Journal of Organometallic Chemistry, 453 (1993) 221–229

JOM 23465

Synthesis, structure, and reactivity of $HMo_2(CO)_9(NO)$

Jiann T. Lin [a], An C. Yeh [b], Thamas Y.R. Tsai [b] and Yuh S. Wen [a]

[a] *Institute of Chemistry, Academia Sinica, Nankang, Taipei (Taiwan)*
[b] *Department of Chemistry, Chun-Yuan Christian University, Chung-Li (Taiwan)*

(Received November 13, 1992; in revised form December 11, 1992)

Abstract

Treatment of $(Na)(HMo_2(CO)_{10})$ with acidic sodium nitrite affords $HMo_2(CO)_9(NO)$ (**1**) in 32% yield. Several derivatives of **1**, $HMo_2(CO)_8(L)(NO)$ (**2**, L = PCy_3; **3**, L = PPh_3; **4**, L = $P(p\text{-}C_6H_4OMe)_3$), $HMo_2(CO)_7(L)_2(NO)$ (**5**, L = $P(OMe)_3$; **6**, L = Ph_2PH), $HMo_2(CO)_7(MeNC)_2(NO_{eq})$ (**7**), $HMo_2(CO)_7(^iPrNC)_2(NO_{ax})$ (**8**), $HMo_2(CO)_7(PCy_3)(^nPrNC)(NO)$ (**9**), and $(NMe_4)(HMo_2(CO)_7(\eta^2\text{-}S_2CNEt_2)(NO))$ (**10**), have been synthesized. X-ray crystal structural analyses for **1**, **2**, **6**, and **9** were carried out. **1**: triclinic, $P\bar{1}$, $Z = 1$, a 6.810(2), b 6.906(3), c 8.741(2) Å, α 103.50(2), β 68.85(2), γ 92.04(2)°, V 372.3(2) Å^3, $R = 0.020$, $R_W = 0.025$. **2**: monoclinic, $P2_1/c$, $Z = 4$, a 12.179(1), b 14.983(1), c 17.068(2) Å, β 92.126(8)°, V 3112.4(5) Å^3, $R = 0.035$, $R_W = 0.041$. **6**: monoclinic, $P2_1/c$, $Z = 4$, a 9.402(2), b 16.614(3), c 21.635(3) Å, β 92.58(3)°, V 3376(1) Å^3, $R = 0.034$, $R_W = 0.035$. **9**: orthorhombic, *Pbca*, $Z = 8$, a 17.113(7), b 17.715(2), c 22.954(3) Å, V 6959(3) Å^3, $R = 0.036$, $R_W = 0.038$.

1. Introduction

Transition-metal complexes with three-centre, two-electron (3c–2e) metal–hydrogen–metal bonds have attracted considerable interest [1]. From this class of compounds, dimeric complexes with a single hydrogen bridge [2*], $HM_2(CO)_{10}^-$(M = Cr, Mo, W) [3], $HW_2(CO)_9(NO)$ [4], $HM_2(CO)_9(L)^-$, and $HM_2(CO)_8(L)_2^-$ (M = Mo, W; L = phosphine) [5], have been extensively investigated. The structural variations of these complexes were found to be dependent on metal [6], counterion and crystal packing [7], and substituent ligands [8].

We previously reported the reaction of $HW_2(CO)_9(NO)$ with various substrates, and isolated complexes of different structures [9–11]. In order to probe the influence of the metal on the structure as well as the reactivity of dinuclear complexes containing a hydrogen bridge, we have extended our study to $HMo_2(CO)_9(NO)$. In this paper, we describe the synthesis, structure, and reactivity of $HMo_2(CO)_9(NO)$.

2. Experimental section

2.1. General procedure

All manipulations were carried out under an atmosphere of N_2 using Schlenk techniques or a N_2-filled glovebox. All solvents were dried and degassed by standard procedures. All column chromatography was performed under N_2 by use of silica gel (230–400 mesh ASTM, Merck) as the stationary phase in a column 2.5 cm in diameter. Compounds $(Na)(HMo_2(CO)_9(NO))$ [12] and Ph_3PN^iPr [13] were prepared by published procedures. Elementary analyses were performed on a Perkin-Elmer 2400 CHN analyzer. Nuclear magnetic resonance spectra were obtained with a Bruker MSL-200 or AM-200 instrument. The ^1H and ^{31}P NMR spectra were referenced to TMS and external 85% H_3PO_4, respectively.

2.1.1. $HMo_2(CO)_9(NO)$ (1)

To an aqueous solution containing $(Na)(HMo_2(CO)_{10})$ prepared *in situ* from 20.0 g (76.0 mmol) of $Mo(CO)_6$ was added $Na^+NO_2^-$ (22.0 g, 200 mmol). The solution was then chilled to 0°C and 6 M acetic acid was added dropwise with vigorous stirring. After the addition of acetic acid was complete, the resulting orange-yellow precipitates were washed with cold water (3 × 50 ml) and dried. $Mo(CO)_6$ was removed from

---

Correspondence to: Dr. J.T. Lin.

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

0022-328X/93/$6.00

the crude product by sublimation at 40°C. Recrystallization of the crude product from cold CH_2Cl_2 (−20°C) afforded 3.6 g (20%) of orange crystalline **1**. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2066sh, 2054s, 1945s, 1934sh; ν(NO) 1735m. ^1H NMR (CD_2Cl_2): δ −12.3 (s). Anal. Found: C, 22.60; H, 0.30; H, 3.19. $C_9HNO_{10}Mo_2$ calcd.: C, 22.76; H, 0.21; N, 2.95%.

Reactions of **1** with PCy_3, PPh_3, $P(p\text{-}C_6H_4OMe)_3$, and $P(OMe)_3$ all followed essentially the same procedure. Only the reaction of **1** with PCy_3 will be described in more detail.

2.1.2. *$HMo_2(CO)_8(PCy_3)(NO)$ (2)*

Complex **1** (1.8 g, 3.79 mmol) and PCy_3 (1.1 g, 3.9 mmol) in 60 ml of CH_2Cl_2 was stirred at room temperature for 10 h and the solvent was removed under vacuum. The crude product was chromatographed. The yellow first band eluted with CH_2Cl_2/hexane (1 : 4) provided 0.68 g (25%) of orange-yellow **2** after removal of the solvent. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2088w, 2063w, 2014s, 1938vs; ν(NO) 1697m. ^1H NMR (acetone-d_6): δ 2.20–1.20 (m, 33H, Cy), −12.2 (d, J(P–H) 18.0 Hz, 1H, μ-H). $^{31}P\{H\}$ NMR (acetone-d_6): δ 53.1 (s). Anal. Found: C, 42.55; H, 4.65; N, 2.61. $C_{26}H_{34}NO_9PMo_2$ calcd.: C, 42.93; H, 4.71; N, 2.61%.

2.1.3. *$HMo_2(CO)_8(PPh_3)(NO)$ (3)*

Orange-yellow complex **3** was isolated from the yellow first band (32% yield). IR (CH_2Cl_2, cm^{-1}): ν(CO) 2094w, 2065w, 2023s, 1932vs; ν(NO) 1698m. ^1H NMR (acetone-d_6): δ 7.65–7.52 (m, 15H, Ph), −11.5 (d, J(P–H) 18.0 Hz, 1H, μ-H). $^{31}P\{H\}$ NMR (acetone-d_6): δ 35.2 (s). Anal. Found: C, 43.86; H, 2.39; N, 1.94. $C_{26}H_{16}NO_9PMo_2$ calcd.: C, 44.03; H, 2.27; N, 1.97%.

2.1.4. *$HMo_2(CO)_8(P(p\text{-}C_6H_4OMe)_3)(NO)$ (4)*

Orange-yellow powdery **4** was obtained from the yellow first band (24%). IR (CH_2Cl_2, cm^{-1}): ν(CO) 2083w, 2063w, 2019s, 1935vs; ν(NO) 1700m. ^1H NMR (acetone-d_6): δ 7.46–7.04 (m, 12H, Ph), 3.84 (s, 3H, OMe), −11.5 (d, J(P–H) 16.0 Hz, 1H, μ-H). $^{31}P\{H\}$ NMR (acetone-d_6): δ 36.8 (s). Anal. Found: C, 45.76; H, 3.53; N, 1.93. $C_{29}H_{22}NO_{12}PMo_2$ calcd.: C, 45.56; H, 3.32; N, 1.82%.

2.1.5. *$HMo_2(CO)_7(P(OMe)_3)_2(NO)$ (5)*

From column chromatography three bands were eluted with CH_2Cl_2/hexane (1 : 4). The yellow first band was found to be $HMo_2(CO)_8(P(OMe)_3)(NO)$. The second band was not characterized. The yellow third band provided **5** after removal of the solvent. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2070w, 2041m, 1991s, 1933vs; ν(NO) 1670m. ^1H NMR (acetone-d_6): δ 3.81 (s, J(P–H) 11.0 Hz, 6H, OMe), −12.4 (t, J(P–H) 20.2 Hz, 1H, μ-H). $^{31}P\{H\}$ (acetone-d_6): δ 59.8 (s). Anal. Found: C, 23.08; H, 2.84; N, 2.20. $C_{13}H_{19}NO_{14}P_2Mo_2$ calcd.: C, 23.41; H, 2.87; N, 2.10%.

2.1.6. *$HMo_2(CO)_7(Ph_2PH)_2(NO)$ (6)*

Yellow crystalline **6** was obtained from the yellow second band (20%). IR (CH_2Cl_2, cm^{-1}): ν(CO) 2069m, 2033m, 1978s, 1935vs, 1911sh; ν(NO) 1677m. ^1H NMR (acetone-d_6): δ 7.72–7.32 (m, 20H, Ph), 6.49 (dd, J(P–H) 343 Hz, J(H–H) 2.80 Hz, 2H, PH), −11.9 (tt, J(P–H) 17.2 Hz), J(H–H) 2.80 Hz, 1H, μ-H). $^{31}P\{H\}$ NMR (acetone-d_6): δ 31.1 (s). Anal. Found: C, 46.99; H, 2.71; N, 1.82. $C_{31}H_{23}NO_8P_2Mo_2$ calcd.: C, 47.07; H, 2.93; N, 1.77%.

2.1.7. *$HMo_2(CO)_7(MeNC)_2(NO_{eq})$ (7)*

A THF solution of **1** (400 mg, 0.85 mmol) was stirred at room temperature for 2 h. After removal of the solvent 3 ml of MeNC was added, and the solution was stirred for 20 minutes. The solution was pumped dry and the residue was recrystallized from Et_2O/hexane to provide red powdery **7** in 53% yield. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2065w, 2032s, 1990s, 1961vs, 1927sh; ν(NO) 1684m. ^1H NMR (acetone-d_6): δ 3.72 (s, 3H, CH_3), 3.49 (s, 3H, CH_3), −12.9 (s, 1H, μ-H). Anal. Found: C, 25.67; H, 1.24; N, 8.36. $C_{11}H_7N_3O_8Mo_2$ calcd.: C, 26.35; H, 1.40; N, 8.39%.

2.1.8. *$HMo_2(CO)_7(^iPrNC)_2(NO_{ax})$ (8)*

To a mixture of **1** (400 mg, 0.85 mmol) and Ph_3PN^iPr (658 mg, 2.06 mmol) was added 60 ml of CH_2Cl_2 prechilled to 0°C, and the solution was stirred at 0°C for 2 h. The solvent was removed *in vacuo* and the residue chromatographed. Complex **8** was obtained from the yellow first band eluted with CH_2Cl_2/hexane (1 : 4). Yield: 35%. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2066w, 2040s, 1991s, 1934vs; ν(NO) 1660m. ^1H NMR (acetone-d_6): δ 4.42 (hept, 2H, CH), 1.53 (d, J(H–H) 11.0 Hz, 12H, CH_3), −12.9 (s, 1H, μ-H). Anal. Found: C, 31.95; H, 3.17; N, 6.02. $C_{15}H_{15}N_3O_8Mo_2$ calcd.: C, 32.32; H, 2.96; N, 6.54%.

2.1.9. *$HMo_2(CO)_7(PCy_3)(^nPrNC)(NO)$ (9)*

Complex **2** (200 mg, 0.28 mmol) and Ph_3PN^nPr (98 mg, 0.31 mmol) were dissolved together in CH_2Cl_2 (30 ml) prechilled to 0°C, and the solution was stirred at 0°C for 2 h. The solution was pumped dry and the residue was chromatographed. Complex **9** was obtained in a yield of 27% from the yellow first band eluted with CH_2Cl_2/hexane (1 : 4). IR (CH_2Cl_2, cm^{-1}): ν(CO) 2066m, 2020s, 1965s, 1931vs; ν(NO): 1667m. ^1H NMR (acetone-d_6): δ 4.02 (q, J(H–H) 7.4 Hz, 2H, CH_2), 2.82–1.13 (m, 35H, Cy & CH_2), 1.10 (t, 3H, CH_3), −11.8 (d, J(P–H) 14.2 Hz, 1H, μ-H). $^{31}P\{H\}$

NMR (acetone-d_6): δ 87.0 (s). Anal. Found: C, 45.83; H, 4.96; N, 1.67. $C_{29}H_{41}NO_8PMo_2$ calcd.: C, 45.32; H, 5.30; N, 1.83%.

2.1.10. $(NMe_4)(HMo_2(CO)_7(\eta^2\text{-}S_2CNEt_2)(NO))$ (10)

Tetrahydrofuran (30 ml) was added to a mixture of **1** (250 mg, 0.53 mmol) and $Na^+S_2CNEt_2^-$ (130 mg, 0.58 mmol) and the solution stirred at room temperature for 2 h. The solvent was removed *in vacuo* and to the residue was added an aqueous solution (0°C) of $Me_4N^+Cl^-$ (66 mg, 0.60 mmol) with vigorous stirring. The orange-yellow precipitates formed were washed with H_2O (3 × 20 ml) and dried. Complex **10** was obtained in 26% yield. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2058w, 2041m, 2001s, 1947vs, 1881m; ν(NO) 1630m. ^1H NMR (acetone-d_6): δ 3.76 (t, J(H–H) 6.2 Hz, 6H, CH_3), 3.06 (s, 12H, NMe_4), 1.20 (q, 4H, CH_2), −12.2 (s, 1H, μ-H). Anal. Found: C, 28.33; H, 3.71; N, 7.13. $C_{20}H_{33}N_3O_8S_2Mo_2$ calcd.: C, 28.96; H, 3.59; N, 7.05%.

2.2. Crystallographic studies

Crystals of $HMo_2(CO)_9(NO)$ (**1**) were obtained by cooling a concentrated solution of the complex in toluene at −80°C, while $HMo_2(CO)_8(PCy_3)(NO)$ (**2**), $HMO_2(CO)_7(Ph_2PH)_2(NO)$ (**6**), and $HMo_2(CO)_7(PCy_3)(^nPrNC)(NO)$ (**9**), were obtained by cooling a concentrated solution of the complex in CH_2Cl_2/hexane (1:5) at −5°C for several days. Crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer by use of graphite-monochromated Mo Kα (λ = 0.7107 Å) in the θ–2θ scan mode. Unit cells were determined from 25 centred reflections in the suitable 2θ range. Other relevant experimental details are listed in Table 1. Absorption corrections based on Ψ scans of three reflections were applied. All the data processing was carried out on a Micro VAX 3600 using the NRCC SDP program [14]. The coordinates of molybdenum 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 $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F_o)^2$ was calculated from the counting statistics. The atomic scattering factors f_0 and the anomalous dispersion terms f', f'' were taken from ref. 15. All nonhydrogen atoms were refined anisotropically. The position of the bridging hydrogen atom was located from the final difference Fourier maps for **1**, **2**, and **6** and refined. Other hydrogen atoms were included in idealized positions with d(C–H) 0.98 Å. The final posi-

TABLE 1. Crystal data for compounds **1**, **2**, **6**, and **9**

	1	**2**	**6**	**9**
Formula	$C_9HNO_{10}Mo_2$	$C_{26}H_{34}NO_9PMo_2$	$C_{31}H_{23}NO_8P_2Mo_2$	$C_{29}H_{41}N_2O_8PMo_2$
Formula weight	474.99	724.41	791.35	768.51
a (Å)	6.810(2)	12.179(1)	9.402(2)	17.113(1)
b (Å)	6.906(3)	14.983(1)	16.614(3)	17.715(2)
c (Å)	8.741(2)	17.068(2)	21.635(3)	22.954(3)
α (°)	103.50(2)			
β (°)	68.85(2)	92.126(8)	92.58(3)	
γ (°)	92.04(2)			
Crystal system	triclinic	monoclinic	monoclinic	orthorhombic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$Pbca$
Z	1	4	4	8
V (Å^3)	372.3(2)	3112.4(5)	3376(1)	6959(3)
D_{calc} (g/cm^3)	2.119	1.552	1.557	1.467
Crystal size (mm)	0.43 × 0.31 × 0.25	0.31 × 0.25 × 0.14	0.39 × 0.08 × 0.17	0.31 × 0.32 × 0.63
Radiation	Mo Kα (λ = 0.7107 Å)	same	same	same
μ (mm^{-1})	1.69	0.88	0.86	0.79
Transmission factors (max; min)	1.00; 0.88	1.00; 0.90	1.00; 0.96	1.00; 0.86
2θ range	0–50	0–45	0–45	0–45
Octants	±h, +k, ±l	±h, +k, +l	±h, +k, +l	+h, +k, +l
	−8 ~ 8 0 ~ 8 −10 ~ 10	−13 ~ 13 0 ~ 16 0 ~ 18	−10 ~ 10 0 ~ 17 0 ~ 23	0 ~ 18 0 ~ 19 0 ~ 24
No. of unique reflections	1315	4053	4396	4551
Reflections with I > nσ	1215 (n = 2)	299 (n = 2)	2392 (n = 2)	2558 (n = 2)
No. of variables	101	356	409	379
R; R_W	0.020; 0.025	0.035; 0.041	0.034; 0.035	0.036; 0.038
GOF	1.57	1.56	1.23	1.44
max Δ/σ	0.001	0.008	0.169	0.014

TABLE 2. Positional parameters and B_{iso} for the atoms in **1**, **2**, **6**, and **9**

Atom	x	y	z	B_{iso}
Complex 1				
Mo	0.33815(4)	0.11804(3)	0.20905(3)	3.24(1)
NC	0.1563(5)	0.2431(4)	0.4310(4)	4.3(2)
O	0.0410(5)	0.3139(4)	0.5647(3)	7.2(2)
O1	0.2386(4)	0.4709(4)	0.0635(3)	5.5(1)
O2	−0.0464(5)	−0.1172(4)	0.1490(4)	6.6(2)
O3	0.4601(5)	−0.2313(4)	0.3455(4)	7.2(2)
O4	0.7278(5)	0.3475(5)	0.2695(4)	7.3(2)
C1	0.2719(5)	0.3459(5)	0.1143(4)	3.8(1)
C2	0.0917(5)	−0.0363(5)	0.1679(4)	4.2(2)
C3	0.4178(5)	−0.1101(5)	0.2946(4)	4.6(2)
C4	0.5914(6)	0.2678(5)	0.2467(5)	4.7(2)
H	0.500	0.000	0.000	10.8(20)
Complex 2				
Mo1	0.60113(5)	0.25142(4)	0.16889(3)	3.62(3)
Mo2	0.40210(4)	0.28156(3)	0.01946(3)	2.72(2)
P	0.21329(13)	0.26359(10)	0.08513(9)	2.76(6)
N	0.3354(4)	0.3001(4)	−0.0753(3)	3.9(3)
O1	0.5132(5)	0.0856(4)	0.2652(4)	7.3(3)
O2	0.7045(5)	0.1145(4)	0.0500(4)	7.9(3)
O3	0.7125(5)	0.4215(4)	0.0945(3)	7.9(3)
O4	0.5187(5)	0.3699(4)	0.3091(3)	7.7(3)
O5	0.8267(5)	0.2312(4)	0.2598(4)	7.9(3)
O6	0.4332(5)	0.0746(3)	−0.0201(4)	7.4(3)
O7	0.6246(4)	0.3027(4)	−0.0701(3)	5.4(3)
O8	0.4098(5)	0.4893(4)	0.0596(3)	8.0(4)
O9	0.2952(5)	0.3130(4)	−0.1384(3)	7.0(3)
C1	0.5412(6)	0.1439(5)	0.2288(4)	4.7(3)
C2	0.6648(6)	0.1641(5)	0.0898(4)	4.9(4)
C3	0.6692(6)	0.3616(5)	0.1187(4)	5.2(4)
C4	0.5445(6)	0.3312(5)	0.2568(4)	4.9(4)
C5	0.7422(7)	0.2382(5)	0.2282(4)	5.3(4)
C6	0.4187(6)	0.1458(5)	−0.0030(4)	4.5(3)
C7	0.5489(5)	0.2952(4)	−0.0338(4)	3.8(3)
C8	0.4056(6)	0.4172(5)	0.0465(4)	4.3(3)
C11	0.1769(5)	0.1489(4)	0.1159(3)	3.0(2)
C12	0.2634(5)	0.1104(4)	0.1732(3)	3.8(3)
C13	0.2313(6)	0.0181(5)	0.2015(4)	5.3(4)
C14	0.2115(6)	−0.0445(4)	0.1334(4)	4.8(4)
C15	0.1269(5)	−0.0082(4)	0.0752(4)	4.2(3)
C16	0.1580(5)	0.0847(4)	0.0471(3)	3.3(3)
C21	0.1914(6)	0.3330(4)	0.1745(4)	4.6(3)
C22	0.0923(6)	0.3136(5)	0.2204(4)	6.1(4)
C23	0.0756(10)	0.3770(7)	0.2867(6)	11.2(7)
C24	0.1500(8)	0.4294(9)	0.3151(6)	12.7(8)
C25	0.2455(7)	0.4507(6)	0.2686(5)	7.9(5)
C26	0.2618(11)	0.3866(11)	0.2028(8)	21.0(12)
C31	0.1025(5)	0.2927(4)	0.0116(3)	3.3(3)
C32	0.1064(5)	0.3887(4)	−0.0179(4)	3.8(3)
C33	0.0285(6)	0.4013(4)	−0.0891(4)	4.8(3)
C34	−0.0884(6)	0.3744(5)	−0.0714(4)	5.3(4)
C35	−0.0931(6)	0.2810(5)	−0.0392(5)	5.5(4)
C36	−0.0159(5)	0.2692(4)	0.0325(4)	4.3(3)
H	0.459(5)	0.262(4)	0.127(3)	5.0(15)
Complex 6				
Mo1	0.25100(8)	0.14855(5)	0.02077(3)	4.60(4)
Mo2	0.21888(7)	0.24599(4)	0.16102(3)	3.84(3)
P1	0.48386(23)	0.27500(12)	0.17120(9)	4.00(9)
P2	0.26291(24)	0.11883(13)	0.22370(9)	4.27(10)
N	0.1607(7)	0.3132(4)	0.2205(3)	5.2(3)
O1	0.1094(9)	−0.0093(4)	0.0698(4)	10.1(5)

TABLE 2 (continued)

Atom	x	y	z	B_{iso}
O2	−0.0619(8)	0.2119(5)	−0.0054(3)	8.7(4)
O3	0.3715(8)	0.3057(4)	−0.0419(3)	8.8(4)
O4	0.5652(8)	0.0812(5)	0.0340(4)	10.3(5)
O5	0.2121(10)	0.0707(6)	−0.1095(3)	13.4(6)
O6	−0.0940(7)	0.1800(5)	0.1420(3)	8.1(4)
O7	0.1675(8)	0.3859(4)	0.0633(3)	7.9(4)
O8	0.1168(7)	0.3591(4)	0.2570(3)	8.2(4)
C1	0.1649(11)	0.0481(6)	0.0531(4)	6.3(5)
C2	0.0517(11)	0.1891(6)	0.0069(4)	6.1(5)
C3	0.3296(10)	0.2510(6)	−0.0180(4)	6.1(5)
C4	0.4514(11)	0.1049(6)	0.0300(4)	6.3(5)
C5	0.2278(12)	0.0998(7)	−0.0626(5)	8.1(7)
C6	0.0184(10)	0.2037(5)	0.1473(4)	5.2(5)
C7	0.1868(10)	0.3348(5)	0.0974(4)	5.7(5)
C11	0.5611(8)	0.3398(4)	0.1143(3)	3.9(4)
C12	0.5337(9)	0.4215(5)	0.1142(4)	4.9(4)
C13	0.5884(11)	0.4724(5)	0.0712(5)	6.4(5)
C14	0.6703(10)	0.4418(7)	0.0274(4)	6.6(6)
C15	0.7014(10)	0.3608(7)	0.0250(4)	6.7(5)
C16	0.6478(9)	0.3108(5)	0.0691(4)	5.5(4)
C21	0.5674(9)	0.3072(4)	0.2446(3)	4.2(4)
C22	0.4866(9)	0.3267(5)	0.2936(4)	5.7(5)
C23	0.5521(11)	0.3456(6)	0.3504(4)	6.7(6)
C24	0.6965(12)	0.3470(6)	0.3579(4)	7.4(6)
C25	0.7772(10)	0.3294(7)	0.3089(5)	8.2(7)
C26	0.7130(10)	0.3093(6)	0.2528(4)	7.0(6)
C31	0.4432(9)	0.0935(4)	0.2495(4)	4.2(4)
C32	0.5012(9)	0.1206(5)	0.3056(4)	4.8(4)
C33	0.6415(11)	0.1056(6)	0.3224(4)	6.3(5)
C34	0.7245(11)	0.0640(7)	0.2840(6)	8.0(7)
C35	0.6694(14)	0.0373(6)	0.2281(5)	8.0(7)
C36	0.5283(11)	0.0512(6)	0.2112(4)	6.3(5)
C41	0.1607(8)	0.0981(6)	0.2916(4)	5.0(4)
C42	0.1104(11)	0.1596(7)	0.3265(4)	7.9(6)
C43	0.0388(13)	0.1421(9)	0.3800(5)	10.0(8)
C44	0.0244(17)	0.0644(13)	0.3985(6)	11.5(13)
C45	0.0718(14)	0.0042(10)	0.3631(7)	11.3(10)
C46	0.1408(10)	0.0186(6)	0.3091(5)	7.4(6)
H	0.305(6)	0.182(3)	0.105(3)	4.9(16)
Complex 9				
Mo1	0.45040(4)	0.29181(4)	0.91895(3)	4.43(3)
Mo2	0.53213(4)	0.16660(4)	1.02210(3)	4.17(3)
P	0.52566(11)	0.23286(10)	1.12335(8)	3.64(9)
N1	0.5849(4)	0.0854(4)	1.0481(3)	5.4(4)
N2	0.3572(5)	0.0948(4)	1.0433(3)	6.6(4)
O1	0.5582(5)	0.4365(4)	0.9332(3)	11.0(5)
O2	0.5836(4)	0.2301(5)	0.8366(3)	10.8(5)
O3	0.3375(5)	0.1522(4)	0.9000(3)	10.2(5)
O4	0.3136(4)	0.3796(4)	0.9829(3)	8.6(4)
O5	0.3845(4)	0.3618(3)	0.8044(3)	7.1(4)
O6	0.5319(4)	0.0765(4)	0.9031(3)	8.6(4)
O7	0.6884(4)	0.2551(4)	0.9930(3)	7.8(4)
O8	0.6223(4)	0.0312(3)	1.0602(3)	8.3(4)
C1	0.5194(5)	0.3837(5)	0.9300(4)	6.3(5)
C2	0.5359(6)	0.2501(6)	0.8686(4)	6.6(5)
C3	0.3797(6)	0.2010(5)	0.9065(4)	6.4(5)
C4	0.3630(5)	0.3461(5)	0.9627(4)	5.6(5)
C5	0.4079(5)	0.3354(5)	0.8474(4)	5.1(4)
C6	0.5313(5)	0.1127(5)	0.9451(4)	5.9(5)
C7	0.6329(5)	0.2226(5)	1.0031(3)	5.5(5)
C9	0.4174(5)	0.1202(4)	1.0376(3)	5.0(4)
C10	0.2807(6)	0.0616(7)	1.0485(5)	9.3(7)

TABLE 2 (continued)

Atom	x	y	z	B_{iso}
C11	0.2661(9)	0.0290(12)	1.0989(7)	20.3(15)
C12	0.3020(8)	0.0236(9)	1.1483(5)	13.3(10)
C21	0.5645(4)	0.1722(4)	1.1822(3)	4.0(3)
C22	0.5179(4)	0.0992(4)	1.1884(3)	4.9(4)
C23	0.5497(6)	0.0486(4)	1.2358(4)	6.4(5)
C24	0.6355(6)	0.0333(6)	1.2284(4)	7.5(6)
C25	0.6818(5)	0.1056(5)	1.2240(4)	6.4(5)
C26	0.6524(4)	0.1560(4)	1.1758(3)	4.9(4)
C31	0.4258(4)	0.2558(4)	1.1493(3)	4.2(4)
C32	0.4177(5)	0.2877(5)	1.2107(3)	5.2(4)
C33	0.3323(5)	0.2935(6)	1.2286(3)	7.1(5)
C34	0.2817(5)	0.3296(6)	1.1873(4)	6.6(5)
C35	0.2905(5)	0.3000(5)	1.1266(4)	6.0(5)
C36	0.3743(5)	0.2959(6)	1.1079(3)	6.8(5)
C41	0.5875(4)	0.3179(4)	1.1271(3)	4.4(4)
C42	0.6039(5)	0.3535(4)	1.1866(3)	5.1(4)
C43	0.6673(5)	0.4139(5)	1.1818(4)	6.5(5)
C44	0.6510(6)	0.4715(5)	1.1354(4)	6.7(5)
C45	0.6321(6)	0.4364(5)	1.0784(4)	6.9(5)
C46	0.5676(5)	0.3783(4)	1.0834(4)	5.7(5)

tional parameters for the atoms are listed in Table 2. Selected interatomic distances and bond angles are in Table 3.

3. Results and discussion

There has been only one brief report on the Raman spectroscopy of $HMo_2(CO)_9(NO)$ (**1**) [16]. We were able to synthesize **1** on a large scale (32%) from $Na^+HMo_2(CO)_{10}^-$ and acidic $Na^+NO_2^-$, procedure similar to that for the preparation of $HW_2(CO)_9(NO)$ [4b], except that acetic acid has to be added very slowly, and the reaction as well as the recrystallization have to be performed at temperatures below 0°C. The compound can be handled only briefly in air and is best stored below 0°C.

Similar to the reaction of $HW_2(CO)_9(NO)$ with phosphines [9], complex **1** reacts with phosphines or phosphites to afford $HMo_2(CO)_8(L)(NO)$ (**2**, $L = PCy_3$; **3**, $L = PPh_3$; **4**, $L = P(p\text{-}C_6H_4OMe)_3$) and $HMo_2(CO)_7(L)_2(NO)$ (**5**, $L = P(OMe)_3$; **6**, $L = Ph_2PH$). Due to extensive decomposition of **1** in CH_2Cl_2, more than four equivalents of L have to be used in order to obtain a reasonable quantity of $HMo_2(CO)_7(L)_2(NO)$. Due to the steric congestion of PCy_3 (cone angle 170° [17]), complex $HMo_2(CO)_7(PCy_3)_2(NO)$ could not be obtained even if large excess of PCy_3 was used.

The extremely air sensitive $HMo_2(CO)_7(THF)_2(NO_{eq})$ (NO resides on the equatorial site) [18 *] was isolated from the reaction of $HMo_2(CO)_9(NO)$ (**1**) with THF in a crude yield of 70%. The compound was found to be a useful precursor to disubstituted derivatives of **1**, such as **6** (60%), $HMo_2(CO)_7(MeNC)_2(NO_{eq})$ (**7**, 53%), and $(NMe_4)(HMo_2(CO)_7(\eta^2\text{-}S_2CNEt_2))$ (**10**, 26%). It is interesting to note that treatment of **1** with $S_2CNEt_2^-$ in CH_2Cl_2 does not lead to the formation of **10**. Nucleophilic attack of phosphinimines [19] at **1** occurs readily and leads to deoxygenation of carbonyl ligands. Complex $HMo_2(CO)_7(^iPrNC)_2(NO_{ax})$ (**8**) was synthesized from **1** and two equivalents of Ph_3PN^iPr in 35% yield. We were also able to isolate complex $HMo_2(CO)_7(PCy_3)(^nPrNC)(NO_{ax})$ (**9**) (27%) from the reaction of **2** with Ph_3PN^nPr.

Most of the derivatives of **1** were obtained in low to moderate yields due to extensive decomposition of **1** during the reaction. The reaction temperature has to be above 0°C in order to achieve a decent concentration of $HMo_2(CO)_9(NO)$ in CH_2Cl_2. Unfortunately, rupture of the dimer occurs even in common non-coordinating solvents, and $M(CO)_6$ is the only detectable decomposition product. Whereas less than 10% of $HW_2(CO)_9(NO)$ decomposes after 24 h in CH_2Cl_2 at room temperature based on IR and ^1H NMR spectra, the lifetime of **1** under similar conditions is less than 4 h. The chemical reactivity of **1** also appears to be higher than that of $HW_2(CO)_9(NO)$, in accordance with the general trend observed for the second and third transition series elements of a given group [19].

The spectroscopic properties for complexes **1**–**10** are consistent with their formulation. They have infrared spectral patterns very similar to those of the corresponding tungsten analogues [9–11] in the CO and NO stretching regions, suggesting that molybdenum and tungsten congeners have similar structures in solution. The chemical shifts of the hydrides in the ^1H NMR spectra are consistent with the existence of a Mo–H–Mo linkage [20]. The two phosphorus atoms in **5** and **6** appear to be magnetically equivalent, based on the ^{31}P NMR spectra. Complex **7** has its NO in equatorial position and thus two magnetically inequivalent MeNC ligands.

3.1. Molecular structures of $HMo_2(CO)_9(NO)$ (1), $HMo_2(CO)_8(PCy_3)(NO)$ (2), $HMo_2(CO)_7(P(p\text{-}C_6H_4\text{-}OMe)_3)_2(NO)$ (6), and $HMo_2(CO)_7(PCy_3)(^nPrNC)(NO)$ (9)

ORTEP drawings of complexes **1**, **2**, **6**, and **9** are shown in Figs. 1–4. Important interatomic distances and angles are listed in Table 3.

A 50–50% packing disorder involving the axial NO and CO groups generated the appearance of a symmetric Mo–H–Mo bond for **1**. Bau [4b] analysed metal–carbon and metal–nitrogen bond distances in mixed carbonyl nitrosyl complexes [21] as well as compounds of the type $M(CO)_5X$ [22] where X is a poorer charge acceptor than the carbonyl groups, and concluded that

TABLE 3. Selected bond distances (Å) and angles (°) for complexes **1**, **2**, **6**, and **9**

	1	**2**	**6**	**9**
Mo(1)–Mo(2); Mo–MoA	3.540(1)	3.4823(8)	3.464(1)	3.533(1)
Mo(1)–C(1); Mo–C(1)	2.073(3)	2.056(8)	2.00(1)	2.03(1)
Mo(1)–C(2); Mo–C(2)	2.052(3)	2.053(8)	2.00(1)	2.01(1)
Mo(1)–C(3); Mo–C(3)	2.059(3)	2.049(8)	2.05(1)	2.03(1)
Mo(1)–C(4); Mo–C(4)	2.068(4)	2.057(8)	2.02(1)	2.043(9)
Mo(1)–C(5)		1.972(8)	1.98(1)	1.955(9)
Mo(2)–C(6)		2.081(8)	2.021(9)	2.009(9)
Mo(2)–C(7)		2.046(7)	2.031(9)	2.04(1)
Mo(2)–C(8)		2.085(7)		
Mo(2)–C(9)				2.158(9)
Mo(2)–P		2.609(2)		2.606(2)
Mo(2)–P(1)			2.537(2)	
Mo(2)–P(2)			2.534(2)	
Mo(2)–N; Mo–NCA	1.898(3)	1.804(5)	1.808(7)	1.801(7)
Mo(2)–N(1)				1.801(7)
Mo(1)–H; Mo–H	1.77		1.86(6)	1.96(5)
Mo(2)–H		1.96(5)	1.82(6)	
C(1)–O(1)	1.122(4)	1.132(9)	1.15(1)	1.15(1)
C(2)–O(2)	1.121(4)	1.13(1)	1.15(1)	1.15(1)
C(3)–O(3)	1.125(4)	1.13(1)	1.15(1)	1.15(1)
C(4)–O(4)	1.119(4)	1.12(1)	1.14(1)	1.13(1)
C(5)–O(5)		1.15(1)	1.13(1)	1.16(1)
C(6)–O(6)		1.121(9)	1.13(1)	1.16(1)
C(7)–O(7)		1.135(8)	1.13(1)	1.14(1)
C(8)–O(8)		1.104(9)		
N–O(9)		1.182(7)		
N–O(8)			1.184(9)	
NC–O	1.149(4)			
Mo(1)–C(1)–O(1)	178.9(3)	175.8(6)	176.1(6)	176.5(8)
Mo(1)–C(2)–O(2)	178.2(3)	175.6(6)	175.2(8)	175.0(8)
Mo(1)–C(3)–O(3)	178.1(3)	175.3(7)	176.8(8)	177.1(9)
Mo(1)–C(4)–O(4)	178.8(3)	173.9(6)	178.4(9)	174.3(7)
Mo(1)–C(5)–O(5)		177.1(7)	178(1)	178.4(7)
Mo(2)–C(6)–O(6)		174.1(6)	177.4(7)	174.6(7)
Mo(2)–C(7)–O(7)		173.3(5)	177.9(7)	178.6(7)
Mo(2)–C(8)–O(8)			176.1(6)	
Mo(2)–N(1)–O(8)				173.9(6)
Mo–NC–O	177.5(3)			
C(1)–Mo(1)–C(2)	90.8(1)	88.7(3)	86.7(4)	86.7(9)
C(1)–Mo(1)–C(3)	177.3(1)	174.6(3)	175.9(3)	178.7(3)
C(1)–Mo(1)–C(4)	89.9(1)	87.6(3)	93.2(4)	89.3(4)
C(1)–Mo(1)–C(5)		89.1(3)	87.0(4)	90.2(3)
C(2)–Mo(1)–C(3)	90.6(1)	94.0(3)	90.6(4)	93.5(4)
C(2)–Mo(1)–C(4)	178.6(1)	174.3(3)	176.8(4)	172.4(3)
C(2)–Mo(1)–C(5)		86.0(3)	86.4(4)	86.1(3)
C(3)–Mo(1)–C(4)	88.7(1)	89.4(3)	89.3(4)	90.3(4)
C(3)–Mo(1)–C(5)		86.4(3)	89.7(4)	88.5(3)
C(4)–Mo(1)–C(5)		89.6(3)	90.4(4)	87.4(3)
C(6)–Mo(2)–C(7)		85.6(3)	92.5(4)	92.8(3)
C(6)–Mo(2)–C(8)		174(2)		
C(6)–Mo(2)–C(9)				87.6(3)
C(6)–Mo(2)–N		90(2)	90.6(3)	
C(6)–Mo(2)–N(1)				85.2(3)
C(6)–Mo(2)–P		94.1(2)		176.8(3)
C(6)–Mo(2)–P(1)			85.3(3)	
C(6)–Mo(2)–P(2)			169.7(2)	
C(7)–Mo(2)–C(8)		89.4(3)		
C(7)–Mo(2)–P		179.1(2)		90.4(2)
C(7)–Mo(2)–N		89.6(2)	89.6(3)	
C(7)–Mo(2)N(1)				92.0(3)

TABLE 3 (continued)

	1	2	6	9
C(7)-Mo(2)-P(1)			92.1(3)	
C(7)-Mo(2)-P(2)			169.7(2)	
C(7)-Mo(2)-C(9)				172.4(3)
C(8)-Mo(2)-P		91.0(2)		
C(8)-Mo(2)-N		93.1(3)		
C(9)-Mo(2)-N(1)				95.6(3)
P(1)-Mo(2)-P(2)			88.61(7)	
N-Mo(2)-P		91.5(2)		
NC-Mo-C(1)	91.4(1)			
NC-Mo-C(2)	89.9(1)			
NC-Mo-C(3)	90.9(1)			
NC-Mo-C(4)	91.3(1)			
Mo(1)-H-Mo(2)		131(3)	132(3)	

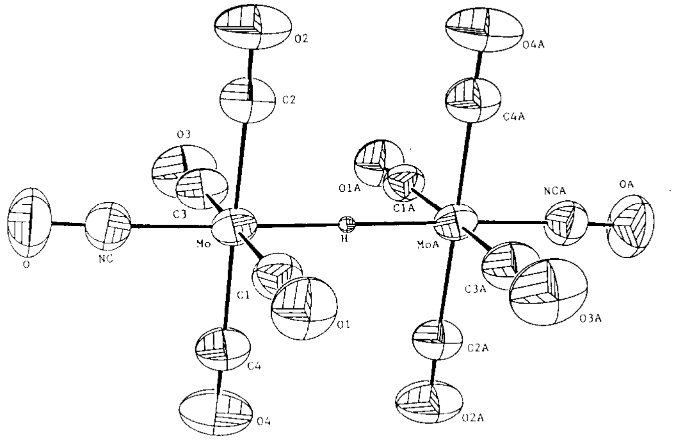

Fig. 1. ORTEP drawing of $HMo_2(CO)_9(NO)$. Thermal ellipsoids are drawn with 50% probability boundaries.

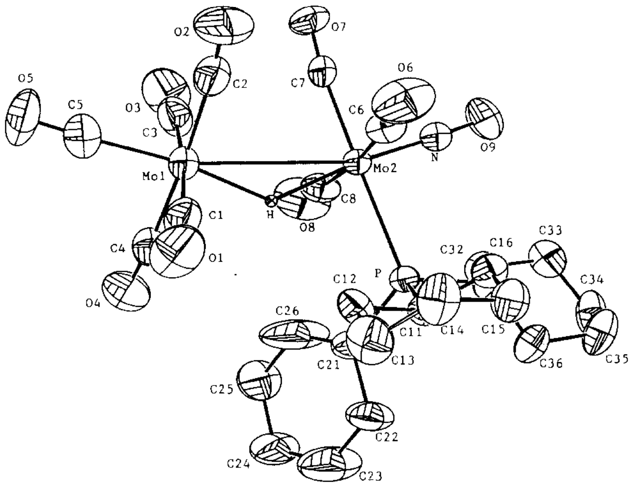

Fig. 2. ORTEP drawing of $HMo_2(CO)_8(PCy_3)(NO)$. Thermal ellipsoids are drawn with 50% probability boundaries.

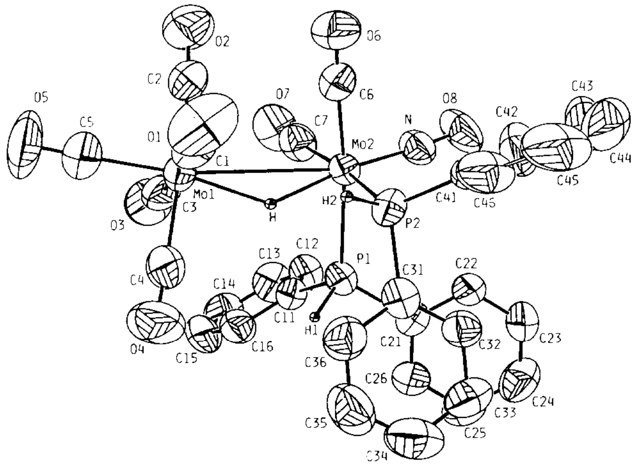

Fig. 3. ORTEP drawing of $HMo_2(CO)_7(Ph_2PH)_2(NO)$. Thermal ellipsoids are drawn with 50% probability boundaries.

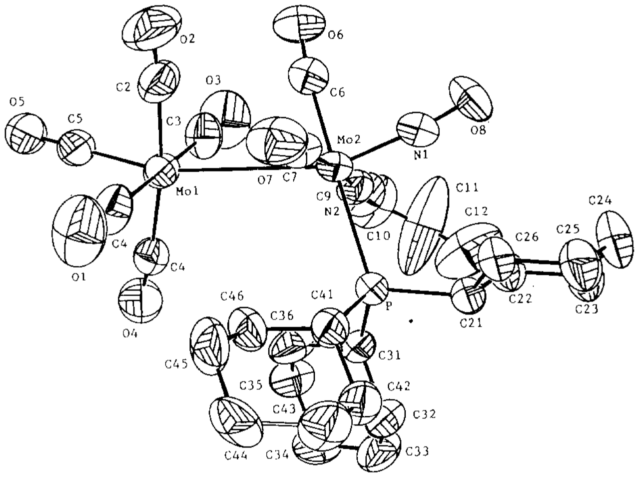

Fig. 4. ORTEP drawing of $HMo_2(CO)_7(PCy_3)(^nPrNC)(NO)$. Thermal ellipsoids are drawn with 50% probability boundaries.

the axial NO should have a metal–ligand distance shorter by 0.17 Å than the average equatorial metal–ligand distance. In complex **1**, the average axial M–X (X = N or C) bond length (1.898(3) Å) opposite hydrogen is shorter by 0.15–0.17 Å than the equatorial metal–carbon distances (2.073(3), 2.052(3), 2.059(3), 2.068(3) Å, which is also close to the corresponding value (0.15 Å) reported for disordered $HW_2(CO)_9(NO)$ [4b]. The location of the axial NO ligand was also distinguished by conspicuous discrepancies in the thermal parameters for the N and C atoms when incorrectly assigned.

The most interesting aspect of the structure of **1** is its eclipsed conformation, in contrast to the staggered conformation of $HW_2(CO)_9(NO)$. This is an example of the metal influence on the structural variation in dimeric M(μ-H)M series. The much longer M–M distance in **1** (3.540(1) Å) than $HW_2(CO)_9(NO)$ (3.328(3); 3.330(3) Å) [4b] is undoubtedly due to interatomic repulsion among mutually eclipsed equatorial ligands. The elongation of M–M distance resulting from interatomic repulsion among eclipsed ligands was also observed for isomeric pairs of $HW_2(CO)_7(MeNC)_2(NO)$ [10]. In terms of the comparable atomic radii of Mo and W, the Mo–Mo distance is estimated to be *ca.* 3.750 Å for a linear Mo–H–Mo bond [23]. Therefore the observed symmetry-imposed bridging hydrogen atom of **1** is likely to be in an off-axis position and the linear, eclipsed structure of **1** is actually a disordered superposition of two or more bent Mo–H–Mo bonds, similar to that reported for $(NEt_4)(HCr_2(CO)_{10})$ [24]. Transformation of an eclipsed $HMo_2(CO)_9(NO)$ (**1**) to a staggered isomer in solution is most likely to be a low energy process, as suggested for M(μ-H)M complexes [25]. Other relevant crystal data appear to be normal. The two molybdenum atoms in **1** reside in almost perfect octahedral environments. Both Mo–N–O and Mo–C–O angles deviate from linearity by less than 3°.

Complexes $HMo_2(CO)_8(PCy_3)(NO)$ (**2**) and $HMo_2(CO)_7(Ph_2PH)_2(NO)$ (**6**) have structures similar to $HW_2(CO)_8(P(p\text{-}C_6H_4F)_3)$ (NO) and $HW_2(CO)_7(P(p\text{-}C_6H_4F)_3)_2(NO)$, respectively [11]. The two molybdenum atoms reside in a roughly octahedral environment, with the nitrosyl ligand occupying the axial position on the phosphine-substituted molybdenum. The nitrosyl (**2**, 177.7(5)°; **6**, 176.1(6)°) and carbonyl (**2**, 175(2)°; **6**, 177(1)°) are linearly coordinated to Mo. The W–N distances (**2**, 1.804(5) Å; **6**, 1.808(7) Å) are shorter than the average W–C distances (**2**, 2.05(3) Å; **6**, 2.01(2) Å). The carbonyl *trans* to the hydride appears to have the shortest Mo–C distance (**2**, 1.972(8) Å; **6**, 1.98(1) Å) among all carbonyls. The overall structure in **2** and **6** is bent, and the equatorial groups are staggered. In **2**, the phosphine ligand occupies the least hindered exo position, whereas in complex **6** both exo sites are occupied by phosphines.

The position of μ-H was located in the final difference Fourier map for **2** and **6**. The observed Mo–H distances (**2**, 1.86(6), 1.96(5) Å; **6**, 1.82(6), 1.96(5) Å) and the Mo–H–Mo angle (**2**, 131(3)°; **6**, 132(3)°) are in agreement with the reported values (Mo–H, 1.68–2.19 Å; Mo–H–Mo, 127–136°) [20]. The Mo–Mo distance in **2** (3.4823(8) Å) is even longer than that in **6** (3.464(1) Å) because PCy_3 has a much larger cone angle (170°) than Ph_2PH (126°).

The complex **9** has a longer Mo–Mo distance (3.533(1) Å) than **6** (3.464(1) Å), apparently due to the greater steric congestion in the former. In contrast to **6**, the ^nPrNC was found to occupy one of the *endo* sites of the parent "$Mo(CO)_3(PCy_3)(NO)$" fragment in **2**. Other structural features of **9**, including linearity of the ligands, the relative Mo–C and Mo–N distances are not much different from those of **2** and **6** discussed earlier.

4. Supplementary material available

All bond distances and angles (Table S1: **1**, 1 page; **2**, 2 pages; **6**, 2 pages; **9**, 2 pages), anisotropic thermal parameters and isotropic thermal parameters (Table S2: **1**, 1 page; **2**, 2 pages; **6**, 2 pages; **9**, 2 pages), positional parameters for calculated hydrogen atoms (Table S3: **2**, 1 page; **6**, 1 page; **9**, 1 page), and structure factors (Table S4: **1**, 5 pages; **2**, 15 pages; **6**, 16 pages; **9**, 16 pages), are all available from the authors.

Acknowledgement

We wish to thank the National Science Council of Republic of China for the support (Grant no. NSC81-0208-M-001-61).

References and notes

1 (a) R. Bau and T.F. Koetzle, *Pure Appl. Chem., 50* (1978) 55; (b) R. Bau and T.F. Teller, *Acc. Chem. Res., 12* (1979) 176; (c) L.M. Venanzi, *Coord. Chem. Rev., 43* (1982) 251; (d) D.M. Slocum and W.R. Moser, *Catalytic Transition Metal Hydrides*, New York Academy of Sciences, New York, 1983, Part I.

2 Two halves of the molecule are held together solely by one 3c-2e M–H–M bond, without other bridging groups.

3 D.W. Hart, R. Bau and T.F. Koetzle, *Organometallics, 4* (1985) 1591 and references therein.

4 (a) M. Andrews, D.L. Tipton, S.W. Kirtley and R. Bau, *J. Chem. Soc., Chem. Commun.*, (1973) 181; (b) J.P. Olsen, T.F. Koetzle, S.W. Kirtley, M.A. Andrews, D.L. Tipton and R. Bau, *J. Am. Chem. Soc., 96* (1974) 6621.

5 M.Y. Darensbourg and C.E. Ash, *Adv. Organomet. Chem., 27* (1987) 1 and references therein.

6 R. Teller and R. Bau, *Struct. Bonding (Berlin), 44* (1982) 1.

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

8 (a) M.Y. Darensbourg, J.L. Atwood, R.R. Burch, Jr., W.E. Hunter and N. Walker, *J. Am. Chem. Soc., 101* (1979) 2631; (b) M.Y. Darensbourg, J.L. Atwood, W.E. Hunter and R.R. Burch, Jr., *J. Am. Chem. Soc., 102* (1980) 3290.

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

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

11 J.T. Lin, P.S. Huang, T.Y.R. Tsai, C.Y. Liao, L.H. Tseng, Y.S. Wen and F.K. Shi, *Inorg. Chem.,* in press.

13 H. Zimmer and G. Singh, *J. Org. Chem., 28* (1963) 483.

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

15 J. Ibers and W.W. Hamilton (Eds.), *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, UK, 1974, Vol. IV.

16 E.D. Schmid, R.S. Krishnan and W. Kiefer (Eds), *Proc. 6th Int. Conf. Raman Spectrosc.,* 1978, Vol. 2, p. 68.

17 C.A. Tolman, *Chem. Rev.,* (1985) 171.

18 We were not able to isolate analytically pure $HMo_2(CO)_7(THF)_2(NO)$. However, the infrared spectra of the compound are very similar to those of $HW_2(CO)_7(THF)_2(NO)$. IR (THF, cm^{-1}): ν(CO) 2065w, 2018m, 1975w, 1933vs, 1902sh; ν(NO) 1670m.

19 (a) H. Alper and R.A. Partis, *J. Organomet. Chem., 35* (1972) C40; (b) T. Kiji, A. Matsumura, T. Haishi and S.F. Osazaki, *J. Bull. Chem. Soc. Jpn., 50* (1977) 2731; (c) C.A. Mirkin, K.L. Lu, G.L. Geoffroy, *J. Am. Chem. Soc., 111* (1989) 7279; (d) L.C. Chen, M.Y. Chen, J.H. Chen, Y.S. Wen and K.L. Lu, *J. Organomet. Chem., 425* (1992) 99.

20 M.Y. Darensbourg, R.El Mehdawi, T.J. Delord, F.R. Fronczek and S.F. Watkins, *J. Am. Chem. Soc., 106* (1984) 2583.

21 B.A. Frenz, J.H. Enemark and J.A. Ibers, *Inorg. Chem., 8* (1969) 1288.

22 S.W. Kirtley, J.P. Olsen and R. Bau, *J. Am. Chem. Soc., 95* (1973) 4532.

23 R.A. Love, H.B. Chin, T.F. Koetzle, S.W. Kirtley, B.R. Whittlesey and R. Bau, *J. Am. Chem. Soc., 98* (1976) 4491.

24 J. Roziere, J.M. Williams, R.P. Stewart, Jr., J.L. Petersen and L.F. Dahl, *J. Am. Chem. Soc., 99* (1977) 4497.

25 B. Jezowska-Trzebiatowska and B. Nissen-Sobocinska, *J. Organomet. Chem., 322* (1987) 331.