Journal of Organometallic Chemistry, 178 (1979) 309—318

CRYSTAL STRUCTURE OF CARBONYLCYCLOPENTADIENYL-1,5-η-[(η-METHYLENE-1)CYCLOPENTENONATO-2]TRIPHENYLPHOSPHINE-MOLYBDENUM(II)

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(Received April 4th, 1979)

Summary

The crystal structure of the title compound was determined at room temperature from 3187 independent reflections. The unit cell is monoclinic, space group $P2_1/c$; the lattice constants are a 8.24 ± 0.02 Å, b 28.12 ± 0.04 Å, c 10.87 ± 0.02 Å, β 104.85° ± 0.04, $Z = 4$. Full matrix least-squares refinement led to a conventional R factor of 0.047. The atomic positions show that phosphine and cyclopentenone are in "*trans*" positions, i.e. on the opposite sides of the plane that bisects the allyl group and which contains the molybdenum: this result is in agreement with a structural assignment based on NMR data. The molybdenum environment is pseudotetrahedral, the four vertices being occupied by the phosphine, the carbonyl group, the cyclopentadienyl group and the allylic ketone.

Introduction

Collin, Roustan and Cadiot [1] have studied the influence of ligands on the conformational equilibrium of π-allyldicarbonylcyclopentadienylmolybdenum. In particular, complexes in which one of the carbonyl groups had been replaced by a ligand L were considered. In solution, these complexes present an equilibrium between two conformations A and B, differing from one another by a pseudorotation around molybdenum—allyl axis. Moreover, these compounds have two chiral centers; the first is the molybdenum atom itself because its environment is pseudotetrahedral, and the second is the π-allyl ligand because it is asymmetric. It is therefore possible to observe two pairs of diastereoisomers, I and II; for each of these, a conformational equilibrium A $\rightleftharpoons$ B exists. Figure 1 shows these equilibria where only one enantiomer of each pair of diastereoimers I and II is shown. When L is triphenylphosphine, Collin et al. obtained only one diastereoisomer, the NMR spectrum of which is well resolved. They

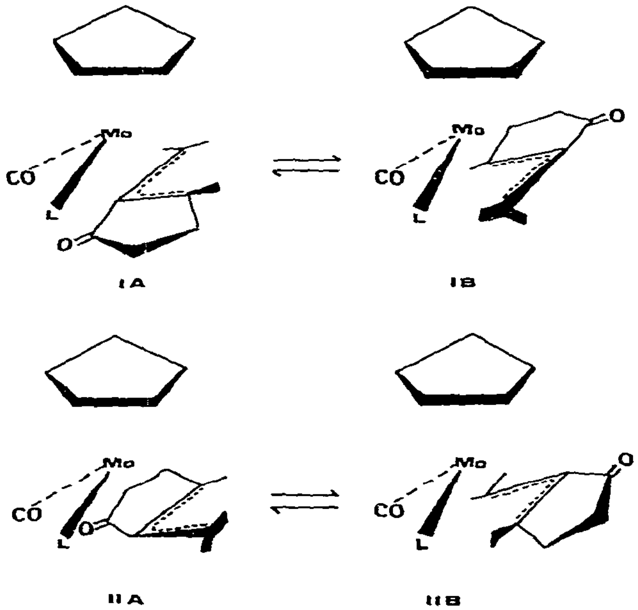

Fig. 1. Conformational equilibria of the two pairs, I and II, of diastereoisomers. Only one enantiomer of each pair is shown.

assigned it the structure IB (Fig. 1) on the basis of NMR data previously obtained for compounds with phosphine or phosphite ligands. Thus they conclude that the cyclopentenone is in a "*trans*" position with respect to the phosphine, the term "*trans*" meaning that both groups are located on opposite sides of the plane containing molybdenum that bisects the allyl group. To check this result, we have determined the structure of the title compound by X-ray diffraction.

Experimental

The crystals are colourless and slightly air unstable. The crystal selected for X-ray analysis was a parallelepiped (0.6 × 0.4 × 0.2 mm). It was sealed under nitrogen in a Lindemann tube. Preliminary Laue and precession photographs led to a monoclinic unit cell, with space group $P2_1/c$. Lattice constants were measured from diffractometer settings; the following values were obtained: a 8.24 ± 0.02 Å, b 28.12 ± 0.04 Å, c 10.87 ± 0.02 Å, β 104.85 ± 0.04°, V 2434 Å^3, $Z = 4$; ρ(calcd.) 1.49 g cm^{-3}, ρ(found) 1.49 g cm^{-3} (flotation in aqueous cadmium sulfate solution). Space group $P2_1/c$.

The crystal was set up on a 300 mm Eulerian cradle along its $0k0$ axis. Intensity data were collected with a laboratory-made automatic diffractometer: Radiation Mo-K_α, take off angle: 3°, crystal—focus distance: 230 mm, crystal—counter distance: 230 mm, scintillation counter connected to a pulse height analyser set on Mo-K_α energy so that 90% of the intensity was counted; graphite monochromator set in front of the counter window; θ—2θ scan technique (1.5° min^{-1}); scan lengths: 1.4° symmetrical scan at zero Bragg angle, corrected for $K_{\alpha1}$—$K_{\alpha2}$ dispersion, background measured in fixed position, for 10 s, before and after each scan; two standard reflections, 006 and 0140, measured every fifty reflections; 3187 independent reflections measured at room temperature up to θ(Bragg) = 22.5°.

Treatment of intensity data

Intensities were corrected for Lorentz and polarization factors. Owing to the weak absorption coefficient, equal to 6.2 cm^{-1}, no attempt was made to correct intensities for absorption. For every observed structure factor F_0, a standard deviation σ was computed: $\sigma = F_0 \Delta C/2C$ where C is the integrated intensity and ΔC the error: $\Delta C = (I_1 + I_2 + I_3 + I_4)^{0.5}$ where I_1 is the measured intensity, I_2 is the background intensity, I_3 is the count loss correction if the counting rate is above 10000 counts s^{-1} and I_4 is the correction computed from variation of standard intensities.

Refinements were made by full-matrix least squares, minimizing the $R\omega$ factor:

$$R_\omega = [\Sigma_i(\omega_i|F_0 - kF_c|^2)/\Sigma_i|\omega_i F_0|^2]^{0.5}$$

where ω is $1/\sigma$ and k is the scale factor. Atomic form factors were taken from Cromer and Waber [3] for all atoms except hydrogen for which the values of Stewart, Davidson and Simpson [4] were used. The real part of the anomalous dispersion was taken into account.

A three-dimensional Patterson map showed molybdenum, phosphorus and seven carbon atoms. Refinement of their coordinates, removing 416 reflections with intensities lower than 3σ, led to R = 0.28. A Fourier synthesis then showed all the other non-hydrogen atoms. Refinement of their coordinates lowered R to 0.15 with isotropic temperature factors and to 0.13 with aniso-

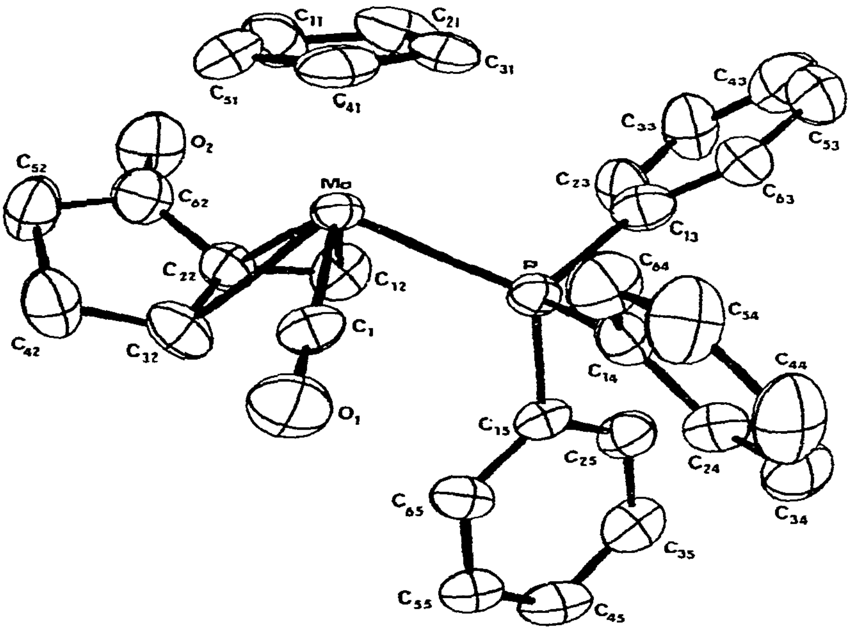

Fig. 2. ORTEP drawing of the asymmetric unit with 50% probability ellipsoids.

TABLE 1

ATOMIC COORDINATES [a] (X 10^4) AND THERMAL PARAMETERS [b]

Metal	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	2649(0)	3847(0)	641(0)	1,91(2)	2,60(3)	2,95(3)	−0,13(3)	0,75(2)	−0,12(3)
P	1809(2)	3830(0)	2626(2)	2,22(7)	2,65(9)	3,02(9)	0,12(9)	0,66(7)	−0,04(9)
C(11)	5225(10)	3968(4)	206(9)	2,9(2)	4.7(6)	5,0(4)	0,2(3)	0,7(3)	−1,5(5)
H(11)	5432(130)	3803(40)	−424(100)	2,9(2)	4.7(6)	5,0(4)	0,2(3)	0,7(3)	−1,5(5)
C(21)	5510(10)	4084(3)	1513(12)	2,5(2)	2,5(3)	8.7(9)	0,2(3)	0,17(0)	−1,4(5)
H(21)	6527(100)	3840(40)	2270(100)	2,5(2)	2,5(3)	8.7(9)	0,2(3)	0,17(0)	−1,4(5)
C(31)	4450(10)	4475(3)	1582(9)	3,9(2)	3,3(3)	5,0(4)	−2,1(3)	1,2(3)	−0,7(3)
H(31)	4470(130)	4530(40)	2440(100)	3,9(2)	3,3(3)	5,0(4)	−2,1(3)	1,2(3)	−0,7(3)
C(41)	3622(10)	4616(4)	327(10)	3,8(5)	2,9(6)	6.6(4)	−1,6(3)	2.0(3)	−0,05(5)
H(41)	2920(140)	4870(40)	130(100)	3,8(5)	2,9(6)	6.6(4)	−1,6(3)	2.0(3)	−0,05(5)
C(51)	4156(10)	4304(4)	−530(10)	4,1(5)	5,3(6)	4,4(4)	−1,1(4)	2.3(3)	0,42(5)
H(51)	3650(140)	4360(50)	−1400(100)	4,1(5)	5,3(6)	4,4(4)	−1,1(4)	2.3(3)	0,42(5)
C(12)	2925(10)	3048(3)	1161(9)	4,4(5)	2,7(3)	4,7(4)	0,7(3)	1,17(3)	0,2(3)
C(22)	2580(10)	3123(3)	−187(8)	3,3(2)	2,6(3)	3,5(4)	−0,2(3)	0,5(3)	0,1(2)
C(32)	1074(10)	3338(3)	−937(9)	3,9(5)	2,7(3)	4,7(4)	0,1(3)	−0,09(3)	−1,1(3)
C(42)	1140(10)	3388(4)	−2289(9)	4,9(5)	5,4(6)	3,6(4)	1,1(4)	0,16(3)	−0,4(5)
H(421)	910(130)	3710(50)	−2800(100)	4,9(5)	5,4(6)	3,6(4)	1,1(4)	0,16(3)	−0,4(5)
H(422)	350(150)	3110(30)	−2900(100)	4,9(5)	5,4(6)	3,6(4)	1,1(4)	0,16(3)	−0,4(5)
C(52)	2913(13)	3229(5)	−2333(9)	5,0(5)	6,0(6)	3,5(4)	1,1(4)	1,6(3)	0,2(5)
H(521)	3560(140)	3570(50)	−2520(100)	5,0(5)	6,0(6)	3,5(4)	1,1(4)	1,6(3)	0,2(5)
H(522)	3050(150)	2990(50)	−3040(100)	5,0(5)	6,0(6)	3,5(4)	1,1(4)	1,6(3)	0,2(5)
C(62)	3727(10)	3053(4)	−1013(9)	4,4(5)	4,1(6)	4,8(4)	0,3(4)	1,4(3)	−0,6(3)
C(1)	379(10)	4057(3)	7(8)	3,1(5)	2,2(3)	4,0(4)	0,03(3)	1,4(3)	0,7(3)
C(13)	3582(8)	3832(4)	4078(7)	2,5(2)	4.0(3)	4,5(4)	0,3(3)	0,9(3)	0.3(5)
C(23)	4631(10)	3439(4)	4370(9)	3,7(5)	4,5(6)	3,0(4)	1,17(35)	−0,007(3)	0,01(3)
H(23)	4420(15)	3250(50)	3870(100)	3,7(5)	4,5(6)	3,0(4)	1,17(35)	−0,007(3)	0,01(3)
C(33)	6010(10)	3446(5)	5400(10)	4,5(5)	5,6(6)	4,2(4)	1,9(4)	0,18(3)	−0,9(5)
H(33)	6270(150)	3120(50)	5570(100)	4,5(5)	5,6(6)	4.2(5)	1,9(4)	0,18(3)	−0,9(5)

C(43)	6364(10)	3826(6)	6188(9)	3,1(5)	11,1(9)	3,43(4)	0,2(6)	0,03(30)	1.10(7)
H(43)	7160(100)	3810(60)	7120(100)	3,1(5)	11,1(9)	3,43(4)	0,2(6)	0,03(30)	1,10(7)
C(53)	5340(10)	4225(4)	5909(9)	4,3(5)	6,0(6)	3,7(4)	−0,5(4)	0,5(3)	−1,0(5)
H(53)	5620(140)	4450(50)	6660(110)	4,3(5)	6,0(6)	3,7(4)	−0,5(4)	0,5(3)	−1,0(5)
C(63)	3952(10)	4228(4)	4859(8)	3,5(5)	4.1(6)	3,7(4)	−0,6(3)	1,0(3)	−0,9(3)
H(63)	3280(130)	4590(40)	4580(100)	3,5(5)	4,1(6)	3,4(4)	−0,6(3)	1,0(3)	−0,9(3)
C(14)	540(10)	4334(3)	2929(8)	2,8(2)	3.0(2)	2,9(4)	0,1(3)	0,2(3)	−0,3(3)
C(24)	−540(10)	4288(3)	3718(9)	2,6(2)	4,1(3)	4,0(4)	−0,2(3)	1,1(3)	−0,3(3)
H(24)	−700(100)	4040(40)	4100(100)	2,6(2)	4,1(3)	4,0(4)	−0,2(3)	1,1(3)	−0,3(3)
C(34)	−1510(10)	4666(4)	3924(9)	2,8(2)	5,5(6)	4,3(4)	0,7(3)	1,3(3)	−0,4(5)
H(34)	−2170(120)	4600(40)	4600(100)	2,8(2)	5,5(6)	4,3(4)	0,7(3)	1,3(3)	−0,4(5)
C(44)	−1390(13)	5101(4)	3387(9)	5,3(5)	4,7(6)	4,2(4)	2,8(4)	0,9(3)	−0,3(5)
H(44)	−1900(150)	5380(50)	3550(100)	5,3(5)	4,7(6)	4,2(4)	2,8(4)	0,9(3)	−0,3(5)
C(54)	−330(13)	5156(3)	2587(9)	6,2(5)	2,9(3)	5,0(4)	1,6(3)	1,8(3)	−0,1(3)
H(54)	−330(150)	5500(40)	1900(100)	6,2(5)	2,9(3)	5,0(4)	1,6(3)	1,8(3)	−0,1(3)
C(64)	610(10)	4774(3)	2351(9)	4,3(5)	3,7(3)	4,9(4)	0,7(3)	1,5(3)	−0,1(3)
H(64)	1320(140)	4740(40)	1670(100)	4,3(5)	3,7(3)	4,9(4)	0,7(3)	1,5(3)	−0,1(3)
C(15)	457(9)	3341(3)	2915(8)	2,4(2)	3,0(3)	3,7(4)	0,2(3)	1,4(3)	0,2(3)
C(25)	684(10)	3116(3)	4085(9)	3,58(9)	4,0(3)	3,9(4)	−0,2(3)	1,5(3)	0,4(3)
H(25)	1750(130)	3263(40)	4850(100)	3,58(5)	4,0(3)	3,9(4)	−0,2(3)	1,5(3)	0,4(3)
C(35)	−470(10)	2785(3)	4275(9)	4,6(5)	3,3(3)	5,2(4)	0,3(3)	2,2(3)	0,4(3)
H(35)	−139(130)	2650(40)	5320(100)	4,6(5)	3,3(3)	5,2(4)	0,3(3)	2,2(3)	0,4(3)
C(45)	−1860(10)	2663(4)	3252(10)	3,2(5)	3,5(3)	6,9(4)	−0,4(3)	2,2(3)	0,1(5)
H(45)	−2700(140)	2410(4)	3410(100)	3,2(5)	3,5(3)	6,9(4)	−0,4(3)	2,2(3)	0,1(5)
C(55)	−2040(10)	2883(3)	2115(9)	2,8(2)	4,7(6)	4,6(4)	−0,8(3)	1,3(3)	−0,03(35)
H(55)	−2860(130)	2750(40)	1340(100)	2,8(2)	4,7(6)	4,6(4)	−0,8(3)	1,3(3)	−0,03(35)
C(65)	−890(10)	3216(3)	1935(9)	2,4(2)	3,8(3)	4,4(4)	−0,3(3)	0,7(3)	−0,2(3)
H(65)	−1110(130)	3350(40)	1140(100)	2,4(2)	3,8(3)	4,4(4)	−0,3(3)	0,7(3)	−0,2(3)
O(15)	−1002(7)	4194(3)	−427(6)	2,8(2)	6,6(3)	5,6(3)	1,1(3)	0,4(3)	0,5(2)
O(25)	5063(9)	2838(3)	−709(7)	5,1(2)	5,9(3)	6,2(4)	2,8(3)	2,0(3)	−0,1(3)

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[a] See Fig. 2 for identification of atoms. [b] The anisotropic thermal parameters have units of Å^2. They enter the expression for the structure factor in the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{23}klb^*c^* + 2B_{13}hla^*c^*)]$.

TABLE 2

SELECTED INTERATOMIC DISTANCES (Å)[a]

Molybdenum surrounding (cf. Fig. 2)				*Triphenylphosphine group (cf. Fig. 2)*				
Mo—P	2,429(4)				P—C(13)	1,855(8)		
Mo—C(1)	1,914(9)				C(13)—C(23)	1,39(1)		
Mo—C(11)	2,314(1)				C(23)—C(33)	1,38(1)	C(23)—H(23)	0,74
Mo—C(21)	2,39(1)			*First*	C(33)—C(43)	1,35(2)	C(33)—H(33)	0,94
Mo—C(31)	2,364(1)			*ring*	C(43)—C(53)	1,39(2)	C(43)—H(43)	1,06
Mo—C(41)	2,360(9)				C(53)—C(63)	1,39(1)	C(53)—H(53)	1,00
Mo—C(51)	2,369(9)				C(13)—C(63)	1,39(1)	C(63)—H(63)	1,16
Mo—C(12)	2,313(9)							
Mo—C(22)	2,220(9)				P—C(14)	1,841(9)		
Mo—C(32)	2,352(9)				C(14)—C(24)	1,39(1)		
Pentadienyl group					C(24)—C(34)	1,38(1)	C(24)—H(24)	0,84
C(11)—C(21)	1,42(1)	C(11)—H(11)	0,88	*Second*	C(34)—C(44)	1,37(1)	C(34)—H(34)	1,00
C(21)—C(31)	1,42(1)	C(21)—H(21)	1,23	*ring*	C(44)—C(54)	1,39(1)	C(44)—H(44)	0,94
C(31)—C(41)	1,42(1)	C(31)—H(31)	0,94		C(54)—C(64)	1,39(1)	C(54)—H(54)	1,24
C(41)—C(51)	1,43(1)	C(41)—H(41)	1,01		C(14)—C(64)	1,39(1)	C(64)—H(64)	1,06
C(51)—C(11)	1,39(1)	C(51)—H(51)	0,93					
Allyl cyclopentenone group					P—C(15)	1,848(9)		
C(12)—C(22)	1,44(1)				C(15)—C(25)	1,39(1)		
C(22)—C(32)	1,43(1)				C(25)—C(35)	1,38(1)	C(25)—H(25)	1,12
C(32)—C(42)	1,49(1)			*Third*	C(35)—C(45)	1,42(1)	C(35)—H(35)	1,16
C(42)—C(52)	1,54(1)	C(42)—H(421)	1,06	*ring*	C(45)—C(55)	1,35(1)	C(45)—H(45)	1,04
C(52)—C(62)	1,50(1)	C(42)—H(422)	1,11		C(55)—C(65)	1,38(1)	C(55)—H(55)	1,00
C(62)—C(22)	1,47(1)	C(52)—H(521)	1,14		C(15)—C(65)	1,37(1)	C(65)—H(65)	0,91
C(62)—O(2)	1,22(1)	C(52)—H(522)	1,06					

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[a] Estimated standard deviations of the least significant figures are given in parentheses.

TABLE 3

SELECTED BOND ANGLES (°) [a]

Molybdenum surrounding (cf. Fig. 2)		*Triphenylphosphine group*	
P—Mo—C(1)	81.5(2)	*1) Phosphorus surrounding*	
P—Mo—C(12)	78.3(2)	Mo—P—C(14)	116.6(3)
P—Mo—C(22)	111.0(2)	Mo—P—C(13)	114.4(3)
P—Mo—C(32)	114.0(2)	Mo—P—C(15)	119.1(3)
C(1)—Mo—C(12)	114.4(3)	C(14)—P—C(15)	98.5(3)
C(1)—Mo—C(22)	102.5(3)	C(14)—P—C(13)	101.9(4)
C(1)—Mo—C(32)	67.6(2)	C(13)—P—C(15)	103.6(4)
Carbonyl group		*2) Benzene rings*	
Mo—C(1)—O(1)	177.3(9)	C(23)—C(13)—C(63)	118.2(8)
		C(13)—C(23)—C(33)	120.7(8)
Pentadienyl group		C(23)—C(33)—C(43)	121.7(9)
C(11)—C(21)—C(31)	106.6(1)	C(33)—C(43)—C(53)	118.7(8)
C(21)—C(31)—C(41)	108.5(1)	C(43)—C(53)—C(63)	120.5(9)
C(31)—C(41)—C(51)	107.6(1)	C(53)—C(63)—C(13)	120.1(9)
C(41)—C(51)—C(11)	107.3(1)		
C(51)—C(11)—C(21)	109.7(2)	C(24)—C(14)—C(64)	117.9(8)
		C(14)—C(24)—C(44)	121.0(8)
Allylcyclopentenone group		C(24)—C(34)—C(44)	120.7(9)
C(32)—C(22)—C(62)	107.8(8)	C(34)—C(44)—C(54)	119.4(8)
C(22)—C(32)—C(42)	110.9(8)	C(44)—C(54)—C(64)	120.0(8)
C(32)—C(42)—C(52)	106.0(8)	C(54)—C(64)—C(14)	120.9(8)
C(42)—C(52)—C(62)	105.1(8)		
C(52)—C(62)—C(22)	109.8(8)	C(25)—C(15)—C(65)	119.1(8)
C(12)—C(22)—C(62)	127.8(8)	C(15)—C(25)—C(35)	120.4(8)
C(12)—C(22)—C(32)	124.0(8)	C(25)—C(35)—C(45)	119.6(8)
C(22)—C(62)—O(2)	125.0(8)	C(35)—C(45)—C(55)	118.8(8)
C(52)—C(62)—O(2)	124.8(9)	C(45)—C(55)—C(65)	121.3(9)
		C(55)—C(65)—C(15)	120.8(9)

[a] Estimated standard deviations of the least significant figures are given in parentheses.

tropic temperature factors. The positions of 24 hydrogens were then computed at distances of 1 Å from the atoms to which they are bound. Their coordinates were refined in such a way that each hydrogen atom moved as the atom to which it was bound: R dropped to 0.07. The two hydrogen atoms of the allyl group were not located by a difference Fourier synthesis. 38 reflections for which ΔF was higher than 15 with $|F_c|$ higher than 14 were removed from the refinement, leading to $R = 0.068$. Introduction of a secondary extinction parameter in the refinement brought no significant improvement in R. The final results were: Non weighted R excluding zeros: 0.068; weighted R excluding zeros: 0.047, $F(000) = 481$. The atomic parameters are shown in Table 1. Main interatomic distances and bond angles are shown in Tables 2 and 3. An ORTEP [5] drawing was computed with 50% probability thermal ellipsoids (Fig. 2).

Results and discussion

Several features are noteworthy.

(1) The study confirms that the title compound is the diastereoisomer IB (Fig. 1), i.e. that phosphine and cyclopentenone are in "*trans*" positions. Fig-

ure 2 shows that the phosphorus atom and cyclopentenone are on the opposite sides of the plane which bisects the allyl group and contains molybdenum. The distances of different atoms from this plane have been computed (Table 4). The values obtained clearly show that the compound is "*trans*". The four carbon atoms of the cyclopentenone ring are on the opposite side to the phosphorus. We thus agree with the conclusions of Collin, Roustan and Cadiot [1].

(2) The second point concerns the molybdenum environment. Ligands supply 14 electrons to the molybdenum if we assume a contribution of 6 electrons from the cyclopentadienyl ring and 4 electrons from the allyl group of cyclopentenone. From a geometric point of view, it is possible to regard the molybdenum environment as pseudotetrahedral, with the following angles (Fig. 2): P—Mo—C(22) 111.0°, P—Mo—C(1) 81.5°, P—Mo—C(f) 114.8°, C(f)—Mo—C(1) 129.4°, C(1)—Mo—C(22) 102.5°, C(22)—Mo—C(f) 122.5°. C(f) is an imaginary atom, corresponding to the middle point of the cyclopentadienyl ring, and atom C(22) is considered to be the mid point of the allyl group. These angle values show that the tetrahedron surrounding the molybdenum is very distorted. The largest angles are those which involve the cyclopentadienyl ring (Mo—C(f) direction); the reason may be that this ring lies like an "umbrella" over the molybdenum. This results in some steric interference with the other atoms coordinated to molybdenum. For instance, the carbonyl group, which is the smallest group, is pushed towards the phosphine ligand (81°) and towards the allyl group (102.5°).

It is of interest to consider structural features of the various ligands.

(a) Triphenylphosphine. The Mo—P distance (Table 2) is not very different from that found in $[\pi\text{-}C_5H_5Mo(CO)_2]_2[P(CH_3)_2](H)$ [6] (Mo^{II}—P = 2.425 ± 0.006 Å), but shorter than that in $[(C_2H_5)_5P_5]Mo(CO)$ [7] (Mo^0—P = 2.52 ± 0.02 Å) or in $\pi\text{-}C_5H_5Mo(CO)_2[P(C_6H_5)_3]COCH_3$ [8] (Mo^{II}—P = 2.473 ± 0.003 Å). It is shorter than the sum of the covalent radii of molybdenum (1.61 Å) and phosphorus (1.10 Å). This is probably the result of back-bonding of π-electrons from molybdenum to phosphorus. Furthermore, the phosphorus—carbon bonds (Table 1) are slightly longer than those in triphenylphosphine [9], where the mean value is 1.828 Å. This stretching could be the result of back-bonding. Carbon—carbon bonds in the three benzene rings range from 1.35 ± 0.01 Å to 1.42 ± 0.01 Å, with mean values for the three rings equal to 1.382 Å, 1.385 Å and 1.382 Å, respectively. The distances of carbon atoms

TABLE 4

DISTANCES (Å) OF SELECTED ATOMS TO THE BISSECTING PLANE OF ALLYL GROUP

Atom	Distance
C(22)	0.00
P	—1.37
C(12)	—1.27
C(32)	+1.27
C(42)	+2.39
C(52)	+0.74
C(62)	+0.26
O(2)	—0.60

TABLE 5

DISTANCES OF CARBON ATOMS TO THE MEAN PLANES OF BENZENE RINGS

	Atom	Distance (Å)	
First ring	C(13)	+0.002	Mean value 0.007
	C(23)	+0.003	
	C(33)	−0.013	
	C(43)	+0.010	
	C(53)	−0.006	
	C(63)	−0.005	
Second ring	C(14)	−0.008	Mean value 0.009
	C(24)	−0.004	
	C(34)	+0.014	
	C(44)	−0.010	
	C(54)	−0.004	
	C(64)	+0.012	
Third ring	C(15)	−0.010	Mean value 0.006
	C(25)	+0.010	
	C(35)	−0.006	
	C(45)	+0.002	
	C(55)	−0.002	
	C(65)	+0.006	

from the mean plane of the ring have been computed (Table 5); the average values are 0.007, 0.009 and 0.006 Å for the rings which appear planar within the limit of error (symmetry D_{6h}).

(b) π-cyclopentadienyl ring. Table 6 shows the distance from atoms to the mean plane of the ring. The average is 0.020 Å; this indicates that the ring is less planar than benzene rings; however, its symmetry is still close to D_{5h}. The mean bond length in the ring (Table 2) is 1.42 Å. This value is not very different from 1.406 Å found by Churchill and Fenessey in *trans*-π-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]COCH_3$ [8]. The mean value of angles in the ring is 107.9° and molybdenum—carbon distances range from 2.32 Å to 2.40 Å.

(c) π-Allylcyclopentenone ring. Distances and bond angles are given in Table 2. The molybdenum is bound to three carbon atoms, C(22) being the central atom. The Mo—C(22) distance is smaller than the two others; overall these three bonds are smaller than those found by Surcouf [10] for a dicarbonyl

TABLE 6

DISTANCES TO THE MEAN PLANE OF CYCLOPENTADIENYL GROUP

Atom	Distance (Å)
C(11)	+0.032
C(21)	−0.027
C(31)	+0.012
C(41)	+0.005
C(51)	−0.023
Mo	+2.032

complex having the same conformation. A carbonyl group needs some back-bonding, which is not necessarily the case for phosphine; thus the molybdenum gives back more electrons to the allyl group, and this decreases the bond lengths between molybdenum and the allylic carbon atoms. The decrease of the observed Mo—P bond length means that there is a competition between "π-acceptor" powers of the triphenylphosphine and the allyl group.

Supplementary material available: a listing of structure factor amplitudes (17 pages).

Acknowledgment

The authors are indebted to P. Cadiot and J. Collin for supplying the crystal and for helpful discussion, and to A.C. Carbonnelle for her technical assistance.

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