The products of the reactions investigated are methane and ethanol in proportions that are relatively sensitive to solvent and metal center but relatively insensitive to H_2 and CO pressure.

Direct Synthesis, Reactivity, Fluxional Behavior, and Molecular Structure of Cp2Mo2(CO)3[PhP(OCH2CH2)2NH] (Cp = η5-C5H5), a Compound with a Dissymmetrically Substituted Mo≡Mo Bond. Synthesis and Molecular Structure of Cp2Mo2(CO)3P(OMe)3[1]

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The reaction of [Cp(CO)2Mo]2 (Cp = η5-C5H5) with the bicyclic aminophosphorane PhPP(H)-(OCH2CH2)2N results, at room temperature, in the formation of Cp2Mo2(CO)3(phoran) (III) (major product), Cp2Mo2(CO)5(phoran) (IV), and Cp2Mo2(CO)4(phoran)2 (V) (in which "phoran" represents the open tautomeric form, i.e., PhP(OCH2CH2)2NH, of the phosphorane). The unexpected and direct formation of the dissymmetrically CO substituted complex III, in which the Mo≡Mo triple bond is retained, appears to be restricted to phoran and was not observed for PhP(OMe)2, which may indicate that the nitrogen atom transannular to phosphorus in phoran plays a role in the reaction. Complex III undergoes addition reactions with CO and isocyanides to form IV and Cp2Mo2(CO)3(μ,η2-CNR)(phoran) (R = CMe3, CH2Ph), respectively. Its reaction with P(OMe)3 results in the formation of Cp2Mo2(CO)3P(OMe)3 (VI). X-ray diffraction studies have been carried out on III and VI. Characteristic of both structures are relatively short Mo–Mo bonds (2.504 Å, average), semibridging CO ligands, and nonlinear Cp–Mo–Mo–Cp arrangements. The dissymmetric substitution of the Mo≡Mo bond allowed the investigation of the dynamic behavior of the CO ligands by means of variable-temperature 13C NMR studies of the 13CO-enriched complex III. Evidence was obtained for a one-for-one switch process of two carbonyls, during which the third one remains unexchanged.

Introduction

The chemistry of the metal–metal triple bond in [Cp(CO)2Mo]2 (I), (Cp = η5-C5H5) has been the subject of numerous investigations. Its reactions with nucleophiles or small unsaturated organic molecules[3] usually lead to the symmetrical addition products, Cp2Mo2(CO)4L2, in which the metal–metal bond order is 1. By contrast, CO substitution reactions in which the Mo≡Mo bond is retained remain practically unknown. The first direct substitution

of *one* CO ligand on the Mo≡Mo bond was relized by using the bicyclic aminophosphorane IIA, which coordinates to the metal through the phosphorus site of its open tautomeric form IIB (eq 1).[2] The resulting complex,
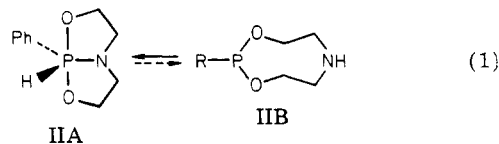
Cp2Mo2(CO)3(phoran) (III), represents a rare example of an easily and directly accessible dissymmetric derivative. More recently, direct substitution of *all* CO groups of I was achieved by using elemental sulfur[4] or selenium.[5] Other

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known derivatives of the type $Cp_2Mo_2(CO)_3L$ containing this triple bond were obtained indirectly from single-bonded Mo–Mo derivatives of type $Cp_2(CO)_4Mo_2L_2$ (L = $^1/_2RC{\equiv}CR$ or PPh_3).[6] The chemistry of the Mo≡Mo bond in such dissymmetrically substituted compounds has not yet been studied, with the exception of $Cp_2Mo_2(CO)(C_{12}H_{20})$.[6b]

In this paper we wish to describe the detailed structure of III, the fluxional behavior of its CO groups, and some selected reactions. These demonstrate both the unique ability of ligand II, whose coordination chemistry already exhibited many original facets,[7] to provoke CO substitution reactions on I and the unique reactivity of the resulting dissymmetrically substituted metal–metal triple bond. We also report the molecular structure of one of the reaction products, $Cp_2Mo_2(CO)_3P(OMe)_3$ (VI).

Experimental Section

General Data. All procedures were carried out under nitrogen with solvents freshly distilled from appropriate drying agents under nitrogen. The phosphorane $PhHP(OCH_2CH_2)_2N$ (II),[8] as well as $[Cp(CO)_2Mo]_2$ (Cp = η^5-C_5H_5),[6c] was prepared according to published procedures. $PhCH_2NC$ and Me_3CNC were obtained from Fluka and Aldrich, respectively. Elemental analyses were performed by the Mikroanalytisches Laboratorium, Universität Regensburg, and by the Analytische Laboratorien Malissa & Reuter, D-5250 Engelskirchen, Germany (P, Mo). They are shown together with selected properties in Table I.

Infrared spectra were obtained with a Beckman 4240 spectrophotometer. Field desorption mass spectra were run on a Varian 311A instrument from toluene and acetone solutions, respectively. NMR spectra were recorded with the instruments indicated in Table IV. Carbon-13-enriched $[Cp(CO)_2Mo]_2$ was prepared according to a published procedure.[9] ^{13}CO (97.1%) was employed for all ^{13}C-enrichment experiments.

Preparations. Reaction of $[Cp(CO)_2Mo]_2$ (I) with Phoran (II). A solution of 0.63 g (3.0 mmol) of II in 20 mL of ether was added dropwise to a solution of 1.30 g (3.0 mmol) of I in a mixture of 20 mL of toluene and 50 mL of ether. Evolution of CO was immediate. After stirring for 15 h at room temperature a red precipitate was collected by filtration, washed twice with 20 mL of toluene, and dried in vacuo to give 0.44 g (17%) of Cp_2Mo_2-$(CO)_4(phoran)_2$ (V). The combined filtrates were concentrated to 10 mL. Chromatography on SiO_2 (column 30 × 3 cm) gave successively $[Cp(CO)_3Mo]_2$, as a red band eluted with toluene; 0.41 g (20%) of $Cp_2Mo_2(CO)_5(phoran)$ (IV), as a dark red product eluted with toluene/acetone 10:1; and $Cp_2Mo_2(CO)_3(phoran)$ (III), contaminated by IV, as a red-orange band eluted with toluene/acetone 1:1. Repeated chromatography of III resulted in 0.40 g of a pure product (21% yield). Complex V is only slightly soluble in common solvents unlike IV which in turn is less soluble than III. Analytically pure samples of III and IV were obtained by recrystallization from CH_2Cl_2/ether or toluene/pentane mixtures at −35 °C.

Attempted Reaction of I with $PhP(OMe)_2$. When equimolar amounts of I and $PhP(OMe)_2$ were treated as above in toluene for 17 h at room temperature, only small amounts of $[CpMo(CO)_3]_2$ were eluted from the SiO_2 column with toluene; the bulk of the reaction product remained adsorbed at the top of the

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Table I. Selected Properties of Compounds III-VIII

compd[a]	mp, °C	mol wt[b] calcd	found	calcd (found) C	H	N	P	Mo
$Cp_2Mo_2(CO)_3$(phoran) (III)	113 dec	617.3	609	44.75 (44.68)	3.92 (4.14)	2.27 (2.83)	5.02 (4.66)	
$Cp_2Mo_2(CO)_5$(phoran) (IV)	171 dec	673.3	665	44.59 (44.30)	3.59 (3.20)	2.08 (1.99)		
$Cp_2Mo_2(CO)_4$(phoran)$_2$ (V)	c	856.5		47.67 (46.98)	4.47 (4.45)	3.27 (4.33)		
$Cp_2Mo_2(CO)_3P(OMe)_3$ (VI)	152 dec	530.2	522	36.25 (36.29)	3.61 (3.37)			36.19 (35.73)
$Cp_2Mo_2(CO)_3(\mu,\eta^2\text{-CNCMe}_3)$phoran (VII)	190 dec	700.4	692	48.01 (48.40)	4.75 (4.87)	4.00 (3.88)		
$Cp_2Mo_2(CO)_3(\mu,\eta^2\text{-CNCH}_2\text{Ph})$phoran (VIII)	155 dec	734.4	726	50.69 (51.01)	4.25 (4.36)	3.81 (4.16)		26.13 (26.70)

^{a} Cp = η^5-C_5H_5. ^{b} Determination by field desorption mass spectroscopy (from toluene or acetone solutions, related to ^{92}Mo). ^{c} Not determined.

<div align="center">Table II. Crystallographic Data</div>

compd	Cp$_2$Mo$_2$(CO)$_3${PhP(OCH$_2$CH$_2$)$_2$NH}	Cp$_2$Mo$_2$(CO)$_3${P(OMe)$_3$}
color	red brown	dark red
cryst symmetry	monoclinic	tetragonal
space group	$P2_1/c$	$P4_2/n$
a, Å	14.902 (3)	21.392 (5)
b, Å	16.681 (3)	21.392 (5)
c, Å	9.631 (2)	8.357 (3)
α, deg	90	90
β, deg	104.84 (2)	90
γ, deg	90	90
V, Å^3	2314	3824
Z	4	8
d_{calcd}, g·cm^{-3}	1.77	1.84
cryst size, mm	0.06 × 0.08 × 0.09 (±0.01)	0.14 × 0.16 × 0.18 (±0.01)
radiation, wavelength, Å	Cu, λ(Kα_1) = 1.54056	Cu, λ(Kα_1) = 1.54056
temp	room	room
diffractometer	Enraf-Nonius CAD-4F	Philips PW 1100/16
monochromator	Ni	graphite
scanning mode	scan $\omega/2\theta$	flying step scan, $\omega/2\theta$
limits in ω	$2 < \omega < 60$	$5 < \omega < 57$
no. of reflcns	2665	5784
abs	none	yes
linear abs coeff, cm^{-1}	102.738	120.308
obsd reflcns ($I > 3\sigma(I)$)	1625	2187
no. of refined parameters by least-squares	289	226
$R(F)$	0.067	0.034
$R_w(F)$	0.087	0.065

column and could not be eluted, even with 1:1 toluene/acetone.

Reaction of III with CO. A solution of 390 mg (0.63 mmol) of III in 50 mL of toluene was stirred for 2.5 h while CO was bubbled through the solution. The solution was then concentrated and chromatographed on SiO$_2$ (7 × 2 cm). Traces of [CpMo-(CO)$_3$]$_2$ were removed by elution with toluene; a dark red band eluted with 2:1 toluene/acetone yielded 400 mg (94%) of IV.

Thermal Conversion of IV into III. A solution of 650 mg (0.97 mmol) of IV in 100 mL of toluene was refluxed for 12 h. The concentrated solution was chromatographed on SiO$_2$ (7 × 2 cm). Impurities were removed with 20:1 toluene/acetone, whereas III (260 mg, 43%) was eluted with 2:1 toluene/acetone as a red-orange band.

^{13}C Enrichment of Cp$_2$Mo$_3$(CO)(phoran) (III). [Cp-(*CO)$_2$Mo]$_2$ (1.13 g, 2.60 mmol) was reacted with an equimolar amount of phoran as described above. After complex V was separated, the resulting mixture of III and IV in toluene was stirred under 0.5 atm of ^{13}CO at room temperature for 2.5 h. Purification on SiO$_2$ (see above) resulted in 650 mg (37%) of Cp$_2$Mo$_2$(*CO)$_5$(phoran), which was converted thermally into Cp$_2$Mo$_2$(*CO)$_3$(phoran) as described above. The degree of ^{13}C enrichment was estimated to be about 40% on the basis of the relative intensities of the CO absorptions at 1784 (^{12}CO) and 1740 (^{13}CO) cm^{-1} in the infrared spectrum (see Figure 1).

Reaction of III with P(OMe)$_3$. A mixture of 410 mg (0.66 mmol) of III with 82 mg (0.66 mmol) of P(OMe)$_3$ was refluxed in 100 mL of toluene for 15 h. The solution was cooled to room temperature and concentrated to 10 mL. Chromatography on SiO$_2$ (column 18 × 3 cm) gave 40 mg (11%) of Cp$_2$Mo$_2$(CO)$_3$P-(OMe)$_3$ (VI) as an orange product eluted with 50:1 toluene/ether and was recrystallized from 2:1 ether/pentane at −35 °C.

When the same reaction was carried out with a 10-fold excess of P(OMe)$_3$ at room temperature, 50 mg (9%) of Cp$_2$-(CO)$_4$Mo$_2$[P(OMe)$_3$]$_2$^{6c} (X) could be isolated by chromatography on SiO$_2$ (18 × 3 cm, toluene/acetone 4:1): IR (cm^{-1}, KBr) ν_{CO} 1880, 1858, 1844; ^{1}H NMR (CDCl$_3$) $\delta_{C_5H_5}$ 5.04 (d, J_{P-H} 1.5 Hz) δ_{CH_3} 3.72 (d, J_{P-H} = 11.5 Hz); mol wt calcd for C$_{20}$H$_{28}$Mo$_2$O$_{10}$P$_2$ 682.2, found 674 (with respect to ^{92}Mo, FD mass spectrum).

Reaction of III with RN≡C (R = CMe$_3$, CH$_2$Ph). To a solution of 0.43 g (0.70 mmol) of III in 100 mL of toluene was added an equimolar amount of the corresponding isonitrile. After stirring for 30 min at room temperature, the concentrated solution was chromatographed on SiO$_2$ (column 30 × 3 cm). Three weak bands were eluted with 4:1 toluene/acetone followed by an orange band with 2:1 toluene/acetone; this band contained the red-brown products VII (or VIII) in 40% (196 mg) (or 34% (110 mg)) yield, respectively. Complex VII was recrystallized from toluene and VIII from 3:1 toluene/pentane.
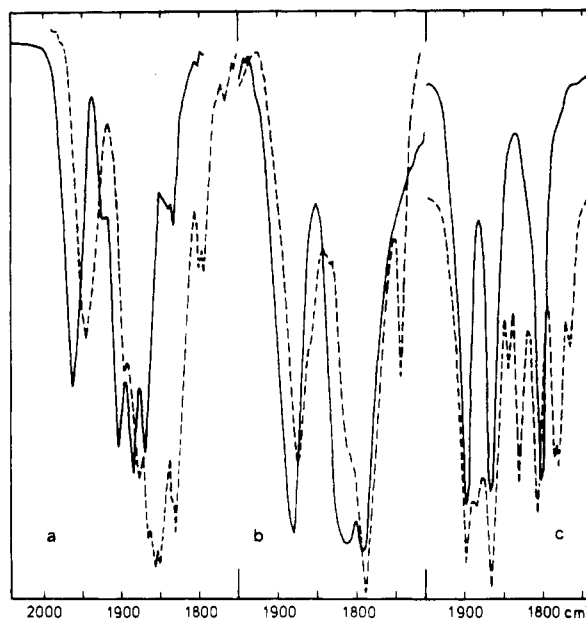
Figure 1. IR spectra of the CO region (in KBr) of (a) Cp$_2$Mo$_2$(CO)$_5$(phoran), (b) Cp$_2$Mo$_2$(CO)$_3$(phoran), and (c) Cp$_2$Mo$_2$(CO)$_3$(μ,η^2-CNCMe$_3$)(phoran) (—) and of their ^{13}CO-enriched analogues (- -).

^{13}C enrichment of VII was achieved through the same procedure as given above from Cp$_2$Mo$_2$(*CO)$_3$(phoran) as starting material.

Solution of the Structures. Accurate unit-cell parameters were determined at room temperature by a least-squares refinement of the diffractometer setting angles of 25 carefully selected reflections (Cu Kα radiation, $20° < \theta < 30°$). Intensity data were collected with standard diffractometer software. For both compounds, all data processing was performed on a Digital PDP 11/60 computer using the Enraf-Nonius SDP program library (version 16).^{10} Absorption corrections of a numerical integration type^{11} were done only for compound VI. For compound III the small crystal sizes led to a nearly constant transmission factor (see Table II). Both structures were solved by

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(11) Coppens, P. "Crystallographic Computing"; Ahmed, F. R., Ed.; Munksgaard: Copenhagen, Denmark, 1970; p 319.

Table III. Infrared Spectral Data of Complexes III–VIII (cm^{-1}, KBr Disks)

compd	ν_{NH}	ν_{CO}	ν_{CN}	ν_{PO}
III	3373 w	1875, 1806, 1784 vs, 1879,^{a} 1794^a		1087 m, 1053, 1028 w, 1007 m
IV	3400 w	1967 s, 1928 m, 1909, 1889, 1872 vs, 1840 m		1087 m, 1052, 1024, 1007 w
V	3380 w	1865 s, 1842 vs		1087 m, 1049, 1025 w, 998 m
VI		1874, 1813, 1789 vs		1052 m, 1017 s
VII	3395 m	1898, 1866, 1800 vs	1650, 1625 m	1087 m, 1055 w, 1030 w, 1006 m
VIII	3402 m	1910, 1860, 1813 vs	1677 s	1087 m, 1057 w, 1026, 1006 m

^{a} In CH$_2$Cl$_2$ solution.

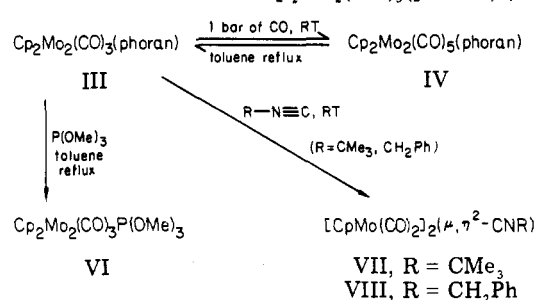Table IV. ^{1}H NMR Spectral Data for Complexes III–VIII^{a,b}

compd	δ_{CH_3}	δ_{CH_3O} (J_{P-H}, Hz)	δ_{CH_2N}	δ_{CH_2O}	δ_{CH_2} (J_{CH-H}, Hz)	$\delta_{C_5H_5}$ (J_{P-H}, Hz)	$\delta_{C_6H_5}$	instrument
III			m 2.96	m 4.03		s 4.73, d 5.06 (1.7)	m 7.40	Varian T-60
IV			m 3.20	m 4.20		d 4.92 (1.2), s 5.14	m 7.43	Varian T-60
VI		d 3.71 (11.6)				d 4.93 (1.5), s 5.10		Varian T-60
VII	s 1.33		m 2.81, m 3.13	m 4.01		s 4.80, d 5.27 (1.1)	m 7.33	Bruker WH 250
VIII			m 2.87, m 3.15	m 4.05	d 4.66 (14), d 4.95 (14)	s 4.83, d 5.16 (1.2)	m 7.31	Bruker WH 250

^{a} CDCl$_3$ solution, internal Me$_4$Si; s = singlet, d = doublet, m = multiplet; coupling constants in Hz. ^{b} The NH proton could not be observed.

combined Patterson and Fourier methods. Hydrogen atoms were introduced in structure factor calculations, but not refined, by their computed coordinates (C–H = 0.95 Å) and for the CH$_3$ hydrogen, by the calculated coordinates closest to the positions picked out from a Fourier difference map. An isotropic fixed temperature factor ($B = 6$ Å^2) was introduced for all hydrogen atoms. The non-hydrogen atoms were refined by full-matrix least-squares. The crystal data of III and VI are listed in Table II.

Results

Synthesis and Spectroscopic Characterization of Cp(CO)$_2$Mo≡Mo(CO)[PhP(OCH$_2$CH$_2$)$_2$NH] (III).

Three products could be isolated from the reaction of equimolar amounts of [Cp(CO)$_2$Mo]$_2$ (I) and phoran (II) in a toluene/ether mixture at room temperature. A red crystalline precipitate, which is sparingly soluble in most common solvents, was identified as [CpMo(CO)$_2$(phoran)]$_2$ (V) on the basis of analytical, infrared, and ^{1}H NMR data (Tables I, III, IV). A trans configuration has been proposed[6c,12] for complexes of this type. The two main products of the reaction were separated by column chromatography and identified as being the dissymmetrically substituted Cp$_2$Mo$_2$(CO)$_3$(phoran) (III) and its carbonyl adduct Cp$_2$Mo$_2$(CO)$_5$(phoran) (IV), the former predomi-

nating slightly as indicated by the IR spectrum of the crude reaction mixture.

Whereas the IR absorption frequencies of the CO groups of IV are in the range typical of terminal ligands, those of III indicate semibridging ligand character (Table III).[13] The different chemical environment of the Mo atoms in
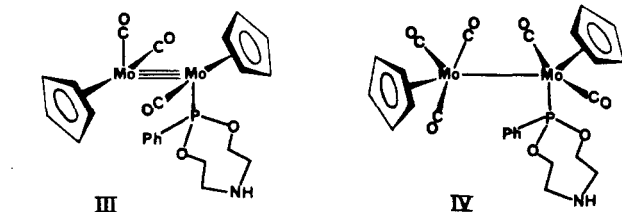
Scheme I. Reactions of Cp$_2$Mo$_2$(CO)$_3$(phoran) (III)

III and IV is reflected by their ^{1}H NMR spectra (Table IV). The chemical shifts of the Cp protons in III, which can be assigned on the basis of the presence or absence of $^3J_{H-P}$ coupling, are inverted with respect to those of IV.

By contrast, the reaction of I with PhP(OMe)$_2$ under comparable experimental conditions failed to give any isolable product.

The Reversible Carbonylation Reaction of III. Compound III incorporates CO very easily at room temperature under 1 atm of CO, to give almost quantitatively Cp$_2$Mo$_2$(CO)$_5$(phoran) (IV). This behavior, which is comparable to that of the parent compound [Cp(CO)$_2$Mo]$_2$,[14] provides a convenient method for the synthesis of ^{13}C-enriched Cp$_2$Mo$_2$(*CO)$_5$(phoran), starting from ^{13}C-enriched I, via a mixture of III and IV, which is then treated with ^{13}CO. When IV is refluxed in toluene, its decarbonylation occurs, leading either to III (Scheme I) or to ^{13}C-enriched III. This result is comparable to the thermal elimination of two CO groups from [CpMo(CO)$_3$]$_2$ or of PPh$_3$ and CO from [CpMo(CO)$_2$PPh$_3$]$_2$.[6c] The IR spectra of the ^{13}CO-labeled and unlabeled compounds are clearly distinguishable, as shown in Figure 1.

^{13}C NMR Studies. The Fluxional Behavior of the CO Groups on the Mo≡Mo Bond. The distinct substitution pattern of the two metal atoms in III provides an opportunity to study the scrambling of the CO groups on a Mo≡Mo triple bond by variable-temperature ^{13}C NMR. Therefore, ^{13}C-enriched compounds were prepared by taking advantage of the equilibrium shown in Scheme

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Table V. ^{13}C NMR Spectral Data for Complexes III, IV, and VII^{a,b}

compd	δ_{CH_3}	δ_{CH_2N}	δ_{CH_2O}	$\delta_{C_5H_5}$	$\delta_{C_6H_5}$	δ_{CO} (J_{P-C}, Hz)	solvent (temp, °C)
III		s 49.0	s 67.3, s 67.1	s 92.0, s 91.8	m 127.7–130.3	d 244.9 (10), d 240.5 (6)^c	CD$_2$Cl$_2$ (0)
IV		s 48.7	s 67.7, s 67.2	s 91.3, s 92.1	m 128.2–130.3	s 228.1,^{d} d 233.9 (31), s 234.6^d	CDCl$_3$ (37)
VII^f	s 31.3	s 49.9	s 66.9	s 91.7, s 93.6	m 127.5–129.1	d 238.3 (26), s 246.4,^{e} s 249.5^e	CDCl$_3$ (32)

^{a} The broad-band decoupled spectra were recorded at 26.63 MHz on a Bruker WH 90 spectrometer. Internal Me$_4$Si, coupling constants in Hz. ^{b} s = singlet, d = doublet, m = multiplet. ^{c} See text. ^{d} J_{C-C} = 10 Hz. ^{e} J_{C-C} = 13 Hz. ^{f} The resonances of other tertiary carbon atoms than ^{13}CO could not be detected.

Scheme II. Synchronous One-to-One Switch Mechanism for the Exchange of Carbonyl Groups in Cp$_2$Mo$_2$(CO)$_3$(phoran)
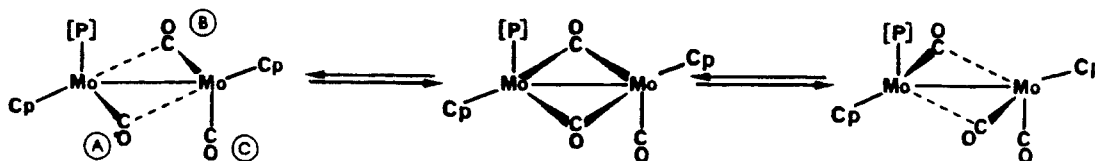
I. The ^{13}C signals due to the CO groups of III and IV are well resolved (Table V), reflecting their different structural environments. Thus for IV, a pattern of three signals with relative intensities of 2:2:1 at 228.1, 233.9 (d), and 234.6 ppm is found. The signals at 228.1 and 234.6 ppm are assigned to carbonyls belonging to the CpMo(CO)$_3$ moiety, by analogy with those found in the spectrum of [CpMo-(CO)$_3$]$_2$;[15] they result from the almost square-pyramidal configuration at the metal center, which yields nonequivalent cis and trans carbonyls. The intermediate signal at δ 233.9 is assigned to the carbonyl groups on the Mo atom bearing the phoran ligand, which gives rise to a P–C coupling of 31 Hz. A similar pattern, but without P–C coupling, was observed for the related Cp(CO)$_3$Mo–Mo-(CO)$_2$(η^2-CS$_2$)Cp complex.[16] Due to the considerable ^{13}C enrichment, C–C coupling constants of 10 Hz can be observed for the nonequivalent carbonyls.

For Cp$_2$Mo$_2$(CO)$_3$(phoran), three distinct types of carbonyls can be observed at −95 °C (Figure 2), which is consistent with the solid-state structure (vide infra). Resonance A, which shows the largest P–C coupling of 18 Hz, should therefore correspond to the CO group directly attached to the phoran-bearing Mo atom. This CO group lies in nearly the same plane as CO group B, and together they form a conjugate pair of approximately C_2 symmetry. Therefore one might expect the activation energy for an exchange process between A and B to be rather low.[17] Indeed, as the temperature is increased to about −60 °C the coalescence of the two peaks of resonance A can be observed. Concomitantly, resonance B broadens slightly: $\nu_{1/2}$ increases from 5 to 8 Hz; it decreases again to 4 Hz above this temperature, indicating that weak, unresolved P–C coupling must exist for carbonyl B. From 0 °C upward, a single doublet with an averaged P–C coupling of 10 Hz is found at 244.9 ppm. It is important to note that the C–P splitting (6 Hz) of resonance C, belonging to the carbonyl trans to the phoran ligand, is not affected by the coalescence process. Only a small coupling with phosphorus through the metal is expected when the CO is π-bonded, as has been found for pure four-electron bridging carbonyls.[18]

Our variable-temperature NMR study thus provides evidence for a two-center exchange of two of the carbonyls,
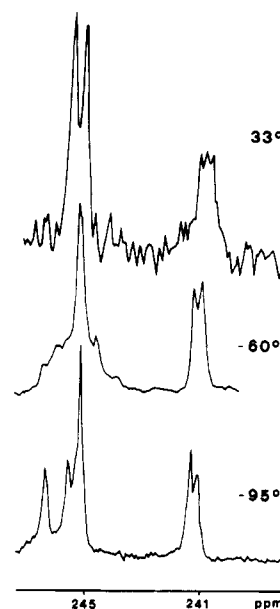

Figure 2. Variable-temperature ^{13}C NMR spectra of the carbonyl groups of Cp$_2$Mo$_2$(CO)$_3$(phoran) (III) (see text for assignments).

in which the third one remains unaffected. It is generally accepted that two-center CO scrambling phenomena in polynuclear carbonyl complexes imply the presence of terminal *and* bridging,[19] or terminal *and* semibridging carbonyls.[18,20]

Molecules containing only semibridging carbonyls, e.g., the parent compound [Cp(CO)$_2$Mo]$_2$, were also supposed to be fluxional,[13] but evidence for this could be obtained only very recently in the heteronuclear dimer Cp$_2$-(CO)$_4$MoW.[21] The participation of *all* the CO groups in the scrambling has been found in the complex Cp$_2$Fe$_2$(µ-CO)$_2$(CO)P(OPh)$_3$,[22] which is isoelectronic with III. MO calculations on [CpFe(CO)$_2$]$_2$[23] as well as experimental findings[22] give evidence for the opening of both bridges and for the rotation around the metal–metal bond in this

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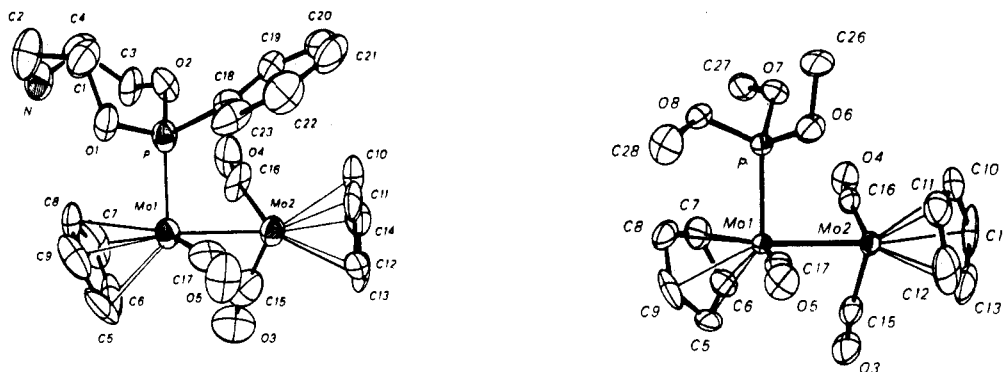(22) Cotton, F. A.; Kruczinsky, L.; White, A. J. *Inorg. Chem.* **1974**, *13*, 1402.
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Figure 3. Perspective ORTEP diagram of Cp$_2$Mo$_2$(CO)$_3$(phoran) (left) and Cp$_2$Mo$_2$(CO)$_3$P(OCH$_3$)$_3$ (right), with thermal ellipsoids at the 50% probability level.

compound. By contrast, molecule III has three semibridging carbonyls, plus a phosphorus ligand which does not participate in the exchange. Our observations are consistent with a one-for-one exchange between carbonyls A and B which could result from a synchronous switch mechanism, as depicted in Scheme II, which goes through a symmetric dibridged intermediate requiring only a low activation energy.[21,23] This process may be facilitated by the nearly coplanar arrangement and approximate C_2 symmetry of these two ligands, which render them "compensatory",[17] and does not require the assistance of terminal CO groups. The nonparticipation of carbonyl group C in the observed exchange process may be explained by the absence of the conjugated CO group needed for a pairwise exchange mechanism. Because III begins to decompose slowly above room temperature, it could not be decided whether another, less favorable process might become effective at higher temperatures, which would involve the exchange of carbonyl C.

The Reaction of III with P(OMe)$_3$. From the reaction, in boiling toluene, of III with an equimolar amount of P(OMe)$_3$, the orange-red complex Cp$_2$Mo$_2$(CO)$_3$P(OMe)$_3$ (VI) has been isolated. Its composition is confirmed by elemental analysis and mass spectroscopy. The IR spectroscopic data (Table III) are comparable to those of the parent compound III. The ^{1}H NMR spectrum (Table IV) shows two signals for the Cp protons, whose chemical shifts are inverted with respect to those of III. In order to rationalize this observation it was important to decide whether or not the phenyl groups present in III could give rise to an anisotropic shielding effect on one of the Cp ligands. As seen from the X-ray stucture of III (Figure 3) such an effect is indeed possible for the uncoupled Cp protons, i.e., those located on the non-P-bound Mo. A similar β-phenyl effect has already been described for a series of mononuclear cyclopentadienyl complexes having a phenyl group in a β-position with respect to the metal.[24] Although complex IV contains the same phosphorus ligand as III, the chemical shift of the Cp protons in the former is very similar to that of complex VI, which has no phenyl groups. This is certainly a consequence of a different structural arrangement in IV (when compared to III), where the expansion of the Mo–Mo bond to bond order 1 causes the conversion of the semibridging CO's into terminal CO's and the increased bending of the Cp–Mo–Mo–Cp axis,[12] which is less favorable to the development of the shielding effect discussed above.

If the reaction of III with P(OMe)$_3$ is carried out at room temperature with a 10-fold excess of the ligand, the for-

mation of the bis(phosphite) adduct, Cp$_2$(CO)$_4$Mo$_2$[P-(OMe)$_3$]$_2$ (X), instead of complex VI is observed, but the yield is very poor. The spectroscopic data measured for X (IR, NMR, mass) are identical with those of the product obtained from the direct reaction of [Cp(CO)$_2$Mo]$_2$ with P(OMe)$_3$.[6c]

The Reaction of III with Isocyanides RN≡C (R = CMe$_3$, CH$_2$Ph). III reacts easily, at room temperature, with equimolar amounts of *tert*-butyl or benzyl isocyanide, leading to complexes VII and VIII, respectively. From
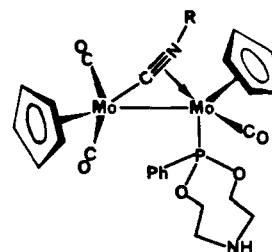
VII : R = CMe$_3$

VIII : R = CH$_2$C$_6$H$_5$

analytical data as well as mass and ^{1}H NMR spectra there is evidence for the addition of only one ligand. The IR spectrum (Table III) is characteristic of bridging isocyanide ligands, whereas the CO region shows three absorptions in both compounds. The IR spectrum of the ^{13}CO-enriched complex VII which is shown in Figure 1 is much more complicated.

The spectroscopic data are consistent with the formulation of a bridged isocyanide complex, such as in Cp$_2$Mo$_2$(CO)$_4$(μ,η^2-CNPh), which was directly obtained from [Cp(CO)$_2$Mo]$_2$ and PhNC.[25] In the latter compound the σ and π coordination of the isocyanide causes a distinct chemical environment at each of the metal atoms, which is reflected by two Cp resonances in the ^{1}H NMR spectrum. It is noteworthy that the semibridging character of the ligand remains preserved even at elevated temperatures.[26] One can therefore deduce the existence of only one isomer from the ^{1}H NMR spectra of VII and VIII, which show only one uncoupled and one phosphorus-coupled Cp resonance. This stereospecificity in the addition of RNC may be explained by a preferential attack of the incoming nucleophile on the unsubstituted CpMo(CO)$_2$ moiety of III rather than on the phosphorus substituted Mo atom. Molecular models suggest indeed that the attack of III should occur between the planes Mo-

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Table VI. Positional Parameters of Complex III and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å²
Mo 1	0.19106 (9)	0.39559 (9)	0.4851 (1)	3.30 (3)
Mo 2	0.34032 (9)	0.39263 (9)	0.6779 (1)	3.40 (3)
P	0.2148 (3)	0.5310 (3)	0.4243 (4)	3.4 (1)
O1	0.1162 (7)	0.5736 (7)	0.356 (1)	4.0 (3)
O2	0.2778 (7)	0.5536 (7)	0.317 (1)	3.8 (3)
C1	0.114 (1)	0.643 (1)	0.267 (2)	5.4 (5)
C2	0.069 (1)	0.625 (1)	0.110 (2)	6.7 (6)
C3	0.270 (1)	0.516 (1)	0.182 (2)	5.2 (5)
C4	0.207 (2)	0.564 (1)	0.058 (2)	6.4 (6)
N	0.109 (1)	0.556 (1)	0.061 (2)	5.9 (4)
C5	0.054 (1)	0.328 (1)	0.450 (2)	6.4 (6)
C6	0.110 (2)	0.283 (1)	0.386 (2)	8.0 (6)
C7	0.124 (1)	0.330 (2)	0.274 (2)	8.2 (7)
C8	0.075 (1)	0.396 (1)	0.271 (2)	6.4 (6)
C9	0.031 (1)	0.397 (1)	0.377 (2)	6.5 (6)
C10	0.474 (1)	0.462 (1)	0.791 (2)	4.7 (5)
C11	0.408 (1)	0.479 (1)	0.866 (2)	4.1 (4)
C12	0.388 (1)	0.404 (1)	0.926 (2)	4.4 (5)
C13	0.444 (1)	0.346 (1)	0.892 (2)	4.8 (5)
C14	0.496 (1)	0.381 (1)	0.805 (2)	4.8 (5)
C15	0.313 (1)	0.284 (1)	0.636 (2)	6.0 (5)
C16	0.370 (1)	0.400 (1)	0.493 (2)	6.0 (6)
C17	0.178 (1)	0.433 (1)	0.668 (2)	4.1 (4)
C18	0.275 (1)	0.601 (1)	0.567 (2)	3.6 (4)
C19	0.365 (1)	0.626 (1)	0.587 (2)	4.1 (4)
C20	0.405 (1)	0.672 (1)	0.698 (2)	4.6 (5)
C21	0.357 (1)	0.702 (1)	0.787 (2)	5.0 (5)
C22	0.263 (1)	0.683 (1)	0.766 (2)	5.3 (5)
C23	0.223 (1)	0.632 (1)	0.660 (2)	4.0 (4)
O3	0.300 (1)	0.2120 (8)	0.616 (1)	7.3 (4)
O4	0.4043 (7)	0.4012 (9)	0.400 (1)	6.2 (4)
O5	0.1502 (8)	0.4529 (8)	0.766 (1)	5.5 (3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

Table VII. Positional Parameters of Complex VI and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å²
Mo 1	0.24976 (2)	0.04572 (3)	-0.01193 (6)	2.75 (1)
Mo 2	0.26684 (3)	-0.05836 (2)	-0.14122 (7)	2.91 (1)
P	0.14313 (8)	0.01710 (8)	0.0129 (2)	3.16 (4)
O3	0.4007 (3)	-0.0129 (3)	-0.0629 (6)	6.6 (2)
O4	0.2576 (3)	-0.0824 (3)	0.2221 (6)	5.7 (1)
O5	0.2203 (3)	0.0605 (3)	-0.3712 (6)	5.4 (1)
O6	0.1185 (2)	-0.0246 (3)	-0.1328 (6)	5.1 (1)
O7	0.1181 (2)	-0.0230 (2)	0.1604 (6)	4.4 (1)
O8	0.0918 (2)	0.0725 (2)	0.0256 (6)	4.0 (1)
C5	0.3242 (4)	0.1230 (4)	0.026 (1)	5.4 (2)
C6	0.3197 (4)	0.0888 (4)	0.167 (1)	5.1 (2)
C7	0.2617 (5)	0.0990 (4)	0.231 (1)	6.5 (2)
C8	0.2306 (4)	0.1379 (4)	0.136 (1)	7.4 (2)
C9	0.2683 (6)	0.1536 (4)	0.006 (1)	7.4 (3)
C10	0.2225 (5)	-0.1537 (4)	-0.205 (1)	7.4 (2)
C11	0.2156 (5)	-0.1165 (4)	-0.333 (1)	6.6 (2)
C12	0.2709 (6)	-0.1054 (5)	-0.394 (1)	7.4 (3)
C13	0.3152 (5)	-0.1333 (5)	-0.305 (1)	7.0 (2)
C14	0.2883 (5)	-0.1641 (4)	-0.185 (1)	7.9 (2)
C15	0.3487 (4)	-0.0259 (4)	-0.091 (1)	4.4 (2)
C16	0.2589 (4)	-0.0684 (3)	0.088 (1)	3.7 (2)
C17	0.2301 (3)	0.0497 (3)	-0.2371 (9)	3.6 (2)
C26	0.0549 (4)	-0.0463 (5)	-0.144 (1)	6.5 (2)
C27	0.1267 (4)	-0.0021 (4)	0.319 (1)	5.0 (2)
C28	0.0877 (5)	0.1180 (5)	-0.098 (1)	6.2 (2)

[a] See footnote a, Table VI.

(1)-C(15)-Mo 2 and Mo(1)-C(17)-Mo(2) (Figure 3) which would require only small changes in the initial structural arrangement during the reaction. The room-temperature ^{13}C NMR spectrum taken on a ^{13}CO-enriched sample of VII (Table V) displays the expected pattern of two singlets

Table VIII. Selected Bond Lengths (Å) for III and VI

	Cp₂Mo₂(CO)₃- {PhP(OCH₂CH₂)₂NH} (III)	Cp₂Mo₂(CO)₃- {P(OMe)₃} (VI)
Mo1-Mo2	2.506 (1)	2.502 (1)
Mo1-P	2.383 (4)	2.371 (2)
Mo1-C15	2.74 (2)	2.70 (1)
Mo1-C16	2.65 (2)	2.59 (1)
Mo1-C17	1.93 (2)	1.93 (1)
Mo1-C5	2.28 (2) ⎫	2.32 (1) ⎫
Mo1-C6	2.30 (2) ⎪	2.31 (1) ⎪
Mo1-C7	2.30 (2) ⎬ 2.31 (2)	2.34 (1) ⎬ 2.34 (2)
Mo1-C8	2.33 (2) ⎪	2.36 (1) ⎪
Mo1-C9	2.34 (2) ⎭	2.35 (1) ⎭
Mo1-Cp(cent)	2.00	2.02
Mo2-C15	1.87 (2)	1.93 (1)
Mo2-C16	1.94 (2)	1.94 (1)
Mo2-C17	2.50 (2)	2.57 (1)
Mo2-C10	2.32 (1) ⎫	2.31 (1) ⎫
Mo2-C11	2.33 (1) ⎪	2.31 (1) ⎪
Mo2-C12	2.32 (2) ⎬ 2.33 (2)	2.34 (1) ⎬ 2.33 (2)
Mo2-C13	2.36 (1) ⎪	2.35 (1) ⎪
Mo2-C14	2.34 (2) ⎭	2.34 (1) ⎭
Mo2-Cp(cent)	2.01	2.02

Table IX. Selected Angles and Torsional Angles (deg) for III and VI

	Cp₂Mo₂(CO)₃- {PhP(OCH₂CH₂)₂NH} III		Cp₂Mo₂(CO)₃- {P(OMe)₃} VI
Mo1-Mo2-C15	75.9 (2)		73.7 (2)
Mo1-Mo2-C16	71.8 (2)		70.0 (2)
Mo2-Mo1-C17	67.1 (2)		69.5 (2)
Mo2-Mo1-P	92.4 (3)		87.0 (4)
Mo2-Mo1-Cp(cent)	154.6		151.5
Mo1-Mo2-Cp(cent)	163.9		164.9
Mo2-C15-O3	175.8 (1.5)		172.6 (6)
Mo2-C16-O4	167.0 (1.5)		170.7 (6)
Mo1-C17-O5	165.9 (1.4)		170.9 (6)
P-Mo1-C17	88.4 (4)		83.5 (3)
C15-Mo2-C16	87.1 (4)		84.6 (3)
Mo1-P-O1	109.9 (4)	Mo1-P-O6	113.2 (2)
Mo1-P-O2	121.9 (4)	Mo1-P-O7	122.0 (2)
Mo1-P-C18	119.3 (4)	Mo1-P-O8	118.0 (2)

Torsional Angles		
C17-Mo1-Mo2-C15	112.9	109.1
C17-Mo1-Mo2-C16	-155.5	-160.8
P-Mo1-Mo2-C15	-159.9	-166.7
P-Mo1-Mo2-C16	-68.3	-76.6

and one doublet for the carbonyl groups, in good agreement with their terminal and consequently nonfluxional character, but tertiary isocyanide carbon atom could not be detected.

X-ray Diffraction Studies. In view of the novel character of complexes III an VI, X-ray diffraction studies were carried out. Some preliminary data for III have already been published.[2] The atomic parameters, bond distances, and bond angles of III and VI are given in Tables VI–IX. ORTEP drawings of III and VI are shown in Figure 3 using an identical numbering scheme for isostructural fragments. The packing diagrams of both molecules are displayed in Figures 4 and 5 (supplementary material), showing that the composition of the unit cell is dependent on the ligand.[27]

The molecular structures of III and VI are very similar; both display short Mo–Mo distances typical of a carbonyl

(27) In this regard it is of interest that (C₅Me₅)₂Mo₂(CO)₃(phoran) crystallizes as III in the monoclinic system with $Z = 4$ (unpublished results).

bridged triple bond,[3a] a nonlinear Cp–Mo–Mo–Cp axis, and Mo–C–O units which are slightly bent back over the Mo–Mo bond (Figure 3). A comparison with the parent compound $Cp_2Mo_2(CO)_4$ (I) reveals striking similarities but also some obvious differences. The Mo–Mo distance (2.506 (1) Å in III and 2.502 (1) Å in VI) is only slightly affected by the substitution (2.448 (1) Å in I).[13] According to the proposal of Curtis, the carbonyl groups all belong to the "donor semibridging" type.[3a] But a closer examination of the carbonyl groups reveals that each "short" Mo–C(CO) distance is shorter, by an average of 0.2 Å, than in I. On the other hand, the indirect "long" Mo–C(CO) bond lengths are not strictly equivalent and are slightly longer than in I,[13] ranging from 2.50 (2) to 2.74 (2) Å. Related to the latter observation is an increase in the acute Mo–Mo–C(CO) angles from 67.1 (2) to 75.9 (2)°. The smallest angle which can be directly compared to the corresponding one in I (67.4 (1.1)°) is found at the Mo atom which bears the phosphorus ligand. A cautious interpretation (because of the relatively high esd's) may take into account a slight increase of the Mo–C=O σ bonding, whereas the π bonding to the second Mo atom seems to be less affected.

Another difference between I and complexes III and VI is the bent Cp–Mo–Mo–Cp axis which renders their structure more similar to that of $Cp_2Cr_2(CO)_4$;[28] the degree of bending in III and VI is comparable. It is more pronounced at Mo(1), probably as a consequence of increased steric crowding. The relevant angles of 154.6° in III and 151.5° in VI, respectively, are even smaller than those in $Cp_2Cr_2(CO)_4$ (159°),[28] whereas they are 180° in $Cp_2Mo_2(CO)_4$.[13]

In summary the replacement of one good π-acceptor ligand (carbonyl) by a ligand whose character is predominantly σ-donor (phoran or $P(OMe)_3$) does not have drastic effects on the structure of the remaining carbonyl ligands. This may be a consequence of the carbonyl π-system being involved in the metal–metal π-system,[13] so that an initially unequal charge distribution is delocalized over all the non-hydrogen atoms in the molecule. In contrast, two different types of carbonyl bridges are observed in $Fe_2(CO)_7(2,2'-bpy)$, which has only a metal–metal "single" bond.[29]

Complex III is the first compound in which the phoran molecule behaves as a monodentate ligand for which a crystal structure has been determined. The conformation of the eight-membered cycle in the solid state approximates the chair–boat conformation found in P- and N-coordinated Rh phoran chelates[30] with the P and N atoms lying on the same side of the mean plane of the cycle, but further apart from each other than in the chelate (ca. 3.5 Å instead of 2.8 Å). It is also of interest to note that the phenyl group points to the Cp ring attached to Mo(2) as in mononuclear cyclopentadienyl complexes of molybdenum having a phenyl group in a β-position.[24]

Discussion

The formation of a dissymmetrically substituted Mo≡Mo derivative of composition $Cp_2Mo_2(CO)_3PPh_3$ has been reported previously, but it could only be obtained indirectly by the thermal elimination (110 °C) of one PPh_3 and one CO from $[CpMo(CO)_2(PPh_3)]_2$.[6c] So far the direct *substitution* of one carbonyl group of I seems to be restricted to the phoran ligand II, where it occurs under much milder conditions, e.g., room temperature. In view

of the general tendency of I to undergo symmetrical *addition* reactions,[6c] one might have expected either the formation of the dinuclear tetracarbonyl complex V, having two phoran ligands, or of the speculative phoran-bridged adduct IX. Instead, the major product was III, and no evidence was found for adduct IX. In order to explain

IX
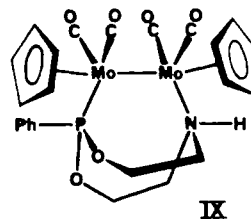
the predominant formation of the former (a part of which is transferred into IV by immediate CO scavenging during the reaction) the substitution of one CO group in I by $PhP(OMe)_2$ has been attempted under comparable experimental conditions. The failure to isolate the corresponding dimolybdenum tricarbonyl substitution complex underlines the unique chemical behavior of ligand II and points again to some assistance by the transannular nitrogen atom in the activation of two coordination sites.

Like its precursor I, complex III readily adds 2 mol of carbon monoxide or 1 mol of isocyanide, thus demonstrating that the high reactivity of the metal–metal triple bond is preserved. On the other hand, the *addition* of a second ligand, e.g., phoran or $PhP(OMe)_2$, to III could not be effected. With $P(OMe)_3$, instead of the expected adduct, the reaction of III gives complex VI, in which the phoran ligand is *substituted* by $P(OMe)_3$ and the Mo≡Mo triple bond is retained. With a large excess of $P(OMe)_3$ a *bisadduct* of composition $Cp_2Mo_2(CO)_4[P(OMe)_3]_2$ (X) could be isolated, which no longer bears the original phoran ligand. The formation of VI could proceed through the intermediate addition compound X, since the reaction is carried out in boiling toluene, and the formation of metal–metal triple bonds under thermal conditions is well documented.[6c] Unfortunately all these reactions proceed only in low yields, thus preventing any safe discussion of the reaction mechanism. Complexes III and VI represent the only two stable complexes of type $Cp_2Mo_2(CO)_3PR_3$ isolated so far.

Among the factors which may explain the differences in the behavior of III with respect to I are the slight increase in electron density expected at Mo(1) which bears the phoran ligand and a possible transannular assistance from the nitrogen atom. In this respect, its behavior differs from that of $Cp_2Mo_2(CO)(C_{12}H_{20})$, which also displays a dissymmetrically substituted Mo≡Mo triple bond; although the latter easily adds CO, no reaction with $P(OMe)_3$ could be observed, which was attributed to steric factors. In conrast, two *tert*-butyl isocyanide ligands were added to this complex and were proposed to be coordinated in a terminal fashion; however, the exact structure of the product is not yet completely known.

In conclusion, the phoran ligand in its reaction with $Cp_2Mo_2(CO)_4$ permitted the development of a new facet of the already numerous reaction patterns known for the Mo≡Mo bond. The high reactivity of the metal–metal triple bond is preserved in the resulting dissymmetrically CO-substituted complex $Cp_2Mo_2(CO)_3(phoran)$ (III) and, among other things, opens the way to other dissymmetrically substituted Mo≡Mo derivatives, e.g., $Cp_2Mo_2(CO)_3P(OMe)_3$.

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(OMe)$_2$, 2946-61-4; CO, 630-08-0; P(OMe)$_3$, 512-56-1; CNCMe$_3$, 7188-38-7; CNCH$_2$C$_6$H$_5$, 10340-91-7; Mo, 7439-98-7.

Supplementary Material Available: Tables of full bond lengths and bond angles, hydrogen atom positional parameters, general temperature factor expressions, and structure factors for III and VI and stereoscopic views (Figures 4 and 5) of the unit-cell packing (27 pages). Ordering information is given on any current masthead page.

Oxidative Addition of Dimethylthiocarbamoyl Chloride to [Rh₂Cl₂(μ-CO)(Ph₂PCH₂PPh₂)₂], the Facile Interconversion between Chelating η² and Bridging Coordination Modes of the SCNMe₂ Group, and the Structure of [Rh₂Cl₂(CO)(SCNMe₂)(Ph₂PCH₂PPh₂)₂][BF₄]·1.833CH₂Cl₂

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Oxidative addition of SC(Cl)NMe$_2$ to [Rh$_2$Cl$_2$(μ-CO)(DPM)$_2$] (1) (DPM = Ph$_2$PCH$_2$PPh$_2$) yields [Rh$_2$Cl$_3$(CO)(SCNMe$_2$)(DPM)$_2$] (2). In the presence of BF$_4^-$ the product of oxidative addition is [Rh$_2$Cl$_2$(CO)(SCNMe$_2$)(DPM)$_2$][BF$_4$] (3). An X-ray structure determination of 3 (space group $P2_1/n$, a = 12.340 (1) Å, b = 32.888 (5) Å, c = 15.374 (2) Å, β = 105.935 (8)°, Z = 4) shows that the SCNMe$_2$ moiety is bound in an η^2 fashion to one metal center. This structure has refined to R = 0.070 and R_w = 0.081 for 4122 observations and 345 parameters varied. The reaction of 3 with Me$_3$NO results in CO loss, yielding [Rh$_2$Cl$_2$(μ-SCNMe$_2$)(DPM)$_2$][BF$_4$] (4) in which the SCNMe$_2$ group bridges the two metals. Compound 4 reacts with CO to regenerate 3 and reacts with methyl isocyanide to give the analogous isocyanide compound, [Rh$_2$Cl$_2$(CNMe)(SCNMe$_2$)(DPM)$_2$][BF$_4$] (5). The reduction of compound 3 employing BH$_4^-$ was carried out to give the very air-sensitive species [Rh$_2$(CO)(μ-SCNMe$_2$)(solvent)(DPM)$_2$][BF$_4$] (solvent = THF (6a), acetonitrile (6b)). Compounds 6a and 6b react with CO to give [Rh$_2$(CO)$_2$(μ-SCNMe$_2$)-(DPM)$_2$][BF$_4$] (7).

Introduction

We have recently been investigating the chemistry of sulfur-containing heteroallenes[1,2] and related molecules with binuclear systems in order to obtain a better understanding of how these molecules interact with more than one metal center. One such group, which has the ability to coordinate to metals in several ways, is the dimethylthiocarboxamido ligand (SCNMe$_2$). In the presence of a single metal center it can coordinate in either the η^1 mode,[3-5] in which it is bound solely through carbon, or the
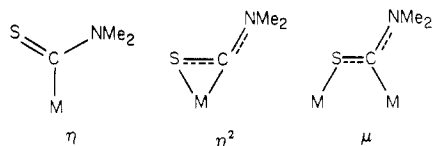
η^2 mode,[3-22] in which it is side-on bound through the C–S

moiety, and in the presence of two metals the third bonding mode (μ), in which this group bridges the metals, bonding to one metal through carbon and to the other through sulfur, is also possible.[3-5,23-25] Although the second[5,7,9-11,14-20] and third[23-25] modes have been confirmed

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