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Dinuclear molybdenum carbonyls bridged by hydride ligands

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Abstract

Complexes $(\mu\text{-H})(\mu\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)\text{Mo}_2(\text{CO})_7(\text{NO})$ ($n = 1\text{--}4$, designated, respectively, as **1**, **2**, **3**, and **4**), $(\mu\text{-H})\text{Mo}_2(\text{CO})_8(\text{L})(\text{NO})$ (**5**, $\text{L} = \text{PPh}_3$; **6**, $\text{L} = \text{P}(p\text{-C}_6\text{H}_4\text{F})_3$; **7**, $\text{L} = \text{P}(p\text{-C}_6\text{H}_4\text{Me})_3$; **8**, $\text{L} = \text{P}(p\text{-C}_6\text{H}_4\text{OMe})_3$), and $(\mu\text{-H})\text{Mo}_2(\text{CO})_7(\text{L})_2(\text{NO})$ (**9**, $\text{L} = \text{P}(\text{OMe})_3$; **10**, $\text{L} = \text{PMe}_2\text{Ph}$) are synthesized from nitrosylation of $(\text{Et}_4\text{N})(\mu\text{-H})(\mu\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)\text{Mo}_2(\text{CO})_8$ ($n = 1\text{--}4$), $(\text{Et}_4\text{N})(\mu\text{-H})\text{Mo}_2(\text{CO})_9(\text{P}(p\text{-C}_6\text{H}_4\text{X})_3)$ ($\text{X} = \text{H}, \text{F}, \text{Me}, \text{OMe}$), and $(\text{Et}_4\text{N})(\mu\text{-H})\text{Mo}_2(\text{CO})_8(\text{L})_2$ ($\text{L} = \text{P}(\text{OMe})_3, \text{PMe}_2\text{Ph}$) with one equivalent of NO^+BF_4^- in CH_2Cl_2 at -60°C . Treatment of **1–4** with $\text{Ph}_3\text{P}=\text{N}^n\text{Pr}$ provides $(\mu\text{-H})(\mu\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)\text{Mo}_2(\text{CO})_6(\text{CN}^n\text{Pr})(\text{NO})$ (**11–14**, $n = 1\text{--}4$). X-ray crystal structure analyses for complexes **3**, **12**, and $(\mu\text{-H})\text{W}_2(\text{CO})_7(\text{PMe}_2\text{Ph})_2(\text{NO})$ (**16**) were carried out to give data as follows. **3**: triclinic, $P\bar{1}$, $Z = 4$, a 11.698(2), b 13.926(2), c 21.605(4) Å, α 93.72(2), β 92.89(3), γ 91.85(3)°, V 3505.5 Å³, $R = 0.034$, $R_w = 0.036$. **12**: triclinic, $P\bar{1}$, $Z = 2$, a 10.100(3), b 12.982(4), c 15.453(4) Å, α 102.60(2), β 83.29(2), γ 105.75(2)°, V 1899.6 Å³, $R = 0.054$, $R_w = 0.055$. **16**: monoclinic, $C2/c$, $Z = 8$, a 15.668(1), b 12.892(2), c 28.764(3) Å, β 98.883(8)°, V 5740.4 Å³, $R = 0.032$, $R_w = 0.034$.

Key words: Molybdenum; Carbonyl; Hydride

1. Introduction

An unsupported three-centre, two-electron metal–hydrogen–metal bond is intrinsically flexible and subject to small changes in its environment [1]. Several factors, such as metal [2], substituent ligand [3], and even counterion and crystal packing [4], are all responsible for structural variation of dimeric complexes with M–H–M bridge. Dinuclear complexes derived from $\text{HW}_2(\text{CO})_9(\text{NO})$ do indeed exhibit structural versatility [5–7]. Recently we extended our study to $\text{HMo}_2(\text{CO})_9(\text{NO})$ and found out that cleavage occurred much more readily with the molybdenum dimer than with its tungsten congener [8]. In order to have a wider spectrum for the correlation between the stability and the structure of dimeric compounds with a Mo–H–Mo linkage, we set out to synthesize complexes $(\mu\text{-H})(\mu\text{-Ph}_2\text{P} \sim \text{PPh}_2)\text{Mo}_2(\text{CO})_7(\text{NO})$, $(\mu\text{-H})\text{Mo}_2(\text{CO})_7(\text{L})_2(\text{NO})$, and $(\mu\text{-H})\text{Mo}_2(\text{CO})_8(\text{L})(\text{NO})$ ($\text{L} = \text{phosphine}$). In this paper we describe the syntheses of these com-

plexes. Structural characterizations for several complexes are also included.

2. Experimental section

2.1. General procedure

All manipulations were carried out under an atmosphere of N_2 using standard Schlenk techniques or a N_2 -filled glovebox. All solvents were dried and degassed with use of standard procedures. All column chromatography was performed under N_2 on silica gel (230–400 mesh ASTM, Merck) as the stationary phase in a column of 2.5 cm in diameter. Complexes $(\text{Et}_4\text{N})(\mu\text{-H})(\mu\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)\text{Mo}_2(\text{CO})_8$ ($n = 1\text{--}4$) [9], $(\text{Et}_4\text{N})(\mu\text{-H})\text{Mo}_2(\text{CO})_9(\text{L})$ ($\text{L} = \text{PPh}_3$; $\text{P}(p\text{-C}_6\text{H}_4\text{X})_3$ ($\text{X} = \text{F}, \text{Me}, \text{OMe}$)) [4a], $(\text{Et}_4\text{N})(\mu\text{-H})\text{Mo}_2(\text{CO})_8(\text{L})_2$ ($\text{L} = \text{P}(\text{OMe})_3$; PMe_2Ph) [4b], and $(\text{Et}_4\text{N})(\mu\text{-H})\text{W}_2(\text{CO})_8(\text{L})_2$ ($\text{L} = \text{PMe}_3$; PMe_2Ph ; $\text{P}(\text{OMe})_3$) [10], were prepared according to published procedures. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer. Infrared measurements were made on a Perkin-Elmer 880 spectrometer. Nuclear magnetic resonance spectra were run on a

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Bruker MSL-200 or AC-200 instrument. The ^1H and ^{31}P NMR spectra were referenced to TMS and external 85% H_3PO_4 , respectively.

2.2. Preparations

2.2.1. $(\mu\text{-H})(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)\text{Mo}_2(\text{CO})_7(\text{NO})$ (**1**)

One equivalent of solid NO^+BF_4^- (121 mg, 1.04 mmol) was added all at once via a Schlenk tube into a vigorously stirred CH_2Cl_2 solution of $(\text{Et}_4\text{N})(\mu\text{-H})(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)\text{Mo}_2(\text{CO})_8$ (1.0 g, 1.04 mmol) prechilled to -60°C . After 5 h at -60°C the deep red solution was evacuated at -20°C . The resulting residue was then recrystallized from Et_2O and hexane at -40°C to provide orange-yellow powdery **1** (176 mg, 21% yield). Anal. Found: C, 47.84; H, 3.12; N, 1.67. $\text{C}_{32}\text{H}_{23}\text{Mo}_2\text{NO}_8\text{P}_2$ calc.: C, 47.84; H, 2.89; N, 1.74%.

Orange-yellow complexes $(\mu\text{-H})(\mu\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)\text{Mo}_2(\text{CO})_7(\text{NO})$ ($n = 2\text{--}4$, designated as **2**, **3**, and **4**) were prepared by essentially the same procedure as that for the synthesis of **1**. Complex **2** had a yield of 41%. Anal. Found: C, 47.98; H, 3.17; N, 1.62. $\text{C}_{33}\text{H}_{25}\text{Mo}_2\text{NO}_8\text{P}_2$ calc.: C, 48.49; H, 3.08; N, 1.71%.

Complex **3**: yield 33%. Anal. Found: C, 48.93; H, 3.07; N, 1.71. $\text{C}_{34}\text{H}_{27}\text{Mo}_2\text{NO}_8\text{P}_2$ calc.: C, 49.12; H, 3.27; N, 1.68%.

Complex **4**: yield 32%. Anal. Found: C, 49.45; H, 3.59; N, 1.57. $\text{C}_{35}\text{H}_{29}\text{Mo}_2\text{NO}_8\text{P}_2$ calc.: C, 49.72; H, 3.46; N, 1.66%.

2.2.2. $(\mu\text{-H})\text{Mo}_2(\text{CO})_8(\text{L})(\text{NO})$ (**5**, $\text{L} = \text{PPh}_3$; **6**, $\text{L} = \text{P}(p\text{-C}_6\text{H}_4\text{F})_3$; **7**, $\text{L} = \text{P}(p\text{-C}_6\text{H}_4\text{Me})_3$; **8**, $\text{L} = \text{P}(p\text{-C}_6\text{H}_4\text{OMe})_3$)

Complexes **5**–**8** were prepared from $(\text{Et}_4\text{N})(\mu\text{-H})\text{Mo}_2(\text{CO})_9(\text{L})$ by the same procedure as for the synthesis of **1** except that the solution was evacuated at 25°C and the residue was chromatographed. The orange-yellow powdery product was obtained from the orange-yellow first band eluted by CH_2Cl_2 /hexane (1/8 v/v).

Complex **5**: yield 10%. Anal. Found: C, 43.86; H, 2.39; N, 1.94. $\text{C}_{26}\text{H}_{16}\text{Mo}_2\text{NO}_9\text{P}$ calc.: C, 44.03; H, 2.27; N, 1.97%.

Complex **6**: yield 10%. Anal. Found: C, 40.98; H, 1.83; N, 1.82. $\text{C}_{26}\text{F}_3\text{H}_{13}\text{Mo}_2\text{NO}_9\text{P}$ calc.: C, 40.92; H, 1.72; N, 1.84%.

Complex **7**: yield 15%. Anal. Found: C, 46.51; H, 3.05; N, 1.84. $\text{C}_{29}\text{H}_{22}\text{Mo}_2\text{NO}_9\text{P}$ calc.: C, 46.36; H, 2.95; N, 1.86%.

Complex **8**: yield 25%. Anal. Found: C, 44.13; H, 2.80; N, 1.66. $\text{C}_{29}\text{H}_{22}\text{Mo}_2\text{NO}_{12}\text{P}$ calc.: C, 43.58; H, 2.77; N, 1.75%.

Complexes **5**–**8** could also be synthesized from $\text{HMo}_2(\text{CO})_9(\text{NO})$ and $\text{P}(p\text{-C}_6\text{H}_4\text{X})_3$ ($\text{X} = \text{H}, \text{F}, \text{Me}$,

OMe) according to the published procedure [8]. The isolated yields (based on $\text{HMo}_2(\text{CO})_9(\text{NO})$) were 32, 28, 36, and 24%, respectively.

2.2.3. $(\mu\text{-H})\text{Mo}_2(\text{CO})_7(\text{L})_2(\text{NO})$ (**9**, $\text{L} = \text{P}(\text{OMe})_3$; **10**, $\text{L} = \text{PMe}_2\text{Ph}$)

Essentially the same procedure as for the synthesis of **1** was followed, but the corresponding $(\text{Et}_4\text{N})(\mu\text{-H})\text{Mo}_2(\text{CO})_8(\text{L})_2$ was used and the solution was evacuated at -40°C . Orange-yellow complex **9** had a yield of 7%. Anal. Found: C, 23.28; H, 2.84; N, 2.20. $\text{C}_{13}\text{H}_{19}\text{Mo}_2\text{NO}_{14}\text{P}_2$ calc.: C, 23.41; H, 2.87; N, 2.10%.

Orange-yellow complex **10** had a yield of 10%. Anal. Found: C, 37.96; H, 3.40; N, 2.36. $\text{C}_{23}\text{H}_{23}\text{Mo}_2\text{NO}_8\text{P}_2$ calc.: C, 39.73; H, 3.33; N, 2.01%.

2.2.4. $(\mu\text{-H})(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)\text{Mo}_2(\text{CO})_6(\text{CN}^n\text{Pr})(\text{NO})$ (**11**)

To a mixture of **1** (300 mg, 0.40 mmol) and $\text{Ph}_3\text{P}=\text{N}^n\text{Pr}$ (140 mg, 0.44 mmol) was added 50 ml of CH_2Cl_2 and the solution was stirred for 3 h. The solvent was removed and the residue was chromatographed. Yellow powdery **11** was isolated from the yellow first band eluted by CH_2Cl_2 /hexane (1/4 v/v) in a yield of 10%. We found that **11** was frequently contaminated with an unidentified impurity, possibly derived from the decomposition of **1**. Anal. Found: C, 47.34; H, 3.51; N, 3.58. $\text{C}_{35}\text{H}_{30}\text{Mo}_2\text{N}_2\text{O}_7\text{P}_2$ calc.: C, 49.78; H, 3.58; N, 3.31%.

2.2.5. Complexes $(\mu\text{-H})(\mu\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)\text{Mo}_2(\text{CO})_6(\text{CN}^n\text{Pr})(\text{NO})$ (**12**–**14**, $n = 2\text{--}4$)

These were prepared similarly. Complex **12** had a yield of 47%. Anal. Found: C, 49.97; H, 3.82; N, 3.04. $\text{C}_{36}\text{H}_{32}\text{Mo}_2\text{N}_2\text{O}_7\text{P}_2$ calc.: C, 50.37; H, 3.76; N, 3.26%. Complex **13** had a yield of 27%. Anal. Found: C, 50.80; H, 3.84; N, 3.42. $\text{C}_{37}\text{H}_{34}\text{Mo}_2\text{N}_2\text{O}_7\text{P}_2$ calc.: C, 50.93; H, 3.93; N, 3.21%. Complex **14** had a yield of 23%. Anal. Found: C, 51.16; H, 4.04; N, 2.52. $\text{C}_{38}\text{H}_{36}\text{Mo}_2\text{N}_2\text{O}_7\text{P}_2$ calc.: C, 51.48; H, 4.09; N, 3.16%.

2.2.6. $(\mu\text{-H})\text{W}_2(\text{CO})_7(\text{L})_2(\text{NO})$ (**15**, $\text{L} = \text{P}(\text{OMe})_3$; **16**, $\text{L} = \text{PMe}_2\text{Ph}$; **17**, $\text{L} = \text{PMe}_3$)

These orange complexes were prepared from $(\text{Et}_4\text{N})(\mu\text{-H})\text{W}_2(\text{CO})_8(\text{L})_2$ by the same procedure as for the synthesis of **5**, but the reaction time was 12 h. The complexes were isolated from the orange second band eluted by CH_2Cl_2 /hexane (1/2 v/v). Complex **15**: yield 38%. Anal. Found: C, 18.48; H, 1.97; N, 1.70. $\text{C}_{13}\text{H}_{19}\text{NO}_{14}\text{P}_2\text{W}_2$ calc.: C, 18.52; H, 2.27; N, 1.66%. Complex **16**: yield 10%. Anal. Found: C, 31.54; H, 2.66; N, 1.49. $\text{C}_{28}\text{H}_{23}\text{NO}_8\text{P}_2\text{W}_2$ calc.: C, 31.71; H, 2.66; N, 1.61%. Complex **17**: yield 15%. Anal. Found: C, 20.88; H, 2.34; N, 1.83. $\text{C}_{13}\text{H}_{19}\text{NO}_8\text{P}_2\text{W}_2$ calc.: C, 20.90; H, 2.56; N, 1.88%.

TABLE 1. Crystal data for compounds **3**, **12**, and **16**

	3	12	16
Formula	C ₃₄ H ₂₇ Mo ₂ NO ₈ P ₂	C ₃₆ H ₃₂ Mo ₂ N ₂ O ₇ P ₂	C ₂₃ H ₂₃ NO ₈ P ₂ W ₂
Formula weight	831.41	858.49	871.08
<i>a</i> (Å)	11.698(6)	10.100(3)	15.668(1)
<i>b</i> (Å)	13.926(2)	12.982	12.892(2)
<i>c</i> (Å)	21.605(4)	15.453	28.764(3)
α (°)	93.72(2)	102.60(2)	
β (°)	92.89(3)	83.29(2)	98.883(8)
γ (°)	91.85(3)	105.75(2)	
Crystal system	triclinic	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
<i>Z</i>	4	2	8
<i>V</i> (Å ³)	3506(2)	1899.6(9)	5740(1)
<i>D</i> _{calc} (g/cm ³)	1.575	1.501	2.016
Crystal size (mm)	0.50 × 0.44 × 0.19	0.31 × 0.19 × 0.13	0.19 × 0.19 × 0.41
Radiation	Mo K α (λ = 0.7107 Å)	same	same
μ (mm ⁻¹)	0.84	0.77	8.33
Transmission factors (max; min)	1.00; 0.92	1.00; 0.89	1.00; 0.86
2 θ -range	0–45	0–45	0–50
Octants	+ <i>h</i> , ± <i>k</i> , ± <i>l</i>	± <i>h</i> , + <i>k</i> , ± <i>l</i>	± <i>h</i> , + <i>k</i> , + <i>l</i>
	0 ~ 12 -14 ~ 14 -23 ~ 23	-10 ~ 10 0 ~ 13 -16 ~ 16	-18 ~ 18 0 ~ 15 0 ~ 34
No. of unique reflections	9127	4945	5031

2.3. Crystallographic studies

Crystals of (μ -H)(μ -Ph₂P(CH₂)₃PPh₂)Mo₂(CO)₇(NO) (**3**), (μ -H)(μ -Ph₂PCH₂CH₂PPh₂)Mo₂(CO)₆(CNⁿPr)(NO) (**12**), and (μ -H)W₂(CO)₇(PMe₂Ph)₂(NO) (**16**) were obtained by cooling a concentrated solution of the corresponding complex in CH₂Cl₂/hexane (1/5 v/v) at -5°C for several days. Crystals were mounted in thin glass capillary tubes. Diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo K α radiation (λ 0.7107 Å) with the θ -2 θ scan mode. Unit cells were determined from centring 25 reflections in the suitable 2 θ range. Other relevant experimental details are listed in Table 1. Absorption corrections according to ψ scans of three reflections were applied. All the data processing was carried out on a MicroVAX 3600 using the NRCC SDP program [11]. The coordinates of molybdenum and 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 $\Sigma \omega(|F_o| - |F_c|)^2$, where $\omega = 1/\sigma(F_o)^2$ was calculated from the counting statistics. The atomic scattering factors f_o and anomalous dispersion terms f' , f'' were taken from ref. 12. The position of the bridging hydrogen atom for **3** was located from the final difference Fourier maps and not refined. Other hydrogen atoms were included in the structure factor calculation in idealized position with d_{C-H} 0.98 Å. The final posi-

tional parameters for the atoms in **3**, **12**, and **16** are in Table 2. Selected interatomic distances and bond angles are in Table 3.

3. Results and discussion

Reaction of phosphine-substituted metal carbonyls with NO⁺ salts frequently results in loss of carbon monoxide and incorporation of NO ligands [13]. We previously applied this strategy to synthesize (μ -H)(μ -Ph₂P ~ PPh₂)W₂(CO)₇(NO) from (μ -H)(μ -Ph₂P ~ PPh₂)W₂(CO)₈ and NO⁺BF₄⁻ [14]. We have extended this methodology to the preparations of molybdenum analogues, (μ -H)(μ -Ph₂P(CH₂)_{*n*}PPh₂)Mo₂(CO)₇(NO) (**1–4**, *n* = 1–4). Complexes containing monodentate phosphine ligands, (CO)₅Mo(μ -H)Mo(CO)₃(NO)(P(*p*-C₆H₄X)₃) (**5**, X = H; **6**, X = F; **7**, X = Me; **8**, X = OMe) and (CO)₄(L)Mo(μ -H)Mo(CO)₃(L)(NO) (**9**, L = P(OMe)₃; **10**, L = PMe₂Ph), could also be prepared in a similar fashion from (CO)₅Mo(μ -H)Mo(CO)₄(P(*p*-C₆H₄X)₃)⁻ and (CO)₄(L)Mo(μ -H)(CO)₄(L)⁻, respectively. For a comparative study, complexes (CO)₄(L)W(μ -H)W(CO)₃(L)(NO) (**15**, L = PMe₃; **16**, L = PMe₂Ph; **17**, L = P(OMe)₃) were also synthesized, and **16** was structurally characterized by single crystal X-ray diffraction (*vide infra*). Although no dinuclear complexes containing a bridging hydrogen atom except for **5–8** were detected during nitrosylation of (CO)₅Mo(μ -H)Mo(CO)₄(P(*p*-C₆H₄X)₃)⁻, formation of (NO)(CO)₄-Mo(μ -H)Mo(CO)₄(P(*p*-C₆H₄X)₃) could not be ruled

(continued on page 206)

TABLE 2. Positional parameters and B_{iso} values for the atoms in compounds 3, 12, and 16

Atom	x	y	z	B_{iso}
<i>Compound 3</i>				
Mo1	0.12071(5)	0.25846(4)	0.16219(2)	3.61(2)
Mo2	0.12805(5)	0.33257(4)	0.31423(2)	3.55(2)
Mo3	0.53861(5)	0.81545(4)	0.36385(2)	3.58(2)
Mo4	0.47880(5)	0.91346(4)	0.22679(3)	3.82(3)
P1	-0.09592(14)	0.26140(11)	0.14639(7)	3.32(7)
P2	-0.02632(13)	0.21392(10)	0.34504(7)	3.03(7)
P3	0.63513(13)	0.66655(10)	0.32152(7)	3.16(7)
P4	0.40830(13)	0.75872(11)	0.16535(7)	3.36(7)
N1	0.1600(5)	0.3820(4)	0.3944(2)	5.2(3)
N2	0.4367(5)	0.9876(4)	0.1593(3)	6.0(3)
O1	0.1447(5)	0.4810(3)	0.1414(2)	8.3(3)
O2	0.3887(4)	0.2657(4)	0.1815(2)	8.7(4)
O3	0.1410(5)	0.0362(3)	0.1833(3)	8.6(3)
O4	0.1310(4)	0.2158(3)	0.0204(2)	6.1(3)
O5	-0.0391(5)	0.4974(3)	0.2802(2)	7.4(3)
O6	0.3234(4)	0.4677(4)	0.2667(2)	7.4(3)
O7	0.3021(5)	0.1645(4)	0.3251(3)	9.1(3)
O8	0.1795(5)	0.4146(4)	0.4455(2)	7.7(3)
O21	0.7671(4)	0.9417(3)	0.3562(2)	5.9(2)
O22	0.4358(5)	1.0027(4)	0.4238(2)	8.7(3)
O23	0.2898(4)	0.7197(4)	0.3569(2)	7.7(3)
O24	0.6015(4)	0.7572(4)	0.4953(2)	6.7(3)
O25	0.7399(4)	0.9085(4)	0.1953(2)	7.1(3)
O26	0.5475(4)	1.1049(3)	0.3089(2)	6.8(3)
O27	0.2312(4)	0.9156(4)	0.2819(2)	6.9(3)
O28	0.4094(5)	1.0316(4)	0.1176(2)	8.2(3)
C1	0.1312(6)	0.4021(5)	0.1498(3)	5.0(3)
C2	0.2900(6)	0.2629(5)	0.1754(3)	5.5(4)
C3	0.1304(6)	0.1149(5)	0.1757(3)	5.4(3)
C4	0.1295(5)	0.2312(4)	0.0742(3)	3.9(3)
C5	0.0182(6)	0.4384(4)	0.2937(3)	4.9(3)
C6	0.2543(6)	0.4182(4)	0.2830(3)	4.8(3)
C7	0.2421(6)	0.2220(5)	0.3230(3)	5.3(3)
C9	-0.1843(5)	0.2733(4)	0.2145(3)	3.7(3)
C10	-0.2044(5)	0.1802(4)	0.2485(3)	3.9(3)
C11	-0.1020(5)	0.1376(4)	0.2823(2)	3.4(3)
C21	0.6871(5)	0.8945(4)	0.3591(3)	4.0(3)
C22	0.4713(6)	0.9365(5)	0.4005(3)	5.5(4)
C23	0.3792(5)	0.7510(5)	0.3598(3)	4.5(3)
C24	0.5769(5)	0.7804(4)	0.4462(2)	3.7(3)
C25	0.6453(5)	0.9091(5)	0.2040(3)	5.2(3)
C26	0.5224(5)	1.0345(4)	0.2803(3)	4.7(3)
C27	0.3167(5)	0.9156(4)	0.2617(3)	4.6(3)
C29	0.6438(5)	0.6476(4)	0.2362(3)	3.6(3)
C30	0.5414(5)	0.5982(4)	0.1989(3)	3.9(3)
C31	0.4245(5)	0.6433(4)	0.2024(3)	3.7(3)
C41	-0.1343(5)	0.3666(4)	0.1040(3)	3.5(3)
C42	-0.1150(5)	0.3629(4)	0.0405(3)	4.2(3)
C43	-0.1319(6)	0.4434(5)	0.0071(3)	5.2(3)
C44	-0.1687(6)	0.5273(4)	0.0354(3)	5.6(4)
C45	-0.1877(6)	0.5313(4)	0.0981(3)	5.6(4)
C46	-0.1717(6)	0.4503(4)	0.1323(3)	4.9(3)
C51	-0.1732(5)	0.1638(4)	0.0994(2)	3.8(3)
C52	-0.1193(6)	0.0810(5)	0.0813(3)	5.6(4)
C53	-0.1770(7)	0.0073(5)	0.0459(4)	7.3(5)
C54	-0.2896(7)	0.0150(5)	0.0290(3)	7.5(5)
C55	-0.3453(6)	0.0953(5)	0.0465(3)	6.8(4)
C56	-0.2877(6)	0.1702(5)	0.0816(3)	5.4(3)
C61	-0.1388(5)	0.2555(4)	0.3945(2)	3.2(2)
C62	-0.2213(5)	0.1917(4)	0.4127(3)	4.2(3)

Table 2 (continued)

Atom	x	y	z	B _{iso}
C63	-0.2996(6)	0.2206(5)	0.4554(3)	5.4(3)
C64	-0.2931(6)	0.3125(5)	0.4811(3)	5.3(3)
C65	-0.2136(6)	0.3784(4)	0.4637(3)	5.2(3)
C66	-0.1360(5)	0.3508(4)	0.4204(3)	4.2(3)
C71	0.0405(5)	0.1268(4)	0.3946(3)	3.4(3)
C72	0.0753(6)	0.1610(4)	0.4543(3)	5.2(3)
C73	0.1325(7)	0.1038(6)	0.4941(3)	6.7(4)
C74	0.1529(6)	0.0110(5)	0.4744(3)	6.9(4)
C75	0.1194(7)	-0.0234(5)	0.4165(3)	6.6(4)
C76	0.0621(6)	0.0338(4)	0.3756(3)	4.9(3)
C81	0.7860(5)	0.6699(4)	0.3470(2)	3.3(3)
C82	0.8223(5)	0.6285(4)	0.4007(3)	4.0(3)
C83	0.9356(5)	0.6367(5)	0.4222(3)	4.7(3)
C84	1.0146(5)	0.6864(5)	0.3912(3)	5.4(4)
C85	0.9800(5)	0.7294(5)	0.3383(3)	5.1(3)
C86	0.8678(5)	0.7224(4)	0.3167(3)	4.3(3)
C91	0.5851(5)	0.5482(4)	0.3443(3)	3.5(3)
C92	0.6232(5)	0.4643(4)	0.3161(3)	4.2(3)
C93	0.5802(6)	0.3759(4)	0.3325(3)	5.5(4)
C94	0.5045(6)	0.3709(4)	0.3784(3)	5.5(3)
C95	0.4688(5)	0.4528(5)	0.4079(3)	5.3(3)
C96	0.5090(5)	0.5419(4)	0.3904(3)	4.3(3)
C101	0.4585(5)	0.7275(4)	0.0882(3)	3.6(3)
C102	0.4063(6)	0.6516(5)	0.0515(3)	5.0(3)
C103	0.4472(7)	0.6239(5)	-0.0057(3)	6.0(4)
C104	0.5403(7)	0.6707(5)	-0.0261(3)	7.0(4)
C105	0.5907(7)	0.7449(5)	0.0095(4)	7.5(5)
C106	0.5520(6)	0.7745(5)	0.0667(3)	5.4(3)
C111	0.2534(5)	0.7607(4)	0.1489(2)	3.6(3)
C112	0.2121(5)	0.8197(4)	0.1042(3)	4.3(3)
C113	0.0970(6)	0.8254(5)	0.0920(3)	5.7(4)
C114	0.0195(6)	0.7764(5)	0.1253(3)	6.2(4)
C115	0.0598(6)	0.7191(5)	0.1700(3)	5.8(4)
C116	0.1752(5)	0.7120(5)	0.1826(3)	4.7(3)
<i>Compound 12</i>				
Mo1	0.68562(20)	0.63552(14)	0.20000(12)	3.97(11)
Mo2	0.84127(21)	0.88887(14)	0.14935(12)	4.06(12)
P1	0.8651(6)	0.6427(4)	0.3038(3)	4.3(3)
P2	0.9333(6)	0.9687(4)	0.3000(3)	4.2(3)
N1	0.9022(16)	1.0158(12)	0.1110(10)	4.8(10)
N2	1.1113(21)	0.7928(17)	0.0848(13)	6.8(13)
O1	0.4898(22)	0.7399(17)	0.3463(13)	12.1(15)
O2	0.4695(15)	0.6194(13)	0.0655(11)	7.8(10)
O3	0.8645(19)	0.5434(13)	0.0351(10)	8.6(11)
O4	0.5300(20)	0.3986(13)	0.2191(14)	10.7(15)
O5	0.5508(19)	0.9330(16)	0.2190(13)	10.1(14)
O6	0.7176(20)	0.7754(14)	-0.0375(10)	8.9(12)
O7	0.9447(18)	1.1008(12)	0.0886(10)	8.5(12)
C1	0.5641(25)	0.7004(17)	0.2951(15)	6.1(14)
C2	0.5543(22)	0.6270(19)	0.1146(16)	6.2(15)
C3	0.8042(24)	0.5789(17)	0.0946(15)	5.7(14)
C4	0.5873(22)	0.4874(18)	0.2153(14)	5.5(13)
C5	0.6581(27)	0.9204(18)	0.1945(15)	5.9(16)
C6	0.7612(23)	0.8126(19)	0.0326(16)	5.8(15)
C8	1.0216(23)	0.8293(17)	0.1063(14)	4.7(13)
C9	1.2214(37)	0.7464(29)	0.0578(28)	13.3(29)
C10	1.2982(51)	0.7622(41)	-0.0244(27)	14.7(37)
C11	1.3566(52)	0.8666(39)	-0.0209(51)	29.8(66)
C12	0.9876(19)	0.7769(16)	0.3313(13)	4.7(12)
C13	0.9113(21)	0.8696(14)	0.3694(11)	4.8(11)
C21	0.8119(26)	0.6128(18)	0.4168(15)	5.5(13)

Table 2 (continued)

Atom	x	y	z	B _{iso}
C22	0.6884(37)	0.6010(37)	0.4510(26)	18.5(38)
C23	0.6433(34)	0.5860(46)	0.5344(22)	23.6(51)
C24	0.7237(34)	0.5667(27)	0.5849(19)	9.4(21)
C25	0.8394(41)	0.5798(44)	0.5555(22)	16.9(40)
C26	0.8871(32)	0.5959(39)	0.4687(25)	17.4(39)
C31	0.9828(25)	0.5551(18)	0.2593(12)	4.7(12)
C32	0.9218(26)	0.4437(21)	0.2288(18)	8.7(18)
C33	1.0105(34)	0.3776(20)	0.1943(17)	7.8(17)
C34	1.1446(45)	0.4131(35)	0.1905(20)	10.6(29)
C35	1.2052(30)	0.5226(30)	0.2203(20)	9.1(21)
C36	1.1187(31)	0.5869(19)	0.2555(16)	7.2(16)
C41	1.1119(23)	1.0406(15)	0.3024(14)	4.8(13)
C42	1.1849(26)	1.0858(23)	0.2329(16)	8.0(17)
C43	1.3193(31)	1.1411(22)	0.2362(20)	8.3(18)
C44	1.3968(28)	1.1498(23)	0.2983(23)	8.8(19)
C45	1.3299(35)	1.1041(37)	0.3696(20)	15.4(30)
C46	1.1916(33)	1.0507(27)	0.3676(19)	12.2(23)
C51	0.8474(21)	1.0688(15)	0.3692(12)	4.6(12)
C52	0.8780(34)	1.1660(23)	0.3528(23)	15.2(26)
C53	0.8016(42)	1.2426(23)	0.3925(25)	15.8(29)
C54	0.7219(36)	1.2238(22)	0.4640(16)	9.1(21)
C55	0.6800(26)	1.1260(24)	0.4789(18)	8.9(18)
C56	0.7481(24)	1.0483(17)	0.4314(18)	7.9(16)
<i>Compound 16</i>				
W1	0.22992(3)	0.32606(3)	0.16602(2)	3.09(2)
W2	0.36384(3)	0.38095(3)	0.08918(1)	3.13(2)
P1	0.15930(20)	0.49815(23)	0.17665(10)	3.64(13)
P2	0.44658(19)	0.53565(22)	0.12762(9)	3.25(12)
N	0.4300(7)	0.3840(7)	0.0423(3)	4.6(5)
O1	0.0997(6)	0.2874(7)	0.0718(3)	6.5(5)
O2	0.3048(7)	0.1018(7)	0.1614(4)	7.2(6)
O3	0.3606(7)	0.3556(8)	0.2598(3)	8.5(6)
O4	0.1033(6)	0.2295(7)	0.2272(3)	6.1(5)
O5	0.2178(6)	0.5089(7)	0.0239(3)	6.3(5)
O6	0.2766(7)	0.1716(7)	0.0460(3)	6.7(3)
O7	0.4911(6)	0.2456(7)	0.1629(3)	5.7(5)
O8	0.4751(7)	0.3901(7)	0.0131(3)	6.9(6)
C1	0.1461(7)	0.3039(8)	0.1057(4)	3.8(5)
C2	0.2792(8)	0.1837(9)	0.1621(4)	4.4(6)
C3	0.3143(8)	0.3490(9)	0.2252(4)	4.5(5)
C4	0.1501(8)	0.2651(8)	0.2040(4)	4.4(6)
C5	0.2690(8)	0.4650(8)	0.0485(4)	3.7(5)
C6	0.3057(8)	0.2456(10)	0.0625(4)	4.5(6)
C7	0.4467(8)	0.2932(9)	0.1367(4)	4.3(6)
C9	0.2275(9)	0.5971(9)	0.2084(4)	5.4(6)
C10	0.0708(9)	0.4889(11)	0.2111(5)	6.8(8)
C11	0.4697(7)	0.5289(9)	0.1916(4)	4.2(5)
C12	0.5525(8)	0.5432(10)	0.1104(5)	5.4(7)
C21	0.1086(6)	0.5627(8)	0.1224(4)	3.3(4)
C22	0.1447(8)	0.6531(9)	0.1054(4)	4.3(6)
C23	0.1038(9)	0.7001(10)	0.0647(5)	5.5(7)
C24	0.0299(10)	0.6571(11)	0.0398(5)	6.1(8)
C25	-0.0054(8)	0.5680(11)	0.0562(5)	5.5(7)
C26	0.0354(7)	0.5207(9)	0.0971(5)	4.6(6)
C31	0.4030(7)	0.6647(8)	0.1160(4)	3.6(5)
C32	0.3759(8)	0.6949(8)	0.0687(4)	4.2(6)
C33	0.3410(8)	0.7921(10)	0.0590(5)	5.2(6)
C34	0.3290(8)	0.8599(9)	0.0926(5)	5.4(7)
C35	0.3567(9)	0.8334(10)	0.1388(5)	5.7(7)
C36	0.3925(8)	0.7363(9)	0.1513(4)	4.4(6)

TABLE 3. Selected bond distances (Å) and angles (°) for complexes 3, 12, and 16

	3	12	16
M(1)–M(2); M(3)–M(4)	3.375(1); 3.391(1)	3.454(3)	3.3499(7)
M(1)–C(1); M(3)–C(21)	2.043(6); 2.040(6)	1.99(2)	2.03(1)
M(1)–C(2); M(3)–C(22)	1.990(7); 2.024(6)	1.94(2)	2.00(1)
M(1)–C(3); M(3)–C(23)	2.052(6); 2.044(6)	2.03(2)	2.01(1)
M(1)–C(4); M(3)–C(24)	1.926(6); 1.914(5)	1.96(2)	1.95(1)
M(1)–P(1); M(3)–P(3)	2.542(2); 2.534(2)	2.528(6)	2.519(3)
M(2)–C(5); M(4)–C(25)	2.051(6); 2.038(7)	2.02(3)	2.05(1)
M(2)–C(6); M(4)–C(26)	2.043(6); 2.020(6)	2.00(3)	2.06(1)
M(2)–C(7); M(4)–C(27)	2.086(6); 2.081(6)		2.07(1)
M(2)–N(1); M(4)–N(2)	1.843(5); 1.899(5)	1.80(2)	
M(2)–N			1.82(1)
M(2)–P(2); M(4)–P(4)	2.551(2); 2.548(2)	2.508(5)	2.537(3)
M(2)–C(8)		2.15(2)	
M(1)–H(1); M(3)–H(2)	1.98; 1.96		
M(2)–H(1); M(4)–H(2)	1.70; 1.88		
C(1)–O(1); C(21)–O(21)	1.129(7); 1.130(7)	1.16(3)	1.14(1)
C(2)–O(2); C(22)–O(22)	1.153(8); 1.118(8)	1.18(3)	1.13(1)
C(3)–O(3); C(23)–O(23)	1.125(8); 1.115(7)	1.12(3)	1.14(1)
C(4)–O(4); C(24)–O(24)	1.167(7); 1.152(7)	1.15(3)	1.16(2)
C(5)–O(5); C(25)–O(25)	1.117(8); 1.130(8)	1.15(3)	1.14(1)
C(6)–O(6); C(26)–O(26)	1.127(7); 1.145(8)	1.17(3)	1.13(2)
C(7)–O(7); C(27)–O(27)	1.081(8); 1.109(8)		1.13(1)
N(1)–O(8); N(2)–O(28)	1.174(7); 1.158(7)		
N(1)–O(7)		1.18(2)	
N–O(8)			1.18(1)
M(1)–C(1)–O(1); M(3)–C(21)–O(21)	175.0(6); 177.2(5)	176(2)	177.4(9)
M(1)–C(2)–O(2); M(3)–C(22)–O(22)	178.3(6); 176.4(6)	177(2)	177(1)
M(1)–C(3)–O(3); M(3)–C(23)–O(23)	176.6(6); 176.4(6)	177(2)	175(1)
M(1)–C(4)–O(4); M(3)–C(24)–O(24)	177.6(5); 178.4(5)	176(2)	179(1)
M(2)–C(5)–O(5); M(4)–C(25)–O(25)	176.5(6); 175.5(6)	177(2)	176.3(9)
M(2)–C(6)–O(6); M(4)–C(26)–O(26)	178.0(6); 177.6(5)	175(2)	176(1)
M(2)–C(7)–O(7); M(4)–C(27)–O(27)	177.7(6); 178.1(5)		179(1)
M(2)–N(1)–O(8); M(4)–N(2)–O(28)	179.0(5); 178.9(5)		
M(2)–N(1)–O(7)		178(2)	
M(2)–N–O(8)			176.7(9)
C(1)–M(1)–C(2); C(21)–M(3)–C(22)	87.8(3); 86.8(3)	88.5(9)	91.6(4)
C(1)–M(1)–C(3); C(21)–M(3)–C(23)	173.4(3); 171.2(2)	173.8(9)	179.1(5)
C(1)–M(1)–C(4); C(21)–M(3)–C(24)	89.8(2); 93.2(2)	91.4(9)	92.0(5)
C(2)–M(1)–C(3); C(22)–M(3)–C(23)	85.6(3); 88.9(3)	86.7(9)	88.5(5)
C(2)–M(1)–C(4); C(22)–M(3)–C(24)	92.0(3); 88.8(2)	89.1(9)	87.0(5)
C(3)–M(1)–C(4); C(23)–M(3)–C(24)	90.1(2); 94.4(2)	92.3(8)	88.9(5)
C(1)–M(1)–P(1); C(21)–M(3)–P(3)	89.6(2); 90.2(2)	94.7(6)	89.4(3)
C(2)–M(1)–P(1); C(22)–M(3)–P(3)	177.2(2); 176.3(2)	176.8(7)	174.4(3)
C(3)–M(1)–P(1); C(23)–M(3)–P(3)	97.0(2); 94.4(2)	90.1(7)	90.7(4)
C(4)–M(1)–P(1); C(24)–M(3)–P(3)	88.9(2); 89.2(2)	91.1(7)	87.4(3)
C(5)–M(2)–C(6); C(25)–M(4)–C(26)	87.0(3); 87.6(3)	89.1(9)	89.7(4)
C(5)–M(2)–C(7); C(25)–M(4)–C(27)	172.6(3); 172.6(3)		171.8(5)
C(5)–M(2)–C(8)		170.6(8)	
C(6)–M(2)–C(7); C(26)–M(4)–C(27)	90.2(3); 89.2(2)		88.4(4)
C(6)–M(2)–C(8)		89.4(8)	
C(5)–M(2)–N(1); C(25)–M(4)–N(2)	93.8(2); 93.2(3)	92.1(8)	
C(6)–M(2)–N(1); C(26)–M(4)–N(2)	91.0(2); 90.6(2)	91.4(7)	
C(7)–M(2)–N(1); C(27)–M(4)–N(2)	93.1(3); 93.5(2)		
C(8)–M(2)–N(1)		97.1(7)	
C(5)–M(2)–N			90.6(4)
C(6)–M(2)–N			90.7(5)
C(7)–M(2)–N			97.5(4)

Table 3 (continued)

	3	12	16
P(2)–M(2)–N(1); P(4)–M(4)–N(2)	93.6(2); 91.1(2)	93.7(5)	
C(5)–M(2)–P(2); C(25)–M(4)–P(4)	95.4(2); 97.2(2)	90.6(7)	96.3(3)
C(6)–M(2)–P(2); C(27)–M(4)–P(4)	174.6(2); 174.8(2)	175.0(6)	174.0(3)
C(7)–M(2)–P(2); C(27)–M(4)–P(4)	86.7(2); 85.8(2)		85.2(3)
C(8)–M(2)–P(2)		90.1(6)	
M(1)–H(1)–M(2); M(3)–H(2)–M(4)	133; 124		

out since they might not be stable in the solution similar to $\text{HMo}_2(\text{CO})_9(\text{NO})$. Complexes **5–8** could alternatively be synthesized from ligand substitution of $\text{HMo}_2(\text{CO})_9(\text{NO})$ with appropriate ligands.

The generally low yields for the aforementioned complexes are partially due to their decomposition during isolation procedures such as chromatography. Dimolybdenum complexes **1–10** and $\text{HMo}_2(\text{CO})_9(\text{NO})$ appear to be much less stable than their corresponding tungsten analogues. For instance, **9** and **10** could only be recrystallized at low temperatures whereas **15–17** survived fast column chromatography. The order of stability of these new dimolybdenum complexes in CH_2Cl_2 at ambient temperature is found to be as follows: $(\text{CO})_4(\text{L})\text{Mo}(\mu\text{-H})\text{Mo}(\text{CO})_3(\text{L})(\text{NO}) < (\mu\text{-H})(\mu\text{-Ph}_2\text{P} \sim \text{PPh}_2)\text{Mo}_2(\text{CO})_7(\text{NO}) < (\text{CO})_5\text{Mo}(\mu\text{-H})\text{Mo}(\text{CO})_3(\text{L})(\text{NO})$. In **9** and **10**, both phosphine ligands are likely to be exo to the bent $(\text{OC})_{\text{ax}}\text{-Mo-Mo-(NO)}_{\text{ax}}$ molecular backbone according to the structural analysis of **16**. The low instability of **9** and **10** could possibly be due to the unfavourable steric contacts between the equatorial ligands of the complexes. Although diphosphine ligands, as frequently used to retain the dimeric metal unit [15], have improved the stability of $(\mu\text{-H})(\mu\text{-Ph}_2\text{P} \sim \text{PPh}_2)\text{Mo}_2(\text{CO})_7(\text{NO})$ (**1–4**) relative to **9** and **10**, in CH_2Cl_2 at ambient conditions, **1–4** still decompose to $(\eta^2\text{-Ph}_2\text{P} \sim \text{PPh}_2)\text{Mo}(\text{CO})_4$ and unidentifiable products within 1 h.

Nucleophilic attack of N-propylphosphinimine at one of the carbonyl ligands of **1–4** occurs readily due to the presence of the strong π -acceptor, NO. Deoxygenation of carbonyl ligand with elimination of O=PPh_3 [16] results in formation of $(\mu\text{-H})(\mu\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{-PPh}_2)[\text{Mo}(\text{CO})_4][\text{Mo}(\text{CO})_2(\text{CNPr})(\text{NO})]$ (**11–14**, $n = 1\text{–}4$). Complex **12** was also structurally characterized. In contrast to complexes **1–4**, **11–14** are stable in solution, possibly owing to the elongation of Mo–Mo distance of the latter which decreases the repulsive interaction among equatorial ligands.

The spectra of the new complexes (Table 4) are consistent with their formulation. The proton chemical shifts of the hydrides are in the range of 10.5–12 ppm upfield from Me_4Si and are consistent with the existence of a Mo–H–Mo linkage [9]. The H–P coupling constants $^2J(\text{H-P})$ also appear to be normal. The two

phosphorus atoms in **1–4** and **9–17** are magnetically inequivalent based on the ^{31}P NMR spectra. The similarity of their infrared spectral pattern to those of the corresponding tungsten analogues [5,7,14] suggests that molybdenum and tungsten congeners have similar structures in the solution.

3.1. Molecular structures of $\mu\text{-H}[\text{W}(\text{CO})_4(\text{PMe}_2\text{Ph})][\text{W}(\text{CO})_3(\text{PMe}_2\text{Ph})(\text{NO})]$ (**16**), $(\mu\text{-H})(\mu\text{-Ph}_2\text{P}(\text{CH}_2)_3\text{-PPh}_2)\text{Mo}_2(\text{CO})_7(\text{NO})$ (**3**), and $(\mu\text{-H})(\mu\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{-PPh}_2)\text{Mo}_2(\text{CO})_6(\text{CN}^n\text{Pr})(\text{NO})$ (**12**)

The ORTEP drawings of **16**, **3**, and **12** are shown in Figs. 1, 2, and 3, respectively. Similar to other dinuclear Group VI metal complexes containing a M–H–M linkage, the two metal atoms reside in a roughly octahedral environment, with the nitrosyl ligand occupying the axial position. The overall structure in these complexes is bent (the framework bends [17*] for **16**: $28.8(2)^\circ$; **3**: $17.7(1)^\circ$; **12**: $13.5(4)^\circ$), and the equatorial ligands are staggered (staggering angle for **16**: $51.9(1)^\circ$; **3**: $48.7(0)^\circ$, $43.0(0)^\circ$; **12**: $33.0(2)^\circ$). Both PMe_2Ph ligands of **16** are exo to the bent $(\text{OC})_{\text{ax}}\text{-W-(NO)}_{\text{ax}}$ molecular backbone. Although substitution of P(OMe)_3 (cone angle 107° [18]) for one CO in $\text{HW}_2(\text{CO})_9(\text{NO})$ (W–W distance $3.329(1) \text{ \AA}$) [19] results in elongation of W–W distance ($3.393(4) \text{ \AA}$ for $\text{HW}_2(\text{CO})_8(\text{P(OMe)}_3)(\text{NO})$ [20]), the W–W distance in **16** ($3.3499(7) \text{ \AA}$) is shorter than that of $\text{HW}_2(\text{CO})_8(\text{P(OMe)}_3)(\text{NO})$ even though the former has two sterically more demanding PMe_2Ph groups (cone angle 122°). Darensbourg [4b] suggested that the framework bend (the angle of intersection defined by two $(\text{OC})_{\text{ax}}\text{-M}$ vectors) being greater in $((\mu\text{-H})(\text{Mo}(\text{CO})_4(\text{PMePh}_2))_2)^-$ (148°) than in $((\mu\text{-H})(\text{Mo}_2(\text{CO})_9(\text{PPh}_3)))^-$ (163°) indicated an increased $\text{Mo} \cdots \text{Mo}$ interaction and shortened Mo–Mo distance in the former. The angles of intersection defined by $(\text{OC})_{\text{ax}}\text{-W}$ and $(\text{ON})_{\text{ax}}\text{-W}$ are 156° and 153° for **16** and $\text{HW}_2(\text{CO})_8(\text{P(OMe)}_3)(\text{NO})$, respectively. It is therefore not unreasonable to correlate the framework bend with the metal–metal distance.

There are two crystallographically independent molecules for **3**. The two molecules differ in metal–

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

TABLE 4. IR spectra and ^1H and $^{31}\text{P}(\text{H})$ NMR spectra for complexes 1–17

Compound	$\nu(\text{CO}), \nu(\text{NO})^a$ (cm^{-1})	δ (ppm) ^{b,c} , $J(\text{Hz})$	δ (ppm) ^{b,d} , $J(\text{Hz})$
1	2088m, 2014s, 1914sh, 1899s, 1889sh; 1684m, br	<i>Ph</i> (7.45–7.26, m, 20H); <i>CH</i> ₂ (3.47, dd, 2H, $^1J(\text{P-H}) = 4.5, 3.1$); $\mu\text{-H}$ (-11.4, dd, 1H, $^2J(\text{P-H}) = 14.5, 14.4$)	<i>PPh</i> ₂ (38.6, d, 1P, $^2J(\text{P-P}) = 175$); <i>PPh</i> ₂ (29.2, d, 1P)
2	2088m, 2013s, 1939sh, 1906s, 1887sh; 1692m, br	<i>Ph</i> (7.81–7.17, m, 20H); <i>CH</i> ₂ (2.74, br, 4H); $\mu\text{-H}$ (-11.9, pseudo triplet, 1H, $^2J(\text{P-H}) = 22.3$)	<i>PPh</i> ₂ (39.8, s, 1P); <i>PPh</i> ₂ (34.7, s, 1P)
3	2088m, 2013s, 1944s, 1912sh, 1894s, 1871sh; 1690m, br	<i>Ph</i> (7.57–7.42, m, 20H); <i>CH</i> ₂ (3.01, m, 2H); <i>CH</i> ₂ (2.56, m, 2H); <i>CH</i> ₂ (1.90, m, 2H); $\mu\text{-H}$ (-11.0, pseudo triplet, 1H, $^2J(\text{P-H}) = 19.5$)	<i>PPh</i> ₂ (31.0, s, 1P); <i>PPh</i> ₂ (26.8, s, 1P)
4	2088m, 2072w, 2073s, 1939s, 1912s, 1894s, 1866sh; 1688m, br	<i>Ph</i> (7.50–7.27, m, 20H); <i>CH</i> ₂ (3.54, m, 4H); <i>CH</i> ₂ (1.32, m, 4H); $\mu\text{-H}$ (-10.7, pseudo triplet, 1H, $^2J(\text{P-H}) = 16.5$)	<i>PPh</i> ₂ (24.0, s, 1P); <i>PPh</i> ₂ (21.8, s, 1P)
5	2094w, 2064w, 2023s, 1932vs; 1698m, br	<i>Ph</i> (7.62–7.51, m, 15H); $\mu\text{-H}$ (-11.5, d, 1H, $^2J(\text{P-H}) = 17.3$)	<i>PPh</i> ₃ (35.2, s)
6	2095w, 2065w, 2021s, 1935vs, 1706m, br	<i>Ph</i> (7.74–7.34, m, 12H); $\mu\text{-H}$ (-11.6, d, 1H, $^2J(\text{P-H}) = 18.0$)	<i>P</i> (34.1, s)
7	2093w, 2064w, 2022s, 1936vs; 1700m, br	<i>Ph</i> (7.51–7.35, m, 12H); <i>CH</i> ₃ (2.39, s, 9H); $\mu\text{-H}$ (-11.5, d, 1H, $^2J(\text{P-H}) = 17.2$)	<i>P</i> (32.7, s)
8	2094w, 2071w, 2022s, 1941vs; 1702m, br	<i>Ph</i> (7.53–7.08, m, 12H); <i>OCH</i> ₃ (3.85, s, 9H); $\mu\text{-H}$ (-11.5, d, 1H, $^2J(\text{P-H}) = 17.2$)	<i>P</i> (30.4, s)
9	2096w, 2025s, 1948sh, 1907s, 1876sh; 1690m, br	<i>OCH</i> ₃ (3.6, s, br, 9H); <i>OCH</i> ₃ (3.5, s, br, 9H); $\mu\text{-H}$ (-11.8, br, 1H)	<i>P(OMe)</i> ₃ (105.9, s, 1P); <i>P(OMe)</i> ₃ (89.8, s, 1P)
10	2084w, 2014s, 1937sh, 1900s, 1860m; 1680m, br	<i>Ph</i> (7.46–7.42, m, 10H); <i>CH</i> ₃ (1.69, d, 6H, $^2J(\text{P-H}) = 15.0$); <i>CH</i> ₃ (1.67, d, 6H, $J(\text{P-H}) = 16.0$); $\mu\text{-H}$ (-10.9, dd, 1H, $^2J(\text{P-H}) = 16.0, 15.0$)	<i>PMe</i> ₂ <i>Ph</i> (34.7, s, 1P); <i>PMe</i> ₂ <i>Ph</i> (33.1, s, 1P)
11	2039s, 2009wm, 1980m, 1889s, 1868sh; 1646m, br 2189w ($\nu(\text{CN})$)	<i>Ph</i> (7.58–7.26, m, 20H); <i>CH</i> ₂ (3.76, m, 4H); <i>CH</i> ₂ <i>CH</i> ₃ (1.62, m, 2H); <i>CH</i> ₃ (0.93, t, 3H, $^3J(\text{H-H}) = 7.2$); $\mu\text{-H}$ (-11.9, dd, 1H, $^2J(\text{P-H}) = 18.7, 18.6$)	<i>PPh</i> ₂ (40.1, d, 1P, $^2J(\text{P-P}) = 162$); <i>PPh</i> ₂ (33.2, d, 1P)
12	2037s, 2007wm, 1973m, 1890s, 1861m; 1634m, br 2186w ($\nu(\text{CN})$)	<i>Ph</i> (7.69–7.42, m, 20H); <i>NCH</i> ₂ (3.51, m, 2H); <i>PCH</i> ₂ (2.90, br, 4H); <i>CH</i> ₂ <i>CH</i> ₃ (1.46, m, 2H); <i>CH</i> ₃ (0.75, t, 3H, $^3J(\text{H-H}) = 7.4$); $\mu\text{-H}$ (-12.1, pseudo triplet, 1H, $^2J(\text{P-H}) = 21.2$)	<i>PPh</i> ₂ (43.1, d, 1P, $^3J(\text{P-P}) = 24.5$); <i>PPh</i> ₂ (38.7, d, 1P)
13	2033s, 2006wm, 1976m, 1905s, 1871m; 1660m, br 2196w ($\nu(\text{CN})$)	<i>Ph</i> (7.63–7.26, m, 20H); <i>NCH</i> ₂ (3.53, m, 2H); <i>PCH</i> ₂ (2.92, br, 4H); <i>CH</i> ₂ (2.55, m, 2H); <i>CH</i> ₂ <i>CH</i> ₃ (1.56, m, 2H); <i>CH</i> ₃ (0.87, t, 3H, $^3J(\text{H-H}) = 7.4$); $\mu\text{-H}$ (-11.2, pseudo triplet, 1H, $^2J(\text{P-H}) = 18.4$)	<i>PPh</i> ₂ (32.9, s, 1P); <i>PPh</i> ₂ (28.6, s, 1P)
14	2032s, 2006wm, 1968m, 1933sh, 1894s, 1857sh; 1648m, br 2201w ($\nu(\text{CN})$)	<i>Ph</i> (7.51–7.26, m, 20H); <i>NCH</i> ₂ (3.54, t, 2H, $^3J(\text{H-H}) = 6.8$); <i>PCH</i> ₂ (2.78, br, 4H); <i>CH</i> ₂ (2.53, m, 4H); <i>CH</i> ₂ <i>CH</i> ₃ (1.45, br, 4H); <i>CH</i> ₃ (0.75, t, 3H, $^3J(\text{H-H}) = 7.4$); $\mu\text{-H}$ (-10.7, pseudo triplet, 1H, $^2J(\text{P-H}) = 16.2$)	<i>PPh</i> ₂ (28.1, s, 1P); <i>PPh</i> ₂ (26.5, s, 1P)
15	2090w, 2020s, 1899s, 1876m; 1694m, br	<i>OCH</i> ₃ (3.86, d, 9H, $^3J(\text{P-H}) = 11.4$); <i>OCH</i> ₃ (3.65, d, 9H, $^3J(\text{P-H}) = 11.3$); $\mu\text{-H}$ (-10.9, dd, 1H, $^2J(\text{P-H}) = 22.7, 25.1$; $^1J(\text{W-H}) = 38.0$)	<i>P(OMe)</i> ₃ (146.8, s, 1P, $^1J(\text{W-P}) = 352$); <i>P(OMe)</i> ₃ (126.8, s, 1P, $^1J(\text{W-P}) = 400$)
16	2079w, 2009s, 1889s, 1864m; 1671m, br	<i>Ph</i> (7.62–7.43, m, 10H); <i>PCH</i> ₃ (1.95, d, 6H, $^2J(\text{P-H}) = 8.7$); <i>PCH</i> ₃ (1.85, d, 6H, $^2J(\text{P-H}) = 8.7$); $\mu\text{-H}$ (-9.88, pseudo triplet, 1H, $^2J(\text{P-H}) = 16.5, ^1J(\text{W-H}) = 46.8$)	<i>PMe</i> ₂ <i>Ph</i> (-20.2, s, 1P, $^1J(\text{W-P}) = 203$); <i>PMe</i> ₂ <i>Ph</i> (-23.5, s, 1P, $^1J(\text{W-P}) = 238$)

TABLE 4 (continued)

17	2079w, 2007s, 1933m, 1891s, 1860m; 1682m, br	CH ₃ (1.88, d, 9H, ² J(P-H) = 6.8); CH ₃ (1.76, d, 9H, ² J(P-H) = 8.4); μ-H (-10.4, pseudo triplet, 1H, ² J(P-H) = 10.8, ¹ J(W-H) = 28.5)	PMe ₃ (-34.3, s, 1P, ¹ J(W-P) = 252); PMe ₃ (-35.1, s, 1P, ¹ J(W-P) = 299)
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^a Measured in CH₂Cl₂ solution. ^b Measured in acetone-*d*₆ except for 1-4, 9, and 10 which were measured in CD₂Cl₂. ^c Reported in ppm relative to δ(Me₄Si) = 0 ppm. ^d Reported in ppm relative to δ(85% H₃PO₄) = 0 ppm. Abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet. These abbreviations do not include the satellites.

metal distance by 0.016 Å, albeit they have approximately similar structures. The two phosphine ligands in **3** are exo to the bent (OC)_{ax}-Mo-Mo-(NO)_{ax} molecular backbone, similar to those observed for (μ-H)(μ-Ph₂P(CH₂)₄PPh₂)Mo₂(CO)₈ [9] and (μ-Ph₂P(CH₂)₃-PPh₂)W₂(CO)₇(NO) [14]. We were able to locate the position of the bridging hydride in the final difference Fourier maps for **3**. The hydride bridge and the phosphine bridge are parallel. The hydride is asymmetrically bridged and closer to the molybdenum atom containing a better π-acceptor, NO. The observed Mo-H distances (1.98; 1.70; 1.96; 1.88 Å) and the Mo-H-Mo angles (133°; 124°) are in agreement with the reported values (Mo-H, 1.68-2.19 Å; Mo-H-Mo, 127-136°) [9]. The Mo-Mo distance in **3** (3.375(1), 3.391(1) Å) is much shorter than those of (μ-H)(μ-Ph₂P(CH₂)₄-PPh₂)Mo₂(CO)₈ (3.4995(8) Å), indicative of the electronic influence of the NO ligand upon the M-M interaction in a 3c-2e M-H-M linkage.

The ⁿPrNC ligand of the complex **12** is coordinated to the molybdenum atom containing NO and is *cis* to the phosphine ligand on the same metal. These structural features are similar to those of (μ-H)(μ-

dppm)W₂(CO)₆(L)(NO) (L = Ph₂PH; PhPH(CH₂CH₂-CN)) [21]. The structural preference of these products derived from (μ-H)(μ-Ph₂P(CH₂)_nPPh₂)M₂(CO)₇(NO) could be rationalized by electronic effects, *i.e.*, the strong π-accepting ability of NO would activate CO ligands on the same metal, and the CO ligand

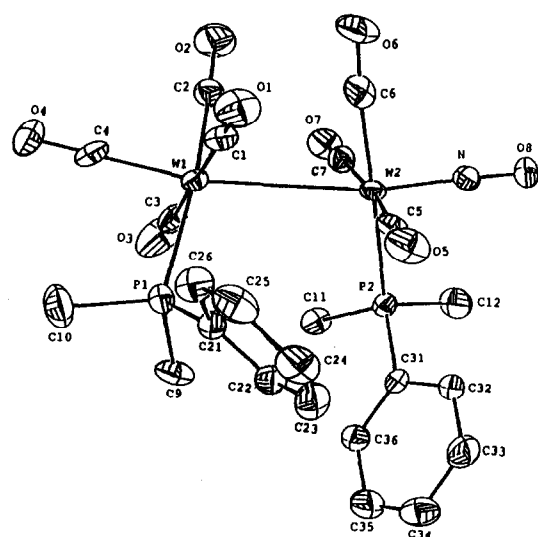


Fig. 1. Molecular structure of **16**. The hydrogen atoms are omitted for clarity.

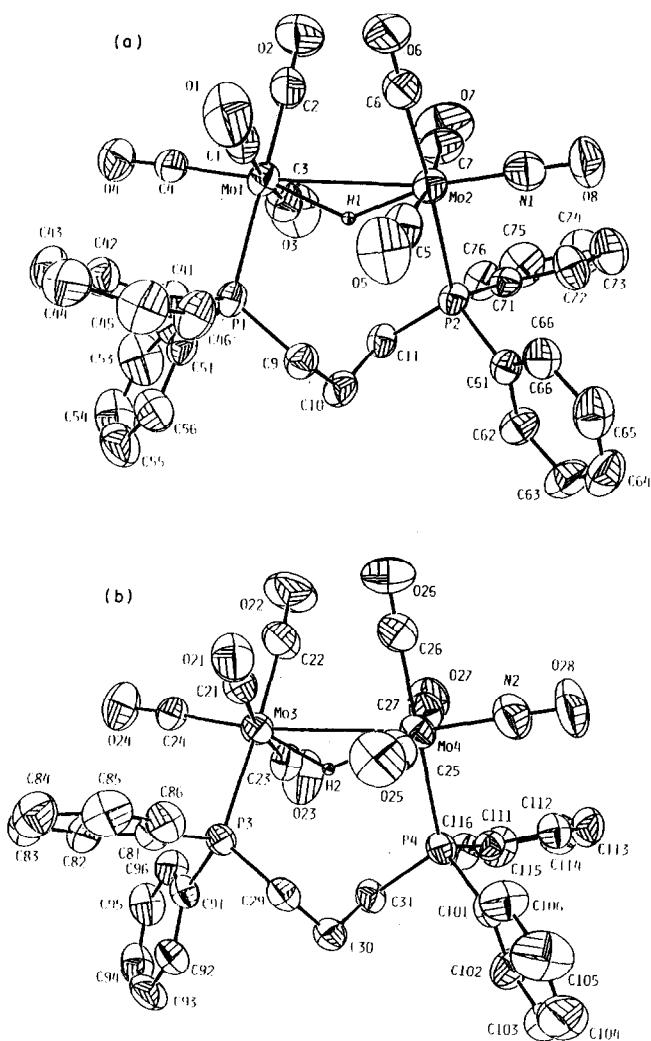


Fig. 2. Molecular structure of **3**. The hydrogen atoms except for μ-H are omitted for clarity.

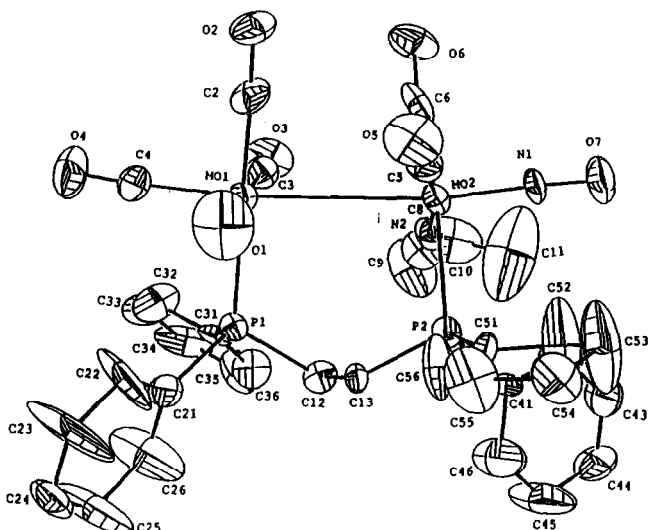


Fig. 3. Molecular structure of **12**. The hydrogen atoms are omitted for clarity.

trans to another CO ligand would be more activated than the CO ligand *trans* to a weaker π -accepting phosphine ligand. Displacement of CO by a sterically more demanding $^n\text{PrNC}$ causes the metal–metal distance (3.454(3) Å) of **12** to be longer than that of $(\mu\text{-H})(\mu\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{W}_2(\text{CO})_7(\text{NO})$ (3.3709(8) Å) [22]. There may also be electronic influence on the lengthened metal–metal distance in **12**, since the $\nu(\text{NO})$ bands for **11–14** are observed in the significantly lower frequency region (around 1690 cm^{-1}) than in **1–4** (around 1650 cm^{-1}), indicating the electron rich nature of the metal centres in these isocyanide complexes.

4. Supplementary material available

All bond distances and angles (Table S1: **16**, 2 pages; **3**, 4 pages; **12**, 2 pages), anisotropic thermal parameters and isotropic thermal parameters (Table S2: **16**, 1 page; **3**, 3 pages; **12**, 2 pages), positional parameters for calculated hydrogen atoms (Table S3: **16**, 1 page; **3**, 1 page; **12**, 1 page), and structure factors (Table S4: **16**, 17 pages; **3**, 31 pages; **12**, 17 pages), are all available from the authors.

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