11) | 0.6943(9) | 0.4883(4) | 24.7(10) |
| C70 | 0.2047(21) | 0.5937(32) | 0.4448(12) | 20.5(27) |
| *Complex 5* | | | | |
| W1 | 0.74865(4) | 0.14795(2) | 0.97846(1) | 4.033(15) |
| W2 | 0.78224(3) | 0.24542(2) | 0.83979(1) | 3.354(12) |
| P1 | 0.73813(22) | 0.11853(12) | 0.77683(9) | 3.80(8) |
| P2 | 0.51649(21) | 0.27466911) | 0.82932(9) | 3.43(8) |
| N | 0.8393(7) | 0.3139(4) | 0.7783(3) | 7.3(4) |
| O1 | 0.8924(10) | −0.0114(5) | 0.9293(4) | 7.8(5) |
| O2 | 1.0631(8) | 0.2130(5) | 1.0043(4) | 6.4(4) |
| O3 | 0.4311(8) | 0.0801(5) | 0.9672(4) | 7.4(5) |
| O4 | 0.6309(9) | 0.3077(5) | 1.0410(3) | 6.4(4) |
| O5 | 0.7858(10) | 0.0718(7) | 1.1106(3) | 9.6(6) |
| O6 | 0.8359(8) | 0.3854(4) | 0.9379(3) | 5.7(3) |
| O7 | 1.0974(7) | 0.1806(5) | 0.8586(3) | 5.0(3) |
| O8 | 0.8815(7) | 0.3582(4) | 0.7401(3) | 5.6(3) |
| C1 | 0.8377(11) | 0.0449(6) | 0.9453(4) | 6.1(5) |
| C2 | 0.9528(11) | 0.1920(5) | 0.9935(4) | 5.4(5) |
| C3 | 0.5422(12) | 0.1026(6) | 0.9695(4) | 6.3(5) |
| C4 | 0.6692(10) | 0.2530(6) | 1.0171(4) | 5.4(5) |
| C5 | 0.7715(11) | 0.0994(7) | 1.0634(5) | 7.2(6) |
| C6 | 0.8136(9) | 0.3353(5) | 0.9044(4) | 4.9(4) |
| C7 | 0.9867(10) | 0.2030(5) | 0.8537(4) | 4.7(4) |
| C11 | 0.5563(8) | 0.0929(4) | 0.7508(3) | 3.8(3) |
| C12 | 0.4686(11) | 0.0508(5) | 0.7897(4) | 5.7(5) |
| C13 | 0.3292(12) | 0.0366(7) | 0.7713(6) | 7.5(6) |
| C14 | 0.2745(11) | 0.0632(7) | 0.7157(6) | 6.8(6) |
| C15 | 0.3593(10) | 0.1053(6) | 0.6773(4) | 5.7(5) |
| C16 | 0.5005(8) | 0.1201(5) | 0.6946(4) | 4.3(3) |
| C21 | 0.8400(8) | 0.0984(6) | 0.7093(4) | 4.8(4) |
| C22 | 0.8893(12) | 0.1598(7) | 0.6735(4) | 7.2(5) |
| C23 | 0.9607(14) | 0.1437(10) | 0.6193(5) | 9.3(8) |
| C24 | 0.9767(14) | 0.0669(12) | 0.6006(5) | 9.5(10) |
| C25 | 0.9281(12) | 0.0032(10) | 0.6372(7) | 10.2(8) |
| C26 | 0.8606(10) | 0.0191(7) | 0.6917(5) | 7.3(5) |
| C31 | 0.4387(7) | 0.3403(4) | 0.8857(3) | 3.5(3) |
| C32 | 0.3526(8) | 0.3098 | 0.9310(4) | 4.6(4) |
| C33 | 0.2975(10) | 0.3615(7) | 0.9733(4) | 6.2(5) |
| C34 | 0.3272(10) | 0.4417(7) | 0.9737(4) | 6.2(5) |
| C35 | 0.4114(10) | 0.4728(5) | 0.9287(4) | 5.7(4) |
| C36 | 0.4694(9) | 0.4220(5) | 0.8856(4) | 4.5(4) |
| C41 | 0.4336(8) | 0.3070(4) | 0.7551(3) | 3.8(3) |
| C42 | 0.5144(9) | 0.3267(6) | 0.7064(4) | 5.5(4) |
| C43 | 0.4493(11) | 0.3452(7) | 0.6481(4) | 6.9(6) |
| C44 | 0.3022(12) | 0.3457(6) | 0.6414(5) | 6.5(5) |
| C45 | 0.2212(11) | 0.3300(8) | 0.6907(5) | 8.0(7) |
| C46 | 0.2876(10) | 0.3092(7) | 0.7475(4) | 6.3(5) |

Table 2 (continued)

| Atom | $x$ | $y$ | $z$ | $B_{\mathrm{iso}}$ |
|---|---|---|---|---|
| *Complex 7* | | | | |
| W1 | 0.19282(2) | 0.35041(2) | −0.09952(2) | 3.18(1) |
| W2 | 0.21629(2) | 0.17885(2) | 0.06615(2) | 2.98(1) |
| P1 | 0.20330(10) | 0.01932(12) | −0.02619(10) | 2.98(6) |
| P2 | 0.35933(10) | 0.09823(12) | 0.07045(10) | 3.13(7) |
| N | 0.2116(4) | 0.1223(4) | 0.1640(3) | 3.8(2) |
| O1 | 0.0147(4) | 0.2481(5) | −0.2008(4) | 6.8(3) |
| O2 | 0.0865(4) | 0.4704(5) | 0.0011(4) | 6.5(3) |
| O3 | 0.2965(4) | 0.2519(5) | −0.2140(4) | 7.0(3) |
| O4 | 0.3531(4) | 0.4815(4) | 0.0036(4) | 6.5(3) |
| O5 | 0.1556(4) | 0.5326(4) | −0.2286(3) | 6.1(3) |
| O6 | 0.2785(4) | 0.3912(4) | 0.1600(3) | 6.7(3) |
| O7 | 0.0194(4) | 0.2269(5) | 0.0190(4) | 7.1(4) |
| O8 | 0.2088(4) | 0.0884(4) | 0.2298(3) | 5.6(3) |
| C1 | 0.0804(5) | 0.2792(5) | −0.1653(5) | 4.5(4) |
| C2 | 0.1255(4) | 0.4248(6) | −0.0323(4) | 4.2(3) |
| C3 | 0.2587(4) | 0.2835(6) | −0.1726(4) | 4.3(3) |
| C4 | 0.2973(5) | 0.4315(6) | −0.0324(4) | 4.3(3) |
| C5 | 0.1668(4) | 0.4658(5) | −0.1811(4) | 4.0(3) |
| C6 | 0.2557(5) | 0.3149(5) | 0.1250(4) | 4.2(3) |
| C7 | 0.0908(5) | 0.2132(6) | 0.0354(5) | 4.5(4) |
| C8 | 0.3141(4) | 0.0297(5) | −0.0299(4) | 3.2(3) |
| C11 | 0.1327(4) | 0.0131(5) | −0.1334(4) | 3.6(3) |
| C12 | 0.1621(5) | 0.0213(6) | −0.2028(4) | 4.7(4) |
| C13 | 0.1043(7) | 0.0172(8) | −0.2824(5) | 6.6(5) |
| C14 | 0.0186(7) | 0.0034(7) | −0.2936(5) | 6.5(5) |
| C15 | −0.0104(5) | −0.0041(8) | −0.2245(6) | 6.7(5) |
| C16 | 0.0460(5) | 0.0000(7) | −0.1445(5) | 5.4(4) |
| C21 | 0.1953(4) | −0.1097(5) | 0.0137(4) | 3.4(3) |
| C22 | 0.1922(5) | −0.1959(6) | −0.0369(5) | 4.6(4) |
| C23 | 0.1914(6) | −0.2938(6) | −0.0046(5) | 5.6(4) |
| C24 | 0.1950(6) | −0.3103(6) | 0.0785(5) | 6.0(5) |
| C25 | 0.1977(7) | −0.2261(7) | 0.1267(5) | 7.4(6) |
| C26 | 0.1966(6) | −0.1262(6) | 0.0959(5) | 6.1(5) |
| C31 | 0.3984(4) | −0.0017(5) | 0.1496(4) | 3.8(3) |
| C32 | 0.4028(5) | 0.0218(7) | 0.2330(5) | 5.5(4) |
| C33 | 0.4333(6) | −0.0546(11) | 0.2942(5) | 7.6(6) |
| C34 | 0.4620(8) | −0.1475(10) | 0.2733(8) | 8.7(7) |
| C35 | 0.4605(8) | −0.1681(7) | 0.1945(7) | 8.2(6) |
| C36 | 0.4286(6) | 0.0961(7) | 0.1315(5) | 6.0(4) |
| C41 | 0.4549(4) | 0.1656(5) | 0.0645(4) | 3.5(3) |
| C42 | 0.4482(5) | 0.2458(6) | 0.0082(6) | 5.8(4) |
| C43 | 0.5187(6) | 0.3000(7) | 0.0039(7) | 6.7(5) |
| C44 | 0.5970(5) | 0.2777(6) | 0.0582(6) | 5.7(5) |
| C45 | 0.6063(4) | 0.1986(7) | 0.1146(5) | 5.0(4) |
| C46 | 0.5355(4) | 0.1414(6) | 0.1184(4) | 4.1(3) |
| *Complex 9* | | | | |
| W1 | 0.39775(2) | 0.20640(2) | 0.16900(2) | 3.21(1) |
| W2 | 0.06853(2) | 0.35667(2) | 0.25208(2) | 2.80(1) |
| P | −0.05697(14) | 0.16483(12) | 0.36966(11) | 2.41(5) |
| N | −0.0898(6) | 0.4664(5) | 0.2867(5) | 4.5(3) |
| O4 | 0.4833(7) | 0.4600(6) | 0.2191(6) | 8.3(4) |
| O3 | 0.4216(6) | 0.0630(7) | 0.4087(5) | 7.5(4) |
| O2 | 0.3615(8) | 0.3250(7) | −0.0734(5) | 8.9(5) |

*(continued)*

Table 2 (continued)

*Complex 9*

| Atom | $x$ | $y$ | $z$ | $B_{iso}$ |
|---|---|---|---|---|
| O1 | 0.3739(8) | −0.0719(6) | 0.1212(5) | 8.1(4) |
| O5 | 0.7211(6) | 0.1502(7) | 0.0752(5) | 7.3(3) |
| O8 | 0.1640(7) | 0.3879(7) | 0.4663(5) | 8.2(4) |
| O6 | 0.2311(6) | 0.5952(5) | 0.1103(6) | 7.7(4) |
| O7 | −0.0028(7) | 0.3185(7) | 0.0307(5) | 7.7(4) |
| O9 | −0.1930(6) | 0.5368(5) | 0.3073(6) | 7.1(3) |
| C4 | 0.4444(8) | 0.3717(7) | 0.2015(7) | 5.4(4) |
| C3 | 0.4103(6) | 0.1175(7) | 0.3232(6) | 4.5(3) |
| C2 | 0.3748(8) | 0.2867(8) | 0.0123(6) | 5.4(4) |
| C1 | 0.3774(8) | 0.0299(7) | 0.1395(6) | 4.9(3) |
| C5 | 0.6030(8) | 0.1690(7) | 0.1088(6) | 5.093) |
| C8 | 0.1300(8) | 0.3780(6) | 0.3906(6) | 4.6(3) |
| C6 | 0.1759(8) | 0.5071(6) | 0.1605(6) | 4.7(3) |
| C7 | 0.0213(8) | 0.3294(7) | 0.1087(6) | 4.693) |
| C10 | 0.0393(5) | 0.0564(5) | 0.4629(5) | 2.7(2) |
| C11 | −0.0990(5) | 0.0465(5) | 0.2983(4) | 2.6(2) |
| C12 | −0.2214(6) | −0.0120(6) | 0.3379(5) | 3.4(3) |
| C13 | −0.2408(8) | −0.1102(7) | 0.2850(6) | 4.6(3) |
| C14 | −0.1403(9) | −0.1477(7) | 0.1958(6) | 5.4(4) |
| C15 | −0.0186(8) | −0.0893(6) | 0.1548(6) | 4.9(3) |
| C16 | 0.0023(7) | 0.0093(6) | 0.2057(5) | 3.8(3) |
| C21 | −0.2186(6) | 0.2244(5) | 0.4631(5) | 2.9(2) |
| C22 | −0.2212(7) | 0.2371(5) | 0.5717(5) | 3.8(3) |
| C23 | −0.3420(8) | 0.2919(7) | 0.6389(6) | 4.9(3) |
| C24 | −0.4566(8) | 0.3336(7) | 0.5992(7) | 5.1(4) |
| C25 | −0.4562(7) | 0.3240(7) | 0.4925(8) | 5.5(4) |
| C26 | −0.3356(6) | 0.2691(6) | 0.4231(6) | 4.0(3) |

tion measurements were made on an Enraf–Nonius CAD-4 diffractometer by use of graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda = 0.7107$ Å) in the $\theta$–$2\theta$ scan mode. Unit cells were determined from 25 centered reflections in the suitable $2\theta$ range. Other relevant experimental details are listed in Table 1. Absorption corrections based on the psi scans of three reflections were applied to all data. All the data were processed on a PDP 11 and a VAX 780 by the NRCC SDP program [8]. The coordinates of the tungsten atoms were obtained from Patterson syntheses. The coordinates of all the remaining atoms except the bridging hydrogen atoms were obtained from a series of structure factor calculations and Fourier syntheses. The structures were refined by minimizing $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F_o)^2$ was calculated from the counting statistics. The atomic scattering factors $f_o$ and anomalous dispersion terms $f'$, $f''$ were taken from ref. 9. All the nonhydrogen atoms were refined anisotropically. The final positional parameters for the atoms in **4**, **5**, **7**, and **9**, are listed in Table 2. Selected interatomic distances and bond angles are listed in Table 3.

*Supplementary material available:* Comprehensive listings of bond lengths and angles for **4** (Table S1A, 3 pages), **5** (Table S1B, 2 pages), **7** (Table S1C, 3 pages) and **9** (Table S1D, 2 pages); anisotropic (non-hydrogen atoms) and isotropic (hydrogen atoms) thermal parameters for **4** (Table S2A, 2 pages), **5** (Table S2B, 2 pages), **7** (Table S2C, 2 pages), **9**, (Table S2D, 1 page); observed and calculated

Table 3

Selected bond distances (Å) and angles ( ° ) for complexes **4**, **5**, **7**, and **9**.

| | **4** | **5** | **7** | **9** |
|---|---|---|---|---|
| W(1)–W(2) | 3.382(1) | 3.418(1) | 3.464(2) | 3.403(2) |
| W(1)–C(1) | 1.98(1) | 2.04(1) | 2.053(8) | 2.015(8) |
| W(1)–C(2) | 2.03(1) | 2.06(1) | 2.030(7) | 2.051(7) |
| W(1)–C(3) | 2.07(1) | 2.07(1) | 2.044(7) | 2.015(7) |
| W(1)–C(4) | 2.01(1) | 2.08(1) | 2.028(8) | 2.012(8) |
| W(1)–C(5) | 1.99(1) | 2.00(1) | 1.970(7) | 1.989(7) |
| W(2)–C(6) | 2.06(1) | 2.047(8) | 2.016(7) | 2.027(7) |
| W(2)–C(7) | 2.03(1) | 2.044(9) | 2.012(8) | 2.074(7) |
| W(2)–C(8) | 2.03(1) | | | 2.069(7) |
| W(2)–P(1) | 2.559(2) | 2.520(2) | 2.535(2) | |
| W(2)–P(2) | | 2.530(2) | 2.542(2) | |
| W(2)–P | | | | 2.534(2) |
| W(2)–N | 1.840(9) | 1.839(7) | 1.808(5) | 1.812(5) |
| C(1)–O(1) | 1.17(2) | 1.12(1) | 1.13(1) | 1.146(9) |
| C(2)–O(2) | 1.12(2) | 1.12(2) | 1.130(9) | 1.114(9) |
| C(3)–O(3) | 1.11(1) | 1.10(1) | 1.131(9) | 1.144(9) |
| C(4)–O(4) | 1.16(2) | 1.11(1) | 1.132(9) | 1.14(1) |
| C(5)–O(5) | 1.14(1) | 1.12(1) | 1.146(8) | 1.140(9) |
| C(6)–O(6) | 1.14(1) | 1.11(1) | 1.145(9) | 1.140(8) |
| C(7)–O(7) | 1.14(1) | 1.10(1) | 1.131(9) | 1.107(9) |
| C(8)–O(8) | 1.14(1) | | | 1.127(9) |
| N–O(8) | | 1.18(1) | 1.192(7) | |
| N–O(9) | 1.16(1) | | | 1.171(7) |
| C(10)–C(10)a | | | | 1.53(1) |
| W(1)–C(1)–O(1) | 176(1) | 176.4(8) | 173.8(6) | 176.1(7) |
| W(1)–C(2)–O(2) | 176(1) | 176.1(8) | 175.8(6) | 176.9(8) |
| W(1)–C(3)–O(3) | 176.9(8) | 177(1) | 176.1(7) | 177.0(6) |
| W(1)–C(4)–O(4) | 177(1) | 175.7(8) | 176.3(6) | 173.6(7) |
| W(1)–C(5)–O(5) | 178(1) | 179(1) | 176.8(6) | 178.3(7) |
| W(2)–C(6)–O(6) | 176.8(7) | 176.7(8) | 178.6(6) | 177.0(6) |
| W(2)–C(7)–O(7) | 173.0(9) | 177.1(7) | 176.2(7) | 177.9(6) |
| W(2)–C(8)–O(8) | | | | 179.1(6) |
| W(2)–N–O(8) | | 177.2(6) | 177.7(5) | |
| W(2)–N–O(9) | 178.4(8) | | | 178.6(6) |
| C(1)–W(1)–C(2) | 88.9(5) | 87.7(4) | 87.5(3) | 89.3(3) |
| C(1)–W(1)–C(3) | 90.7(4) | 93.4(4) | 92.5(3) | 87.0(3) |
| C(1)–W(1)–C(4) | 175.3(4) | 176.0(3) | 174.7(3) | 172.0(3) |
| C(1)–W(1)–C(5) | 91.4(5) | 87.5(4) | 89.7(3) | 87.9(3) |
| C(2)–W(1)–C(3) | 172.3(4) | 176.3(4) | 176.2(3) | 175.6(3) |
| C(2)–W(1)–C(4) | 91.0(5) | 89.3(4) | 87.8(3) | 94.8(3) |
| C(2)–W(1)–C(5) | 85.6(5) | 86.4(4) | 89.1(3) | 91.2(3) |
| C(3)–W(1)–C(4) | 90.1(4) | 89.5(4) | 92.1(3) | 89.2(3) |
| C(3)–W(1)–C(5) | 86.7(4) | 90.1(4) | 87.1(3) | 91.1(3) |
| C(4)–W(1)–C(5) | 93.2(5) | 89.7(4) | 87.9(3) | 85.1(3) |
| C(6)–W(2)–C(7) | 89.6(4) | 92.5(3) | 94.9(3) | 89.0(3) |
| C(6)–W(2)–C(8) | 172.1(4) | | | 89.9(3) |
| C(7)–W(2)–C(8) | 86.5(4) | | | 175.9(3) |
| C(6)–W(2)–N | 92.6(4) | 90.3(3) | 90.3(2) | 91.0(3) |
| C(7)–W(2)–N | 90.8(4) | 91.0(3) | 90.0(3) | 91.1(3) |
| C(8)–W(2)–N | 94.3(4) | | | 92.8(3) |
| C(6)–W(2)–P(1) | 89.4(2) | 169.7(3) | 162.7(2) | |
| C(6)–W(2)–P(2) | | 91.9(2) | 100.6(2) | |
| C(6)–W(2)–P | | | | 177.6(2) |

Table 3 (continued)

| | **4** | **5** | **7** | **9** |
|---|---|---|---|---|
| C(7)–W(2)–P(1) | 177.8(3) | 85.6(2) | 97.5(2) | |
| C(7)–W(2)–P(2) | | 170.3(3) | 163.4(2) | |
| C(7)–W(2)–P | | | | 92.5(2) |
| C(8)–W(2)–P | | | | 88.5(2) |
| N–W(2)–P(1) | 87.2(3) | 99.8(2) | 101.7(2) | |
| N–W(2)–P(2) | | 97.6(2) | 95.7(2) | |
| N–W(2)–P | | | | 90.8(2) |
| P(1)–C(8)–P(2) | | | 97.8(3) | |

structure factors for **4** (Table S3A, 51 pages), **5**, (Table S3B, 39 pages), **7** (Table S3C, 40 pages), **9**, (Table S3D, 29 pages), are available from the authors.

## Results and discussion

The complexes, $HW_2(CO)_8(NO)(L)$ (L = $Ph_2PH$ (1), $PPh_3$ (2), $PCy_3$ (3), $\eta^1$-($\eta^5$-$C_5H_4PPh_2)_2Fe$ (**4**)), $HW_2(CO)_7(NO)(L')_2$ (L' = $Ph_2PH$ (5), $PPh_3$ (6), $Ph_2PCH_2PPh_2/2$ (7), $Ph_2PCH_2CH_2PPh_2/2$ (**8**)), $[HW_2(CO)_8(NO)]_2(\mu$-L ~ L) (L ~ L = $Ph_2PCH_2CH_2PPh_2$ (**9**), ($\eta^5$-$C_5H_4PPh_2)_2Fe$ (**10**)), were obtained from the reactions of $HW_2(CO)_9(NO)$ with appropriate phosphines. The spectroscopic data together with single crystal X-ray diffraction studies for **4**, **5**, **7**, **9** have revealed several novel structures.

*Crystal structure of* $HW_2(CO)_8(NO)(\eta^1$-*dppf*) *(4)*, $HW_2(CO)_9(NO)(Ph_2PH)_2$ *(5)*, $HW_2(CO)_7(NO)(\eta^2$-*DPPM*) *(7), and* $[HW_2(CO)_8(NO)]_2(\mu$-*DPPE*) *(9)*. The ORTEP drawings of the complexes **4**, **5**, **7**, and **9** are shown in Figs. 1, 2, 3, and 4, respectively. Important interatomic distances and angles are listed in Table 3. The $^1H$ NMR spectra (vide infra) are consistent with the existence of a three-center, two-electron (3c-2e) W–H–W linkage in these complexes. The following structural data provide additional supporting evidence.

Some of the structural features of the complexes studied are shared by $HW_2(CO)_8(NO)(P(OCH_3)_3)$ (**11**) [6b]. Firstly, the steric congestion of phosphine ligands causes the metal-metal distances (**4**, 3.382 (1) Å; **5**, 3.418(1) Å; **7**, 3.464(2) Å; **9**, 3.403(2) Å; **11**, 3.381(2) Å) to be somewhat longer than that in $HW_2(CO)_9(NO)$ (3.329(1) Å) [5]. In comparison, the unsupported W–W single bond in $Cp_2W_2(CO)_6$ is 3.222(1) Å [10]. Secondly, the two tungsten atoms with W–H–W linkage reside in a roughly octahedral environment, with the nitrosyl ligand occupying the axial position on the phosphine-substituted tungsten. The overall structure in these complexes is also bent; thus the equatorial groups are staggered instead of being eclipsed (Fig. 5). A unique feature of complex **9** is the existence of an inversion center which renders the two phosphine groups magnetically equivalent (vide infra). It is noteworthy that the packing disorder found in $HW_2(CO)_9(NO)$ [5] is not encountered in these complexes and so the NO ligand can be located precisely.

The nitrosyl (**4**, 178.4(8)°, **5**, 177.2(6)°; **7**, 177.7(4)°; **9**, 178.6(6)°) and carbonyl (**4**, 176(1)°; **5**, 176.7 (9)°; **7**, 176 (1)°; **9**, 177 (2)°) are linearly coordinated to W. Since $NO^+$ is a better $d\pi \rightarrow p\pi^*$ acceptor ligand than CO, the W–N distances (**4**, 1.840(9) Å; **5**, 1.839(7) Å; **7**, 1.807(5) Å; **9**, 1.812(5) Å) are shorter than the average

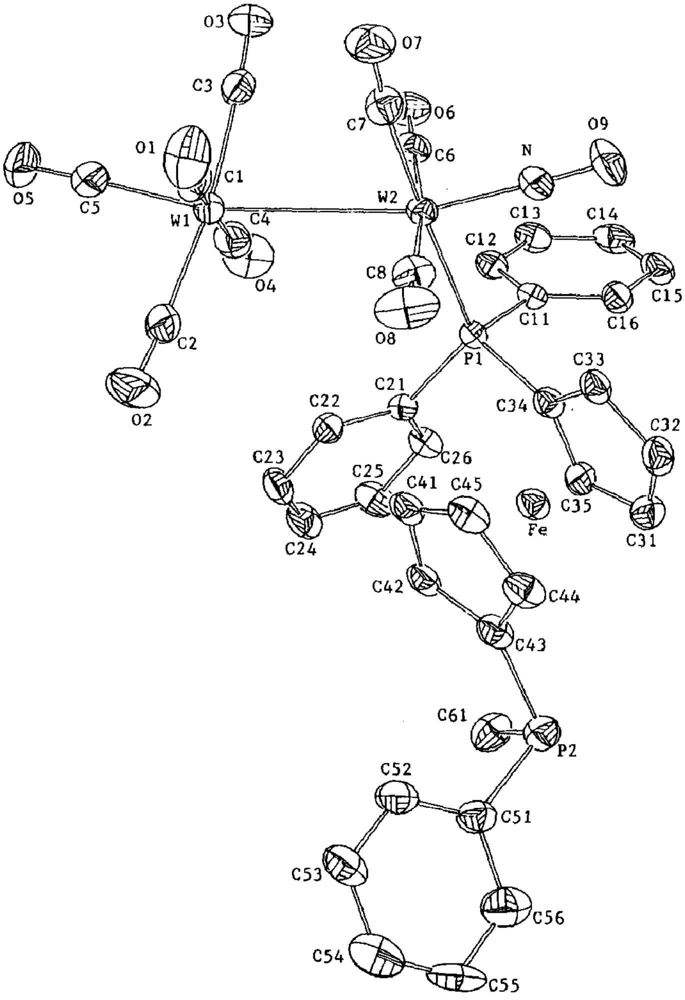

Fig. 1. ORTEP drawing of $HW_2(CO)_8(NO)(\eta^1\text{-dppf})\cdot CH_2Cl_2$. The $CH_2Cl_2$ molecule is omitted and one of the phenyl groups is represented only by its *ipso* carbon atom for clarity. Thermal ellipsoids are drawn with 30% probability boundaries.

W–C distances (**4**, 2.02(3) Å; **5**, 2.05(2) Å; **7**, 2.02(2) Å; **9**, 2.03(4) Å) by about 0.2 Å. These distances are similar to those found for *trans,trans*-$W[\eta^1\text{-OPO(OH)}_2](CO)_2(NO)(PPh_3)_2$ (W–N = 1.793 (13) Å; W–C = 2.077(15), 2.06(2) Å) [11], *trans*-$W(\eta^2\text{-}O_2CCH_3)(CO)(NO)(PPh_3)_2$ (W–N = 1.836(7) Å; W–C = 1.914(8) Å) [11], and *mer*-$W(\eta^1\text{-FSbF}_5)(CO)_3(NO)(PMe_2Ph)$ (W–N = 1.80(2) Å; W–C = 2.09(2), 2.09(2), 2.05(2) Å) [12]. Another notable feature in these complexes is that the carbonyl ligand in the axial position of "$W(CO)_5$" unit, i.e., C(5)–O(5), has a significantly shorter metal–carbon bond length (**4**, 1.99(1) Å; **5**, 2.00(1) Å; **7**, 1.970(7) Å; **9**, 1.989(7) Å) than the average of the remaining carbonyls (**4**, 2.03(3) A; **5**, 2.06(2) Å; **7**, 2.03(2) Å; **9**, 2.04(2) Å).

That substitution occurs only at the metal which is bonded to the NO group is not attributable to steric effects (vide infra). Of the coordination sites in $HW_2(CO)_9(NO)$ (Fig. 6), the phosphorus atoms prefer the the exo positions 9 (in complexes **5**, **7**, **9**, and $HW_2(CO)_8(NO)(P(OCH_3)_3)$ [6b]) and/or 8 (in complexes **4**,

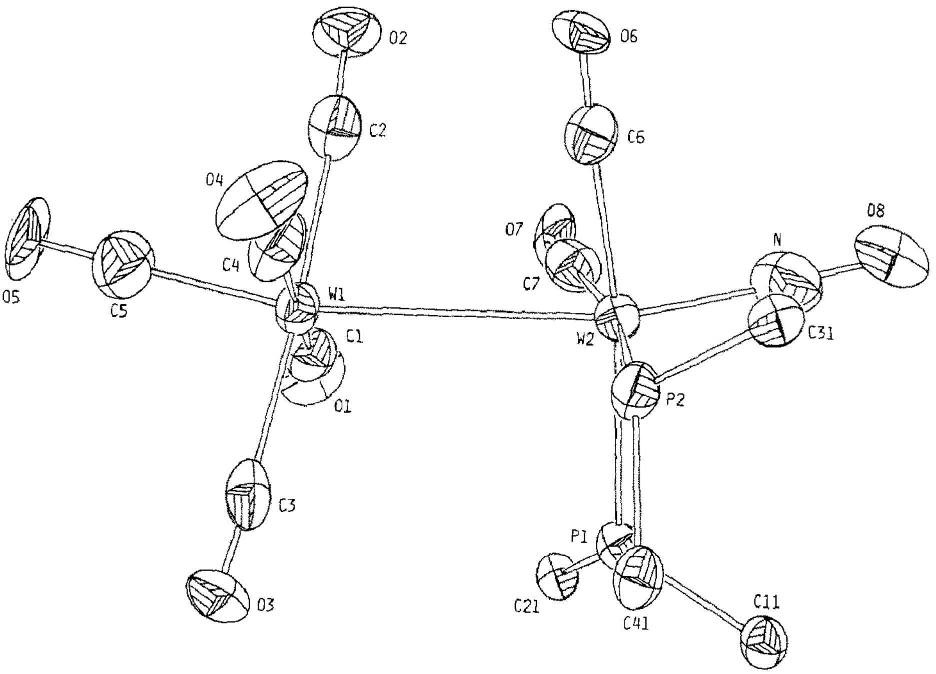

Fig. 2. ORTEP drawing of $HW_2(CO)_7(NO)(Ph_2PH)_2$. The four phenyl groups are represented only by their *ipso* carbon atoms for clarity. Thermal ellipsoids are drawn with 30% probability boundaries.

5 and 7) to the positions 6 and 7. Such a substitution is likely to minimize steric hindrance between the organic groups attaching to phosphorus atom and the CO ligands. By contrast, steric influence normally favors the mutual trans orientation of the phosphine groups in monomeric di-substituted complexes [12].

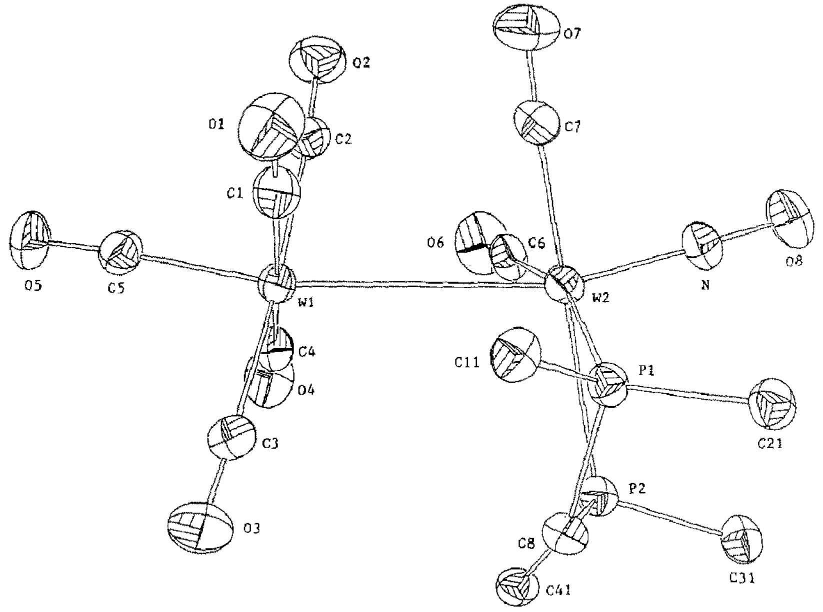

Fig. 3. ORTEP drawing of $HW_2(CO)_7(NO)(Ph_2PCH_2PPh_2)$. The four phenyl groups are represented only by their *ipso* carbon atoms for clarity. Thermal ellipsoids are drawn with 30% probability boundaries.

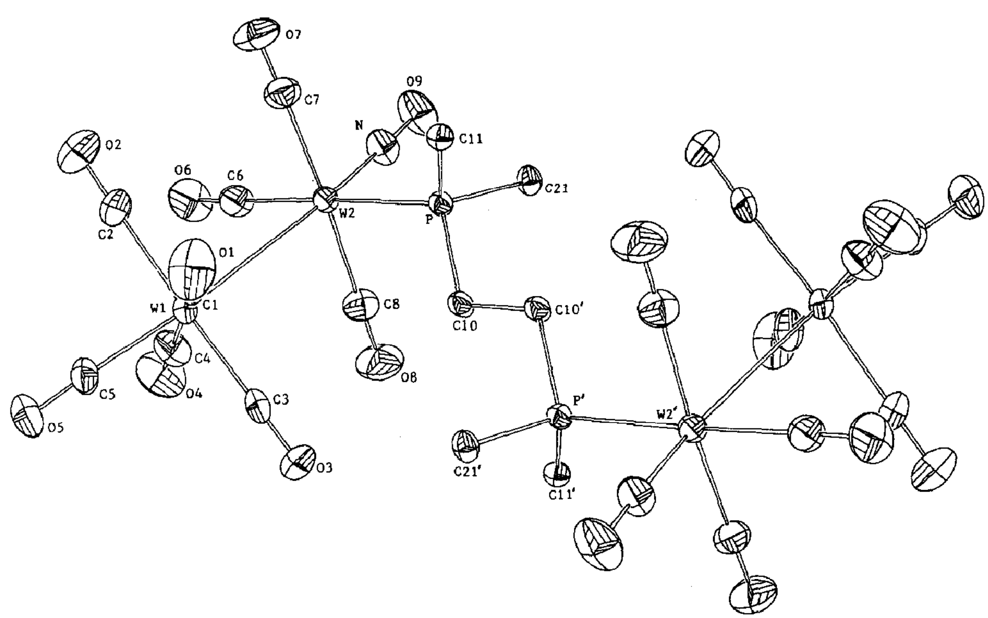

Fig. 4. ORTEP drawing of $[HW_2(CO)_8(NO)]_2(\mu\text{-}Ph_2PCH_2CH_2PPh_2)$. Half of the molecule is not labelled owing to the presence of an inversion center. Phenyl groups are omitted for clarity. Thermal ellipsoids are drawn with 30% probability boundaries.

The extremely long W–W distance found in complex 7 apparently stems from the unfavorable steric crowdedness in one of the phenyl groups attached to the P1 atom. We are presently attempting to synthesize derivatives of $HW_2(CO)_9(NO)$ with

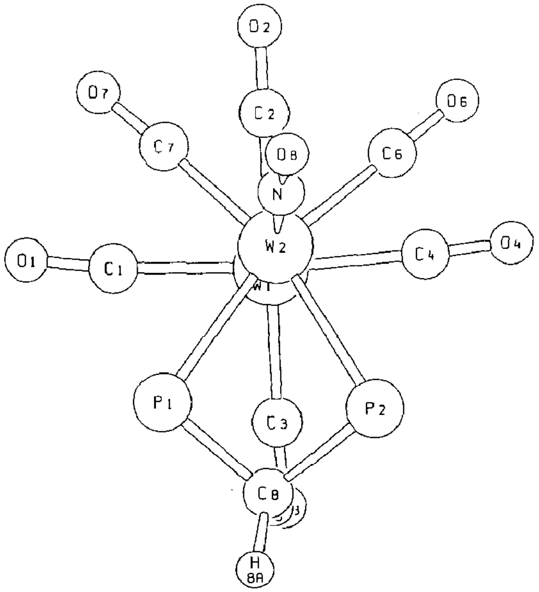

Fig. 5. The "end-on" view of $HW_2(CO)_7(Ph_2PCH_2PPh_2)$ showing the staggered conformation of the molecule.

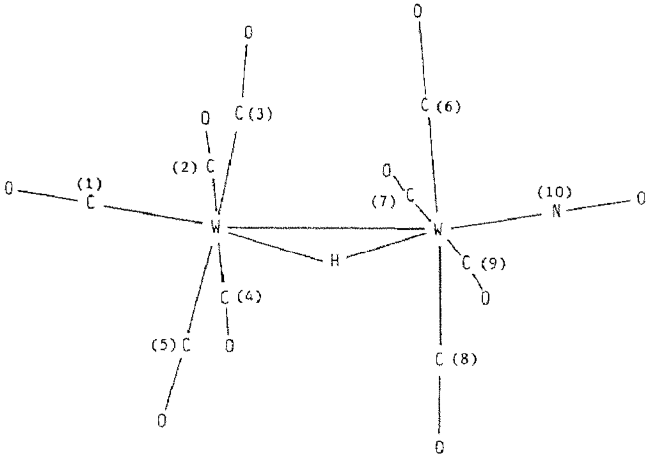

Fig. 6. Architecture of $HW_2(CO)_9(NO)$ molecule, which possesses a carbonyl-staggered geometry and a bent W–H–W fragment [5].

various ligands in order to determine the influence of the coordination core of tungsten atoms on the W–W interaction (i.e. W–W distance).

*Spectroscopic properties.* The mono-substituted complexes, $(CO)_5W(\mu\text{-}H)W(CO)_3(NO)L$ ($L = Ph_2PH$ (**1**), $PPh_3$ (**2**), $PCy_3$ (**3**), $\eta^1\text{-}(\eta^5\text{-}C_5H_4PPh_2)_2Fe$ (**4**)), $[HW_2(CO)_8(NO)]_2(\mu\text{-dppf})$ (**10**), have very similar infrared spectral patterns in the CO and NO stretching regions, which suggesting that they have very similar structures. Complex (**9**), $[HW_2(CO)_8(NO)]_2(\mu\text{-DPPE})$, has a slightly different structure (vide supra), although the infrared spectral pattern differs only slightly from those of **1**, **2**, **3**, **4**, and **10**. Five prominent $\nu(CO)$ absorptions ($CH_2Cl_2$) are observed: three weak bands around 2090, 2060, and 1980 $cm^{-1}$, a strong band around 2010 $cm^{-1}$, and a very strong band around 1935 $cm^{-1}$. The $\nu(NO)$ absorptions appear as a medium band around 1700 $cm^{-1}$. All the di-substituted complexes, $HW_2(CO)_7(NO)(L)$ ($L = Ph_2PH$ (**5**), $PPh_3$ (**6**)). $HW_2(CO)_7(NO)(\eta^2\text{-}L \sim L)$ ($L \sim L$ = DPPM (**7**), DPPE (**8**)), also have distinctive infrared spectral patterns in the CO and NO stretching regions. Four prominent $\nu(CO)$ absorptions ($CH_2Cl_2$) are observed: two medium bands around 2070 and 2020 $cm^{-1}$, a very strong band around 1960 $cm^{-1}$, and a strong band around 1930 $cm^{-1}$, The $\nu(NO)$ absorption appears as a medium band around 1670 $cm^{-1}$.

The $^1H$ NMR spectra (Table 4) are consistent with the three-center, two-electron (3c-2e) W–H–W linkage [14] which is retained in these phosphine-substituted derivatives of $HW_2(CO)_9(NO)$. The proton chemical shifts of the hydride lie 9.5–12 ppm upfield from $Me_4Si$, and flanked by two sets of tungsten satellite signals; The nature of the W satellites should also throw light on the bonding of the hydride ligand. The P–H coupling constants (11–20 Hz) suggest that the hydride is cis to the ligated phosphorus atoms [14b]. An interesting feature of complex 7 is that there is a long-range coupling ($^4J$(H–H) = 1.8 Hz) between the bridging hydrogen atom and one of the diastereotopic methylene protons in DPPM (Fig. 7).

The $^{31}P$ NMR spectra of complexes **1** ~ **10** are also consistent with their formulation. The chemical shifts of the phosphine ligands are flanked by one set of tungsten satellite signals, with W–P coupling constants between 200 and 250 Hz. The two phosphine groups appear to be magnetically equivalent in di-substituted complexes

Table 4

NMR data [a] for complexes **1** ~ **10**.

| | $^{1}$H NMR [b] | $^{31}$P{H} NMR [b] |
|---|---|---|
| **1** | *Ph* (7.79–7.52, m, 20 H); *H*PPh$_2$ (7.32, dd, 1 H $^{3}H$(H–H) = 2.60, $^{1}J$(P–H) = 372); W-*H* (−11.7, dd, 1 H, $^{3}J$(H–H) = 2.40, $^{2}J$(P–H) = 21.4, $^{1}J$(W–H) = 42.8, 38.4) | H*P*Ph$_2$ (−14.6, s, $^{1}J$(W–P) = 230) |
| **2** | *Ph* (7.54–7.22, m, 15 H); W-*H* (−10.86, d, 1 H, $^{2}J$(P–H) = 17.0, $^{1}J$(W–H) = 45.0, 40.6) | *P*Ph$_3$ (15.4, s, $^{1}J$(W–P) = 246) |
| **3** | P(C$_6$*H*$_{11}$)$_3$ (1.75–1.32, m, 33 H); W-*H* (−11.80, d, 1 H, $^{2}J$(P–H) = 14.9, $^{1}J$(W–H) = 45.8, 40.3) | *P*(C$_6$H$_{11}$)$_3$ (27.8, s, $^{1}J$(W–P) = 238) |
| **4** | P*Ph*$_2$ (7.61–7.26, m, 20 H); C$_5$*H*$_4$ (4.52, m, 2 H), (4.33, m, 2 H), (4.26, m, 2 H), (3.92, m, 2 H); W-*H* (−11.13, d, 1 H, $^{2}J$(P–H) = 6.6, $^{1}J$(W–H) = 45.0, 44.2) | W-*P*Ph$_2$ (7.1, s, 1 P, $^{1}J$(W–P) = 246); *P*Ph$_2$ (−12.7, s, 1 P) |
| **5** | HP*Ph$_2$* (7.58–7.26, m, 20 H); *H*PPh$_2$ (6.81, dd, 2 H, $^{3}J$(H–H) = 2.6, $^{2}J$(P–H) = 334); W-*H* (−11.62, tt, 1 H, $^{3}J$(H–H) = 2.6, $^{2}J$(P–H) = 17.8, $^{1}J$(W–H) = 42.8, 36.6) | H*P*Ph$_2$ (−4.2, s, $^{1}J$(W–P) = 222) |
| **6** | P*Ph$_3$* (7.48–7.12, m, 30 H); W-*H* (−11.40, d, 1 H, $^{2}J$(P–H) = 11.4, $^{1}J$(W–H) = 45.1, 40.0) | *P*Ph$_3$ (17.2, s, $^{1}J$(W–P) = 244) |
| **7** | P*Ph$_2$* (7.54–7.14, m, 20 H); C*Ha*Hb (5.85, dtd, 1 H, $^{2}J$(Ha–Hb) = 15.2, $^{2}J$(P–H) = 9.0, $^{4}J$(Hc–Ha) = 1.8); CHa*Hb* (4.80, dt, 1 H, $^{2}J$(Ha–Hb) = 15.2, $^{2}J$(P–H) = 10.8); W-*Hc* (−10.79, td, 1 H, $^{2}$J(P–Hc) = 16.8, $^{4}$J(Ha–Hc) = 1.8, $^{1}$J(W–H) = 40.8, 38.0) | *P*Ph$_2$ (−21.6, s, $^{1}J$(W–P) = 200) |
| **8** | P*Ph$_2$* (7.66–7.42, m, 20 H); C*H*$_2$ (3.14, m, 2 H), (2.83, m, 2 H); W-*H* (−11.73, t, 1 H, $^{2}J$(P–H) = 16.8, $^{1}J$(W–H) = 48.0, 38.0) | *P*Ph$_2$ (32.3, s, $^{1}J$(W–P) = 234) |
| **9** | P*Ph$_2$* (7.60–7.34, m, 20 H); C*H*$_2$ (2.49, br, 4 H); W-*H* (−11.26, d, 1 H, $^{2}J$(P–H) = 18.0, $^{1}J$(W–H) = 44.0, 40.0) | *P*Ph$_2$ (3.17, s, $^{1}J$(W–P) = 214) |
| **10** | P*Ph$_2$* (7.81–7.41, m, 20 H); C$_5$*H*$_4$ (4.64, m, 4 H), (4.52, m, 4 H); W-*H* (−11.30, d, $^{2}J$(P–H) = 6.6, $^{1}J$(W–H) = 45.0, 40.5) | *P*Ph$_2$ (7.12, s, $^{1}J$(W–P) = 246) |

[a] $^{1}$H NMR data are reported as follows: assignment (chemical shift in ppm, multiplicity, relative intensity, H–H and heteronuclear coupling constants in Hz). The solvent used was acetone-$d_6$ [b] Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad.

(**5**, **6**, **7**, **8**) as well as in the mono-substituted complexes that have bridging phosphines (**9**, **10**). It is important to note that the ligated and un-ligated phosphine group in complex **4** can be unambiguously differentiated in $^{31}$P NMR.

The formation of the phosphine-substituted derivatives of $HW_2(CO)_9(NO)$ deserves comment. Coordinated NO ligands are usually much more resistant to ligand substitution than CO groups [3]. The displacement of CO from the metal center occurs readily under mild conditions in several complexes containing both NO and CO ligands [6a,15]. Replacement of carbonyl in $HW_2(CO)_9(NO)$ by $Ph_2PH$, $PPh_3$, $PCy_3$, $Ph_2PCH_2PPh_2$ (DPPM), $Ph_2PCH_2CH_2PPh_2$ (DPPE), and $(\eta^5\text{-}C_5H_4PPh_2)_2Fe$ (dppf), also proceeds under ambient conditions. IR monitoring of

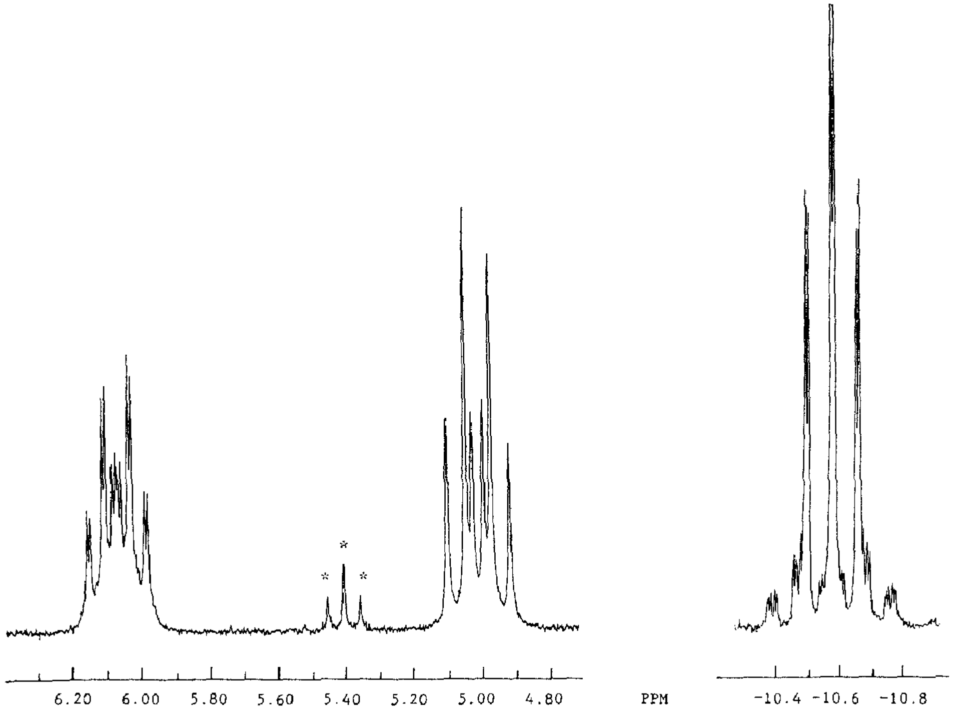

Fig. 7. The $^1H$ NMR spectra of $HW_2(CO)_7(NO)(\eta^2\text{-DPPM})$ in acetone-$d_6$ signals from the phenyl protons are not shown and those marked with asterisks are from free DPPM.

the reactions indicated that $HW_2(CO)_9(NO)$ was completely consumed within two days. In view of the sluggishness of ligand substitution of $HW_2(CO)_{10}^-$ [4a], it becomes clear that NO plays an important role in the reactions. Indeed, up to two carbonyl ligands in the "$W(CO)_4(NO)$" unit of $HW_2(CO)_9(NO)$ can be displaced. The steric congestion of the ligands certainly affects the degree of substitution. For example, both $HW_2(CO)_8(NO)(L)$ and $HW_2(CO)_7(NO)(L)_2$ were obtained from the reaction of $HW_2(CO)_9(NO)$ with $Ph_2PH$ or $PPh_3$, whereas the $^1H$ NMR spectra of the crude product from the reaction of $HW_2(CO)_9(NO)$ with $PCy_3$ ruled out the possibility of $HW_2(CO)_7(NO)(PCy_3)_2$. The large cone angle of $PCy_3$ (170°) [16] clearly prevents the accommodation of two $PCy_3$ by the same metal.

The $^1H$ NMR monitoring of the reaction of $HW_2(CO)_9(NO)$ or (**2**) with $PPh_3$ shows that the mono-substituted complex (**2**) and its isomer (**2′**) are the precursors of the di-substituted complex (**6**), which derives mainly from (**2′**). No monomeric hydrido tungsten complexes were detected in solution, suggesting that if rupture of $HW_2(CO)_9(NO)$ to "$W(CO)_5$"/"$HW(CO)_4(NO)$" does occur, then ligand substitution of $HW(CO)_4(NO)$ and recombination of "$W(CO)_5$"/"$HW(CO)_{4-x}(L)_x(NO)$" must be fast.

The phosphine-substituted complexes, once formed, are much more chemically robust than $HW_2(CO)_9(NO)$. For example: (a) they are indefinitely stable in $CH_2Cl_2$, THF, and $CH_3CN$ under nitrogen, whereas $HW_2(CO)_9(NO)$ decomposes gradually in these solvents [17*]. (b) Both 3-butyn-1-ol [18*] and $Et_4NCS_2^-$ react with $HW_2(CO)_9(NO)$ in $CH_2Cl_2$ within 1 h under ambient conditions, whereas

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* Reference number with asterisk indicates a note in the list of references.

$HW_2(CO)_7(NO)(\eta^2$-DPPE) in THF remains intact in the presence of these reagents even after one day at 45 ° C.

Although we have successfully synthesized complexes ($\mu$-H)($\mu$-L ~ L)$W_2(CO)_n$-(NO) (L ~ L is a bidentate ligand) by a different route [19], they are elusive from the reaction of $HW_2(CO)_9(NO)$ with the bidentate ligands we have used, even though they are stable under the reaction conditions.

## Acknowledgement

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17 J.T. Lin and J.S. Sun, unpublished observations. (a) Less than 10% of $HW_2(CO)_9(NO)$ decomposes after 24 h in $CH_2Cl_2$ based on IR and $^1H$ NMR spectra. Only $W(CO)_6$ could be detected in the reaction. (b) $HW_2(CO)_7(NO)(THF)_2$ was isolated from the reaction of $HW_2(CO)_9(NO)$ with THF in 70% yield. IR(THF, $cm^{-1}$): $\nu$(CO) 2064 (w), 2003(m), 1970(w), 1928(vs), 1905(s); $\nu$(NO) 1662(m, br). $^1H$ NMR($CD_2Cl_2$, ppm): $\delta$ 4.33 (m, 4H), $\delta$ 4.00 (m, 4H), $\delta$ 2.12 (m, 4H), $\delta$ 2.02 (m, 4H), $\delta$ −5.21 (s, 1H, $^1J$(W–H) = 49.4, 59.6 Hz). This complex was found to be a good precursor for the disubstituted products mentioned in the text.
18 The product from the reaction was mainly $W(CO)_6$. A trace amount of $(CO)_5W(CCH_2CH_2CH_2O)$ was also detected. IR (THF, $cm^{-1}$) $\nu$(CO): 2073 (w), 1957 (sh), 1945 (s); $^1H$ NMR ($CD_3CN$) $\delta$ = 4.97 (t, $J$(H–H) = 7.8 Hz, 2H), 3.52 (t, $J$(H–H) = 7.8 Hz, 2H), 2.00 (m, 2H). $^{13}C\{H\}$ NMR ($CD_3CN$): $\delta$ = 316.4 (s, 1C, W=C), 205.6 (s, 1C, trans CO), 198.3 (s, 4C, *cis*-CO), 88.3 (s, 1C), 64.8 (s, 1C), 19.8 (s, 1C).
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