ORGANOMETALLICS

Volume 1, Number 2, February 1982

© Copyright 1982
American Chemical Society

Addition of Isocyanides to $[CpMo(CO)_2]_2$. The Crystal and Molecular Structure of $Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2\text{-CNPh})$ Which Contains a Bridging η^2-Isocyanide Ligand

Richard D. Adams,* Dean A. Katahira, and Li-Wu Yang

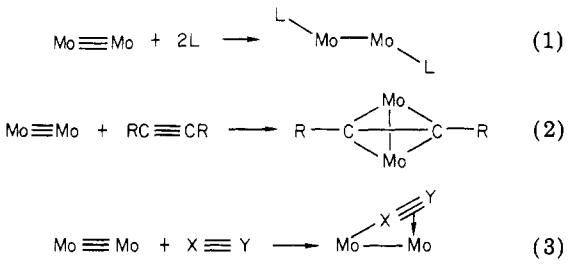
Department of Chemistry, Yale University, New Haven, Connecticut 06511

Received June 26, 1981

The isocyanides, CNR, R = Me, Ph, *t*-Bu, react with $[CpMo(CO)_2]_2$ to form the 1:1 adducts $Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2\text{-CNR})$, R = Me, Ph, *t*-Bu. The products have been investigated by IR, ^1H NMR, and ^{13}C NMR spectroscopy. The phenyl isocyanide adduct has also been characterized by X-ray crystallographic methods: space group $P2_1/n$, at 23 °C, a = 9.144 (1) Å, b = 19.574 (3) Å, c = 11.409 (2) Å, β = 96.10 (1)°, V = 2030.5 (9) Å^3, Z = 4, ρ_{calcd} = 1.757 g/cm^3. For 2951 reflections ($F_o \geq 3.0\sigma(F_o^2)$) R_1 = 0.023 and R_2 = 0.025. The molecule contains two molybdenum atoms joined by a Mo–Mo single bond, Mo–Mo = 3.212 (1) Å. The two metal atoms are bridged by an isocyanide ligand which is σ bonded to one metal atom and π bonded to the other. The C–N multiple bond at 1.244 (3) Å is significantly longer than that normally found for terminally coordinated isocyanide ligands. ^{13}C NMR shifts of the isocyano carbons of the $\sigma + \pi$-bonded isocyanide ligands occur at approximately 215-ppm downfield from Me_4Si.

Introduction

Organometallic molecules containing metal–metal multiple bonds have been shown to exhibit a wealth of new and unusual reaction chemistry.[1,2] Probably the most thoroughly studied of these is $[CpMo(CO)_2]_2$ (**I**).[3-11] Formally this molecule contains a Mo≡Mo triple bond.[3] It readily adds donors, either two two-electron donors or one four-electron donor,[4,6] to yield molecules containing a Mo—Mo single bond (eq 1–3). The third reaction X≡Y = N≡C—R[5] or CN$^-$[7] has resulted in a few of the rare examples of the $\sigma + \pi$ coordination of the heteronuclear triple bond. It has been proposed that such coordination may play an important role in the activation of these lig-



ands toward catalytic reduction about polynuclear metal centers.[12] We have now found that isocyanides also react with **I** according to eq 3 to produce 1:1 adducts where the isocyanide ligand engages in the $\sigma + \pi$-bonding mode.

Experimental Section

General Information. Since the compounds, particularly when in solution, were air sensitive, all reactions and purifications were routinely performed under a prepurified nitrogen atmosphere. Hexane and toluene solvents were purified by distillation from sodium–benzophenone; other solvents were stored over 4-Å molecular sieves and degassed with a dispersed stream of nitrogen. $[CpMo(CO)_2]_2$ was prepared according to the method of Curtis.[13] MeNC and PhNC were prepared by reported methods.[14,15]

(1) Chisholm, M. H.; Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 356.
(2) (a) Clauss, A. D.; Dimas, P. A.; Shapley, J. R. *J. Organomet. Chem.* **1980**, *201*, C31. (b) Boag, N. M.; Green, M.; Mills, R. M.; Pain, G. N.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1980**, 1171.
(3) Klinger, R. J.; Butler, W. M.; Curtis, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 5034.
(4) Bailey, W. I.; Chisholm, M. H.; Cotton, F. A.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 5764.
(5) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 807.
(6) Curtis, M. D.; Klingler, R. J. *J. Organomet. Chem.* **1978**, *161*, 23.
(7) Curtis, M. D.; Han, K. R.; Butler, W. M. *Inorg. Chem.* **1980**, *19*, 2096.
(8) Curtis, M. D.; Butler, W. M. *J. Chem. Soc., Chem. Commun.* **1980**, 988.
(9) Curtis, M. D.; Messerle, L. *J. Am. Chem. Soc.* **1980**, *102*, 7791.
(10) Wachter, J.; Mitschler, A.; Riess, J. G. *J. Am. Chem. Soc.* **1981**, *103*, 2121.
(11) Brunner, H.; Meier, W.; Wachter, J. *J. Organomet. Chem.* **1981**, *210*, C23.
(12) (a) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1976**, *85*, 451. (b) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479.
(13) Klingler, R. J.; Butler, W.; Curtis, M. D. *J. Am. Chem. Soc.* **1975**, *97*, 3535.

0276-7333/82/2301-0231$01.25/0 © 1982 American Chemical Society

Table I. Spectral Properties[a]

compd	NMR, δ (J, Hz) ^{1}H	NMR, δ (J, Hz) ^{13}C	IR, cm^{-1}
$Cp_2Mo_2(CO)_4CNMe$ (II)	5.34 (C_5H_5), 5.33 (C_5H_5) 3.62 (CH_3)	245.99 (CO), 244.37 (CO) 233.84 (CO), 232.50 (CO) 210.53 (CN), 94.56 (C_5H_5) 92.26 (C_5H_5), 40.65 (CH_3)	ν_{CN} 1725 (m br) ν_{CO} 1825 (s), 1898 (s) 1930 (vs), 1971 (s)
$Cp_2Mo_2(CO)_4CNPh$ (III)	7.50 (d, ^3J = 8.1, C_6H_5) 7.40 (dd, ^3J = 8.1, ^3J = 7.0, C_6H_5) 7.21 (d, ^3J = 7.0, C_6H_5) 5.44 (C_5H_5), 5.42 (C_5H_5)	246.16 (CO), 244.47 (CO)[b] 232.96 (CO), 231.02 (CO) 213.90 (CN), 139.32 (C_6H_5) 129.29 (C_6H_5), 125.98 (C_6H_5) 122.74 (C_6H_5), 94.76 (C_5H_5) 92.89 (C_5H_5)	ν_{CN} 1666 (m br) ν_{CO} 1850 (s), 1898 (s) 1927 (vs), 1968 (s)
$Cp_2Mo_2(CO)_4CN$-*t*-Bu (IV)	5.33 (C_5H_5), 5.32 (C_5H_5) 1.39 (CH_3)	246.49 (CO), 244.48 (CO) 233.98 (CO), 232.90 (CO) 211.36 (CN), 94.41 (C_5H_5) 94.44 (C_5H_5), 59.49 (C_4H_9, tertiary) 31.09 (C_4H_9, primary)	ν_{CN} 1690 (m br) ν_{CO} 1849 (s), 1892 (s) 1920 (vs), 1963 (s)

[a] NMR spectra of compounds in $CDCl_3$ at 298 K; IR spectra of compounds in hexane solvent, ±5 cm^{-1}. [b] At −50 °C.

tert-Butyl isocyanide was obtained from Strem Chemicals Inc. Alumina for chromatography was Baker acid-washed aluminum oxide deactivated with 6% w/w water.

Melting points were determined in evacuated capillary tubes using a Thomas-Hoover apparatus are are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 237B spectrophotometer. A Bruker HX270 NMR spectrometer was used to obtain ^{1}H and ^{13}C NMR spectra at 270 and 67.89 MHz, respectively.

Reaction of $[CpMo(CO)_2]_2$ with CNPh. At room temperature phenyl isocyanide (85.5 mg, 0.829 mmol) was added to a stirred solution of $[CpMo(CO)_2]_2$ (300.0 mg, 0.691 mmol) in methylene chloride (100 mL). As monitored by IR spectroscopy, the reaction was complete in 5 min. Volatile components of the reaction were removed under vacuum. The remaining red-browm residue was taken up in a minimal amount of methylene chloride and chromatographed on alumina. A single red-brown band was eluted with a methylene chloride/hexane solvent mixture (30%/70%, v/v) to yield 315.6 mg (85%) of crude $Cp_2Mo_2(CO)_4(CNPh)$ (III). Dark red-brown, rhombohedral crystals were obtained by slow crystallization of the crude product from hexane/methylene chloride (20%/80%, v/v) or from benzene at 6 °C; mp 156 °C.

The reactions of methyl and *tert*-butyl isocyanides with $Cp_2Mo_2(CO)_4$ were performed similarly. $Cp_2Mo_2(CO)_4$-(CNMe) (II): yield, 87%; mp 120 °C. Anal. Calcd: C, 40.44; H, 2.76; N, 2.95. Found: C, 40.18; H, 2.85; N, 3.03. $Cp_2Mo_2(CO)_4$(CN-*t*-Bu) (IV): yield 88%, mp 121 °C. Anal. Calcd: C, 44.12; H, 3.70; N, 2.71. Found: C, 44.13; H, 3.89; N, 2.44. See Table I for IR and NMR spectra.

Crystallographic Analyses. A crystal of Cp_2Mo_2-$(CO)_4(\mu\text{-}\eta^2\text{-CNPh})$ suitable for diffraction measurements was obtained from a benzene solution. It was mounted in a thin-walled glass capillary. Diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer using graphite-monochromatized Mo K$\bar{\alpha}$ radiation. Unit cells were determined and refined from 25 selected reflections ($2\theta > 45°$) by using the CAD-4 automatic center and least-squares routines. The space group $P2_1/n$ was identified by observation of the appropriate systematic absences during data collection. Crystal data and data collection parameters are listed in Table II. All data processing was performed on a Digital PDP 11/45 computer using the Enraf-Nonius SDP program library.

Table II. Crystallographic Data for X-ray Diffraction Study for $Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2\text{-CNPh})$ (III)

(A) Crystal Data	
formula	$C_{21}H_{15}NO_4Mo_2$
temp, ±5 °C	23
space group	$P2_1/n$
a, Å	9.144 (1)
b, Å	19.574 (3)
c, Å	11.409 (2)
β, deg	96.10 (1)
V, Å^3	2030.5 (9)
mol wt	537.24
Z	4
ρ_{calcd}, g/cm^3	1.757
ρ_{obsd}, g/cm^3	1.78
(B) Measurement of Intensity Data	
radiation	Mo K$\bar{\alpha}$ (0.710 73 Å)
monochromator	graphite
detector aperture, mm	
horizontal ($A + B \tan \theta$)	
A	3.0
B	1.0
vertical	4.0
crystal faces	100, $\bar{1}$00, 010; 0$\bar{1}$0, 001, 00$\bar{1}$
crystal size, mm	0.23 × 0.33 × 0.30
crystal orientatn: direction; deg from ϕ axis	normal to 21$\bar{4}$; 14.0°
reflections measd	$+h, +k, \pm l$
max 2θ	52°
scan type	moving crystal-stationary counter
ω-scan width	
$A + 0.347 \tan \theta$	A = 0.90°
bkgd	one-fourth additional scan at each end of scan
ω-scan rate (variable)	
max, deg/min	10.0°
min, deg/min	1.3°
no. of reflections measd	5333
data used ($F^2 \geq 3.0\sigma(F)^2$)	2951
(C) Treatment of Data	
P factor	0.01
final residuals R	0.023
R_w	0.025
esd of unit weight	1.89
largest shift/error value on final cycle	0.01
largest peak in final diff Fourier, e/Å^3	0.35

The linear absorption coefficient is 12.4 cm^{-1}. No absorption correction was applied. Three standard reflections monitored every 4000 s showed only random ±2% fluctuation. Neutral atom scattering factors were calculated by the standard procedures.[16a] Anomalous dispersion

(14) Casanova, J.; Schuster, E. R.; Werner, N. D. *J. Chem. Soc.* **1963**, 4280.
(15) Ugi, I.; Meyer, R.; Lipinski, M.; Bodesheim, F.; Rosendahl, F. *Org. Synth.* **1961**, *41*, 13.

Table III. Fractional Atomic Coordinates, Thermal Parameters,[a] and Their Esds for $Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2\text{-}CNPh)$ (III)

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(1)	0.29947 (3)	0.10929 (1)	0.22387 (2)	2.806 (9)	2.61 (1)	2.677 (9)	−0.14 (1)	0.703 (8)	−0.35 (1)
Mo(2)	0.03298 (3)	0.21699 (1)	0.20517 (2)	3.35 (1)	3.42 (1)	2.79 (1)	0.67 (1)	0.394 (9)	0.22 (1)
O(1)	0.4329 (3)	0.2483 (1)	0.1562 (2)	6.8 (1)	4.2 (1)	7.4 (1)	−1.6 (1)	2.7 (1)	0.2 (1)
O(2)	0.5570 (3)	0.1397 (2)	0.4159 (2)	5.3 (1)	9.5 (2)	6.3 (1)	1.0 (1)	−1.8 (1)	−3.3 (1)
O(3)	0.0602 (4)	0.1869 (2)	−0.0613 (2)	9.6 (2)	8.8 (2)	3.1 (1)	1.8 (2)	0.2 (1)	−0.2 (1)
O(4)	−0.2616 (3)	0.1412 (2)	0.1369 (3)	4.7 (1)	11.8 (2)	11.0 (2)	−2.8 (2)	−1.6 (1)	3.3 (2)
N	0.1561 (3)	0.0932 (1)	0.365 (2)	3.3 (1)	3.4 (1)	3.0 (1)	0.39 (9)	1.03 (9)	0.42 (9)
Cp(11)	0.3056 (4)	0.0715 (2)	0.032 (3)	7.6 (2)	4.0 (2)	3.3 (1)	−1.2 (2)	1.5 (1)	−1.4 (1)
Cp(12)	0.4326 (4)	0.0477 (2)	0.100 (3)	4.1 (2)	4.7 (2)	6.1 (2)	−0.7 (1)	2.1 (1)	−2.7 (1)
Cp(13)	0.3907 (4)	0.0014 (2)	0.1821 (3)	5.0 (2)	3.4 (1)	5.8 (2)	0.6 (1)	0.6 (2)	−1.0 (1)
Cp(14)	0.2372 (4)	−0.0053 (2)	0.1639 (3)	6.0 (2)	2.9 (1)	6.0 (2)	−1.4 (1)	2.3 (1)	−1.1 (1)
Cp(15)	0.1839 (4)	0.0381 (2)	0.0716 (3)	4.8 (2)	4.3 (2)	5.2 (2)	−1.0 (1)	−0.2 (2)	−2.0 (1)
Cp(21)	0.1665 (5)	0.3073 (2)	0.3075 (3)	7.4 (2)	3.8 (2)	5.2 (2)	0.5 (2)	−0.8 (2)	−1.5 (1)
Cp(22)	0.0446 (6)	0.2926 (2)	0.3673 (3)	11.4 (3)	5.0 (2)	3.7 (2)	1.5 (2)	1.5 (2)	−1.1 (2)
Cp(23)	−0.0829 (5)	0.3072 (2)	0.2906 (4)	6.8 (2)	6.8 (2)	8.4 (2)	2.4 (2)	2.8 (2)	−1.7 (2)
Cp(24)	−0.0377 (5)	0.3311 (2)	0.1856 (4)	7.0 (2)	4.3 (2)	6.0 (2)	2.7 (2)	−0.0 (2)	0.1 (2)
Cp(25)	0.1149 (5)	0.3302 (2)	0.1944 (3)	7.9 (2)	3.1 (2)	5.2 (2)	0.1 (2)	0.5 (2)	0.1 (2)
C(1)	0.3760 (4)	0.1982 (2)	0.1823 (3)	4.2 (1)	3.7 (2)	3.9 (1)	−0.5 (1)	1.2 (1)	−0.2 (1)
C(2)	0.4587 (4)	0.1285 (2)	0.3465 (3)	3.9 (1)	5.1 (2)	3.9 (1)	0.5 (1)	0.4 (1)	−1.3 (1)
C(3)	0.0538 (4)	0.1968 (2)	0.0371 (3)	5.0 (2)	4.7 (2)	3.4 (1)	0.6 (1)	−0.1 (1)	0.2 (1)
C(4)	−0.1527 (4)	0.1696 (2)	0.1627 (3)	3.9 (2)	6.9 (2)	5.3 (2)	0.1 (2)	0.0 (1)	2.0 (2)
C(5)	0.0921 (3)	0.1379 (2)	0.3014 (3)	2.7 (1)	3.7 (1)	3.0 (1)	0.0 (1)	0.8 (1)	−0.0 (1)
C(31)	0.1528 (3)	0.0717 (2)	0.4845 (2)	3.0 (1)	3.1 (1)	2.7 (1)	−0.2 (1)	0.4 (1)	0.3 (1)
C(32)	0.0733 (4)	0.1087 (2)	0.5589 (3)	4.0 (1)	3.8 (1)	3.8 (1)	0.4 (1)	1.2 (1)	0.3 (1)
C(33)	0.0722 (4)	0.0874 (2)	0.6752 (3)	5.2 (2)	5.2 (2)	3.4 (1)	−0.6 (1)	1.7 (1)	−0.8 (1)
C(34)	0.1474 (4)	0.0302 (2)	0.7147 (3)	5.2 (2)	5.6 (2)	2.8 (1)	−0.9 (2)	0.4 (1)	0.5 (1)
C(35)	0.2252 (4)	−0.0066 (2)	0.6409 (3)	5.3 (2)	4.8 (2)	3.9 (2)	0.8 (2)	0.1 (1)	1.4 (1)
C(36)	0.2307 (4)	0.0147 (2)	0.5244 (3)	4.5 (2)	3.8 (2)	3.5 (1)	0.7 (1)	1.0 (1)	0.4 (1)

atom[b]	x	y	z	atom[b]	x	y	z
H(32)	0.0180	0.1487	0.5293	H(13)	0.4562	−0.0225	0.2427
H(33)	0.0183	0.1126	0.7296	H(14)	0.1783	−0.0352	0.2080
H(34)	0.1442	0.0152	0.7953	H(15)	0.0798	0.0436	0.0414
H(35)	0.2792	−0.0474	0.6702	H(21)	0.2717	0.3025	0.3394
H(36)	0.2872	−0.0108	0.4714	H(22)	0.0474	0.2749	0.4472
H(11)	0.3026	0.1058	−0.0310	H(23)	−0.1855	0.3021	0.3080
H(12)	0.5333	0.0603	0.0920	H(24)	−0.1011	0.3455	0.1153
				H(25)	0.1751	0.3428	0.1321

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + B_{12}hka^*b^* + B_{13}hla^*c^* + B_{23}klb^*c^*)]$. [b] Hydrogen atom positions were not refined. $B = 5.00$ Å^2.

corrections were applied for all nonhydrogen atoms.[16b] The structure was solved by a combination of Patterson and difference Fourier techniques. Hydrogen atom positions were calculated on the basis of geometric considerations. Hydrogen atom contributions were included in structure factor calculations, but their positions were not refined. Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$. All nonhydrogen atoms were refined with anisotropic temperature factors. Final fractional atomic coordinates and interatomic distances and angles with errors obtained from the inverse matrix calculated on the final cycle of least-squares refinement are listed in Tables III–V. Structure factor amplitudes are available (see supplementary material).

Results and Discussion

When I is allowed to react with 1 equiv of isocyanide at room temperature, products with the formula $Cp_2Mo_2(CO)_4(CNR)$ (II, R = Me; III, R = Ph; IV, R = *t*-Bu) can be isolated in high yield. Their IR spectra show four absorptions in the terminal CO stretching region and a broad low-energy absorption (1725, 1666, and 1695 cm^{-1} for II, III, and IV, respectively) indicative of a bridging ligand. No absorptions are observed in the region 2000–2200 cm^{-1} which is characteristic of terminally coordinated isocyanide ligands.

Table IV. Interatomic Distances with Esds for $Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2\text{-}CNPh)$ (III)

atoms	dist, Å	atoms	dist, Å
Mo(1)-Mo(2)	3.212 (1)	C(31)-C(32)	1.380 (3)
Mo(1)-C(1)	1.953 (3)	C(32)-C(33)	1.391 (3)
Mo(1)-C(2)	1.946 (3)	C(33)-C(34)	1.367 (4)
Mo(1)-C(5)	2.247 (2)	C(34)-C(35)	1.364 (4)
Mo(1)-N	2.207 (2)	C(35)-C(36)	1.398 (3)
Mo(1)-Cp(11)	2.317 (2)	C(36)-C(31)	1.376 (3)
Mo(1)-Cp(12)	2.301 (2)	Cp(11)-Cp(12)	1.406 (4)
Mo(1)-Cp(13)	2.339 (3)	Cp(12)-Cp(13)	1.387 (4)
Mo(1)-Cp(14)	2.397 (3)	Cp(13)-Cp(14)	1.403 (4)
Mo(1)-Cp(15)	2.384 (2)	Cp(14)-Cp(15)	1.399 (4)
Mo(2)-C(3)	1.986 (3)	Cp(15)-Cp(11)	1.406 (4)
Mo(2)-C(4)	1.950 (3)	Cp(21)-Cp(22)	1.397 (5)
Mo(2)-C(5)	1.942 (2)	Cp(22)-Cp(23)	1.410 (5)
Mo(2)-Cp(21)	2.382 (3)	Cp(23)-Cp(24)	1.388 (5)
Mo(2)-Cp(22)	2.363 (3)	Cp(24)-Cp(25)	1.389 (4)
Mo(2)-Cp(23)	2.326 (3)	Cp(25)-Cp(21)	1.400 (4)
Mo(2)-Cp(24)	2.330 (3)	C(1)-O(1)	1.163 (3)
Mo(2)-Cp(25)	2.347 (3)	C(2)-O(2)	1.154 (3)
C(5)-N	1.244 (3)	C(3)-O(3)	1.147 (3)
N-C(31)	1.426 (3)	C(4)-O(4)	1.151 (3)

The ^{1}H NMR spectra of II, III, and IV show resonances which can be assigned to inequivalent cyclopentadienyl rings and the R groups of the isocyanide ligands (see Table I). The ^{13}C NMR spectra show five low-field resonances in addition to those characteristic of the cyclopentadienyl ligands and R groups. These low-field resonances are arranged in two groups of two with the remaining reso-

(16) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1975; Vol. IV: (a) Table 2.2B, pp 99–101; (b) Table 2.3.1, pp 149–50.

Table V. Interatomic Angles with Esds for $Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2\text{-}CNPh)$ (III)

atoms	angles, deg	atoms	angles, deg	atoms	angles, deg
Mo(2)-Mo(1)-C(5)	36.55 (6)	C(2)-Mo(1)-Cp(13)	93.8 (1)	Mo(2)-C(5)-N	167.7 (2)
Mo(2)-Mo(1)-N	68.69 (5)	C(2)-Mo(1)-Cp(14)	121.6 (1)	Mo(1)-N-C(5)	75.5 (1)
Mo(2)-Mo(1)-C(1)	71.81 (8)	C(2)-Mo(1)-Cp(15)	151.3 (1)	Mo(1)-N-C(31)	144.4 (2)
Mo(2)-Mo(1)-C(2)	115.15 (8)	Mo(1)-Mo(2)-C(5)	43.56 (6)	C(5)-N-C(31)	135.2 (2)
C(5)-Mo(1)-N	32.41 (7)	Mo(1)-Mo(2)-C(3)	77.50 (8)	N-C(31)-C(32)	119.8 (2)
C(5)-Mo(1)-C(1)	102.3 (1)	Mo(1)-Mo(2)-C(4)	109.8 (1)	N-C(31)-C(36)	119.5 (2)
C(5)-Mo(1)-C(2)	105.48 (9)	C(5)-Mo(2)-C(3)	109.7 (1)	C(36)-C(31)-C(32)	120.6 (2)
C(5)-Mo(1)-Cp(11)	123.9 (1)	C(5)-Mo(2)-C(4)	86.8 (1)	C(31)-C(32)-C(33)	119.2 (2)
C(5)-Mo(1)-Cp(12)	153.62 (9)	C(5)-Mo(2)-Cp(21)	102.5 (1)	C(32)-C(33)-C(34)	120.4 (2)
C(5)-Mo(1)-Cp(13)	129.8 (1)	C(5)-Mo(2)-Cp(22)	94.0 (1)	C(33)-C(34)-C(35)	120.4 (2)
C(5)-Mo(1)-Cp(14)	99.25 (9)	C(5)-Mo(2)-Cp(23)	118.7 (1)	C(34)-C(35)-C(36)	120.4 (3)
C(5)-Mo(1)-Cp(15)	96.02 (9)	C(5)-Mo(2)-Cp(24)	151.2 (1)	C(35)-C(36)-C(31)	119.1 (2)
N-Mo(1)-C(1)	124.07 (9)	C(5)-Mo(2)-Cp(25)	135.4 (1)	Cp(15)-Cp(11)-Cp(12)	107.7 (3)
N-Mo(1)-C(2)	87.65 (9)	C(3)-Mo(2)-C(4)	80.6 (1)	Cp(11)-Cp(12)-Cp(13)	108.5 (3)
N-Mo(1)-Cp(11)	136.16 (9)	C(3)-Mo(2)-Cp(21)	121.6 (1)	Cp(12)-Cp(13)-Cp(14)	107.8 (3)
N-Mo(1)-Cp(12)	140.22 (9)	C(3)-Mo(2)-Cp(22)	151.6 (1)	Cp(13)-Cp(14)-Cp(15)	108.5 (2)
N-Mo(1)-Cp(13)	105.84 (9)	C(3)-Mo(2)-Cp(23)	130.5 (1)	Cp(14)-Cp(15)-Cp(11)	107.4 (3)
N-Mo(1)-Cp(14)	86.23 (8)	C(3)-Mo(2)-Cp(24)	98.8 (1)	Cp(25)-Cp(21)-Cp(22)	107.9 (3)
N-Mo(1)-Cp(15)	101.40 (9)	C(3)-Mo(2)-Cp(25)	94.2 (1)	Cp(21)-Cp(22)-Cp(23)	107.8 (3)
C(1)-Mo(1)-C(2)	75.0 (1)	C(4)-Mo(2)-Cp(21)	149.6 (1)	Cp(22)-Cp(23)-Cp(24)	107.5 (3)
C(1)-Mo(1)-Cp(11)	90.6 (1)	C(4)-Mo(2)-Cp(22)	117.3 (2)	Cp(23)-Cp(24)-Cp(25)	108.8 (3)
C(1)-Mo(1)-Cp(12)	95.2 (1)	C(4)-Mo(2)-Cp(23)	92.4 (1)	Cp(24)-Cp(25)-Cp(21)	108.0 (3)
C(1)-Mo(1)-Cp(13)	127.6 (1)	C(4)-Mo(2)-Cp(24)	102.0 (1)	Mo(1)-C(1)-O(1)	174.1 (2)
C(1)-Mo(1)-Cp(14)	147.7 (1)	C(4)-Mo(2)-Cp(25)	135.3 (1)	Mo(1)-C(2)-O(2)	177.3 (2)
C(1)-Mo(1)-Cp(15)	119.1 (1)	Mo(1)-C(5)-Mo(2)	99.89 (9)	Mo(2)-C(3)-O(3)	176.9 (3)
C(2)-Mo(1)-Cp(11)	130.5 (1)	Mo(1)-C(5)-N	72.0 (1)	Mo(2)-C(4)-O(4)	179.4 (3)
C(2)-Mo(1)-Cp(12)	98.0 (1)				

nance occurring at a somewhat higher field. In III these occur at at δ 246.16, 244.47, 232.96, 231.02, and 217.50 at −50 °C. We choose to assign the first four to the terminal carbonyl ligands since on the basis of the structural analysis (see below), these can be arranged into groups of two. The remaining resonance we assign to the isocyano (*C*=N) carbon atom. This shift is considerably lower than that normally found for terminally coordinated isocyanide ligands which lie in the range δ 140–170[17-19] but is similar to those found for bridging isocyanide ligands.[15] The ^{1}H and ^{13}C NMR peaks remain sharp at room temperature; thus, unlike other molecules in this family,[4,7] these are stereochemically rigid.

Details of the molecular structure of III were established by an X-ray crystallographic analysis. An ORTEP diagram of the molecular structure is shown in Figure 1. The molecule contains two $(\eta^5\text{-Cp})Mo(CO)_2$ units joined by a metal–metal bond which on the basis of bond length (3.212 (1) Å) can be formulated as a single bond (e.g., $[CpMo(CO)_3]_2$, Mo—Mo = 3.235 (1) Å,[20] and $Cp_2Mo_2(CO)_5CNCH_3$, Mo—Mo = 2.320 (1) Å[21]). The metal–metal bond is bridged by an isocyanide ligand coordinated in a $\sigma + \pi$ fashion. The isocyano carbon is σ bonded to metal Mo(2), Mo(2)—C(5) = 1.942 (2) Å, while the C—N function is π bonded to Mo(1), Mo(1)—C(5) = 2.247 (2) Å and Mo(1)—N = 2.207 (1) Å. The C(5)=N bond length at 1.244 (3) Å is significantly longer than those found for terminal isocyanide ligands.[19,21-26] For example, the C≡N

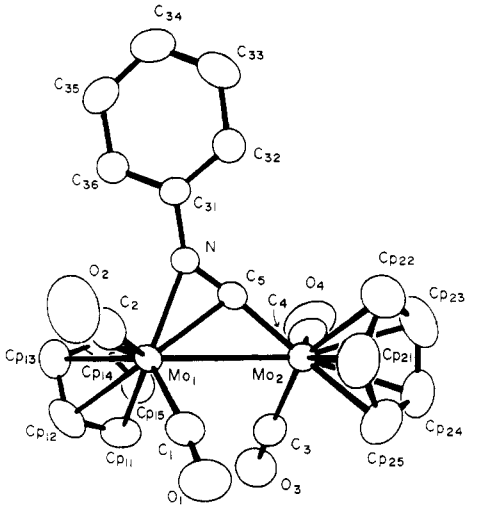


Figure 1. A perspective ORTEP diagram of $Cp_2Mo_2(CO)_4(\mu\text{-}\eta_2\text{-}CNPh)$ showing 50% electron density probability ellipsoids.

bond lengths of the terminal isocyanide ligands are 1.17 (1) Å in $Cp_2Mo_2(CO)_5CNMe$[21] and 1.153 (13) Å in $CpMo(CO)_2CNPhI$.[22] It is even longer than those found for the more common C-briding isocyanide ligands.[19,27,28] C=N bond lengths for C-bridging isocyanide ligands generally lie in the range 1.19–1.23 Å.[15,23,24] The only other reported example of a $\sigma + \pi$-bonded isocyanide ligand was for the molecule $Mn_2(dpm)_2(CO)_4(\mu\text{-}\eta^2\text{-}CN\text{-}p\text{-}tol)$, and it had a C=N bond length of 1.25 (1) Å.[29] The long bond length suggests a weakening of the C—N bond order, and this is supported by the low-energy position of the C—N absorption in the IR spectrum. Both observations support the notion advanced by Muetterties that polynuclear coordination will significantly reduce bond order in unsat-

(17) Novotny, M.; Lewis, D. F.; Lippard, S. J. *J. Am. Chem. Soc.* **1972**, *94*, 6961.
(18) Fanell, L. F.; Randall, E. W.; Rosenberg, E. *J. Chem. Soc. D* **1971**, 1078.
(19) Green, M.; Howard, J. A. K.; Murray, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1509.
(20) Adams, R. D.; Collins, D. M.; Cotton, F. A. *Inorg. Chem.* **1974**, *13*, 1086.
(21) Adams, R. D.; Brice, M.; Cotton, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 6954.
(22) Sim, G. A.; Sime, J. G.; Woodhouse, D. I.; Knox, G. R. *Acta Crystallogr., Sect. B* **1979**, *B35*, 2406.
(23) Green, M.; Nyathi, J. Z.; Scott, C.; Stone, F. G. A.; Welch, A. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1978**, 1067.
(24) Davidson, J. L.; Green, M.; Nyathi, J. Z.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1977**, 2246.
(25) Lam, C. T.; Novotny, M.; Lewis, D. L.; Lippard, S. J. *Inorg. Chem.* **1978**, *17*, 2127.
(26) Lewis, D. L.; Lippard, S. J. *J. Am. Chem. Soc.* **1975**, *97*, 2697.
(27) Cotton, F. A.; Frenz, B. A. *Inorg. Chem.* **1974**, *13*, 253.
(28) Adams, R. D.; Cotton, F. A.; Rusholme, G. A. *J. Coord. Chem.* **1971**, *1*, 275.
(29) Benner, L. S.; Olmstead, M. M.; Balch, A. J. *J. Organomet. Chem.* **1978**, *159*, 289.

urated ligands.[12] Although the $\sigma + \pi$ unit is nearly linear, Mo(2)–C(5)–N = 167.7 (2)°, the C(5)–N–C(31) angle of 135.2 (2)° indicates a change in hybridization at the nitrogen atom away from the linear sp-type normally found for terminally coordinated isocyanide ligands.

Two other compounds in this series which have the $\sigma + \pi$ coordination are $Cp_2Mo_2(CO)_4(NCNMe_2)$[5] and $Et_4N[Cp_2Mo_2(CO)_4CN]$ (V).[7] The former has the nitrile function of the cyanimide ligand σ bonded via the nitrogen atom. In the latter the cyanide ligand is σ bonded via the carbon to one metal atom and π bonded to the other. This molecule was disordered in the crystal, and only crude structural parameters were obtained, but we feel a few useful comparisons can still be made. The π-bonding Mo–C and Mo–N distances in V lie in the range 2.3–2.6 Å and are significantly longer than the corresponding distances in III. One could reasonably infer that the cyanide ligand in V is not as strongly π bonded as the isocyanide in III. This notion is supported by the observation that V is a fluxional molecule which apparently rearranges to an equivalent form in which the σ- and π-bonding modes of the cyanide ligand have been interchanged between the two metal atoms. Intuitively, such a rearrangement would require some degree of metal-ligand bond breaking. Accordingly, we find that the molecules II–IV are not fluxional.

III also contains four terminal carbonyl ligands which could be grouped into pairs. C(1)–O(1) and C(3)–O(3) project toward the adjacent metal atom, Mo(2)–Mo(1)–C(1) = 71.81 (8)° and Mo(2)–Mo(1)–C(2) = 77.50 (8)°, while the other two, C(2)–O(2) and C(4)–O(4), point away from the second metal atom, Mo(2)–Mo(1)–C(2) = 115.15 (8)° and Mo(1)–Mo(2)–C(4) = 109.76 (10)°. We would hesitate to call the former semibridging CO's because the Mo···C distances at approximately 3.2 Å are clearly nonbonding, but the pairing of the environments of the CO ligands might explain the pairing of the resonance shifts of these ligands in the ^{13}C NMR spectra (see above).

Acknowledgment. This research has been supported by the Office of Basic Energy Sciences of the U.S. Department of Energy under Contract No. DE-AC02-78ER04900 and by the Alfred P. Sloan Foundation through a Fellowship to R.D.A. NMR studies were supported by Grant No. CHE-7916210 from the National Science Foundation.

Registry No. I, 56200-27-2; II, 79703-92-7; III, 79703-93-8; IV, 79703-94-9.

Supplementary Material Available: A listing of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

Cleavage of Aryl Carbon–Sulfur Bonds by a Trinuclear Cluster. The Reaction of Alkyl Phenyl Sulfides with $Os_3(CO)_{12}$

Richard D. Adams,* Dean A. Katahira, and Li-Wu Yang

Department of Chemistry, Yale University, New Haven, Connecticut 06511

Received June 30, 1981

The reactions of the alkyl phenyl sulfides, RSPh (R = Me, *i*-Pr), with $Os_3(CO)_{12}$ have been shown to produce cleavage of the phenyl group from the sulfur atom and yield the molecules $HOs_3(\mu\text{-SR})(\mu_3\text{-}\eta^2\text{-}C_6H_4)(CO)_9$ (I, R = Me; II, R = *i*-Pr). I has been analyzed by an X-ray crystallographic analysis: space group $P2_1/n$, at 23 °C, a = 8.697 (2) A, b = 13.442 (5) Å, c = 17.779 (7) Å, β = 99.29 (3)°, V = 2551 (2) Å^3, Z = 4, ρ_{calcd} = 3.07 g/cm^3. For 1999 reflections ($F_o \geq 3.0\sigma(F_o^2)$ R_1 = 0.052 and R_2 = 0.051. I contains an "open" cluster of three osmium atoms with a methanethiolato group bridging the open edge and a triply bridging benzyne, C_6H_4, ligand. In solution I exists as two rapidly equilibrating isomers at room temperature. ^1H DNMR studies have revealed two dynamical processes. A low-energy degenerate process (ΔG^* = 12.7 kcal/mol) which involves a migration of the hydride ligand between the two metal–metal bonds was established through a DNMR study of II. The higher energy isomerization process ($\Delta G^* \cong$ 14.7 kcal/mol) is believed to involve inversions of configuration of the trivalent sulfur atom of the bridging methanethiolato group.

Introduction

A number of workers have shown that triosmium cluster compounds can readily cleave aryl groups from phosphines and other ligands. Frequently, cluster compounds containing benzyne, C_6H_4, ligands are obtained.[1-6] Recently, the cleavage of carbon–sulfur bonds in CS_2 and related ligands by triosmium clusters has been demonstrated,[7] and it occurred to us that such cleavages in alkyl or aryl sulfide molecules might also be possible. Such processes are of fundamental importance to the desulfurization and purification of fossil fuels.[8] Herein we report results of our investigation of the cleavage of carbon–sulfur bonds of alkyl phenyl sulfide molecules by $Os_3(CO)_{12}$. Similar to the reactions with arylphosphines, these reactions also give a number of products. Not all of these have been characterized yet. In this report we will describe the structure and fluxional properties of the family of molecules which

(1) Bradford, C. W.; Gainsford, G. J.; Guss, J. M.; Ireland, P. R.; Mason, R. *J. Chem. Soc., Chem. Commun.* **1972**, 87.
(2) Gainsford, G. J.; Guss, J. M.; Ireland, P. R.; Mason, R.; Bradford, C. W.; Nyholm, R. S. *J. Organomet. Chem.* **1972**, *40*, C70.
(3) Deeming, A. J.; Kimber, R. E.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1973**, 2589.
(4) Brown, S. C.; Evan, J.; Smart, L. E. *J. Chem. Soc., Chem. Commun.* **1980**, 1021.
(5) Bradford, C. W.; Nyholm, R. S. *J. Chem. Soc., Dalton Trans.* **1973**, 529.
(6) Adams, R. D.; Golembeski, N. M. *J. Organomet. Chem.* **1979**, *172*, 239
(7) Adams, R. D.; Golembeski, N. M.; Selegue, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 546.
(8) Schuman, S. C.; Shalit, H. *Catal. Rev.* **1970**, *4*, 245.

0276-7333/82/2301-0235$01.25/0 © 1982 American Chemical Society