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Binuclear Tungsten Carbonyls Bridged both by Hydride and by Bidentate Phosphine Ligands: $(\mu\text{-H})(\mu\text{-Ph}_2\text{P(CH}_2)_n\text{PPh}_2)\text{W}_2(\text{CO})_7(\text{NO})$ (n = 1–5) and $(\mu\text{-H})(\mu\text{-(Ph}_2\text{PCH}_2)_3\text{CMe})\text{W}_2(\text{CO})_7(\text{NO})$

Jiann T. Lin,[*,†] Kuo-Yang Chang,[†,‡] Shiow Y. Wang,[†] Yuh S. Wen,[†] Li-Hong Tseng,[†]
Chung-Cheng Chang,[‡] Shie-Ming Peng,[§] Yu Wang,[*,§] and G. H. Lee[§]

Institute of Chemistry, Academia Sinica, Nankang, Taipei, Taiwan, Republic of China,
National Sun Yat-Sen University, Kaohsiung, Taiwan, Republic of China,
and National Taiwan University, Taipei, Taiwan, Republic of China

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Nitrosylation of $[\text{Et}_4\text{N}][(\mu\text{-H})(\mu\text{-Ph}_2\text{P(CH}_2)_n\text{PPh}_2)\text{W}_2(\text{CO})_8]$ (n = 1–5) and $[\text{Et}_4\text{N}][(\mu\text{-H})(\mu\text{-(Ph}_2\text{PCH}_2)_3\text{CMe})\text{W}_2(\text{CO})_8]$ with 1 equiv of NO^+BF_4^- in CH_2Cl_2 at –60 °C provides 30–45% yields of orange complexes, $(\mu\text{-H})(\mu\text{-Ph}_2\text{P(CH}_2)_n\text{PPh}_2)\text{W}_2(\text{CO})_7(\text{NO})$ (n = 1–5, designated, respectively, as **1**, **2**, **3**, **4**, and **5**) and $(\mu\text{-H})(\mu\text{-(Ph}_2\text{PCH}_2)_3\text{CMe})\text{W}_2(\text{CO})_7(\text{NO})$ (**6**). X-ray crystal structure analyses for complexes **1**, **3**, and $[\text{Et}_4\text{N}][(\mu\text{-H})(\mu\text{-Ph}_2\text{P(CH}_2)_n\text{PPh}_2)\text{W}_2(\text{CO})_8]$ (n = 1, **7**; n = 3, **8**) were carried out to give the data as follows. **1**: Triclinic; $P\bar{1}$; $Z = 4$; a = 12.989 (3), b = 15.271 (6), c = 18.16 (1) Å; α = 112.22 (3), β = 95.91 (3), γ = 90.48 (2)°; V = 3316.0 Å^3; R = 0.037; R_w = 0.037. **3**: Orthorhombic; *Pnna*; $Z = 4$; a = 14.566 (2), b = 23.512 (3), c = 10.471 (2) Å; V = 3586.1 Å^3; R = 0.035; R_w = 0.037. **7**: Monoclinic; $P2_1/c$; $Z = 4$; a = 20.692 (4), b = 12.326 (2), c = 17.436 (3) Å; β = 105.32 (1)°; V = 4288.9 Å^3; R = 0.027, R_w = 0.032. **8**: Monoclinic; $P2_1/n$; $Z = 4$; a = 21.159 (3), b = 10.243 (2), c = 21.486 (4) Å; β = 109.64 (1)°; V = 4386.0 Å^3; R = 0.044; R_w = 0.047. The W–W distances in **1** (3.349 (1); 3.350 (1) Å) and **3** (3.315 (1) Å) are significantly shorter than those in $[\text{Et}_4\text{N}][(\mu\text{-H})(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)\text{W}_2(\text{CO})_8]$ (3.4286 (7) Å) and $[\text{Et}_4\text{N}][[(\mu\text{-H})(\mu\text{-PPh}_2\text{P(CH}_2)_3\text{PPh}_2)\text{W}_2(\text{CO})_8]$ (3.434 (1) Å), respectively. Complexes $(\mu\text{-H})(\mu\text{-Ph}_2\text{P(CH}_2)_n\text{PPh}_2)\text{W}_2(\text{CO})_6(\text{Ph}_2\text{PH})(\text{NO})$ (n = 1–3) were isolated from the ligand substitution of complexes **1**, **2**, and **3**, respectively.

Introduction

The existence of both the staggered and eclipsed conformations in the solid-state structures of $(\mu\text{-H})\text{Cr}_2(\text{CO})_{10}^-$ and $(\mu\text{-H})\text{W}_2(\text{CO})_{10}^-$ pinpoints the flexibility of the M–H–M bridge in these dimeric hydride anions.[1] Previous investigations by Darensbourg[2,3] on phosphine derivatives of $(\mu\text{-H})\text{Mo}(\text{CO})_{10}^-$ showed that substituent ligands also affected the metal–metal interaction in a M–H–M bridge. We recently found that substantial variation of the M–H–M linkage also occurred in isocyanide-[4] or phosphine-substituted[5] derivatives of $(\mu\text{-H})\text{W}_2(\text{CO})_9(\text{NO})$.[6] Most derivatives adopt the bent, staggered structure, and in no case did we find ligand substitution occurring at the "W(CO)_5" segment. Owing to the instability of $(\mu\text{-H})\text{W}_2(\text{CO})_9(\text{NO})$ in many common solvents, we set out to synthesize analogues of $(\mu\text{-H})\text{W}_2(\text{CO})_9(\text{NO})$ with an extra phosphine bridge, $(\mu\text{-H})(\mu\text{-Ph}_2\text{P–PPh}_2)\text{W}_2(\text{CO})_7(\text{NO})$, in the hope of strengthening the W–H–W linkage. While these complexes are elusive from the reaction of $(\mu\text{-H})\text{W}_2(\text{CO})_9(\text{NO})$ with $\text{Ph}_2\text{P(CH}_2)_n\text{PPh}_2$,[5] they can be synthesized from nitrosylation of $(\mu\text{-H})(\mu\text{-Ph}_2\text{P(CH}_2)_n\text{PPh}_2)\text{W}_2(\text{CO})_8^-$.[7]

This paper will be mainly concerned with the synthesis, structure, and reactivity of $(\mu\text{-H})(\mu\text{-Ph}_2\text{P–PPh}_2)\text{W}_2(\text{CO})_7(\text{NO})$. The structural study on $[\text{Et}_4\text{N}][(\mu\text{-H})(\mu\text{-Ph}_2\text{P(CH}_2)_n\text{PPh}_2)\text{W}_2(\text{CO})_8]$ (n = 1, 3) is also included for comparison.

Experimental Section

General Procedure. Infrared measurements were made on a Perkin-Elmer 880 spectrophotometer. The NMR spectra were recorded on a Bruker MSL 200 or AM 200 spectrometer. 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 operations were carried out under nitrogen with use of standard Schlenk techniques or a drybox. All solvents were purified by standard procedures or degassed prior to use. All the column chromatography was performed under N_2 by use of silica gel (230–400 mesh ASTM, Merck) as the stationary phase in a column 35 cm long and 2.5 cm in diameter. Anhydrous Me_3NO was obtained from heating of $\text{Me}_3\text{NO}\cdot2\text{H}_2\text{O}$ at 105 °C under a partial vacuum followed by sublimation. Complexes $[\text{Et}_4\text{N}][(\mu\text{-H})(\mu\text{-Ph}_2\text{P(CH}_2)_n\text{PPh}_2)\text{W}_2(\text{CO})_8]$ (n = 1–5) and $[\text{Et}_4\text{N}][(\mu\text{-H})(\mu\text{-Ph}_2\text{PCH}_2)_3\text{CMe})\text{W}_2(\text{CO})_8]$ were prepared according to the published procedure.[7]

$(\mu\text{-H})(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)\text{W}_2(\text{CO})_7(\text{NO})$ (1). One equivalent of solid NO^+BF_4^- (300 mg, 0.271 mmol) was added all at once via a Schlenk tube into a vigorously stirring CH_2Cl_2 solution of $[\text{Et}_4\text{N}][(\mu\text{-H})(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)\text{W}_2(\text{CO})_8]$ (**7**) (316 mg, 0.271 mmol) prechilled to –60 °C. After 12 h at –60 °C the deep red solution was warmed gradually to room temperature and the solvent was removed in vacuo. The residue was extracted with Et_2O and filtered, and the solvent was removed under reduced pressure. The crude reaction mixture was dissolved in a minimum volume of CH_2Cl_2 and separated by column chromatography. Two bands were first developed with use of hexane as eluent. The mixture of CH_2Cl_2 and hexane (2:3 by volume) was then used as eluent.

[†] Academia Sinica.

[‡] National Sun Yat-Sen University.

[§] National Taiwan University.

(1) (a) Petersen, J. L.; Brown, R. K.; Williams, J. M. *Inorg. Chem.* **1981**, *20*, 158. (b) Petersen, J. L.; Masino, A.; Stewart, R. P., Jr. *J. Organomet. Chem.* **1981**, *208*, 55. (c) Roziere, J.; Teulon, P.; Grillone, M. D. *Inorg. Chem.* **1983**, *22*, 557.

(2) Darensbourg, M. W.; Atwood, J. L.; Burch, R. R., Jr.; Hunter, W. E.; Walker, N. *J. Am. Chem. Soc.* **1979**, *101*, 2631.

(3) Darensbourg, M. Y.; Atwood, J. L.; Hunter, W. E.; Walker, N. *J. Am. Chem. Soc.* **1980**, *102*, 3290.

(4) Lee, M. K.; Huang, P. S.; Wen, Y. S.; Lin, J. T. *Organometallics* **1990**, *9*, 2181.

(5) Lin, J. T.; Wang, S. Y.; Huang, P. S.; Hsiao, Y. M.; Wen, Y. S.; Yeh, S. K. *J. Organomet. Chem.* **1990**, *388*, 151.

(6) Olsen, J. P.; Koetzle, T. F.; Kirtley, S. W.; Andrews, M.; Tipton, D. L.; Bau, R. *J. Am. Chem. Soc.* **1974**, *96*, 6621.

(7) Lin, J. T.; Hsiao, Y. M.; Wen, Y. S.; Yeh, S. K. *J. Organomet. Chem.* **1987**, *334*, C31.

0276-7333/91/2310-2377$02.50/0

Table I. IR Spectra in the ν(CO) Region and ^{1}H and ^{31}P{H} NMR Spectra of (μ-H) (μ-Ph_2P–PPh_2)$W_2(CO)_7(NO)$

compd	ν(CO), $\underline{\nu(\text{NO})}$,[a] cm^{-1}	δ(ppm),[b,c] J(Hz)	δ(ppm),[b,d] J(Hz)
1	2084 m, 2014 vs, 2002 sh, 1915 sh, 1887 s, $\underline{1662}$ m	7.59–7.28 (m, 20 H, Ph), 4.28 (ddd, 2 H, $J_{\text{H-P}}$ = 11.0, 9.6, $^4J_{\text{H-H}}$ = 1.00, CH_2), –10.2 (ddt, 1 H, $J_{\text{H-P}}$ = 15.6, 14.4; $J_{\text{H-W}}$ = 41.5, 37.5 Hz)	24.1 (d, 1 P, $J_{\text{P-P}}$ = 60.4, $J_{\text{P-W}}$ = 221), 12.3 (d, 1 P, $J_{\text{P-W}}$ = 253)
2	2083 m, 2007 vs, 1998 sh, 1906 sh, 1887 s, $\underline{1657}$ m	7.64–7.34 (m, 20 H, Ph), 3.10 (br, 4 H, CH_2), –11.0 (dd, 1 H, $J_{\text{H-P}}$ = 22.0, 20.6; $J_{\text{H-W}}$ = 39.2)	22.1 (d, 1 P, $J_{\text{P-P}}$ = 5.60; $J_{\text{P-W}}$ = 207), 15.3 (d, 1 P, $J_{\text{P-W}}$ = 240)
3	2082 m, 2006 s, 1934 sh, 1911 sh, 1885 s, $\underline{1650}$ m	(m, 2 H, CH_2), 2.89 (m, 2 H, CH_2), 2.00 (m, 2 H, CH_2), –9.94 (pseudo triplet, 1 H, $J_{\text{H-P}}$ = 19.4; $J_{\text{H-W}}$ = 42.4)	9.91 (s, 1 P, $J_{\text{P-W}}$ = 204), 3.35 (s, 1 P, $J_{\text{P-W}}$ = 238)
4	2082 m, 2070 sh, 2007 vs, 1990 sh, 1935 sh, 1908 w, 1887 s, $\underline{1678}$ ms	7.70–7.75 (m, 20 H, Ph), 3.04 (m, 4 H, CH_2), 1.41 (m, 4 H, CH_2), –9.33 (dd, 1 H, $J_{\text{H-P}}$ = 16.5, 15.3; $J_{\text{H-W}}$ = 45.4, 43.1)	5.27 (s, 1 P, $J_{\text{P-W}}$ = 199), 5.02 (s, 1 P, $J_{\text{P-W}}$ = 242)
5	2082 m 2070 sh, 2015 sh, 2005 vs, 1987 wm, 1936 m, 1908 s, 1892 s, 1887 sh, 1867 w, $\underline{1679}$ ms	7.73–7.57 (m, 20 H, Ph), 2.90 (m, 2 H, CH_2), 2.70 (m, 2 H, CH_2), 1.60 (m, 2 H, CH_2), 1.40 (m, 2 H, CH_2), 1.18 (m, 2 H, CH_2), –9.82 (pseudo triplet, 1 H, $J_{\text{H-P}}$ = 13.4; $J_{\text{H-W}}$ = 44.8)	12.9 (s, 1 P, $J_{\text{P-W}}$ = 212), 4.46 (s, 1 P, $J_{\text{P-W}}$ = 242)
6	2081 m, 2016 s, 2004 s, 1985 s, 1912 s, 1886 vs, $\underline{1648}$ m	7.51–6.98 (m, 30 H, Ph), 3.39–3.28 (m, 4 H, CH_2), 1.73 (br, 2 H, CH_2), 0.80 (s, 3 H, Me), –9.53 (pseudo triplet, 1 H, $J_{\text{H-P}}$ = 24.2; $J_{\text{H-W}}$ = 49.8)	–1.17 (s, 1 P, $J_{\text{P-W}}$ = 202), –8.47 (s, 1 P, $J_{\text{P-W}}$ = 230), –22.1 (s, 1 P)
9	2027 s, 2001 m, 1955 ms, 1910 sh, 1886 s, 1870 sh, $\underline{1631}$ m	7.48–7.25 (m, 30 H, Ph), 6.31 (dm, 1 H, $^1J_{\text{P-H}}$ = 349 Hz, P*H*), 4.64 (m, 1 H, CH_2), 3.88 (m, 1 H, CH_2), –9.85 (dddm, 1 H, $J_{\text{H-P}}$ = 21.6, 14.6, 8.98; $J_{\text{H-W}}$ = 41.2, 47.6 Hz, μ-H)	20.9 (d, 1 P, $J_{\text{P-P}}$ = 64.0; $J_{\text{P-W}}$ = 228 Hz, PPh_2), 11.8 (d, 1 P, $J_{\text{P-P}}$ = 64.0, 15.7; $J_{\text{P-W}}$ = 240 Hz, PPh_2), –1.31 (d, 1 P, $J_{\text{P-P}}$ = 15.7; $J_{\text{P-W}}$ = 266 Hz, Ph_2PH)
10	2028 s, 2001 m, 1955 ms, 1904 sh, 1888 s, 1868 sh, $\underline{1628}$ m	7.78–7.24 (m, 30 H, Ph), 6.01 (dm, 1 H, $^1J_{\text{H-P}}$ = 352 Hz, P*H*), 2.01 (br, 4 H, CH_2), –10.9 (unresolved m, 1 H, μ-H)	24.1 (d, 1 P, $J_{\text{P-P}}$ = 7.80; $J_{\text{P-W}}$ = 211 Hz, PPh_2), 16.3 (dd, 1 P, $J_{\text{P-P}}$ 15.8, 7.80; $J_{\text{P-W}}$ = 233 Hz, PPh_2), 1.40 (d, 1 P, $J_{\text{P-P}}$ = 15.8; $J_{\text{P-W}}$ = 232 Hz, Ph_2PH)
11	2028 s, 2001 m, 1956 ms, 1903 sh, 1881 s, 1865 sh, $\underline{1664}$ m	7.58–7.46 (m, 30 H, Ph), 6.75 (dm, 1 H, $^1J_{\text{H-P}}$ = 351 Hz, P*H*), 3.25 (m, 2 H, Ch_2), 3.00 (br, 2 H, CH_2), 2.80 (m, 2 H, CH_2), –11.8 (pseudo tdd, 1 H, $J_{\text{H-P}}$ = 15.9, 15.9, 11.8; $^3J_{\text{H-H}}$ = 2.0; $J_{\text{H-W}}$ = 44.0, 40.0 Hz, μ-H)	15.1 (s, 1 P, $J_{\text{P-W}}$ = 213 Hz, Ph_2PH), 4.89 (d, 1 P, $J_{\text{P-P}}$ = 19.1; $J_{\text{P-W}}$ = 233 Hz, PPh_2), –1.08 (d, 1 P, $J_{\text{P-P}}$ = 19.1; $J_{\text{P-W}}$ = 233 Hz, PPh_2)

[a] Measured in CH_2Cl_2 solution. [b] Measured in acetone-d_6. [c] Reported in ppm relative to δ(Me_4Si) 0 ppm. [d] Reported in ppm relative to δ (85% H_3PO_4) 0 ppm. Abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet. These abbreviations do not include the satellites.

The solvent was removed from the fractions. The product in the first band was found to be $W(CO)_4(Ph_2PCH_2PPh_2)$. The orange-red second band provided 106 mg (40% yield) of powdery 1. Anal. Calcd for $C_{32}H_{23}NP_2O_8W_2$: C, 39.25; H, 2.37; N, 1.43. Found: C, 38.69; H, 2.48; N, 1.18.

Orange-red complexes (μ-H)(μ-$Ph_2P(CH_2)_nPPh_2$)$W_2(CO)_7(NO)$ (*n* = 2–5, designated as 2, 3, 4, and 5) and (μ-H)(μ-$(Ph_2PCH_2)_3CMe$)$W_2(CO)_7(NO)$ (6) were prepared by essentially the same procedure for the synthesis of 1. The spectroscopic data for complexes 1–6 are collected in Table I. Complex 2 has a yield of 45%. Anal. Calcd for $C_{33}H_{25}NO_8P_2W_2$: C, 39.91; H, 2.54; N, 1.41. Found: C, 39.82; H, 2.49; N, 1.42.

Complex 3 has a yield of 41%. Anal. Calcd for $C_{34}H_{27}NO_8P_2W_2$: C, 40.52; H, 2.68; N, 1.39. Found: C, 40.30; H, 2.64; N, 1.28.

Complex 4 has a yield of 40%. Anal. Calcd for $C_{35}H_{29}NO_8P_2W_2$: C, 41.14; H, 2.84; N, 1.37. Found: C, 41.42; H, 3.14; N, 1.29.

Complex 5 has a yield of 34%. Anal. Calcd for $C_{36}H_{31}NO_8P_2W_2$: C, 41.74; H, 3.00; N, 1.35. Found: C, 41.59; H, 2.87; N, 1.29.

Complex 6 has a yield of 43%. Anal. Calcd for $C_{49}H_{40}NO_8P_3W_2$: C, 47.28; H, 3.31; N, 1.15. Found: C, 47.15; H, 3.02; N, 0.97.

(μ-H)(μ-$Ph_2PCH_2PPh_2$)$W_2(CO)_6(Ph_2PH)(NO)$ (9). Complex 1 (300 mg, 0.31 mmol) in 50 mL of CH_3CN prechilled to –30 °C was treated dropwise with Me_3NO (23 mg, 0.31 mmol) in CH_3CN also at –30 °C. After 2 h at –30 °C the solution was added Ph_2PH (0.053 mL, 0.31 mmol) and stirred at the same temperature for another 2 h. The solution was then warmed to room temperature, and the solvent was removed under vacuum. The crude reaction product was then chromatographed. The light yellow compound obtained from the first band (CH_2Cl_2/hexane, 1:4 by volume) was not identified. The yellow-orange powders obtained from the second major band (CH_2Cl_2/hexane, 2:3 by volume) recrystallized to give yellow-orange crystals of 9 (152 mg, 43%). Anal. Calcd for $C_{43}H_{34}NO_7P_3W_2$: C, 45.41; H, 3.01; N, 1.23. Found: C, 45.02; H, 3.29; N, 1.15.

Yellow-orange complexes (μ-H)(μ-$Ph_2P(CH_2)_nPPh_2$)$W_2(CO)_6(Ph_2PH)(NO)$ (*n* = 2, 10; *n* = 3, 11) were prepared by the same procedure described for the preparation of compound 9.

Complex 10 has a yield of 55%. Anal. Calcd for $C_{44}H_{36}NO_7P_3W_2$: C, 45.90; H, 3.15; N, 1.22. Found: C, 46.25; H, 2.90; N, 1.21.

Complex 11 has a yield of 32%. Anal. Calcd for $C_{45}H_{38}NO_7P_3W_2$: C, 46.38; H, 3.28; N, 1.20. Found: C, 45.96; H, 2.98; N, 1.19.

X-ray Structural Determination of 1, 3, 7, and 8. Crystals of 1 and 3 were grown by cooling a concentrated solution of the complex in CH_2Cl_2/hexane (1:3 by volume) at –5 °C for several days. Crystals 7 and 8 were grown by slow diffusion of Et_2O into a concentrated solution of 7 and 8 in acetone. Crystals were mounted in the thin-wall 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 $\theta - 2\theta$ scan mode. Unit cells were determined from centering 25 reflections in the suitable 2θ range. Other relevant experimental details are listed in Table II (complexes 1, 3, 7, and 8). Absorption corrections according to ψ scans of three reflections were applied. All the data processing was carried out on a MICRO VAX 3600 by using the NRCC SDP program.[8] 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 $\sum\omega(|F_o| - |F_c|)^2$, where $\omega = 1/\sigma(F_o)^2$ was calculated from the counting statistics. The atomic scattering factors f_o and anomalous dispersion terms f' and f'' were taken from ref 9. The cations of 7 and 8 were found to have some disorder atoms. All atoms in the cations were thus fixed in the last least-square refinement. All other non-hydrogen atoms were refined anisotropically. The position of the bridging hydrogen atom was located from the final difference Fourier maps for 3, 7, and 8, and then refined. Other hydrogen atoms were included in the structure factor calculation in idealized positions with $d_{\text{C-H}}$ = 0.98 Å. The final positional parameters for the atoms in 1, 3, 7, and 8 are in Table III. Selected interatomic distances and bond angles are in Table IV.

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(8) (a) Gabe, E. J.; Lee, F. L. *Acta Crystallogr.* **1981**, *37*, S339. (b) Gabe, E. J.; LePage, Y.; White, P. S.; Lee, F. L. *Acta Crystallogr.* **1987**, *43*, C294.

(9) *International Tables for X-ray Crystallography*: Kynoch, Birmingham, England, 1974; Vols. IV and Vol III, p 276.

Table II. Crystal Data for Compounds 1, 3, 7, and 8

	1	3	7	8
formula	$C_{32}H_{23}NO_8P_2W_2$	$C_{34}H_{27}NO_8P_2W_2$	$C_{41}H_{43}NO_8P_2W_2$	$C_{43}H_{47}NO_8P_2W_2$
fw	977.83	1008.2	1107.4	1135.5
a, Å	12.989 (3)	14.566 (2)	20.692 (4)	21.159 (3)
b, Å	15.271 (6)	23.512 (3)	12.326 (2)	10.243 (2)
c, Å	18.16 (1)	10.471 (2)	17.436 (3)	21.486 (4)
α, deg	112.22 (3)			
β, deg	95.91 (3)		105.32 (1)	109.64 (1)
γ, deg	90.48 (2)			
cryst syst	triclinic	orthorhombic	monoclinic	monoclinic
space group	$P\bar{1}$	*Pnna*	$P2_1/c$	$P2_1/n$
Z	4	4	4	4
V, Å^3	3315.03	3586.1	4288.9	4386.0
d_{calc}, g/cm^3	1.959	1.869	1.714	1.718
cryst size, mm	0.45 × 0.40 × 0.30	0.25 × 0.18 × 0.16	0.35 × 0.40 × 0.45	0.30 × 0.13 × 0.13
radiation	Mo Kα (λ = 0.7107 Å)	same	same	same
μ, cm^{-1}	72.3	66.8	56.0	54.7
transmission factors (max; min)	1.00; 0.45	1.00; 0.90	1.00; 0.62	1.00; 0.88
2θ range, deg	0–50	0–50	3–50	0–45
octants	$\pm h$ (−15 to 15), $+k$ (0–18), $\pm l$ (−21 to 19)	$+h$ (0–17), $+k$ (0∼27), $-l$ (−12 to 0)	$\pm h$ (−24 to 23), $+k$ (0∼14), $+l$ (0–20)	$\pm h$ (−22 to 21), $+k$ (0∼11), $+l$ (0–22)
no. of unique rflns	11656	3162	7583	5721
no. of rflns with $I > n\sigma$	6661 (n = 3)	1509 (n = 2)	5227 (n = 2)	3634 (n = 2)
no. of variables	811	214	488	425
R, R_w	0.037; 0.037	0.035; 0.037	0.027; 0.032	0.044; 0.047
GOF	1.297	1.17	1.53	2.75
max Δ/σ	0.831	0.061	0.262	0.249

Results and Discussion

Instead of forming $(\mu\text{-H})(\mu\text{-}Ph_2P(CH_2)_nPPh_2)W_2(CO)_7(NO)$, the reaction of $(\mu\text{-H})W_2(CO)_9(NO)$ with $Ph_2P(CH_2)_nPPh_2$ results in ligand substitution only at the metal containing NO.[5] This is in sharp contrast to the reaction of $(\mu\text{-H})Mo_2(CO)_{10}^-$ with $Ph_2P(CH_2)_nPPh_2$, which provides $(\mu\text{-H})(\mu\text{-}Ph_2P(CH_2)_nPPh_2)Mo_2(CO)_8^-$.[10] The failure in forming $(\mu\text{-H})(\mu\text{-}Ph_2P\text{–}PPh_2)W_2(CO)_7(NO)$ for the former reaction can be attributable to the influence of NO.[11] By using NO^+ salt, a well-known reagent for the synthesis of tungsten nitrosyl compounds,[12] we have successfully synthesized $(\mu\text{-H})(\mu\text{-}Ph_2P\text{–}PPh_2)W_2(CO)_7(NO)$. Addition of 1 equiv of solid $NO^+BF_4^-$ to a vigorously stirred CH_2Cl_2 solution of $[Et_4N][(\mu\text{-H})(\mu\text{-}Ph_2P\text{–}PPh_2)W_2(CO)_8]$ at −60 °C resulted in the formation of $(\mu\text{-H})(\mu\text{-}Ph_2P(CH_2)_nPPh_2)W_2(CO)_7(NO)$ (n = 1–5, designated as, respectively, **1**, **2**, **3**, **4**, and **5**) and $(\mu\text{-H})(\mu\text{-}(Ph_2PCH_2)_3CMe)W_2(CO)_7(NO)$ (**6**). Complex $(\mu\text{-H})(\mu\text{-}(\eta^5\text{-}C_5H_4PPh_2)_2Fe)W_2(CO)_7(NO)$ could also be prepared similarly, albeit not in pure form. The isolated yields for complexes **1**–**6** were only moderate. We found that excess $NO^+BF_4^-$ and silica gel were detrimental to these complexes and would reduce the yields of which, especially **1**. Complex obtained from the first eluted yellow band from column chromatography was identified to be $W(CO)_4(\eta^2\text{-}Ph_2P\text{–}PPh_2P)$.[13]

Molecular Structure of $(\mu\text{-H})(\mu\text{-}Ph_2P(CH_2)_nPPh_2)W_2(CO)_7(NO)$ (n = 1 (1); n = 3 (3)) and $[Et_4N][(\mu\text{-H})(\mu\text{-}Ph_2P(CH_2)_nPPh_2)W_2(CO)_8]$ (n = 1 (7); n = 3 (8)). The ORTEP drawings of **1**, **3**, as well as anions of **7** and **8** are shown in Figures 1, 2, 3, and 4, respectively. Two crystallographically independent molecules, A and B, are found in **1**. The two molecules differ only slightly in corresponding bond distances and angles. It is interesting to note that these two independent molecules are approximately related by a pseudo b-glide plane (∼0.27, y, z).[14] There exists a 2-fold axis passing through the center of W–Wa axis and carbon C(6) for complex **3** (Figure 2). In all of these complexes the tungsten atoms reside in roughly octahedral environments. They are of the bent (the bending angles in the framework[15] for **1**, **3**, **7**, and **8** are 13.7 (4)°/12.3 (4)°, 19.1 (2)°, 18.9 (2)°, and 13.0 (4)°, respectively), staggered configuration (the staggering angles[15] for **1**, **3**, **7**, and **8** are 25.7 (1)°/17.0 (1)°, 45.5 (1)°, 20.6 (1)°, and 53.8 (2)°, respectively), similar to their dimolybdenum analogues, $[Et_4N][(\mu\text{-H})(\mu\text{-}Ph_2P(CH_2)_nPPh_2)Mo_2(CO)_8]$ (n = 1, 4).[10] The NO ligand in **1** and **3** is found to occupy the axial site[16] (i.e., trans to the bridging hydride), although a 50%–50% nitrosyl–carbonyl disorder was found in **3**. Complex $HW_2(CO)_9(NO)$[6] and its phosphine derivatives[5] also have their NO ligand in axial site.

The products formed by substitution of NO^+ for one of axial CO in $(\mu\text{-H})(\mu\text{-}Ph_2P(CH_2)_nPPh_2)W_2(CO)_8^-$ should be different from that obtained by displacement of the other axial CO due to the bent nature of the W–H–W bond[17] in these complexes. Indeed these two geometrical isomers are related by a mirror reflection in the crystal lattice of **1** and **3**.[18] The existence of two such geometrical isomers

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[10] Darensbourg, M. Y.; Mehdawi, R. El.; Delord, T. J.; Fronczek, F. R.; Watkins, S. F. *J. Am. Chem. Soc.* **1984**, *106*, 2583.

[11] Complex $HMo_2(CO)_9(NO)$ was found to react with phosphines similarly to its tungsten analogue. Yeh, A. C.; Lin, J. T. Unpublished research.

[12] Honeychuck, R. V.; Hersh, W. H. *Inorg. Chem.* **1989**, *28*, 2869.

[13] The spectroscopic properties are identical with those of bona fide complexes. Compound $W(CO)_4(Ph_2PCH_2PPh_2)$ was also identified by crystal structure determination. Grim, S. O.; Briggs, B. W.; Tolman, C. A.; Jesson, J. P. *Inorg. Chem.* **1974**, *13*, 1095.

[14] The pseudosymmetry only exists around the heavy atoms. There is no exact symmetry between the two molecules in the asymmetric unit. The atomic coordinates were checked through with MISSYM program (Le Page, Y. *J. Appl. Crystallogr.* **1987**, *20*, 264), no extra symmetry element was found. The lattice parameters were also tried with several transformations, no monoclinic cell was resulted.

[15] The bending angle is defined as the dihedral angle between the two least-squares planes through the two sets of equatorial ligands. For example, atoms W(1), C(1), C(2), C(3), and P(1) in compound 1 constitute one of the planes, and W(2), C(5), C(6), C(7), and P(2) constitute the other. The staggering angle is defined as the $P_1\text{–}W_1\text{–}W_2\text{–}P_2$ torsion angle.

[16] 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 incorrectedly assigned.

[17] It was also suggested that the favored geometry of the metal–hydrogen linkage in the $[HM_2(CO)_{10}]^-$ is that of the bent M–H–M bond. Hart, D. W.; Bau, R.; Koetzle, T. F. *Organometallics* **1985**, *4*, 1591.

Table III. Positional Parameters and B_{iso} Values for the Atoms in Compounds 1, 3, 7, and 8

atom	x	y	z	B_{iso}, Å^2	atom	x	y	z	B_{iso}, Å^2
				Compound 1					
W1A	0.95903 (4)	0.33622 (3)	0.24108 (3)	3.33 (2)	C14A	0.7252 (13)	0.5019 (13)	0.4413 (8)	7.7 (11)
W2A	1.16110 (4)	0.57684 (3)	0.31606 (3)	3.24 (2)	C15A	0.7079 (13)	0.5680 (12)	0.4134 (8)	6.8 (10)
W1B	0.59978 (4)	1.15972 (3)	0.24756 (3)	3.48 (2)	C16A	0.7530 (11)	0.5719 (10)	0.3493 (7)	5.2 (8)
W2B	0.41655 (4)	1.06510 (4)	0.31677 (3)	3.58 (2)	C21A	0.7563 (9)	0.4667 (7)	0.1478 (6)	3.1 (6)
P1A	0.87116 (25)	0.50879 (21)	0.22316 (17)	2.95 (14)	C22A	0.7502 (11)	0.4844 (9)	0.0789 (7)	4.5 (7)
P2A	1.08604 (25)	0.41213 (21)	0.23263 (18)	3.03 (15)	C23A	0.6623 (11)	0.4549 (10)	0.0249 (7)	5.4 (9)
P1B	0.68159 (25)	1.00551 (21)	0.22583 (18)	3.04 (14)	C24A	0.5828 (11)	0.4074 (9)	0.0374 (7)	5.0 (8)
P2B	0.46748 (26)	0.90360 (21)	0.22624 (17)	3.10 (15)	C25A	0.5879 (11)	0.3899 (10)	0.1046 (8)	5.3 (8)
N1A	1.2764 (8)	0.5407 (7)	0.3646 (6)	4.4 (6)	C26A	0.6739 (10)	0.4186 (8)	0.1608 (7)	3.9 (6)
N1B	0.3168 (9)	1.0262 (8)	0.3606 (6)	5.9 (7)	C31A	1.1597 (9)	0.3550 (8)	0.1480 (7)	3.1 (6)
O1A	1.0191 (8)	0.5956 (7)	0.0638 (5)	6.4 (6)	C32A	1.2477 (12)	0.3115 (10)	0.1591 (8)	5.7 (9)
O2A	0.9248 (9)	0.7614 (6)	0.4254 (5)	6.5 (6)	C33A	1.3115 (11)	0.2731 (12)	0.0995 (10)	7.1 (10)
O3A	1.0741 (9)	0.8569 (6)	0.2714 (6)	7.7 (7)	C34A	1.2883 (13)	0.2788 (11)	0.0279 (8)	6.7 (9)
O4A	0.7508 (7)	0.7288 (6)	0.1860 (5)	5.3 (5)	C35A	1.2056 (12)	0.3240 (11)	0.0175 (8)	5.9 (9)
O5A	1.2202 (8)	0.7958 (6)	0.4068 (6)	7.0 (6)	C36A	1.1410 (12)	0.3614 (10)	0.0746 (7)	5.1 (8)
O6A	1.0269 (8)	0.5938 (7)	0.4578 (5)	6.2 (6)	C41A	1.0844 (9)	0.3242 (8)	0.2794 (7)	3.5 (6)
O7A	1.2832 (9)	0.5690 (8)	0.1702 (6)	8.3 (7)	C42A	1.1185 (11)	0.3476 (9)	0.3583 (7)	4.4 (7)
O8A	1.3516 (7)	0.5178 (8)	0.3916 (6)	7.2 (7)	C43A	1.1194 (12)	0.2797 (10)	0.3933 (9)	5.7 (9)
O1B	0.4946 (8)	1.0962 (7)	0.0686 (5)	6.5 (6)	C44A	1.0808 (12)	0.1905 (11)	0.3489 (9)	5.9 (9)
O2B	0.6768 (10)	1.2537 (7)	0.4333 (5)	7.3 (7)	C45A	1.0459 (11)	0.1675 (9)	0.2694 (10)	6.0 (9)
O3B	0.4950 (9)	1.3536 (7)	0.2811 (6)	7.7 (7)	C46A	1.0468 (10)	0.2331 (9)	0.2334 (8)	4.3 (7)
O4B	0.7962 (7)	1.2261 (6)	0.1965 (5)	5.1 (5)	C11B	0.7504 (9)	0.9971 (8)	0.3151 (6)	3.1 (6)
O5B	0.3872 (10)	1.2825 (7)	0.4157 (7)	9.3 (8)	C12B	0.7287 (10)	0.9258 (8)	0.3438 (7)	3.8 (6)
O6B	0.5775 (8)	1.0721 (7)	0.4624 (5)	7.1 (6)	C13B	0.7827 (11)	0.9275 (10)	0.4146 (8)	5.2 (8)
O7B	0.2489 (10)	1.0650 (9)	0.1769 (7)	9.8 (8)	C14B	0.8564 (11)	0.9951 (11)	0.4541 (8)	5.9 (9)
O8B	0.2477 (9)	1.0034 (8)	0.3891 (7)	8.5 (8)	C15B	0.8829 (12)	1.0645 (11)	0.4274 (8)	6.1 (9)
C1A	0.9927 (10)	0.6170 (8)	0.1266 (8)	4.2 (7)	C16B	0.8283 (12)	1.0662 (9)	0.3594 (8)	5.3 (8)
C2A	0.9374 (11)	0.7247 (8)	0.3593 (8)	4.8 (7)	C21B	0.7784 (9)	0.9696 (7)	0.1538 (6)	3.1 (6)
C3A	1.0343 (11)	0.7843 (9)	0.2605 (7)	4.8 (8)	C22B	0.7599 (11)	0.9846 (9)	0.0820 (7)	4.7 (7)
C4A	0.8277 (10)	0.7077 (8)	0.2090 (7)	3.6 (6)	C23B	0.8332 (13)	0.9595 (10)	0.0285 (8)	6.3 (9)
C5A	1.1989 (10)	0.7175 (9)	0.3745 (7)	4.5 (7)	C24B	0.9210 (12)	0.9197 (10)	0.0416 (8)	5.9 (9)
C6A	1.0713 (10)	0.5863 (8)	0.4052 (7)	3.9 (6)	C25B	0.9404 (11)	0.9056 (10)	0.1107 (9)	5.5 (8)
C7A	1.2408 (10)	0.5727 (9)	0.2233 (8)	4.9 (7)	C26B	0.8694 (10)	0.9287 (9)	0.1673 (8)	4.6 (7)
C9A	0.9517 (9)	0.4071 (8)	0.1854 (6)	3.2 (6)	C31B	0.3719 (9)	0.8518 (8)	0.1393 (7)	3.2 (6)
C1B	0.5328 (10)	1.1168 (8)	0.1339 (8)	4.4 (7)	C32B	0.2844 (12)	0.8075 (10)	0.1493 (8)	5.5 (8)
C2B	0.6517 (12)	1.2172 (9)	0.3668 (8)	5.2 (8)	C33B	0.2037 (11)	0.7740 (11)	0.0864 (10)	6.6 (10)
C3B	0.5315 (11)	1.2823 (9)	0.2700 (7)	4.9 (7)	C34B	0.2101 (12)	0.7848 (10)	0.0165 (8)	5.5 (8)
C4B	0.7209 (10)	1.2052 (8)	0.2191 (7)	3.7 (6)	C35B	0.2937 (12)	0.8306 (10)	0.0085 (7)	5.5 (9)
C5B	0.3995 (11)	1.2047 (9)	0.3815 (9)	5.7 (8)	C36B	0.3754 (10)	0.8652 (9)	0.0684 (7)	4.3 (7)
C6B	0.5251 (12)	1.0680 (9)	0.4085 (7)	5.1 (7)	C41B	0.4781 (9)	0.8081 (8)	0.2645 (6)	3.1 (6)
C7B	0.3084 (13)	1.0676 (10)	0.2266 (8)	6.2 (9)	C42B	0.4562 (11)	0.8202 (9)	0.3414 (7)	4.7 (7)
C9B	0.5908 (9)	0.9009 (7)	0.1818 (6)	3.0 (5)	C43B	0.4665 (12)	0.7454 (10)	0.3665 (8)	5.3 (8)
C11A	0.8215 (9)	0.5025 (8)	0.3115 (6)	3.1 (6)	C44B	0.4951 (11)	0.6619 (10)	0.3174 (9)	5.7 (9)
C12A	0.8434 (9)	0.4332 (9)	0.3415 (7)	4.0 (6)	C45B	0.5182 (11)	0.6459 (9)	0.2411 (9)	5.5 (9)
C13A	0.7947 (12)	0.4336 (11)	0.4063 (8)	6.0 (9)	C46B	0.5097 (10)	0.7190 (8)	0.2137 (7)	4.2 (7)
				Compound 3					
W	0.49174 (3)	0.31952 (2)	0.22369 (5)	3.85 (2)	C12	0.3622 (10)	0.4379 (6)	0.4536 (14)	5.0 (8)
P	0.33274 (21)	0.34042 (13)	0.30987 (35)	3.40 (17)	C13	0.3703 (12)	0.4704 (7)	0.5633 (17)	6.0 (9)
N(C)	0.5108 (9)	0.3985 (5)	0.2060 (14)	6.3 (7)	C14	0.3577 (13)	0.4454 (9)	0.6798 (19)	7.5 (11)
O1	0.4427 (9)	0.3016 (5)	−0.0668 (12)	8.3 (8)	C15	0.3380 (13)	0.3873 (8)	0.6832 (17)	6.6 (11)
O2	0.5598 (8)	0.3244 (6)	0.5088 (13)	9.0 (8)	C16	0.3306 (10)	0.3555 (6)	0.5778 (15)	5.1 (8)
O3	0.6932 (7)	0.2936 (5)	0.1301 (12)	8.0 (7)	C21	0.2530 (9)	0.3837 (5)	0.2182 (17)	4.3 (7)
O4	0.5221 (8)	0.4475 (4)	0.1884 (12)	8.5 (7)	C22	0.1734 (10)	0.4027 (7)	0.2707 (15)	5.3 (8)
C1	0.4572 (10)	0.3103 (6)	0.0396 (17)	5.0 (7)	C23	0.1107 (10)	0.4350 (7)	0.2010 (22)	6.7 (10)
C2	0.5360 (9)	0.3220 (7)	0.4070 (18)	5.8 (9)	C24	0.1295 (17)	0.4454 (9)	0.0785 (21)	9.0 (14)
C3	0.6195 (9)	0.3020 (5)	0.1659 (14)	4.3 (7)	C25	0.2067 (17)	0.4270 (9)	0.0265 (17)	9.8 (14)
C5	0.2613 (8)	0.2793 (5)	0.3544 (14)	4.1 (7)	C26	0.2700 (12)	0.3957 (7)	0.0934 (19)	7.0 (10)
C6	0.2078 (12)	0.2500	0.2500	6.0 (13)	H	0.423 (10)	0.250	0.250	5.4 (44)
C11	0.3394 (8)	0.3802 (5)	0.4581 (13)	3.4 (6)					
				Compound 7					
W1	0.22418 (2)	0.05308 (4)	0.45659 (3)	3.30 (2)	C3	0.2750 (6)	0.1201 (10)	0.5552 (7)	4.1 (5)
W2	0.31969 (2)	−0.17622 (4)	0.50758 (3)	3.62 (2)	C4	0.1787 (6)	0.1898 (10)	0.4210 (7)	4.7 (6)
P1	0.16560 (13)	−0.04689 (22)	0.33018 (16)	3.11 (12)	C5	0.3878 (7)	−0.0758 (11)	0.5751 (8)	5.4 (6)
P2	0.22503 (14)	−0.26769 (23)	0.40827 (17)	3.47 (12)	C6	0.2935 (7)	−0.2270 (11)	0.6062 (8)	5.2 (7)
O1	0.3421 (5)	0.1263 (8)	0.3825 (6)	6.5 (5)	C7	0.3579 (6)	−0.1381 (10)	0.4166 (8)	4.6 (6)
O2	0.1090 (7)	0.0221 (11)	0.5429 (8)	10.5 (9)	C8	0.3826 (7)	−0.3011 (11)	0.5282 (8)	5.0 (6)
O3	0.3042 (5)	0.1622 (8)	0.6139 (6)	6.6 (5)	C9	0.1978 (5)	−0.1855 (8)	0.3193 (6)	3.3 (5)
O4	0.1503 (5)	0.2717 (8)	0.4051 (6)	7.3 (6)	C11	0.1705 (5)	0.0166 (9)	0.2357 (6)	3.4 (5)
O5	0.4247 (5)	−0.0162 (8)	0.6112 (7)	8.2 (6)	C12	0.1778 (8)	0.1248 (10)	0.2304 (8)	5.7 (8)
O6	0.2847 (7)	−0.2599 (10)	0.6634 (6)	9.1 (8)	C13	0.1796 (8)	0.1757 (12)	0.1626 (9)	6.8 (9)
O7	0.3836 (5)	−0.1211 (8)	0.3663 (7)	7.2 (6)	C14	0.1750 (8)	0.1186 (14)	0.0967 (9)	6.6 (8)
O8	0.4185 (5)	−0.3729 (8)	0.5428 (7)	7.1 (6)	C15	0.1668 (13)	0.0106 (14)	0.0986 (9)	11.0 (16)
C1	0.2996 (6)	0.0947 (9)	0.4070 (7)	4.2 (6)	C16	0.1636 (10)	−0.0396 (11)	0.1683 (8)	8.5 (12)
C2	0.1496 (7)	0.0272 (12)	0.5108 (8)	5.6 (7)	C21	0.0748 (5)	−0.0676 (10)	0.3089 (7)	3.9 (5)

Table III (Continued)

atom	*x*	*y*	*z*	B_{iso}, Å^2	atom	*x*	*y*	*z*	B_{iso}, Å^2
				Compound 7					
C22	0.0368 (7)	0.0099 (16)	0.3334 (9)	7.7 (9)	C44	0.0221 (9)	−0.3337 (20)	0.4608 (14)	10.6 (14)
C23	−0.0321 (8)	0.0028 (19)	0.3169 (11)	9.2 (13)	C45	0.0680 (8)	−0.2631 (15)	0.5090 (10)	7.6 (10)
C24	−0.0627 (7)	−0.0807 (20)	0.2746 (14)	9.9 (13)	C46	0.1289 (7)	−0.2442 (11)	0.4932 (8)	5.6 (7)
C25	−0.0266 (10)	−0.1498 (17)	0.2437 (22)	17.5 (23)	N	0.4596	0.1504	0.1736	4.6
C26	0.0406 (8)	−0.1483 (14)	0.2706 (14)	11.6 (13)	C51	0.3912	0.1041	0.1516	5.9
C31	0.2447 (6)	−0.3977 (9)	0.3676 (8)	4.5 (6)	C52	0.3703	0.0231	0.1987	5.1
C32	0.2410 (6)	−0.4161 (10)	0.2894 (8)	4.8 (6)	C53	0.5107	0.0653	0.1647	5.9
C33	0.2579 (8)	−0.5193 (13)	0.2656 (10)	6.6 (9)	C54	0.5761	0.0883	0.1682	5.5
C34	0.2744 (8)	−0.5991 (12)	0.3158 (14)	7.5 (10)	C55	0.4615	0.2498	0.1181	6.1
C35	0.2804 (8)	−0.5835 (12)	0.3970 (13)	7.7 (10)	C56	0.4518	0.2407	0.0403	5.5
C36	0.2639 (7)	−0.4828 (11)	0.4215 (9)	6.0 (8)	C57	0.4813	0.1928	0.2612	6.0
C41	0.1462 (5)	−0.2979 (10)	0.4329 (7)	4.1 (5)	C58	0.4544	0.2554	0.2995	5.9
C42	0.1019 (8)	−0.3754 (15)	0.3894 (10)	8.0 (9)	H	0.256 (5)	−0.086 (8)	0.503 (6)	4.7 (24)
C43	0.0395 (10)	−0.3880 (19)	0.4044 (12)	10.2 (13)					
				Compound 8					
W1	0.77847 (4)	0.96162 (8)	0.03328 (3)	3.00 (4)	C31	0.8972 (8)	0.7754 (18)	−0.0373 (8)	3.1 (9)
W2	0.61858 (4)	0.96477 (10)	−0.07925 (4)	4.26 (5)	C32	0.9258 (10)	0.8917 (19)	−0.0483 (10)	4.7 (11)
P1	0.81752 (25)	0.77524 (46)	−0.02237 (23)	3.21 (24)	C33	0.9826 (10)	0.8863 (23)	−0.0661 (11)	5.0 (12)
P2	0.65821 (24)	0.98561 (49)	−0.17702 (23)	3.48 (23)	C34	1.0131 (10)	0.7745 (23)	−0.0723 (10)	4.7 (11)
O1	0.7253 (10)	0.7557 (17)	0.1127 (9)	8.6 (12)	C35	0.9861 (11)	0.6587 (24)	−0.0625 (11)	5.3 (13)
O2	0.8295 (7)	1.2004 (15)	−0.0300 (6)	5.3 (8)	C36	0.9302 (10)	0.6563 (18)	−0.0423 (8)	3.9 (10)
O3	0.7198 (8)	1.1634 (14)	0.1087 (8)	6.1 (9)	C41	0.6497 (10)	1.1564 (18)	−0.2044 (9)	3.8 (10)
O4	0.9131 (7)	0.9827 (15)	0.1472 (7)	5.7 (8)	C42	0.5878 (10)	1.2041 (22)	−0.2434 (10)	4.9 (11)
O5	0.5763 (9)	0.9544 (27)	0.0476 (7)	12.3 (17)	C43	0.5790 (12)	1.3386 (27)	−0.2552 (12)	6.5 (14)
O6	0.6339 (11)	1.2727 (20)	−0.0561 (8)	9.2 (13)	C44	0.6307 (16)	1.4213 (22)	−0.2303 (12)	6.4 (16)
O7	0.5947 (12)	0.6633 (21)	−0.0829 (11)	11.2 (16)	C45	0.6916 (14)	1.3759 (22)	−0.1908 (12)	6.2 (15)
O8	0.4733 (8)	1.0094 (22)	−0.1761 (9)	10.3 (14)	C46	0.7016 (10)	1.2440 (20)	−0.1773 (9)	4.4 (11)
C1	0.7434 (10)	0.8278 (22)	0.0811 (10)	4.7 (12)	C51	0.6162 (9)	0.8998 (18)	−0.2539 (9)	3.6 (9)
C2	0.8106 (9)	1.1089 (21)	−0.0104 (10)	4.3 (10)	C52	0.5737 (11)	0.8002 (23)	−0.2566 (9)	5.0 (12)
C3	0.7395 (10)	1.0913 (20)	0.0809 (10)	4.3 (11)	C53	0.5469 (12)	0.7249 (23)	−0.3148 (12)	6.1 (13)
C4	0.8624 (10)	0.9698 (19)	0.1048 (9)	3.9 (10)	C54	0.5643 (12)	0.7553 (22)	−0.3673 (11)	6.0 (13)
C5	0.5927 (10)	0.9604 (28)	0.0019 (11)	7.0 (15)	C55	0.6058 (12)	0.8555 (24)	−0.3657 (10)	5.7 (14)
C6	0.6305 (12)	1.1566 (30)	−0.0625 (10)	6.1 (15)	C56	0.6320 (10)	0.9283 (18)	−0.3095 (9)	4.3 (10)
C7	0.6062 (14)	0.7751 (29)	−0.0797 (12)	7.7 (17)	N	0.6187	0.4661	0.1710	7.5
C8	0.5274 (12)	0.9913 (26)	−0.1373 (12)	6.9 (15)	C61	0.6260	0.4712	0.1070	8.7
C9	0.7618 (9)	0.7257 (17)	−0.1049 (9)	3.5 (9)	C62	0.5806	0.3837	0.0710	9.0
C10	0.7645 (9)	0.8041 (20)	−0.1636 (9)	4.1 (10)	C63	0.6671	0.5673	0.2206	9.9
C11	0.7465 (8)	0.9470 (20)	−0.1655 (8)	3.8 (9)	C64	0.7294	0.4685	0.2396	9.4
C21	0.8250 (10)	0.6286 (18)	0.0271 (9)	3.7 (10)	C65	0.5535	0.5346	0.1703	9.1
C22	0.7781 (11)	0.5294 (22)	0.0133 (11)	5.5 (12)	C66	0.5492	0.6548	0.1254	10.5
C23	0.7848 (15)	0.4261 (20)	0.0537 (14)	6.8 (17)	C67	0.6035	0.3263	0.1947	9.3
C24	0.8360 (17)	0.4145 (25)	0.1121 (15)	7.4 (18)	C68	0.6259	0.2883	0.2541	9.5
C25	0.8839 (13)	0.5110 (24)	0.1275 (11)	6.2 (14)	H	0.707 (7)	0.894 (15)	−0.050 (7)	4.8 (39)
C26	0.8774 (10)	0.6204 (21)	0.0857 (11)	5.3 (12)					

illustrates the equal probabilities of displacement of two axial CO ligands in 7 by NO^+.

We were able to locate the position of μ-H in the final difference Fourier maps for complexes 3, 7, and 8. The observed W–H distances (3, 1.94 Å; 7, 1.9/1.7 Å; 8, 2.0/1.9 Å) and the W–H–W angles (3, 117°; 7, 140°; 8, 120°) are in agreement with the reported values (W–H, 1.8–1.9 Å; W–H–W, 115–135°).[19] It was reported that the relative position of the hydride bridge to the phosphine bridge varied from being perpendicular in $(\mu\text{-H})(\mu\text{-}Ph_2PCH_2PPh_2)Mo_2(CO)_8^-$ to being parallel in $(\mu\text{-H})(\mu\text{-}Ph_2P(CH_2)_4PPh_2)Mo_2(CO)_8^-$.[10] We also observed a similar trend in the aforementioned complexes, i.e., the hydride bridge and the phosphine bridge are mutually perpendicular in 7 and mutually parallel in complexes 3 and 8 which contain phosphine bridge of longer backbone.

The W–W distance in 1 (3.349 (1), 3.350 (1) Å) is significantly shorter than that in 7 (3.4286 (7) Å) and so is 3 (3.315 (1) Å) compared to 8 (3.434 (1) Å), suggesting the electronic influence of the NO ligand upon the W–W interaction in 3c–2e W–H–W linkage. It is interesting to note that 3 has a shorter W–W distance than 1, although the W–W distance in 8 is longer than that in 7. We reasoned that there might be a compromise between the following two factors: (1) the interatomic repulsion between the equatorial ligands belonging to different tungsten atoms of the same molecule; (2) the steric congestion witin the diphosphine ligands. It seems that the phosphine bridge serves to bring the two metal atoms into closer contact; for instance, the W–W distance in 1 (3.349 (1), 3.350 (1) Å) is considerably shorter than those in isomeric $(CO)_5(\mu\text{-H})W(CO)_2(\eta^2\text{-}Ph_2PCH_2PPH_2)(NO)$ (3.464 (2) Å) and $(CO)_5W(\mu\text{-H})W(CO)_2(Ph_2PH)_2(NO)$ (3.418 (1) Å).[5] Even $(\mu\text{-H})(\mu\text{-}Ph_2PCH_2PPh_2)W_2(CO)_8^-$ has a shorter W–W distance (3.4286 (7) Å) than $(CO)_5W(\mu\text{-H})W(CO)_2(\eta^2\text{-}Ph_2PCH_2PPh_2)(NO)$.

Other relevant crystal data for 1, 3, 7, and 8 appear to be normal. The W–C–O and W–N–O linkages do not deviate significantly from linearity. The W–N distances of 1.86 (1)/1.79 (1) Å (complex 1) and 1.89 (1) Å (complex 3) are 0.1–0.2 Å shorter than those of W–C, ranging from 1.96–2.05 Å. In general the W–C bonds of carbonyl groups trans to the bridging hydride (1.92–1.96 Å) are shorter than those trans to each other (1.96–2.05 Å), whereas those of carbonyl groups (1.95–2.03 Å) trans to the P donor lie

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[18] The two independent molecules in compound 1 are these geometrical isomers. The disordered NO–CO model of compound 3 is actually the two geometrical isomers distribute evenly in the lattice. Compound 2 which is currently under investigation also has such two geometrical isomers in the lattice.

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

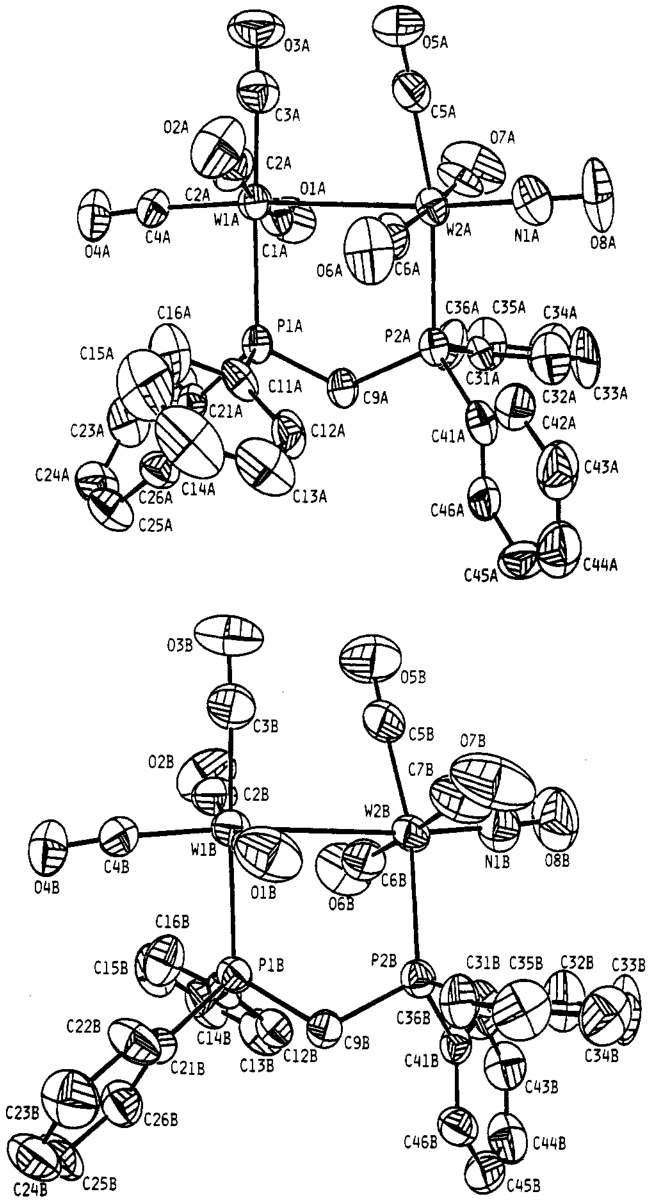

Figure 1. Molecular structure of 1. The ellipsoids are drawn with 30% probability boundaries.

between the two. These observations are consistent with the relative π-electron-accepting ability of CO > phosphine > H.

The spectroscopic properties (Table I) for complexes 1–6 are consistent with their formulation. The proton chemical shifts of the hydrides are centered between 9.5 to 11 ppm upfield from Me_4Si and the H–P coupling constants ($^2J_{H-P}$) range from 15 to 25 Hz. The coupling constant, $^1J_{H-W}$, ranges from 39 to 50 Hz. However, only in complex 4 can the two sets of tungsten satellites due to the magnetic inequivalence of the two tungsten atoms be resolved. The magnetically inequivalent phosphorus atoms in the same molecule have their chemical shifts differ by several parts per million. The one-bond tungsten–phosphorus coupling constants, ranging from 199 to 253 Hz, are consistent with those frequently observed.[20]

Three prominent ν(CO) absorption are observed for 1–6: one medium band around 2080 cm^{-1}, a strong band around 2010 cm^{-1}, and a strong band near 1890 cm^{-1}. A ν(NO) absorption appears around 1660 cm^{-1}. The region between

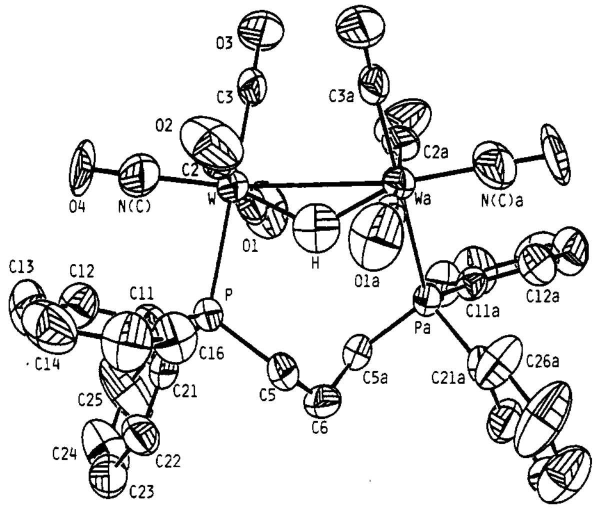

Figure 2. Molecular structure of 3. Atoms labeled with "a" are related to the corresponding unlabeled atoms by a 2-fold axis passing through the center of W–Wa axis and carbon C(6). The ellipsoids are drawn with 30% probability boundaries.

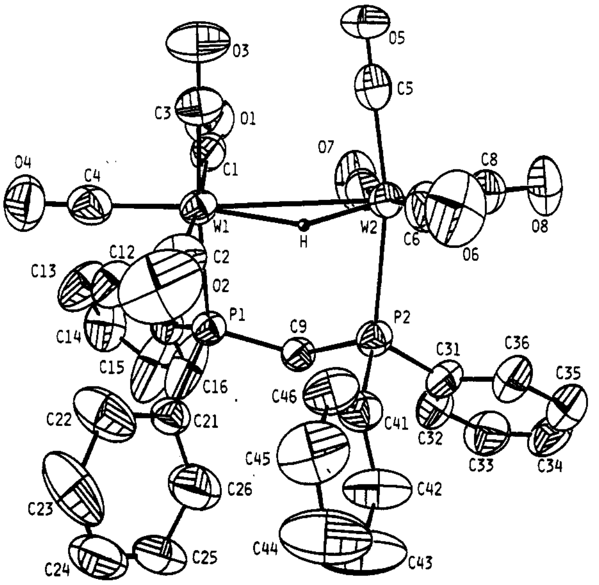

Figure 3. Molecular structure of the anion for 7. The ellipsoids are drawn with 30% probability boundaries.

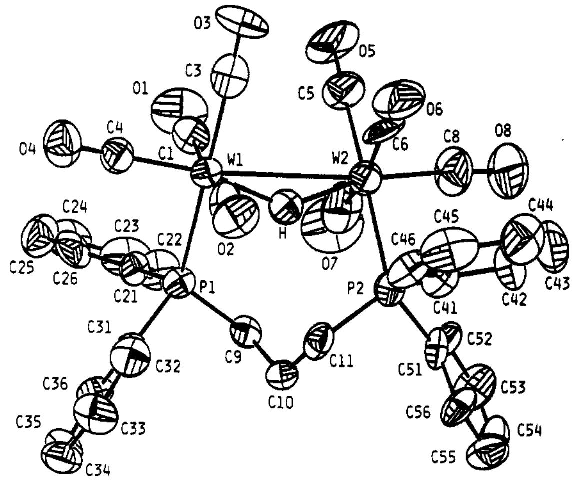

Figure 4. Molecular structure of the anion for 8. The ellipsoids are drawn with 30% probability boundaries.

the lower two bands becomes more complex as chain length increases. The higher ν(CO) stretchings in 1–6 than in

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[20] Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer-Verlag: New York, 1979.

Table IV. Selected Bond Distances (Å) and Angles (deg) for Complexes 1, 3, 7, and 8

	1^a	3	7	8
		Distances		
W(1)–W(2) or W–Wa	3.349 (1); 3.350 (1)	3.315 (1)	3.4286 (7)	3.434 (1)
W(1)–C(1)	2.02 (1); 2.02 (1)		2.04 (1)	2.00 (2)
W–C(1)		2.00 (2)		
W(1)–C(2)	2.04 (1); 2.05 (1)		2.04 (1)	2.01 (2)
W–C(2)		2.02 (2)		
W(1)–C(3)	1.98 (1); 1.99 (1)		1.95 (1)	2.01 (2)
W–C(3)		2.00 (1)		
W(1)–C(4)	1.96 (1); 1.91 (1)		1.95 (1)	1.92 (2)
W(1)–P(1)	2.505 (3); 2.500 (3)		2.536 (3)	2.534 (5)
W–P		2.534 (3)		
W(2)–C(5)	2.03 (1); 2.04 (1)		2.01 (1)	2.00 (2)
W(2)–C(6)	2.05 (1); 2.06 (1)		2.03 (1)	2.00 (3)
W(2)–C(7)	2.04 (1); 2.06 (2)		2.01 (1)	1.96 (3)
W(2)–C(8)			1.98 (1)	1.93 (2)
W(2)–P(2)	2.523 (3); 2.528 (3)		2.513 (3)	2.519 (5)
W(2)–N(1)	1.86 (1); 1.79 (1)			
W–N(C)		1.89 (1)		
W(1)–H			1.9 (1)	2.0 (2)
W(2)–H			1.7 (1)	1.9 (2)
W–H		1.94 (8)		
C(1)–O(1)	1.15 (2); 1.16 (2)	1.15 (2)	1.14 (2)	1.15 (3)
C(2)–O(2)	1.15 (2); 1.14 (2)	1.12 (2)	1.13 (2)	1.15 (3)
C(3)–O(3)	1.16 (2); 1.14 (2)	1.15 (2)	1.16 (2)	1.12 (3)
C(4)–O(4)			1.16 (2)	1.16 (2)
C(5)–O(5)	1.13 (2); 1.13 (2)		1.12 (2)	1.15 (3)
C(6)–O(6)	1.14 (2); 1.12 (2)		1.14 (2)	1.20 (4)
C(7)–O(7)	1.14 (2); 1.12 (2)		1.16 (2)	1.17 (4)
C(8)–O(8)			1.14 (2)	1.18 (3)
N(1)–O(8)	1.17 (1); 1.19 (2)			
N(C)–O(4)		1.18 (2)		
		Angles		
W(1)–C(1)–O(1)	174 (1); 177 (1)		174 (1)	175 (2)
W–C(1)–O(1)		174 (1)		
W(1)–C(2)–O(2)	178 (1); 176 (1)		174 (1)	173 (2)
W–C(2)–O(2)		179 (1)		
W(1)–C(3)–O(3)	177 (1); 177 (1)		178 (1)	178 (2)
W–C(3)–O(3)		178 (1)		
W(1)–C(4)–O(4)	176 (1); 174 (1)		175 (1)	176 (2)
W(2)–N(1)–O(8)	176.3 (9); 177 (1)			
W–N(C)–O(4)		177 (1)		
W(2)–C(5)–O(5)	180 (1); 178 (1)		177 (1)	178 (2)
W(2)–C(6)–O(6)	176 (1); 174 (1)		174 (1)	176 (2)
W(2)–C(7)–O(7)	178 (1); 177 (1)		175 (1)	176 (2)
W(2)–C(8)–O(8)			178 (1)	176 (2)
C(1)–W(1)–C(2)	172.6 (5); 171.8 (5)		174.1 (5)	174.7 (8)
C(1)–W–C(2)		174.0 (6)		
C(1)–W(1)–C(3)	88.3 (5); 88.1 (5)		88.5 (5)	84.5 (8)
C(1)–W–C(3)		85.5 (6)		
C(1)–W(1)–C(4)	89.5 (5); 90.9 (5)		90.4 (5)	91.3 (8)
C(1)–W–N(C)		92.8 (6)		
C(1)–W(1)–P(1)	93.5 (3); 93.8 (3)		89.8 (3)	87.8 (6)
C(1)–W–P		97.7 (4)		
C(2)–W(1)–C(3)	84.4 (5); 84.2 (5)		87.4 (5)	90.2 (8)
C(2)–W–C(3)		89.8 (6)		
C(2)–W(1)–C(4)	91.8 (5); 92.3 (5)		95.5 (6)	88.5 (8)
C(2)–W–N(C)		91.0 (7)		
C(2)–W(1)–P(1)	93.7 (4); 93.8 (4)		94.6 (4)	97.5 (6)
C(2)–W–P		87.0 (4)		
C(3)–W(1)–C(4)	92.4 (5); 92.6 (5)		91.0 (5)	89.5 (8)
C(3)–W–N(C)		92.1 (5)		
C(3)–W(1)–P(1)	176.5 (4); 176.9 (4)		175.1 (4)	172.1 (5)
C(3)–W–P		176.7 (4)		
C(5)–W(2)–C(6)	88.0 (5); 86.9 (6)		89.8 (6)	85 (1)
C(5)–W(2)–C(7)	90.9 (5); 91.1 (6)		87.6 (6)	85 (1)
C(5)–W(2)–C(8)			92.7 (5)	93.4 (9)

(μ-H)(μ-Ph_2P–PPh_2)$W_2(CO)_8^-$ agrees with the better π-accepting ability of NO than CO.

Chemical Reactivity. Complexes 1–6 are found to be less stable than their precursor, (μ-H)(μ-Ph_2P–PPh_2)$W_2(CO)_8^-$. For example, in refluxing THF complex 1 decomposes to yield $W(CO)_4(Ph_2PCH_2PPh_2)$ within 30 min, while (μ-H)(μ-$Ph_2PCH_2PPh_2$)$W_2(CO)_8^-$ survives in refluxing THF for at least 3 days. On the other hand, 1–6 are more robust than (μ-H)$W_2(CO)_9(NO)$ which does not contain phosphine bridge. The latter decomposes in all common solvents while 1–6 remain intact in CH_2Cl_2 and Et_2O. We found that ligand substitution of 1–3 occurred at the tungsten atom containing NO via the assistance of Me_3NO. Complexes (μ-H)(μ-$Ph_2P(CH_2)_nPPh_2$)$W_2(CO)_6(Ph_2PH)(NO)$ (n = 1–3, designated as **9**, **10**, and **11**) were obtained from the reaction. The formulation of these complexes has been confirmed by X-ray structural determination on compound **9**.[21] The spectroscopic properties of **9**–**11** (Table I) are consistent with their formulation: one hydride chemical shift at −10 to −12 ppm (δ value) in the ^{1}H NMR, three different chemical shifts for the phosphorus atoms in the ^{31}P NMR, and a ν(NO) stretching between 1630–1665 cm^{-1}. The three different phosphorus atoms can be differentiated from one another without ambiguity: only two-bond phosphorus–phosphorus couplings are resolved, and one-bond phosphorus–hydrogen coupling (**9**, 349; **10**, 352; **11**, 350 Hz) is characteristic for Ph_2PH. The assymmetric nature of these complexes is most clearly seen from the presence of diastereometric methylene protons in **9**. The successful synthesis of **9**–**11** nicely illustrated the crucial role of the diphosphine ligands in retaining the dimeric metal unit as frequently observed[22] and the NO ligand in activating the coordinated CO ligand.[23] The chemical reactivity of the complexes **1**–**6** will be pursued further and be reported in due course.

Acknowledgment. We wish to thank the National Science Council of Republic of China for the support (Grant NSC 79-0208-M001-07).

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 compounds 1, 3, 7, and 8 (23 pages); listings of structure factors (91 pages). Ordering information is given on any current masthead page.

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(21) Lin, J. T.; Chang, K. Y. Unpublished results. Orange crystals of **9** were grown by cooling a concentrated solution of **9** in CH_3CN. Crystal data: orthorhombic, space group *Pbca*, a = 19.408 (5), b = 36.100 (8), c = 12.025 (1) Å.

(22) (a) Blagg, A.; Robson, R.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1987**, 2171. (b) Jacobsen, G. B.; Shaw, B .L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1987**, 1509. (c) Ibid. Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* 1987, 1489.

(23) Richter-Addo, G. B.; Legzdins, P. *Chem. Rev.* **1988**, *88*, 1010.

Isomerism in 47- and 48-Electron (Methylidyne)triruthenium Clusters. Crystal Structures[1] of $(\mu\text{-H})_3Ru_3(\mu_3\text{-COMe})(CO)_6\{\mu_3\text{-}(PPh_2CH_2)_3CMe\}$ and $(\mu\text{-H})_3Ru_3(\mu_3\text{-COMe})(CO)_7\{\mu_2\text{-}(PPh_2)_3CH\}\cdot1.25CH_2Cl_2$

Melvyn Rowen Churchill,* Charles H. Lake, William G. Feighery, and Jerome B. Keister*

Department of Chemistry, University at Buffalo, State University of New York, Buffalo, New York 14214

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Ligand substitution on $(\mu\text{-H})_3Ru_3(\mu_3\text{-COMe})(CO)_9$ has been used to prepare the clusters $(\mu\text{-H})_3Ru_3(\mu_3\text{-COMe})(CO)_6\{\mu_3\text{-}(PPh_2CH_2)_3CMe\}$ and $(\mu\text{-H})_3Ru_3(\mu_3\text{-COMe})(CO)_7\{\mu_2\text{-}(PPh_2)_3CH\}$. The complex $(\mu\text{-H})_3Ru_3(\mu_3\text{-COMe})(CO)_6\{\mu_3\text{-}(PPh_2CH_2)_3CMe\}$ crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with a = 10.053 (2) Å, b = 12.920 (3) Å, c = 19.185 (4) Å, α = 87.23 (2)°, β = 75.80 (2)°, γ = 77.62 (2)°, V = 2359.6 (9) Å^3, and Z = 2. The molecule has approximate C_3 symmetry, with the μ_3-COMe group and the $\mu_3\text{-MeC}(CH_2PPh_2)_3$ ligand capping opposite faces of the planar triruthenium core; the P-donor atoms thus are all in axial sites. Electrochemical and chemical oxidation of $(\mu\text{-H})_3Ru_3(\mu_3\text{-COMe})(CO)_6\{\mu_3\text{-}(PPh_2CH_2)_3CMe\}$ forms the corresponding 47-electron radical cation, characterized by EPR spectroscopy. The complex $(\mu\text{-H})_3Ru_3(\mu_3\text{-COMe})(CO)_7\{\mu_2\text{-}(PPh_2)_3CH\}$ crystallizes from CH_2Cl_2 in the centrosymmetric monoclinic space group $P2_1/n$ with a = 21.653 (6) Å, b = 19.078 (4) Å, c = 25.238 (8) Å, β = 106.63 (3)°, V = 9989 (5) Å^3, and Z = 8. The crystallographic asymmetric unit contains 2 triruthenium cluster molecules and 2.5 CH_2Cl_2 molecules. The $(PPh_2)_3CH$ ligand behaves only as a bidentate bridging ligand and spans adjacent equatorial sites on two ruthenium atoms.

Introduction

Recently the importance of redox processes in organometallic chemistry has become apparent.[2] Of particular interest are the redox properties of transition-metal cluster compounds, which can in principle display a wide range of oxidation states. A number of electrochemical studies have focused upon clusters containing a triangular metal core capped by a main-group atom.[3-8] Many of these

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(1) Structural Studies on Ruthenium Carbonyl Hydrides. 16. Part 15: Churchill, M. R.; Buttrey, L. A.; Keister, J. B.; Ziller, J. W.; Janik, T. S.; Striejewske, W. S. *Organometallics* **1990**, *9*, 766.

(2) (a) Tyler, D. R. *Prog. Inorg. Chem.* **1988**, *36*, 125. (b) Kochi, J. K. *J. Organomet. Chem.* **1986**, *300*, 139. (c) Connelly, N. G. *Chem. Soc. Rev.* **1989**, *18*, 153. (d) Geiger, W. E. *Prog. Inorg. Chem.* **1985**, *33*, 275. (e) Connelly, N. G.; Geiger, W. E. *Adv. Organomet. Chem.* **1985**, *24*, 87. (f) Drake, S. R. *Polyhedron* **1990**, *9*, 455.

(3) (a) Wei, C. H.; Dahl, L. F. *Inorg. Chem.* **1967**, *6*, 1229. (b) Strouse, C. E.; Dahl, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 6032. (c) Honrath, U.; Vahrenkamp, H. *Z. Naturforsch.* **1984**, *39B*, 555.

(4) (a) Peake, B. M.; Robinson, B. H.; Simpson, J.; Watson, D. J. *Inorg. Chem.* **1977**, *16*, 405. (b) Bond, A. M.; Peake, B. M.; Robinson, B. H.; Simpson, J.; Watson, D. J. *Inorg. Chem.* **1977**, *16*, 410. (c) Bond, A. M.; Dawson, P. A.; Peake, B. M.; Rieger, P. H.; Robinson, B. H.; Simpson, J. *Inorg. Chem.* **1979**, *18*, 1413. (d) Downard, A. J.; Robinson, B. H.; Simpson, J. *Organometallics* **1986**, *5*, 1122. (e) Kotz, J. C.; Petersen, J. V.; Reed, R. C. *J. Organomet. Chem.* **1976**, *120*, 433.

0276-7333/91/2310-2384$02.50/0