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REACTIVITY OF THE METAL–METAL MULTIPLE BOND IN METAL CARBONYL DERIVATIVES

X *. REINVESTIGATION OF THE REACTION OF $[\eta^5\text{-}C_5Me_5(CO)_2Mo]_2$-(*Mo≡Mo*) WITH PHOSPHORUS LIGANDS: FORMATION OF $(C_5Me_5)_2Mo_2(CO)_3PR_3$-(*Mo≡Mo*) ($PR_3 = P(OMe)_3$; $PhP(OCH_2CH_2)_2NH$) AND $C_5Me_5(CO)_2[P(OMe)_3]Me$, AND THE CRYSTAL STRUCTURE OF $(C_5Me_5)_2Mo_2(CO)_3[PhP(OCH_2CH_2)_2NH]$

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Summary

In spite of the increase in steric crowding, $[C_5Me_5(CO)_2Mo]_2$ (II), was found to react with $P(OMe)_3$ or with the bicyclic aminophosphorane $PhP(H)(OCH_2CH_2)_2N$ in boiling toluene to give the CO-replacement products $(C_5Me_5)_2Mo_2(CO)_3P(OMe)_3$ (V) and $(C_5Me_5)_2Mo_2(CO)_3$(phoran) (VI), respectively, in which "phoran" represents the open tautomeric form of the phosphorane. As a further product of the $P(OMe)_3$ reaction, $C_5Me_5(CO)_2Mo[P(OMe)_3]CH_3$ (VII) was isolated in yields varying with the reaction conditions. The two dinuclear compounds are the first examples of pentamethylcyclopentadienyl molybdenum dimers containing phosphorus ligands, as well as the first dissymmetrically substituted derivatives of II. Their isolation is in contrast with the previously reported inertness of II towards phosphorus ligands, and extends the range of its reactions in which Mo≡Mo is preserved. The crystal structure of VI is surprisingly close to that of the much less crowded $(C_5H_5)_2Mo_2(CO)_3$(phoran) as far as the environment of the Mo≡Mo core is concerned, but differs in the arrangement of the phoran ligand.

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* For part IX see ref. 1.

** Structure determination.

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Introduction

Among transition metal complexes having a metal–metal multiple bond, the molybdenum cyclopentadienylcarbonyl complexes $[\eta^5\text{-}C_5R_5(CO)_2Mo]_2$ (R = H: I, R = CH_3: II) are of outstanding interest, owing to their easy accessibility and also, in the case of the unsubstituted dimer I, to the rich chemistry that derives from the addition of a wide range of reactants across the Mo–Mo triple bond [2]. In contrast, reactions of II proceeding without metal–metal bond scission seem so far to be restricted to those involving small molecules. Thus, CO [3], CS_2 [4], and diazoalkanes [5] gave addition products, as did Me–N=C=S, reaction of which resulted, after sulfur abstraction, in the formation of a $\mu,\eta^1:\eta^2$-isocyanide adduct [6]. A completely novel type of reaction which has so far been observed to occur only with II, is the replacement of all four carbonyl ligands by elemental sulfur [7] or selenium [8]. These findings further illustrate the major differences in behavior that can be observed between the methyl-substituted and unsubstituted cyclopentadienyl derivatives. Similarly, in contrast to I, II was reported not to react with $P(OMe)_3$ [9], and from this a general inertness of II towards phosphorus ligands has been inferred [2b].

In previous papers we described the unusual reaction of $[C_5H_5(CO)_2Mo]_2$ with the bicyclic aminophosphorane $PhP(H)(OCH_2CH_2)_2N$ (III, whose monocyclic, potentially bidentate tautomeric open-form [10] is denoted by phoran), leading to a dissymmetrically substituted Mo≡Mo derivative of composition $(C_5H_5)_2$-$Mo_2(CO)_3$(phoran) (IV) [11], even at room temperature, whereas the usual phosphorus ligands such as PPh_3 or $P(OMe)_3$ take part in addition reactions at the metal–metal triple bond [12]. Stereochemical considerations led us to suspect that the pentamethyl homologue of IV, VI, might be as stable as IV. In this paper we show that, in contradiction of the general view expressed in the literature [2b], phoran and even $P(OMe)_3$ do give stable $(C_5Me_5)_2Mo_2(CO)_3PR_3$ derivatives, and therefore that the influence of the pentamethylcyclopentadienyl ligand is less dramatic than was expected in the light of an X-ray crystallographic investigation of II [13].

Experimental section

General data. Infrared spectra were obtained with a Beckman 4240 spectrophotometer, ^1H NMR spectra were recorded at 60 MHz on a Varian T-60 spectrometer when not otherwise noted. Molecular weights were determined by field desorption mass spectra on a 311 A instrument (MAT) from acetone solutions. All procedures were carried out under nitrogen with solvents freshly distilled under nitrogen from appropriate drying agents. Nitrogen saturation of SiO_2 (Kieselgel 60, 0.125–0.200 mm, purchased from Merck, Darmstadt, Germany) was carried out at room temperature by three short pump/nitrogen cycles.

Solution of the structure of $(C_5Me_5)_2Mo_2(CO)_3$(phoran) (VI). Rotating crystal, Weissenberg and precession photographs showed the crystal to be monoclinic with the following lattice constants (23°C): a 13.786(2), b 22.130(3), c 15.538(2) Å, β 136.35 (1)°; V 3271.7 Å^3, $Z = 4$, ρ_{calcd} 1.538 g cm^{-3}, space group $P2_1/n$. Data collection was carried out on a Nonius CAD 4 diffractometer with Mo-K_α radiation (0.7107 Å, graphite monochromator). The heavy atoms were located by using

MULTAN, and subsequent difference Fourier syntheses were used to locate all other atoms except the hydrogens. The structure was solved by using 1926 independent reflections with $I > 3\sigma(I)$ collected in the range $2° < \theta < 18°$. The final residuals are $R = 0.038$ and $R_w = 0.046$.

Preparations

$(C_5Me_5)_2Mo_2(CO)_3P(OMe)_3$ (V), and $C_5Me_5(CO)_2Mo[P(OMe)_3]CH_3$ (VII). A mixture of 0.30 g (0.52 mmol) of $[C_5Me_5(CO)_2Mo]_2$ (II) with 0.65 g (5.2 mmol) of $P(OMe)_3$ was refluxed in 100 ml of toluene for 17 h. The solution was cooled to room temperature and concentrated to 10 ml. Chromatography on SiO_2 (column 30 × 3 cm) gave an orange band of minor amounts of $[C_5Me_5(CO)_3Mo]_2$ and a pale yellow band containing trace amounts of VII (identification by IR), both eluted with toluene, followed by a dark red band eluted with toluene/ether 10/1, containing 0.14 g (40%) of complex V. Recrystallization of the latter from 10 ml of ether gave dark red prisms.

Anal. Found: C, 46.60; H, 5.69; P, 4.67; mol wt. 662 (^{92}Mo). $C_{26}H_{39}Mo_2O_6P$ calcd.: C, 46.58; H, 5.86; P, 4.62%; mol wt. 670.42. mp. 192°C (beg. decomp.). IR (cm^{-1}, CH_2Cl_2) ν(CO) 1870s, 1781vs; ^{1}H NMR ($CDCl_3$) $\delta(CH_3)$ 1.84(s), 1.90(s); $\delta(CH_3O)$ 3.75 (d, J(P-H) 11.6 Hz).

When 1.78 g (3.10 mmol) of II and 3.85 g (31 mmol) of $P(OMe)_3$ were refluxed in 100 ml of toluene for 17 h, chromatography on SiO_2 resulted in a yellow band, eluted with toluene, containing 0.75 g (56%) of complex VII. With toluene/ether 10/1 a red band was eluted containing complex V in about 1% yield. Recrystallization from pentane gave yellow prisms of VII. Anal. Found: C, 44.52; H, 6.13; P, 7.35; mol wt. 428 (^{98}Mo) $C_{16}H_{27}MoO_5P$ calcd.: C, 45.08; H, 6.38; P, 7.27%; mol wt. 426.3. IR (cm^{-1}, KBr) 1932, 1858. ^{1}H NMR ($CDCl_3$, Bruker WM 250 instrument) *cis*-VII: $\delta(CH_3)$ −0.30 (d, ^3J(P-H) 10.0 Hz); $\delta(CCH_3)$ 1.83 (d, ^4J(P-H) 0.9 Hz); $\delta(OCH_3)$ 3.50 (d, ^3J(P-H) 11.2 Hz); *trans*-VII: $\delta(CH_3)$ 0.58 (d, ^3J(P-H) 2.9 Hz); $\delta(CCH_3)$ 1.80 (d, ^4J(P-H) 0.8 Hz); $\delta(OCH_3)$ 3.56 (d, ^3J(P-H) 11.4 Hz).

$(C_5Me_5)_2Mo_2(CO)_3$(phoran) (VI). A mixture of 1.0 g (1.74 mmol) of $[C_5Me_5(CO)_2Mo]_2$ with 0.37 g (1.75 mmol) of phoran was refluxed in 100 ml of toluene for 3 d. The solution was cooled to room temperature and concentrated to 10 ml. Chromatography on SiO_2 (column 8 × 2 cm) gave 0.78 g (78%) of unreacted redbrown starting material eluted with toluene, followed by a dark red band with toluene/acetone 1/1. Repeated chromatography of the second band with toluene/acetone 3/1 as eluent resulted in the isolation of violet-brown VI. Recrystallization from toluene/pentane 1/1 gave 105 mg (8% yield) of black shining crystals.

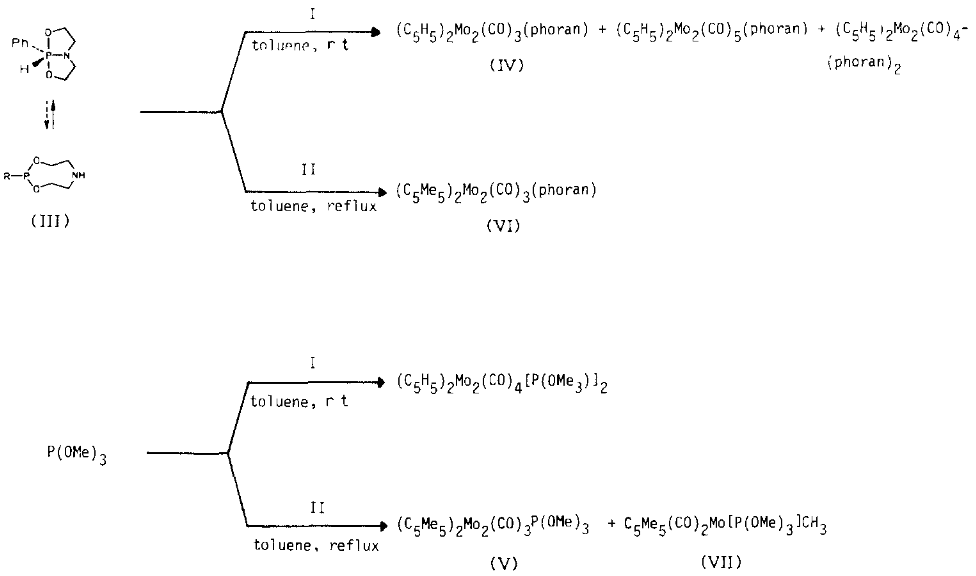
Anal. Found: C, 52.35; H, 6.08; Mo, 25.75; N, 2.15; mol wt. 749 (^{92}Mo). $C_{33}H_{44}Mo_2NO_5P$ calcd.: C, 52.35; H, 5.85; Mo, 25.33; N, 1.85%; mol wt. 757.54. IR (cm^{-1}, CH_2Cl_2) 1871s, 1777vs. ^{1}H NMR ($CDCl_3$) $\delta(CH_3)$ 1.58(s), 1.86(s); $\delta(CH_2N)$ 3.03(m); $\delta(CH_2O)$ 3.92(m); $\delta(C_6H_5)$ 7.38(m), 7.96(m).

Attempted reaction of V or VI with CO. A solution containing 100 mg of either V or VI in 50 ml of toluene was stirred for 1 h at room temperature with CO bubbling through the solution. After concentration to 10 ml the solution was transferred to SiO_2 (column 8 × 2 cm). In the case of $(C_5Me_5)_2Mo_2(CO)_3P(OMe)_3$ a broad orange band was eluted with toluene and shown by its IR spectrum to be $[C_5Me_5(CO)_3Mo]_2$, which was formed in nearly quantitative yield. When $(C_5Me_5)_2Mo_2(CO)_3$(phoran) was used as the starting material a reaction occurred, but all the product remained absorbed at the top of the SiO_2 column, even when elution with toluene/acetone 1/1 was attempted.

Results and discussion

Reactivity of $[C_5Me_5(CO)_2Mo]_2$ *with phosphorus ligands*

In contrast to $[C_5H_5(CO)_2Mo]_2$, which reacts with $P(OMe)_3$ [12] or phoran [11] even at room temperature, refluxing in toluene was required with $[C_5Me_5(CO)_2Mo]_2$ (Scheme 1). The complexes isolated were shown by means of analytical and spectroscopic data to have the compositions $(C_5Me_5)_2Mo_2(CO)_3[P(OMe)_3]$ (V), and $(C_5Me_5)_2Mo_2(CO)_3$(phoran) (VI), respectively. In the IR spectra (KBr pellets) the presence of semi-bridging CO groups is indicated by strong absorptions at 1869, 1789, and 1771 cm^{-1} (V), and at 1856, 1787, and 1755 cm^{-1} (VI), while in the ^1H NMR spectra the different chemical shifts of the cyclopentadienyl methyl protons establish in both cases the different chemical environment of the two Mo atoms. From spectroscopic data it is obvious that the nature of the Mo≡Mo core is the same in complexes V and VI, although the two reactions appeared to proceed differently. In the case of $P(OMe)_3$ all the starting material II was consumed, but some dark, unidentified material remained at the top of the column. On the other hand considerable amounts of II were still recovered after, for example, three days of refluxing under the same conditions when phoran was employed as the ligand, even when the latter was used in a tenfold excess.



SCHEME 1. Comparison between the reactions of $[C_5H_5(CO)_2Mo]_2$ (I), and $[C_5Me_5(CO)_2Mo]_2$ (II), with PR_3 ligands

Furthermore the reaction with $P(OMe)_3$ seems to be highly concentration dependent. When a six times more concentrated solution of $[C_5Me_5(CO)_2Mo]_2$ and $P(OMe)_3$ was refluxed in 100 ml of toluene, the standard volume used in all the experiments described here, only a very small amount of complex V was present in the products, and instead a yellow complex analyzing as $C_5Me_5(CO)_2Mo[P(OMe)_3]CH_3$ (VII) was isolated in more than 50% yield. The ^1H NMR spectrum showed this compound to exist as *cis/trans* isomers, as was found earlier in the case of the unsubstituted cyclopentadienyl complex [14]; the isomer ratio of 62/38 was readily established by integration of the methyl signals. A Michaelis–Arbuzov-like rearrangement has been proposed in interpretation of the similar formation of $C_5H_5Mo(CO)_2[P(OMe)_3]CH_3$ along with $C_5H_5Mo(CO)_2[P(OMe)_3][P(O)(OR)_2]$ in the reaction of $[C_5H_5Mo(CO)_3]_2$ with excess $P(OMe)_3$ [15]. No complex containing the phosphonate ligand was be detected in the present case, however. In contrast, phoran which is a phosphonite ligand, does not take part in such a rearrangement.

It is of interest to note, when comparing the reactions described here with those of $[C_5H_5(CO)_2Mo]_2$ with the same ligands, that only CO-replacement products were obtained (Scheme 1). Neither the pentamethylcyclopentadienyl analogues of $(C_5H_5)_2Mo_2(CO)_4[P(OMe)_3]_2$ [12] nor those of $[C_5H_5(CO)_2Mo(phoran)]_2$ and $(C_5H_5)_2(CO)_5Mo_2(phoran)$ [11] were observed. Attempts to prepare $(C_5Me_5)_2(CO)_5Mo_2PR_3$ complexes by subsequent addition of carbon monoxide to the Mo≡Mo triple bond in V or VI (room temp., 1 bar) resulted either (i) (for $PR_3 = P(OMe)_3$) in the formation of $[C_5Me_5(CO)_3Mo]_2$ in nearly quantitative yield, or (ii) (for PR_3 = phoran) in mixtures from which no neutral product could be isolated, even though all the starting material was consumed. The stability of the CO-addition products thus appears to be much lower than that of their cyclopentadienyl homologs. This may be due to the enhanced steric crowding resulting from the introduction of two additional ligands, which would then lead to elimination of the $P(OMe)_3$ ligand or to heterolysis of the metal–metal bond. The latter alternative is probably responsible for the formation of the mononuclear compound VII isolated from the reaction of II with an excess of $P(OMe)_3$, but it is not yet clear why the ratio of binuclear to mononuclear complexes VI/VII formed is dependent on the concentration.

The isolation of complexes V and VI containing additional bulky ligands at the Mo≡Mo bond is particularly noteworthy in view of the previously reported inertness of $[C_5Me_5(CO)_2Mo]_2$ towards phosphorus ligands [2b], which was ascribed to a blocking of the access to the metal sites by the bulky pentamethylcyclopentadienyl groups.

X-ray diffraction analysis of $(C_5Me_5)_2Mo_2(CO)_3(phoran)$

Because of the considerable crowding expected in VI, and the distinctly different structures of the parent compounds I and II [13], it seemed desirable to carry out an X-ray structural investigation of this molecule in order to compare the result with the structure of $(C_5H_5)_2Mo_2(CO)_3(phoran)$ IV [11]. Figures 1 and 2 show an ORTEP drawing of the structure of VI and the numbering scheme, which is identical to that earlier used for complex IV. The atomic parameters, bond distances and bond angles of VI are given in Tables 1–3.

Although the Mo≡Mo distance of 2.527(1) Å in VI is larger than that in IV (2.506(1) Å), it nevertheless lies within the range accepted for triple bond interactions. For the rest, the differences between VI and IV are, surprisingly, much smaller, where the environment of the Mo≡Mo center is concerned, than in the structures of their corresponding parent compounds $[C_5H_5(CO)_2Mo]_2$ [16] and

TABLE 1

POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS OF $(C_5Me_5)_2Mo_2(CO)_3$(phoran) (esd's are given in parentheses)[a]

Atom	x	y	z	B (Å^2)
Mo(1)	0.6556(7)	0.0895(4)	0.8386(6)	2.74(2)
Mo(2)	0.4343(7)	0.1295(4)	0.7660(6)	2.59(2)
P	0.5689(2)	0.1843(1)	0.9558(2)	3.09(8)
N	0.7160(8)	0.0978(5)	1.2303(7)	6.1(3)
O(1)	0.5066(5)	0.1893(3)	1.0124(4)	3.5(2)
O(2)	0.7263(5)	0.1595(3)	1.0733(4)	3.7(2)
O(3)	0.5998(6)	0.2172(3)	0.7300(5)	5.1(2)
O(4)	0.4318(6)	0.0399(4)	0.5695(5)	5.9(3)
O(5)	0.4702(5)	0.5135(3)	0.5772(5)	4.8(2)
C(1)	0.8042(9)	0.1868(6)	1.1973(7)	4.7(4)
C(2)	0.8373(1)	0.1364(6)	1.2826(8)	5.8(4)
C(3)	0.4758(8)	0.1369(5)	1.0456(7)	3.9(3)
C(4)	0.5917(9)	0.1265(6)	1.1857(8)	5.1(4)
C(5)	0.2023(8)	0.1144(5)	0.6742(7)	3.8(3)
C(6)	0.2078(8)	0.0971(5)	0.5885(7)	3.7(3)
C(7)	0.2375(8)	0.1511(5)	0.5573(7)	3.7(3)
C(8)	0.2514(8)	0.2001(5)	0.6252(7)	3.8(3)
C(9)	0.2263(8)	0.1777(5)	0.6951(7)	3.8(3)
C(10)	0.7955(8)	0.0316(5)	0.8310(7)	3.7(3)
C(11)	0.8603(8)	0.0896(5)	0.8826(7)	3.7(3)
C(12)	0.9018(7)	0.0956(5)	0.9998(7)	3.6(3)
C(13)	0.8594(7)	0.0414(5)	1.0155(7)	3.7(3)
C(14)	0.7934(8)	0.0025(5)	0.9116(7)	3.9(3)
C(15)	0.6084(8)	0.1700(5)	0.7703(7)	3.8(3)
C(16)	0.5066(7)	0.0610(5)	0.6695(7)	3.6(3)
C(17)	0.4955(8)	0.5581(5)	0.6323(7)	3.4(3)
C(18)	0.6014(8)	0.2654(5)	0.9627(5)	3.8(3)
C(19)	0.7066(9)	0.2806(6)	0.9708(7)	5.1(4)
C(20)	0.734(1)	0.3438(6)	0.9747(8)	6.8(4)
C(21)	0.658(1)	0.3870(6)	0.9704(8)	6.8(4)
C(22)	0.553(1)	0.3707(6)	0.9632(9)	6.4(5)
C(23)	0.528(1)	0.3091(5)	0.9626(8)	4.9(4)
C(24)	0.1618(8)	0.0735(5)	0.7233(7)	4.9(3)
C(25)	0.1678(9)	0.0351(5)	0.5290(8)	4.7(4)
C(26)	0.2364(9)	0.1565(6)	0.4586(7)	5.0(3)
C(27)	0.2720(9)	0.2665(5)	0.6103(9)	5.2(4)
C(28)	0.2032(8)	0.2170(6)	0.7590(7)	4.8(3)
C(29)	0.7438(9)	−0.0612(5)	0.8974(9)	5.3(4)
C(30)	0.7512(9)	0.0033(6)	0.7182(7)	5.1(4)
C(31)	0.8897(8)	0.1348(6)	0.8300(7)	5.2(3)
C(32)	0.9868(9)	0.1478(5)	1.0915(8)	4.8(4)
C(33)	0.8872(8)	0.0272(6)	1.1281(7)	5.1(3)

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

$[C_5Me_5(CO)_2Mo]_2$ [13]. Thus, there are no significant changes in the distances of the metal atoms from the C_5H_5 and the C_5Me_5 planes, in the Mo(1)–P bond length, nor in the degree of bridging character of the carbonyls (Tables 2, 3). Probably as a result of larger steric crowding at Mo(1), the Mo(2)–Mo(1)–Cp angle decreases

TABLE 2

SELECTED BOND LENGTHS (d, Å) OF $(C_5Me_5)_2Mo_2(CO)_3$(phoran)

Mo(1)–Mo(2)	2.527(1)
Mo(1)–P	2.386(2)
Mo(1)–C(5)	2.403(6)
Mo(1)–C(6)	2.325(6)
Mo(1)–C(7)	2.317(6)
Mo(1)–C(8)	2.367(6)
Mo(1)–C(9)	2.450(6)
Mo(1)–C(15)	2.518(7)
Mo(1)–C(16)	2.775(8)
Mo(1)–C(17)	1.927(8)
Mo(1)–Cp′(1(cent))	2.03
Mo(2)–C(10)	2.387(6)
Mo(2)–C(11)	2.374(6)
Mo(2)–C(12)	2.347(6)
Mo(2)–C(13)	2.324(6)
Mo(2)–C(14)	2.340(6)
Mo(2)–C(15)	1.931(8)
Mo(2)–C(16)	1.926(8)
Mo(2)–C(17)	2.528(6)
Mo(2)–Cp′(2(cent))	2.01
P–O(1)	1.617(4)
P–O(2)	1.617(4)
P–C(18)	1.833(7)
C(15)–O(3)	1.177(7)
C(16)–O(4)	1.174(7)
C(17)–O(5)	1.182(7)

TABLE 3

SELECTED BOND ANGLES (ω, deg) OF $(C_5Me_5)_2Mo_2(CO)_3$(phoran)

Mo(2)–Mo(1)–P	91.07(4)
Mo(2)–Mo(1)–C(17)	67.6(2)
Mo(2)–Mo(1)–Cp′(1(cent))	151.1
P–Mo(1)–C(17)	85.6(2)
Mo(1)–Mo(2)–C(15)	67.2(2)
Mo(1)–Mo(2)–C(16)	75.8(2)
Mo(1)–Mo(2)–Cp′(2(cent))	168.0
C(15)–Mo(2)–C(16)	87.1(3)
Mo(2)–C(15)–O(3)	167.0(6)
Mo(2)–C(16)–O(4)	169.9(5)
Mo(1)–C(17)–O(5)	171.1(5)
Mo(1)–P–O(1)	117.6(2)
Mo(1)–P–O(2)	115.5(2)
Mo(1)–P–C(18)	120.6(2)
O(1)–P–O(2)	102.4(2)
O(1)–P–C(18)	96.0(3)
O(2)–P–C(18)	101.3(3)

slightly from 154.6 to 151.9° in VI, whereas the Mo(1)–Mo(2)–Cp angle increases from 163.9 in IV to 168° in VI.

The most striking structural difference between complexes IV and VI concerns the arrangement of the phoran ligand, which otherwise has nearly the same bond parameters in both cases with respect to the Mo–Mo axis. In IV this ligand, which is bound to Mo(1), is oriented in such a way that its phenyl group points towards the C_5H_5 ring attached to Mo(2). This gives rise to a definite anisotropic shielding effect on the corresponding C_5H_5 ligand, as can be observed in the ^1H NMR spectrum in solution [11]. In the case of VI, a similar orientation would bring the phoran ligand into unacceptably short intramolecular contacts with the methyl groups of the cyclopentadienyl ligand. In order to avoid this, the ligand is moved around the P–Mo bond by about 90°, the mean Ph–P–N plane becoming perpendicular to the Mo–Mo axis. It thus appears that it is the more flexible phoran ligand, and not the organometallic core, which adjusts its conformation and orientation so as to ease the additional steric constraints introduced in complex VI by the pentamethylcyclopentadienyl groups.

Crystal structures are available for $[C_5H_5(CO)_2Cr]_2$ [17], $[C_5Me_5(CO)_2Cr]_2$ [18], $[C_5Me_5(CO)_2Mo]_2$ [13], and $[C_5H_5(CO)_2Mo]_2$ [16], which all contain the CpM≡MCp moiety, but only the last complex has a linear Cp–M–M–Cp axis. Electronic factors were held to be responsible for this [16]. Bending of the Cp–M–M–Cp axis in the PR_3 substituted complexes $(C_5H_5)_2Mo_2(CO)_3$(phoran), [11] $(C_5H_5)_2Mo_2(CO)_3$-$P(OMe)_3$ [11] and $(C_5Me_5)_2Mo_2(CO)_3$(phoran) seems to be reasonable in view of the steric requirements of the bulky phoran ligand. Fortunately the crystal structures of the above-mentioned PR_3 complexes do not display any structural disorder of the type of those which prevented a proper stereochemical analysis of the semibridging character of the carbonyls in the case of the $[C_5R_5(CO)_2M]_2$ dimers (M = Cr, Mo; R = H, Me) [13]. Taking into account the $\sigma + \pi$ bonding mode for the CO groups [16], their σ-C–M–M bond angles vary from 67.1(2) to 75.9(2)° in IV [11] and VI, as well as in $(C_5H_5)_2Mo_2(CO)_3P(OMe)_3$ [11]. Thus, they fall into the range covered by their precursors I [16] and II [13]. But it must be noted that the largest M–M–C angle is found for carbonyl group C(15) in IV whereas it is for carbonyl C(16) in complex VI. As there is evidence for the fluxional behavior of the carbonyls in

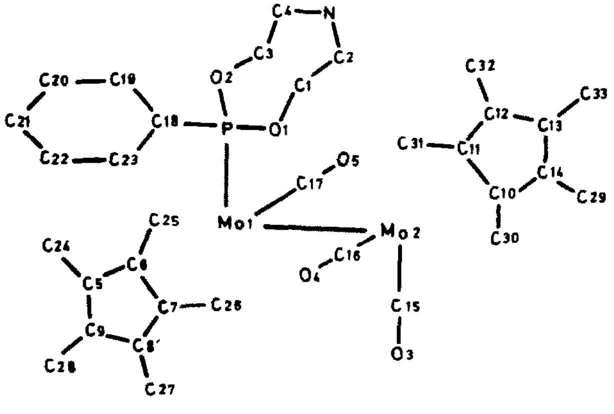


Fig. 1. Numbering scheme of $(C_5Me_5)_2Mo_2(CO)_3$(phoran).

solution for $(C_5H_5)_2(CO)_4MoW$ [19] and $(C_5H_5)_2Mo_2(CO)_3$(phoran) [11] from dynamic ^{13}C NMR spectroscopy, the arrangement found in the solid state may be regarded as a "stop-action" photograph which lies within the limits of 66.0(5)°, found in for $[C_5H_5(CO)_2Mo]_2$ [16], and 75.9(2)°, found for IV [11].

In an attempt to correlate the structural findings and infrared carbonyl vibration data, intramolecular and intermolecular steric forces were assumed to be predominantly responsible for the bridging character of the carbonyls [20]. In the dissymmetrically substituted complexes IV–VI the CO stretching frequencies are considerably lower than in their precursors I or II. Therefore, reduced π-electron density in the C–O bonds may be assumed, arising from enhanced electron density at the Mo atom bearing the phosphorus ligand, which leads to enhanced back donation from metal *d*-orbitals into π^*-C–O orbitals. This interpretation is also consistent with the fact that the σ-M–C bonds are 0.1–0.2 Å shorter in complexes IV–VI than in their respective parent compounds. But it is also of interest to note that the corresponding M–M–C angles, which are indicative of C–O to metal π-interactions, [16] remain practically unaffected. These results are not sufficient to account for the semibridging nature of the carbonyls attached to metal–metal multiple bonds in terms of one of the two proposals described in the literature, [16,21], but they show that electronic effects cannot be neglected in the discussion.

In conclusion, dissymmetrically substituted compounds containing the $C_5Me_5Mo{\equiv}MoC_5Me_5$ core are now available from the reaction of $[C_5Me_5(CO)_2Mo]_2$ with $P(OMe)_3$ or phoran. This contrasts with previously reported results, which led to the belief that phosphorus ligands were inert with respect to $[C_5Me_5(CO)_2Mo]_2$. Furthermore it has been shown that, despite their different molecular structures, $[C_5H_5(CO)_2Mo]_2$ and $[C_5Me_5(CO)_2Mo]_2$ exhibit closer chemical behavior with

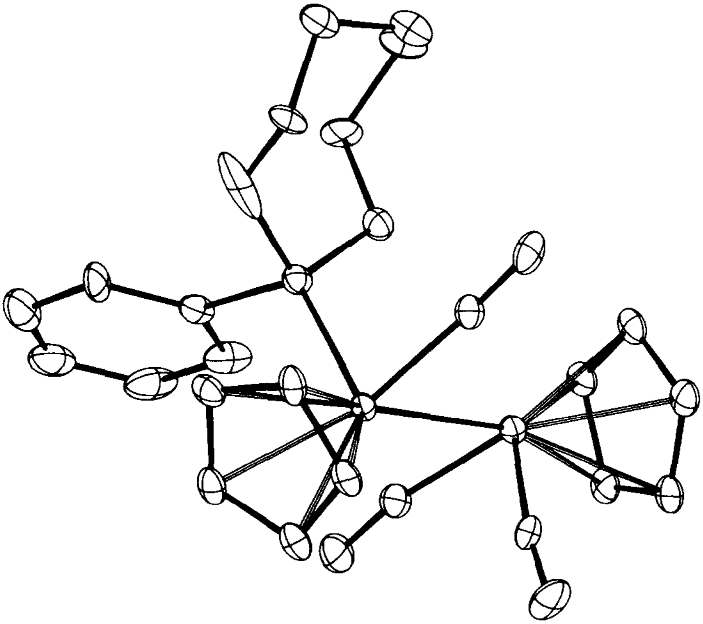


Fig. 2. Perspective drawing of $(C_5Me_5)_2Mo_2(CO)_3$(phoran), the methyl groups of the C_5Me_5 ligands are omitted for clarity.

respect to these ligands than would have been expected. It is noteworthy that the arrangement of the bonds around the Mo≡Mo core is closer for IV and VI than for the pentamethylated and unsubstituted cyclopentadienyl parent compounds, and that it is the more flexible phosphorus ligand that adjusts to the new steric conditions by adopting different configurations.

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