

**PREPARATION OF $cis\text{-Mo}(\text{CO})_2(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)_2$ ($n = 1, 2, 3$)
 FROM $cis\text{-DICARBONYLBIS(NORBORNADIENE)MOLYBDENUM}$
 AND CRYSTAL STRUCTURE OF $[cis\text{-Mo}(\text{CO})_2(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)_2]$**

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Summary

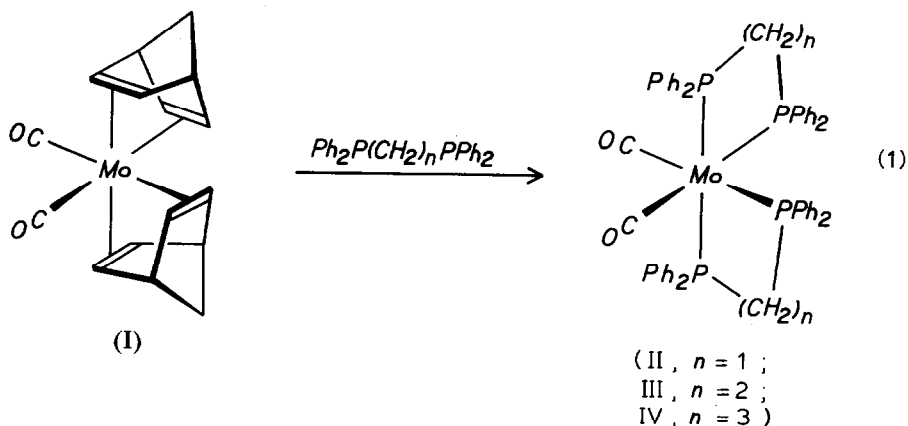
The complexes $cis\text{-Mo}(\text{CO})_2(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)_2$ ($n = 1, 2, 3$) are synthesized by heating benzene solutions of $cis\text{-dicarbonylbis(norbornadiene)molybdenum}$ and the corresponding diphosphines. The X-ray structural analysis of $cis\text{-Mo}(\text{CO})_2\text{-}(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)_2$ is reported, with the following crystal data: $\text{C}_{56}\text{H}_{52}\text{MoO}_2\text{P}_4 \cdot 2\text{CH}_2\text{Cl}_2 \cdot 0.5\text{C}_6\text{H}_{14}$, mol wt. 1189.81, monoclinic, space group $P2_1/n$, a 15.643(2), b 21.453(7), c 17.105(3) Å, β 100.75(1)°, V 5639.59 Å³, $Z = 4$, D_c 1.39, D_m 1.36 g/cm³.

Introduction

Norbornadiene (NBD) has been used as an intermediate bidentate in the syntheses of many transition metal complexes. The labile nature of NBD makes it readily replaceable by stronger ligands. A series of such labile ligands is known, e.g. tetrahydrofuran [1] and acetonitrile [2] as two-electron donors, NBD [2,3] and 1,5-cyclooctadiene [4] as four-electron donors, benzene and mesitylene [5,6] as six-electron donors. Accordingly, complexes such as $\text{M}(\text{CO})_5\text{L}$, $\text{M}(\text{CO})_4\text{L}_2$, and $\text{M}(\text{CO})_3\text{L}_3$ for Group VIB metals can be viewed as active species, of $[\text{M}(\text{CO})_5]$, $[\text{M}(\text{CO})_4]$ and $[\text{M}(\text{CO})_3]$, respectively. These intermediate complexes sometimes play a crucial role in syntheses since they provide a milder route to the target compounds. Most of them are stable enough to be stored at 25°C before use.

Recently we have synthesized a molybdenum carbonyl complex with two NBD ligands, i.e. $cis\text{-Mo}(\text{CO})_2(\text{NBD})_2$ (I) [7,8]. It is a stable complex and can be made quite easily in large quantities. The two NBD ligands together supply eight electrons to the metal, thus it may serve as an entry for preparing complexes containing a $[\text{Mo}(\text{CO})_2]$ moiety. It had been recognized that molybdenum carbonyls containing a smaller number of CO's are generally more difficult to prepare. In this report we demonstrate the potential versatility of I in ligand exchange reactions by utilizing it in the synthesis of three diphos complexes; i.e. $cis\text{-dicarbonylbis[bis(diphe-$

nylphosphino)methane]molybdenum (*cis*-Mo(CO)₂(DPM)₂, II) [9,10], *cis*-dicarbonylbis[1,2-bis(diphenylphosphino)ethane]molybdenum (*cis*-Mo(CO)₂(DPE)₂, III) [11-13], and *cis*-dicarbonylbis[1,3-bis(diphenylphosphino)propane]molybdenum (*cis*-Mo(CO)₂(DPP)₂, IV). The preparation of IV has been described previously [14], but lacks the details of structural information. Aided by the present method we were able to produce single crystals of good quality for X-ray diffraction structural analysis.



Experimental

Uncorrected melting points were determined using a Yamato MP-21. Infrared spectra were recorded on a Perkin-Elmer 297 infrared spectrophotometer. Mass spectra were carried out on a JEOL JMS-D300 mass spectrometer.

Norbornadiene was purchased from Alfa Products and was distilled before use. Hexacarbonylmolybdenum was purchased from Merck, and the ligands DPM, DPE and DPP were purchased from Strem Chemicals. They were used as received.

Dicarbonylbis(norbornadiene)molybdenum (I)

A solution of norbornadiene (1.00 g, 11 mmol) and hexacarbonylmolybdenum (1.00 g, 3.80 mmol), in 25 ml of petroleum ether was refluxed in a round bottomed flask, under nitrogen for 40 h and cooled. The resultant dark-brown precipitate was extracted several times with n-hexane. All the liquid portions were combined and evaporated to dryness. Complex I was directly recrystallized from n-hexane to form light yellow needles, m.p. 85°C (585 mg, 1.74 mmol, 46%). The crystal was quite stable under nitrogen at room temperature, but decomposed very slowly in air. It darkens after a few hours when dissolved in chloroform or benzene, but stays intact in methanol in a sealed tube for 20 d at 0°C. ¹H NMR (CDCl₃): δ 5.6 (t, 1H, *J* 4 Hz), 5.1 (t, 1H, *J* 4 Hz), 3.7 and 3.5 (2m's, 2H), 2.2 (t, 1H, *J* 4 Hz), 2.2 (t, 1H, *J* 4 Hz), 1.2 (AB pattern with multiplets, 2H, *J* 8 Hz). IR (KBr): ν(CO) 1880s, 1930s cm⁻¹. MS: *m/z* 338 (*M*⁺ for Mo = 98), 310 (*M*⁺ - CO), 278, 254, 241, 228, 214, 203, 188. Anal. Found: C, 57.51; H, 4.76. C₁₆H₁₆MoO₂ calcd.: C, 57.10; H, 4.76%.

cis-Dicarbonylbis[bis(diphenylphosphino)methane]molybdenum (II)

The procedures were similar to those outlined for complex IV. Refluxing a benzene solution of I (100 mg, 0.30 mmol) and bis(diphenylphosphino)methane (290

mg, 0.76 mmol) for 32 h produced II as yellow solids (69 mg, 0.075 mmol, 25% yield). It decomposed (crystals turned dark-brown) gradually over 175°C. IR (KBr): $\nu(\text{CO})$ 1780s, 1850s cm^{-1} . MS: m/z 922 (M^+ for Mo = 98), 894 ($M^+ - \text{CO}$), 866 ($M^+ - 2\text{CO}$), 482 ($M^+ - 2\text{CO} - \text{DPM}$), 384 (DPM).

cis-Dicarbonylbis[1,2-bis(diphenylphosphino)ethane]molybdenum (III)

The procedures were also similar to those described for complex IV. A benzene solution of I (100 mg, 0.30 mmol) and 1,2-bis(diphenylphosphino)ethane (300 mg, 0.76 mmol) was refluxed for 40 h. The yellow solids (210 mg crude) were recrystallized from benzene/methanol to yield 150 mg (0.16 mmol, 52%), m.p. 258°C (decomp.) (lit. 324–325°C [11]). IR (KBr): $\nu(\text{CO})$ 1780s, 1850s cm^{-1} . MS: m/z 950 (M^+ for Mo = 98), 922 ($M^+ - \text{CO}$).

cis-Dicarbonylbis[1,3-bis(diphenylphosphino)propane]molybdenum (IV)

A two-necked round-bottomed flask containing complex I (103 mg, 0.31 mmol) and 1,3-bis(diphenylphosphino)propane (318 mg, 0.77 mmol) was fitted with a refluxing condenser and a nitrogen inlet. The system was purged with nitrogen twice and then freshly distilled benzene was added by syringe to the flask. The solution was refluxed for 40 h. The color of the solution changed gradually from light-yellow to orange with the formation of a yellow precipitate. It was cooled and benzene was evaporated off using a rotary evaporator. The solid was washed three times with benzene/n-hexane ($v/v = 1/2$) to remove unreacted diphosphine. Complex IV was recrystallized from dichloromethane/n-hexane. The yellow crystal, (240 mg, 65% yield corrected for incorporated solvent molecules) was found to contain 2.0 mol of dichloromethane as well as 0.5 mol of n-hexane in its lattice. It decomposed at 137°C with vigorous effervescence. IR (KBr): $\nu(\text{CO})$ 1785s, 1860s cm^{-1} . MS: m/z 978 (M^+ for Mo = 98), 950 ($M^+ - \text{CO}$).

Crystal data for cis-Mo(CO)₂(Ph₂P(CH₂)₃PPh₂)₂. C₅₆H₅₂MoO₂P₄ · 2CH₂Cl₂ · 0.5C₆H₁₄, mol. wt. 1189.81, monoclinic, space group $P2_1/n$, a 15.643(2), b 21.453(7), c 17.105(3) Å, β 100.75(1)°, V 5639.59 Å³, $Z = 4$, D_c 1.39, D_m 1.36 g/cm³, (Mo- K_α) 0.7093 Å, μ 5.73 cm^{-1} , $F(000) = 2439.61$.

Collection and reduction of X-ray data

A chunky yellow crystal, of $0.2 \times 0.2 \times 0.4$ mm, was used for data collection. Diffraction data were collected on a CAD4 diffractometer using graphite-monochromated Mo- K_α radiation. Unit cell dimensions were determined from a least-squares refinement of 25 carefully centered reflections ($20.6^\circ < 2\theta < 26.7^\circ$). Intensity data within $2\theta < 52^\circ$ were collected at various scan speeds of 20/3–20/17° s^{-1} by using $\omega-2\theta$ scan techniques, with a scan range calculated according to the expression $0.6 + 0.35 \tan \theta$. Stationary background measurements were taken before, and after each scan for a period of time equal to a 0.25 of the scan time. The three intensity monitors were checked every 2 h and were fluctuated randomly within 5% over the entire collection. After correction for background, the intensities were reduced to F and $\sigma(F)$ according to counting statistics, and the weights were assigned as $1/\sigma^2(F)$. Of 7902 total reflections, 4786 had $I > 3\sigma(I)$ and were considered as observations. Intensity data were corrected for Lorentz-polarization effects and elliptical absorption.

TABLE 1

FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS FOR THE CRYSTAL OF IV (2.0 mol of dichloromethane (labeled C(9), Cl(1), Cl(2), and C(10), Cl(3), Cl(4)) and 0.5 mol of n-hexane (labeled C(91), C(92), and C(93)) are contained in the lattice)

Atom	x	y	z	B_{iso}
Mo	0.27389(5)	0.14408(4)	0.13923(5)	2.34(3)
P(1)	0.3970(2)	0.1367(1)	0.0681(2)	3.0(1)
P(2)	0.3527(2)	0.0587(1)	0.2302(2)	3.0(1)
P(3)	0.1684(2)	0.0641(1)	0.0601(2)	2.7(1)
P(4)	0.1575(2)	0.1664(1)	0.2154(2)	2.8(1)
O(1)	0.3587(4)	0.2595(3)	0.2290(4)	4.6(5)
O(2)	0.2127(5)	0.2530(3)	0.0238(4)	4.9(4)
C(1)	0.3309(6)	0.2132(4)	0.1977(6)	2.8(5)
C(2)	0.2318(6)	0.2099(4)	0.0643(6)	3.1(5)
C(3)	0.4656(6)	0.0657(5)	0.0696(6)	3.3(5)
C(4)	0.4894(6)	0.0300(5)	0.1471(6)	3.9(6)
C(5)	0.4122(6)	0.0025(4)	0.1794(6)	3.4(5)
C(6)	0.0835(6)	0.0315(4)	0.1099(6)	3.2(5)
C(7)	0.0288(6)	0.0775(5)	0.1478(6)	3.7(6)
C(8)	0.0760(6)	0.1064(5)	0.2256(6)	3.6(5)
C(11)	0.3808(6)	0.1496(4)	-0.0418(6)	3.6(5)
C(12)	0.2952(6)	0.1538(4)	-0.0856(6)	3.7(6)
C(13)	0.2818(8)	0.1622(5)	-0.1683(7)	5.5(8)
C(14)	0.3535(9)	0.1669(6)	-0.2054(7)	6.4(9)
C(15)	0.4383(8)	0.1630(5)	-0.1611(7)	5.6(8)
C(16)	0.4540(7)	0.1555(5)	-0.0788(6)	5.1(7)
C(21)	0.4791(6)	0.1980(5)	0.0992(6)	3.7(5)
C(22)	0.5617(6)	0.1869(5)	0.1434(6)	4.4(7)
C(23)	0.6176(7)	0.2387(6)	0.1667(7)	5.6(9)
C(24)	0.5909(7)	0.2989(6)	0.1468(7)	5.6(7)
C(25)	0.5078(7)	0.3104(5)	0.1020(7)	5.4(7)
C(26)	0.4527(7)	0.2608(5)	0.0780(7)	4.5(7)
C(31)	0.4423(6)	0.0792(5)	0.3129(6)	3.4(5)
C(32)	0.4820(6)	0.1379(5)	0.3132(6)	3.8(6)
C(33)	0.5534(7)	0.1527(5)	0.3737(7)	4.9(7)
C(34)	0.5835(7)	0.1097(6)	0.4330(7)	5.8(9)
C(35)	0.5473(7)	0.0502(7)	0.4306(7)	6.1(10)
C(36)	0.4745(7)	0.0354(5)	0.3724(6)	4.7(6)
C(41)	0.2879(6)	0.0048(4)	0.2796(6)	3.6(6)
C(42)	0.2574(7)	-0.0504(5)	0.2401(7)	4.6(8)
C(43)	0.2071(7)	-0.0910(5)	0.2774(8)	5.6(9)
C(44)	0.1868(8)	-0.0762(6)	0.3507(8)	7.0(9)
C(45)	0.2700(7)	0.0176(5)	0.3551(7)	5.2(7)
C(46)	0.2186(9)	-0.0229(6)	0.3908(9)	7.9(10)
C(51)	0.2057(6)	-0.0095(4)	0.0212(6)	3.1(5)
C(52)	0.1750(7)	-0.0681(5)	0.0399(7)	4.3(6)
C(53)	0.2061(8)	-0.1225(5)	0.0079(8)	5.7(8)
C(54)	0.2649(8)	-0.1186(5)	-0.0449(8)	5.8(8)
C(55)	0.2944(7)	-0.0591(5)	-0.0642(7)	5.0(7)
C(56)	0.2662(6)	-0.0049(5)	-0.0303(6)	3.4(5)
C(61)	0.1007(6)	0.0967(4)	-0.0314(6)	2.9(5)
C(62)	0.0930(6)	0.0676(5)	-0.1050(6)	3.6(5)
C(63)	0.0436(7)	0.0959(5)	-0.1727(7)	4.6(7)
C(64)	0.0001(7)	0.1532(6)	-0.1664(7)	5.2(7)
C(65)	0.0065(7)	0.1815(5)	-0.0937(7)	4.8(8)

TABLE 1 (continued)

Atom	x	y	z	B_{iso}
C(66)	0.0577(6)	0.1541(4)	-0.0241(7)	4.0(7)
C(71)	0.1868(6)	0.1877(4)	0.3221(5)	3.0(5)
C(72)	0.2716(6)	0.1807(5)	0.3617(6)	3.5(5)
C(73)	0.2922(7)	0.1926(5)	0.4439(6)	4.4(6)
C(74)	0.2266(7)	0.2118(5)	0.4846(6)	4.6(7)
C(75)	0.1407(7)	0.2204(5)	0.4432(6)	4.6(7)
C(76)	0.1212(7)	0.2086(5)	0.3624(6)	4.2(6)
C(81)	0.0887(6)	0.2345(4)	0.1799(5)	3.1(5)
C(82)	-0.0032(6)	0.2313(5)	0.1581(6)	3.7(6)
C(83)	-0.0495(7)	0.2860(5)	0.1293(6)	4.6(7)
C(84)	-0.0069(7)	0.3411(5)	0.1237(7)	4.9(7)
C(85)	0.0837(7)	0.3451(5)	0.1454(7)	4.9(7)
C(86)	0.1321(7)	0.2915(5)	0.1745(6)	4.0(6)
C(9)	0.8114	0.4907	0.1882	13.3
Cl(1)	0.7717	0.4318	0.1004	11.0
Cl(2)	0.7339	0.4862	0.2366	17.1
C(10)	0.8471	0.1766	0.3723	17.5
Cl(3)	0.8246	0.1272	0.4346	14.0
Cl(4)	0.8328	0.1561	0.2748	15.4
C(91)	0.5254(12)	0.4803(9)	0.0345(11)	12.0(6)
C(92)	0.4591(13)	0.5492(10)	0.0438(13)	15.0(7)
C(93)	0.5160(11)	0.5002(9)	0.1127(11)	11.2(5)

Solution and refinement of structure

All the calculations were carried out using the NRCC SDP PDP-11 package [15]; ORTEP from Enraf-Nonius structure determination package [16], on a PDP-11/23 computer. The molybdenum atom was located from a Patterson map, subsequent Fourier syntheses based on the heavy atom revealed the position of the non-hydrogen atoms of the complex. The solvent molecules of dichloromethane and n-hexane and the H atoms of the complex were found on difference Fourier synthesis. The final least-squares cycle with anisotropic thermal parameters for all non-hydrogen atoms of the complex and isotropic thermal parameters of the n-hexane gave R and R_w factors of 6.84% and 6.88%, respectively. The positional and isotropic thermal parameters of all the atoms are given in Table 1. Tables of anisotropic thermal parameters and structure factors may be obtained from the authors.

Results and discussion

The methods used for the preparation of II, III were either directly from $\text{Mo}(\text{CO})_6$ [9] or via intermediates like $\text{Mo}(\text{CO})_4(\text{diphos})$ [10,11] and $\text{Mo}(\text{N}_2)_2(\text{diphos})_2$ [17]. It had been recognized that expulsion of carbonyl groups from $\text{Mo}(\text{CO})_6$ by phosphines proceeds stepwise with increasing difficulty [11]. Therefore it requires a relatively high temperature to produce the dicarbonylmolybdenum species. Ligand exchanges on NBD of I have thus provided an alternative route for its preparation at a lower temperature.

The reactions were observed to proceed slowly, even at room temperature, after I and the diphosphines were mixed. However, all the reactions were carried out by refluxing in benzene for a prolonged period of time, to ensure a complete exchange

TABLE 2
BOND LENGTHS (Å) AND BOND ANGLES (°) OF IV

Mo–P(1)	2.468(2)	Mo–P(2)	2.564(2)	Mo–P(3)	2.582(2)
Mo–P(4)	2.476(2)	Mo–C(1)	1.913(8)	Mo–C(2)	1.938(9)
P(1)–C(3)	1.861(9)	P(1)–C(11)	1.87(1)	P(1)–C(21)	1.844(9)
P(2)–C(5)	1.84(1)	P(2)–C(31)	1.849(9)	P(2)–C(41)	1.844(9)
P(3)–C(6)	1.844(9)	P(3)–C(51)	1.850(9)	P(3)–C(61)	1.855(9)
P(4)–C(8)	1.842(9)	P(4)–C(71)	1.854(9)	P(4)–C(81)	1.848(9)
O(1)–C(1)	1.17(1)	O(2)–C(2)	1.16(1)	C(3)–C(4)	1.52(1)
C(4)–C(5)	1.54(1)	C(6)–C(7)	1.53(1)	C(7)–C(8)	1.53(1)
C(11)–C(12)	1.41(1)	C(11)–C(16)	1.41(1)	C(12)–C(13)	1.40(1)
C(13)–C(14)	1.39(1)	C(14)–C(15)	1.40(1)	C(15)–C(16)	1.39(1)
C(21)–C(22)	1.39(1)	C(21)–C(26)	1.44(1)	C(22)–C(23)	1.42(1)
C(23)–C(24)	1.38(1)	C(24)–C(25)	1.40(1)	C(25)–C(26)	1.38(1)
C(31)–C(32)	1.40(1)	C(31)–C(36)	1.41(1)	C(32)–C(33)	1.41(1)
C(33)–C(34)	1.39(1)	C(34)–C(35)	1.39(1)	C(35)–C(36)	1.40(1)
C(41)–C(42)	1.40(1)	C(41)–C(45)	1.40(1)	C(42)–C(43)	1.40(1)
C(43)–C(44)	1.39(2)	C(44)–C(46)	1.38(2)	C(45)–C(46)	1.40(1)
C(51)–C(52)	1.40(1)	C(51)–C(56)	1.41(1)	C(52)–C(53)	1.41(1)
C(53)–C(54)	1.41(1)	C(54)–C(55)	1.42(1)	C(55)–C(56)	1.41(1)
C(61)–C(62)	1.39(1)	C(61)–C(66)	1.42(1)	C(62)–C(63)	1.40(1)
C(63)–C(64)	1.42(1)	C(64)–C(65)	1.37(1)	C(65)–C(66)	1.43(1)
C(71)–C(72)	1.38(1)	C(71)–C(76)	1.41(1)	C(72)–C(73)	1.41(1)
C(73)–C(74)	1.41(1)	C(74)–C(75)	1.41(1)	C(75)–C(76)	1.38(1)
C(81)–C(82)	1.42(1)	C(81)–C(86)	1.41(1)	C(82)–C(83)	1.42(1)
C(83)–C(84)	1.37(1)	C(84)–C(85)	1.40(1)	C(85)–C(86)	1.42(1)
C(9)–Cl(1)	1.97(1)	C(9)–Cl(2)	1.59(1)	Cl(1)–Cl(2)	2.77(1)
C(10)–Cl(3)	1.59(1)	C(10)–Cl(4)	1.70(1)	Cl(3)–Cl(4)	2.83(1)
C(91)–C(91)	1.55(3)	C(91)–C(92)	1.83(2)	C(91)–C(92)	1.54(2)
C(91)–C(93)	1.44(2)	C(92)–C(93)	1.70(2)		
P(1)–Mo–P(2)	85.55(8)	P(1)–Mo–P(3)	100.39(8)		
P(1)–Mo–P(4)	172.04(9)	P(1)–Mo–C(1)	88.7(2)		
P(1)–Mo–C(2)	85.5(2)	P(2)–Mo–P(3)	91.82(8)		
P(2)–Mo–P(4)	97.82(9)	P(2)–Mo–C(1)	96.4(2)		
P(2)–Mo–C(2)	170.8(2)	P(3)–Mo–P(4)	86.76(8)		
P(3)–Mo–C(1)	168.2(2)	P(3)–Mo–C(2)	91.8(2)		
P(4)–Mo–C(1)	83.8(2)	P(4)–Mo–C(2)	90.9(2)		
C(1)–Mo–C(2)	81.3(3)	Mo–P(1)–C(3)	123.1(3)		
Mo–P(1)–C(11)	120.9(3)	Mo–P(1)–C(21)	112.2(3)		
C(3)–P(1)–C(11)	96.1(4)	C(3)–P(1)–C(21)	102.2(4)		
C(11)–P(1)–C(21)	98.1(4)	Mo–P(2)–C(5)	114.2(3)		
Mo–P(2)–C(31)	120.4(3)	Mo–P(2)–C(41)	118.9(3)		
C(5)–P(2)–C(31)	98.0(4)	C(5)–P(2)–C(41)	100.0(4)		
C(31)–P(2)–C(41)	101.6(4)	Mo–P(3)–C(6)	117.0(3)		
Mo–P(3)–C(51)	122.8(3)	Mo–P(3)–C(61)	113.6(2)		
C(6)–P(3)–C(51)	98.4(4)	C(6)–P(3)–C(61)	100.7(4)		
C(51)–P(3)–C(61)	100.8(4)	Mo–P(4)–C(8)	120.3(3)		
Mo–P(4)–C(71)	119.7(3)	Mo–P(4)–C(81)	114.8(3)		
C(8)–P(4)–C(71)	97.3(4)	C(8)–P(4)–C(81)	102.3(4)		
C(71)–P(4)–C(81)	98.7(4)	Mo–C(1)–O(1)	172.6(7)		
Mo–C(2)–O(2)	173.3(8)	P(1)–C(3)–C(4)	118.2(6)		
C(3)–C(4)–C(5)	115.2(7)	P(2)–C(5)–C(4)	114.7(6)		
P(3)–C(6)–C(7)	117.4(6)	C(6)–C(7)–C(8)	114.5(7)		
P(4)–C(8)–C(7)	115.5(6)	P(1)–C(11)–C(12)	118.8(7)		

TABLE 2 (continued)

P(1)-C(11)-C(16)	119.6(7)	C(12)-C(11)-C(16)	121.7(9)
C(11)-C(12)-C(13)	119.5(9)	C(12)-C(13)-C(14)	119.(1)
C(13)-C(14)-C(15)	121.(1)	C(14)-C(15)-C(16)	122.(1)
C(11)-C(16)-C(15)	117.(1)	P(1)-C(21)-C(22)	124.1(8)
P(1)-C(21)-C(26)	116.4(7)	C(22)-C(21)-C(26)	119.4(9)
C(21)-C(22)-C(23)	119.(1)	C(22)-O(23)-C(24)	121.(1)
C(23)-C(24)-C(25)	120.(1)	C(24)-C(25)-C(26)	119.(1)
C(21)-C(26)-C(25)	121.(1)	P(2)-C(31)-C(32)	119.1(7)
P(2)-C(31)-C(36)	120.9(7)	C(32)-C(31)-C(36)	119.9(9)
C(31)-C(32)-C(33)	119.5(9)	C(32)-C(33)-C(34)	120.(1)
C(33)-C(34)-C(35)	120.(1)	C(34)-C(35)-C(36)	120.(1)
C(31)-C(36)-C(35)	120.(1)	P(2)-C(41)-C(42)	118.4(8)
P(2)-C(41)-C(45)	121.5(7)	C(42)-C(41)-C(45)	120.1(9)
C(41)-C(42)-C(43)	118.(1)	C(42)-C(43)-C(44)	121.(1)
C(43)-C(44)-C(46)	121.(1)	C(41)-C(45)-C(46)	121.(1)
C(44)-C(46)-C(45)	119.(1)	P(3)-C(51)-C(52)	122.5(7)
P(3)-C(51)-C(56)	117.3(6)	C(52)-C(51)-C(56)	120.3(8)
C(51)-C(52)-C(53)	119.6(9)	C(52)-C(53)-C(54)	121.(1)
C(53)-C(54)-C(55)	119.(1)	C(54)-C(55)-C(56)	121.(1)
C(51)-C(56)-C(55)	119.8(9)	P(3)-C(61)-C(62)	122.3(7)
P(3)-C(61)-C(66)	117.3(7)	C(62)-C(61)-C(66)	120.4(8)
C(61)-C(62)-C(63)	119.7(9)	C(62)-C(63)-C(64)	121.(1)
C(63)-C(64)-C(65)	119.9(9)	C(64)-C(65)-C(66)	120.(1)
C(61)-C(66)-C(65)	119.0(9)	P(4)-C(71)-C(72)	119.7(7)
P(4)-C(71)-C(76)	119.3(7)	C(72)-C(71)-C(76)	121.0(8)
C(71)-C(72)-C(73)	119.4(9)	C(72)-C(73)-C(74)	119.8(9)
C(73)-C(74)-C(75)	120.3(9)	C(74)-C(75)-C(76)	119.4(9)
C(71)-C(76)-C(75)	120.1(9)	P(4)-C(81)-C(82)	123.2(7)
P(4)-C(81)-C(86)	116.7(6)	C(82)-C(81)-C(86)	120.0(8)
C(81)-C(82)-C(83)	118.6(9)	C(82)-C(83)-C(84)	121.0(9)
C(83)-C(84)-C(85)	121.2(9)	C(84)-C(85)-C(86)	119.(1)
C(81)-C(86)-C(85)	119.8(9)	Cl(1)-C(9)-Cl(2)	101.3(7)
C(9)-Cl(1)-Cl(2)	34.4(4)	C(9)-Cl(2)-Cl(1)	44.3(5)
Cl(3)-C(10)-Cl(4)	118.8(7)	C(10)-Cl(3)-Cl(4)	31.8(4)
C(10)-Cl(4)-Cl(3)	29.5(4)	C(91)-C(91)-C(92)	54.(1)
C(91)-C(91)-C(92)	73.(1)	C(91)-C(91)-C(93)	115.(1)
C(92)-C(91)-C(92)	126.(1)	C(92)-C(91)-C(93)	61.(1)
C(92)-C(91)-C(93)	172.(1)	C(91)-C(92)-C(91)	54.(1)
C(91)-C(92)-C(93)	47.9(9)	C(91)-C(92)-C(93)	102.(1)

of ligands. The yields of II, III, and IV after purification were 25%, 52%, and 65%, respectively. Although the results for II, III were not exceptionally good, the 65% yield of IV indeed provided a practical way of making this rather uncommon complex.

All three products showed two very strong absorptions of IR at ca. 1855 and 1785 cm^{-1} , which were consistent with *cisoid* structures [17,18]. The presence of significant intensities for parent peaks on mass spectra and the subsequent loss of CO groups confirmed their molecular formulas. However, an ambiguity had arisen on the elemental analysis of IV; the C/H ratios were not consistent with the proposed formula after repeated measurements. So crystals of larger sizes were grown and subjected to X-ray analysis.

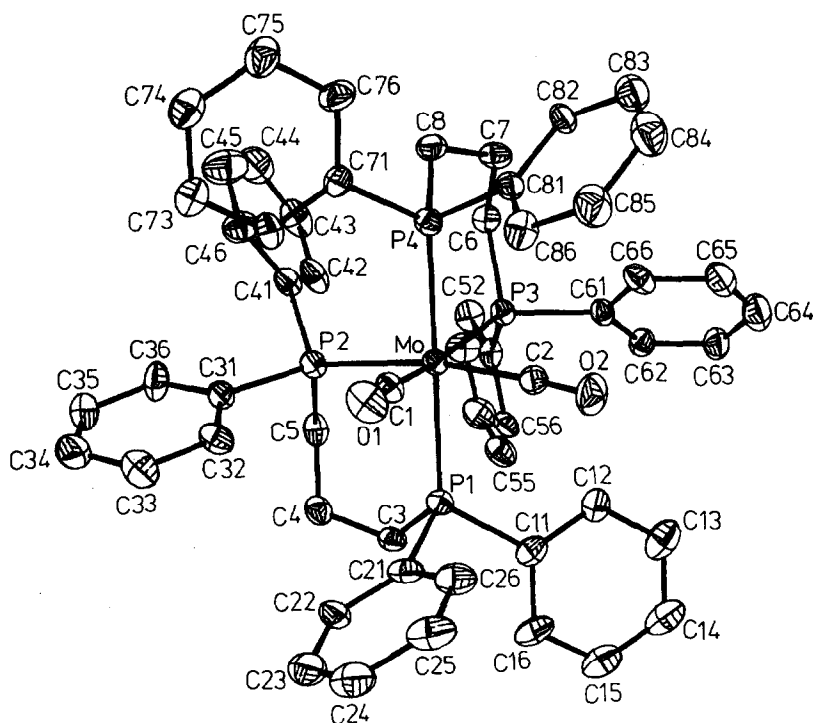


Fig. 1. The ORTEP drawing of IV and its numbering scheme.

The structure of the dicarbonyl complex is shown in Fig. 1, whilst selected bond lengths and angles are given in Table 2. The unit cell contains four discrete molecules and loosely packed solvents of dichloromethane and *n*-hexane. The molecular complex has a *cisoid* octahedral structure consistent with the IR data. The crystal structure of 1,3-bis(diphenylphosphino)propane has not received much attention and the "bite" angles of the ligands have thus been investigated by our group. The "bite" angles of $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ bidentate increase with increasing n , which are $63.5(2)^\circ$ [19], $78.0(2)^\circ$ [20] and $86.1(5)^\circ$ for $n = 1, 2$ and 3 , respectively. Therefore the six ligating atoms around the molybdenum in IV, form an octahedron with minimum distortion. Moreover, the appearance of two sets of Mo–P distances is probably a reflection of the relative *trans* influences of the CO and P bonds across the metal. The carbonyls have induced a considerable increase in length of (ca 0.1 Å) the *trans*-located Mo–P bonds.

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