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THE MOLECULAR AND CRYSTAL STRUCTURE OF PENTACARBONYL(PHOSPHABENZENE)MOLYBDENUM(0)

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Summary

Pentacarbonyl(phosphabenzene)molybdenum(0) crystallizes in the *Pbam* space group with $Z = 8$, a 15.880(4), b 20.162(4) and c 7.971(3) Å. The crystal structure was determined and refined from 1404 independent reflections to $R_1 = 0.034$. The pentacarbonylmolybdenum moiety is symmetrically coordinated to the phosphorus atom of the phosphabenzene ring, which closely resembles the free ligand in geometry.

Introduction

The phosphabenzene (phosphorin) ring **1** can serve as a versatile ligand towards transition metals. Three types of complexes are known, a σ-type [1–8] a π-type [6,7,9], and a mixed σ-π type [7,8,10,11]. Which kind of complex is formed seems to depend on the degree of substitution of the phosphabenzene ring. For example, 2,4,6-triphenylphosphabenzene **1a** reacts with THF-$Mo(CO)_5$ to give the corresponding σ-molybdenum pentacarbonyl **2a**, which on heating to 140°C rearranged with loss of CO to the π-molybdenum tricarbonyl **3a** [6]. The unsubstituted phosphabenzene **1c** forms a similar σ-complex **2c** which fails to rearrange to π-complex **3c** even on heating to 200°C [5]. Phosphabenzenes with an intermediate degree of substitution, such as 4-cyclohexylphosphabenzene **1b**, react with $Mo(CO)_6$ to give a σ-π adduct (**4b**) [10].

Structural data are available for several of the π-complexes [12,13] and free phosphabenzenes [15,16]. However, the only σ-complex for which a crystal structure has been reported is the 2,4,6-triphenylphosphabenzenechromium pentacarbonyl (**5**) related to **2a** [16]. We have now obtained an X-ray structure for **2c** in order to focus on the effects of substitution on the phosphabenzene ring.

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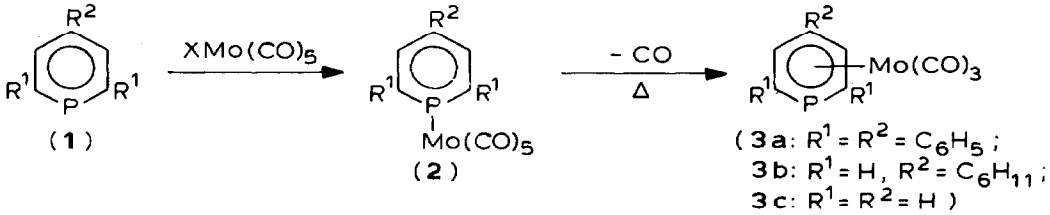

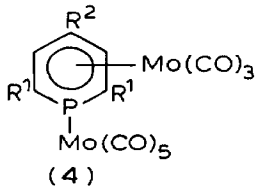

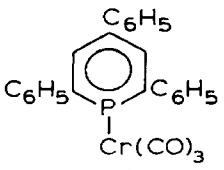

Experimental

Preparation and properties. Hexacarbonylmolybdenum (1.35 g, 5.1 mmol) in 350 ml of tetrahydrofuran was placed in a Pyrex photolysis reaction vessel equipped with a magnetic stirrer and argon inlet. After irradiation with a medium pressure mercury lamp (Hanovia) for 5 h, a solution of phosphabenzene (0.5 g, 5.2 mmol) in 5 ml of tetrahydrofuran was added and the resulting mixture stirred for 24 h. After the solvent was removed under reduced pressure, the residue was taken up in pentane. The pentane solution was cooled to −78°C and filtered to remove unreacted hexacarbonylmolybdenum. Removal of pentane yielded a yellow-green solid which was sublimed (55°C at 0.25 torr), then recrystallized from pentane to 0.4 g (24% yield) of pale yellow crystals of **3c**, m.p. 76–77°C. Anal. Found: C, 36.12; H, 1.55. $C_{10}H_5MoO_5P$ calcd.: C, 36.17; H, 1.52%. IR ($CHCl_3$): ν(CO) 2078 m, 1962 (s) cm^{-1}. MS *m/e*: 334 (M^+, $C_{10}H_5\,^{98}MoO_5P$).

X-ray crystallography. Crystals of pentacarbonyl(phosphabenzene)molybdenum(0) were grown by sublimation. A 0.21 × 0.24 × 0.22 mm crystal was mounted on a Syntex $P2_1$ automatic diffractometer and the space group determined to be *Pbam* with $Z = 8$, *a* 15.880(4), *b* 20.162(4), *c* 7.971(3) Å, *V* 2552(1) Å^3 and *d*(calcd) 1.73 g/cm^3. A total of 1404 independent reflections with $2\theta < 45°$ were obtained using Mo-K_α radiation monochromated from a graphite crystal whose diffraction vector was perpendicular to the diffraction vector of the sample. Three standard reflections were measured every 50 reflections. The data were reduced by procedures previously described [17]. The structure was solved using standard Patterson techniques. Hydrogen atoms were included in the final refinements as fixed atom contributors. Final residuals were $R^1 = 0.034$ and $R^2 = 0.038$ [18].

Results and discussion

The structure consists of discrete molecules linked only by Van der Waals contacts. There are two independent molecules each confined to a crystallographic mirror containing the Mo atom; the phosphabenzene ring atoms and one of the carbonyl groups.

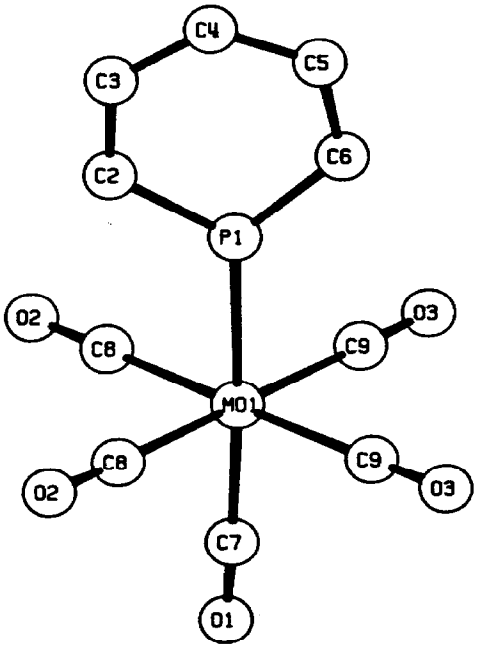

Fig. 1. The molecular structure of pentacarbonyl(phosphabenzene)molybdenum(0) showing the numbering scheme.

The molecular structure of pentacarbonyl(phosphabenzene)molybdenum(0) is illustrated in Fig. 1. Table 1 contains the refined positional and final thermal parameters for the non-hydrogen atoms. Tables 2 and 3 give the bond distances and angles for non-hydrogen atoms, while Table 4, a list of observed and calculated structure factors, is available on request from AJA.

The molybdenum atoms of **2c** are almost perfectly octahedrally coordinated with CMoC angles of 90.4° (ave) and PMoC angles of 89.7° (ave). Both the MoC and CO distances of **2c** are well within the range observed for similar phosphine-$Mo(CO)_5$ complexes (see Table 5). Interestingly, the MoP distance of 2.46 Å is relatively short, in fact 0.10 Å shorter than that of $(C_6H_5)_3PMo(CO)_5$ [19]. The data in Table 5 show that the $Mo(CO)_5$ complexes of the rigid, cyclic phosphines [20,21] generally have shorter MoP bond distances than complexes of the acyclic phosphines. This suggests a steric origin for the effect.

The structure of the phosphabenzene moiety closely resembles that of the free ligand [14] and of **5** [16]. The rings are planar in all cases, while the corresponding internal bond angles do not vary significantly. However, the mean CC (1.38 Å) and CP (1.70 Å) bond lengths are slightly shorter than those of **1c** (1.40 and 1.73 Å, respectively) and considerably shorter than those of the π-complex $(C_5H_5)Mn(PC_5H_2(C_6H_5)_3)$ (1.46 and 1.76 Å, respectively). It has been argued that the lengthening of the ligand bonds in the π-complex is due to a removal of electron density for the triphenylphosphabenzene ring on complexation. By extension of this argument the short bonds of **2c** imply that there is little removal of electron density from the ring on complexation.

The juxtaposition of the metal pentacarbonyl group relative to the plane of the phosphabenzene ring is different in **2c** and **5**. In **5**, the P–metal bond is bent about

(Continued on p. 238)

TABLE 1

THE POSITIONAL PARAMETERS AND FINAL THERMAL PARAMETERS OF PENTACARBONYL(PHOSPHABENZENE)MOLYBDENUM(0) [a]

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo(1)	0.3903(1)	0.8843(0)	0.0	0.0600(6)	0.0543(5)	0.0822(7)	0.0	0.0	0.0021(4)
P(1)	0.4390(2)	0.7683(1)	0.0	0.0610(16)	0.0559(15)	0.0723(18)	0.0	0.0	−0.0011(!3)
C(2)	0.3739(8)	0.7010(5)	0.0	0.0795(98)	0.0656(69)	0.1009(97)	0.0	0.0	−0.0074(65)
C(3)	0.4024(10)	0.6361(15)	0.0	0.1025(70)	0.0578(73)	0.1010)99)	0.0	0.0	−0.0110(85)
C(4)	0.4853(10)	0.6208(6)	0.0	0.1069(69)	0.0607(79)	0.1083(9)	0.0	0.0	0.0043(0)
C(5)	0.5493(11)	0.6654(6)	0.0	0.0665(44)	0.0798(81)	0.2220(0)	0.0	0.0	0.0203(94)
C(6)	0.5355(8)	0.7340(6)	0.0	0.0563(90)	0.1022(2)	0.1695(49)	0.0	0.0	−0.0054(74)
C(7)	0.3455(8)	0.9779(5)	0.0	0.0844(94)	0.0717(86)	0.0936(83)	0.0	0.0	−0.0019(74)
O(1)	0.3175(6)	1.0303(4)	0.0	0.1251(76)	0.0693(48)	0.1357(80)	0.0	0.0	0.0290(51)
C(8)	0.3055(5)	0.8602(4)	0.1818(11)	0.0728(56)	0.0783(51)	0.1026(69)	0.0019(53)	0.0092(54)	0.0114(42)
O(2)	0.2569(4)	0.8457(3)	0.2811(9)	0.0856(43)	0.1405(53)	0.1296(57)	0.0194(47)	0.0331(45)	−0.0007(39)
C(9)	0.4777(5)	0.9084(3)	0.1818(10)	0.0671(50)	0.0555(39)	0.0930(64)	0.0017(44)	0.0076(49)	0.0034(37)
O(3)	0.5262(4)	0.9211(3)	0.2820(8)	0.0831(41)	0.0979(42)	0.1144(50)	−0.0140(38)	−0.0196(37)	−0.0016(32)
Mo(1)′	0.7831(1)	0.9294(0)	0.5000	0.0585(6)	0.0527(5)	0.0764(7)	0.0	0.0	−0.0004(4)
P(1)′	0.9012(2)	0.8508(1)	0.5000	0.0628(18)	0.0723(18)	0.0729(19)	0.0	0.0	0.0074(13)
C(2)′	0.8927(11)	0.7667(5)	0.5000	0.1081(60)	0.0751(74)	0.1140(10)	0.0	0.0	0.0373(89)
C(3)′	0.9601(13)	0.7235(8)	0.5000	0.1878(46)	0.1205(10)	0.0801(21)	0.0	0.0	0.0747(67)
C(4)′	1.0402(14)	0.7475(11)	0.5000	0.0933(87)	0.2401(31)	0.1127(36)	0.0	0.0	0.0766(91)
C(5)′	1.0669(14)	0.8119(11)	0.5000	0.0341(91)	0.3410(60)	0.1700(25)	0.0	0.0	0.0103(22)
C(6)′	1.0055(10)	0.8628(9)	0.5000	0.0474(77)	0.1731(28)	0.1842(93)	0.0	0.0	0.0019(27)
C(7)′	0.6846(8)	0.9934(6)	0.5000	0.0859(74)	0.0703(76)	0.0823(79)	0.0	0.0	0.0074(65)
O(1)′	0.6327(6)	1.0315(4)	0.5000	0.0939(62)	0.0911(61)	0.1237(73)	0.0	0.0	0.0371(53)
C(8)′	0.7264(4)	0.8724(3)	0.3210(10)	0.0653(42)	0.0659(42)	0.0836(55)	−0.0015(43)	0.0023(41)	−0.0025(36)
O(2)′	0.6957(4)	0.8390(3)	0.2256(8)	0.0855(40)	0.0950(38)	0.1095(47)	−0.0205(37)	−0.0089(36)	−0.0133(32)
C(9)′	0.8407(5)	0.9851(4)	0.3206(11)	0.0878(56)	0.0624(44)	0.0885(62)	−0.0016(45)	0.0053(52)	−0.0052(39)
O(3)′	0.8713(5)	1.0165(3)	0.2196(9)	0.1509(6)	0.0911(40)	0.1187(52)	0.0133(41)	0.0331(47)	−0.0238(41)

[a] Atoms of the second independent molecule are indicated by a prime (′).

TABLE 2

BONDED DISTANCES (Å) FOR PENTACARBONYL(PHOSPHABENZENE)MOLYBDENUM(0) [a]

				mean
Mo(1)–P(1)	2.464(2)	Mo(1)′–P(1)′	2.456(3)	2.46
Mo(1)–C(7)	2.015(9)	Mo(1)′–C(7)′	2.038(11)	2.03
Mo(1)–C(8)	2.037(7)	Mo(1)′–C(8)′	2.044(7)	2.04
Mo(1)–C(9)	2.069(7)	Mo(1)′–C(9)′	2.035(7)	2.05
P(1)–C(2)	1.717(8)	P(1)′–C(2)′	1.711(8)	1.71
P(1)–C(6)	1.695(8)	P(1)′–C(6)′	1.693(9)	1.69
C(2)–C(3)	1.381(9)	C(2)′–C(3)′	1.363(11)	1.37
C(3)–C(4)	1.348(10)	C(3)′–C(4)′	1.357(12)	1.35
C(4)–C(5)	1.353(10)	C(4)′–C(5)′	1.377(12)	1.36
C(5)–C(6)	1.396(10)	C(5)′–C(6)′	1.417(12)	1.41
C(7)–O(1)	1.150(9)	C(7)′–O(10)′	1.120(11)	1.14
C(8)–O(2)	1.143(7)	C(8)′–O(2)′	1.124(7)	1.13
C(9)–O(3)	1.136(7)	C(9)′–O(3)′	1.134(7)	1.14

[a] Atoms of the second independent molecule are indicated by a prime (′).

TABLE 3

BOND ANGLES (deg) FOR PENTACARBONYL(PHOSPHABENZENE)MOLYBDENUM(0) [a]

				mean
P(1)–Mo(1)–C(7)	177.6(3)	P(1)′–Mo(1)′–C(7)′	179.1(3)	178
P(1)–Mo(1)–C(8)	88.9(2)	P(1)′–Mo(1)′–C(8)′	88.4(2)	89
C(7)–Mo(1)–C(8)	89.4(3)	C(7)′–Mo(1)′–C(8)	91.0(3)	90
P(1)–Mo(1)–C(9)	90.7(2)	P(1)′–Mo(1)′–C(9)′	90.8(2)	91
C(7)–Mo(1)–C(9)	91.0(3)	C(7)′–Mo(1)′–C(9)′	89.8(3)	90
C(8)–Mo(1)–C(9)	90.1(3)	C(8)′–Mo(1)′–C(9)′	91.1(3)	91
C(2)–P(1)–C(6)	103.1(5)	C(2)′–P(1)′–C(6)′	103.2(6)	103
P(1)–C(2)–C(3)	122.9(8)	P(1)′–C(2)′–C(3)′	125(1)	124
C(2)–C(3)–C(4)	123.1(9)	C(2)′–C(3)′–C(4)′	120(1)	122
C(3)–C(4)–C(5)	125.0(9)	C(3)′–C(4)′–C(5)′	130(2)	128
C(4)–C(5)–C(6)	123(1)	C(4)′–C(5)′–C(6)′	118(1)	121
P(1)–C(6)–C(5)	122.7(8)	P(1)′–C(6)′–C(5)′	124(1)	123

[a] Atoms of the second independent molecule are indicated by a prime (′).

TABLE 5

COMPARISON OF SELECTED BOND DISTANCES (Å) FOR THE COMPOUNDS $Mo(CO)_5PR_3$

Compound	MoP	$Mo(CO_{ax})$	$Mo(CO_{eq})$	CO_{ax}	CO_{eq}	Ref.
$Mo(CO)_5P(C_6H_5)_3$	2.56	2.00	2.05	1.14	1.13	19
$Mo(CO)_5P(CH_2CH_2CN)_3$	2.51	2.01	2.04	1.15	1.13	19
$Mo(CO)_5[P(CH_2)_6N_3]$	2.48	2.03	2.01	1.12	1.16	21
$Mo(CO)_5[P_4S_3]$	2.48	2.08	2.05	1.12	1.14	20
$Mo(CO)_5[PC_5H_5]$	2.46	2.03	2.05	1.14	1.13	this work

8° out of the plane of the ring, while in **2c** the P–Mo bond is completely coplanar with the ring. Apparently the bulky 2,6-phenyl substituents of **5** buttress the $Cr(CO)_5$ group, while in the less congested **2c** the $Mo(CO)_5$ group is able to straddle the ring plane without steric problems. Very likely the lack of steric congestion of **2c** is responsible for its greater thermal stability toward rearrangement to π-complex **3c**.

Finally, it should be noted that the plane of the phosphabenzene ring of **2c** precisely bisects the C(9)Mo(1)C(9) and C(8)Mo(1)C(8) angles. This staggering rather than a possible eclipsing of two of the (CO) groups is also found in **5** and the related pentacarbonyl (mesitylenediphenylmethylene)phosphine (**6**) [22]. Recent theoretical studies on similar carbene-$M(CO)_5$ complexes have indicated only very small rotational barriers about the carbene–metal bonds [23]. By analogy, the observed staggered conformations in **2c**, **5** and **6** are probably preferred only on steric grounds.

Acknowledgment

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