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An unexpected molybdenum(0) complex with "MoP_6" coordination: crystal structure of $[Mo\{P(CH_2CH_2PPh_2)_3\}_2] \cdot C_5H_{10}$

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Abstract

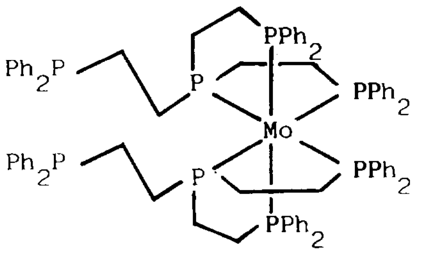
The reaction of *trans*-$[Mo(N_2)_2(PPh_2Me)_4]$ with the tripodal phosphine tris(2-diphenylphosphinoethyl)phosphine, PP_3, in benzene has been studied. The product was recrystallized from a mixture of benzene and petroleum ether to give $[Mo(PP_3)_2] \cdot C_5H_{10}$, whose crystal structure shows a distorted octahedral "MoP_6" coordination with both phosphines acting as tridentate ligands.

Introduction

Studies of the chemistry of dinitrogen complexes continue in order to clarify aspects relevant to nitrogen fixation. Despite the numerous contributions to the field, the synthesis of molybdenum dinitrogen complexes is still difficult and usually requires reduction processes under very controlled conditions [1]. An attractive alternative is the preparation of new complexes through substitution reactions starting from suitable well-characterized dinitrogen complexes. In this sense, *trans*-$[Mo(N_2)_2(PPh_2Me)_4]$ (**1**) is one of the few examples of dinitrogen complexes able to undergo substitution of a coordinated phosphine without loss of coordinated nitrogen [2–5], and use has been made of this to prepare dinitrogen complexes containing mono- and poly-dentate phosphines [3,5–7] or pyridine or other N-donor molecules [8]. Of particular relevance to this work is the preparation of $[Mo(N_2)_2(\text{triphos})(PPh_2Me)]$ [3]. In our study of substitution reactions of dinitrogen complexes we have examined the reaction of **1** with tris(2-diphenylphosphinoethyl)phosphine, PP_3, a tripodal phosphine able to coordinate through four P atoms. The reaction was studied separately under N_2 and Ar because different products could be reasonably expected under the two atmospheres.

Results and discussion

The reaction under Ar gave a red compound. Its infrared spectrum showed no band assignable to coordinated dinitrogen, either in the solid (KBr or Nujol) or in



Scheme 1

solution (benzene) under Ar or N_2. Air-stable red crystals were grown from a benzene–light petroleum solution of the compound under nitrogen during several weeks. Their elemental analysis was in agreement with the formula $[Mo(PP_3)_2] \cdot C_5H_{10}$ (**2**). The $^{31}P\{^1H\}$ NMR spectrum shows a doublet ($J = 17.1$ Hz) at -11.82 ppm indicative of the presence of uncoordinated PPh_2 units. The signal of the central P of PP_3 appears at 96.68 ppm, with a large coupling constant of 101.8 Hz in addition to other unresolved coupling. Between 64 and 67 ppm there are three overlapping multiplets corresponding to coordinated PPh_2 units. Both the analytical and spectroscopic data suggest the structure shown in Scheme 1.

However, examples of compounds with molybdenum(0) hexacoordinated by six P atoms are rare, and usually contain phosphines with small cone angles [9–12]. For this reason an X-ray analysis of the structure was carried out, and this confirmed the structure shown in Scheme 1.

Final atomic coordinates for all non-hydrogen atoms are listed in Table 1. The structure of the complex molecule with the atom labelling scheme is shown in Fig. 1. It can be described as having a highly distorted octahedral arrangement of six phosphorus atoms around molybdenum (Fig. 2). Both PP_3 ligands coordinate as tridentate ligands through the central P and two PPh_2 units in a *fac*-like coordination, with both central phosphorus atoms in *cis*-positions. There is also one free PPh_2 unit for each PP_3 molecule.

Selected bond lengths and angles are listed in Table 2. Mo–P distances range from 2.393(3) to 2.525(3) Å, with smaller values for all three phosphorus atoms in one PP_3 ligand than in the other one. This could suggest that there is a stronger interaction of one of the two tridentate phosphines but the NMR spectrum indicates that they become equivalent in solution, and the results found in the crystal structure are probably an artifact of the structure determination, especially since the absolute structure was not defined. The distances between Mo and the central P of both PP_3 ligands, 2.393(3) and 2.427(3) Å, are among the shortest known for molybdenum(0)-phosphine complexes [9–13]. On the other hand, the four Mo–PPh_2 bonds are relatively long, 2.468(3) to 2.525(3) Å, and similar to those in **1**, 2.496(2) Å [14]. The distortion from octahedral coordination is even more evident from the P–Mo–P angles, which range from 77.8(1) to 107.3(1)°, very far from the ideal value of 90°. The average values show that the distortion arises mainly from a decrease of the P–Mo–P angles for the chelate rings to ca. 80°, with a consequent increase in other angles, especially those involving P atoms of different PP_3 units.

Table 1

Final atomic coordinates for $[Mo\{P(CH_2CH_2PPh_2)_3\}_2]\cdot C_5H_{10}$; e.s.d.'s are in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	−0.0006(0)	0.2046(0) [a]	−0.0012(0)	C504	−0.1331(7)	0.5241(9)	−0.0003(9)
P1	0.0036(1)	0.0932(2)	−0.0821(1)	C505	−0.1046(6)	0.5203(9)	−0.0597(9)
P2	0.0117(1)	0.3168(2)	0.0748(1)	C506	−0.0862(5)	0.4503(8)	−0.0864(7)
P3	0.0652(1)	0.2619(2)	−0.0785(2)	C511	−0.1338(5)	0.2414(7)	−0.1176(6)
P4	−0.0748(1)	0.1686(2)	0.0845(1)	C512	−0.1855(5)	0.2447(8)	−0.0853(6)
P5	−0.0669(1)	0.2788(2)	−0.0775(1)	C513	−0.2360(5)	0.2150(9)	−0.1156(7)
P6	0.0744(1)	0.1528(2)	0.0802(2)	C514	−0.2335(6)	0.1837(9)	−0.1789(8)
P7	0.0118(2)	0.5883(2)	0.0847(2)	C515	−0.1833(6)	0.1775(9)	−0.2116(6)
P8	0.2308(2)	0.4020(3)	−0.0943(2)	C516	−0.1323(5)	0.2047(8)	−0.1807(6)
C13	0.0420(5)	0.1264(7)	−0.1594(5)	C601	0.0692(5)	0.0590(7)	0.1308(6)
C24	−0.0406(5)	0.3157(8)	0.1460(6)	C602	0.0852(5)	−0.0128(7)	0.1011(7)
C26	0.0797(5)	0.3102(7)	0.1248(6)	C603	0.0812(7)	−0.0846(10)	0.1362(8)
C27	0.0130(5)	0.4239(7)	0.0547(6)	C604	0.0614(7)	−0.0844(8)	0.2005(7)
C31	0.0857(5)	0.1935(8)	−0.1476(6)	C605	0.0444(7)	−0.0139(9)	0.2305(7)
C35	0.0305(5)	0.3405(7)	−0.1297(6)	C606	0.0489(6)	0.0571(8)	0.1962(6)
C38	0.1336(5)	0.3128(8)	−0.0586(6)	C611	0.1507(5)	0.1368(7)	0.0597(6)
C42	−0.0612(5)	0.2322(7)	0.1613(6)	C612	0.1933(7)	0.1273(13)	0.1081(8)
C53	−0.0279(5)	0.3097(8)	−0.1521(5)	C613	0.2494(7)	0.1093(13)	0.0923(9)
C62	0.0862(5)	0.2260(7)	0.1506(6)	C614	0.2659(6)	0.1036(10)	0.0271(9)
C72	0.0285(6)	0.4840(7)	0.1100(6)	C615	0.2224(7)	0.1104(10)	−0.0236(8)
C83	0.1654(7)	0.3507(14)	−0.1159(8)	C616	0.1682(5)	0.1272(8)	−0.0057(7)
C101	−0.0607(5)	0.0496(7)	−0.1217(6)	C701	0.0518(5)	0.6397(7)	0.1531(6)
C102	−0.1118(6)	0.0507(8)	−0.0886(7)	C702	0.0303(7)	0.6300(9)	0.2170(8)
C103	−0.1601(6)	0.0161(9)	−0.1150(8)	C703	0.0549(8)	0.6650(11)	0.2727(7)
C104	−0.1579(7)	−0.0204(10)	−0.1760(9)	C704	0.1056(7)	0.7070(9)	0.2652(7)
C105	−0.1101(7)	−0.0213(11)	−0.2099(9)	C705	0.1271(6)	0.7193(9)	0.2041(7)
C106	−0.0601(6)	0.0128(8)	−0.1846(7)	C706	0.1001(6)	0.6840(8)	0.1466(7)
C111	0.0411(5)	−0.0060(8)	−0.0692(6)	C711	0.0579(7)	0.6007(8)	0.0132(6)
C112	0.0981(6)	−0.0154(9)	−0.0844(7)	C712	0.0330(8)	0.6335(8)	−0.0460(8)
C113	0.1263(6)	−0.0871(9)	−0.0741(7)	C713	0.0656(11)	0.6368(11)	−0.1038(9)
C114	0.0965(8)	−0.1524(11)	−0.0489(8)	C714	0.1209(15)	0.6165(14)	−0.1040(13)
C115	0.0410(8)	−0.1445(9)	−0.0352(8)	C715	0.1469(10)	0.5842(13)	−0.0469(11)
C116	0.0102(6)	−0.0722(7)	−0.0461(7)	C716	0.1134(8)	0.5773(10)	0.0113(8)
C401	−0.1548(5)	0.1802(7)	0.0795(5)	C801	0.2378(5)	0.4718(8)	−0.1618(7)
C402	−0.1843(5)	0.2477(7)	0.1022(6)	C802	0.2089(8)	0.4693(11)	−0.2236(8)
C403	−0.2428(6)	0.2534(9)	0.0964(7)	C803	0.2132(8)	0.5311(12)	−0.2717(9)
C404	−0.2748(6)	0.1915(10)	0.0688(7)	C804	0.2494(7)	0.5924(10)	−0.2574(9)
C405	−0.2473(5)	0.1229(9)	0.0475(7)	C805	0.2779(8)	0.6011(12)	−0.1968(8)
C406	−0.1881(5)	0.1178(7)	0.0538(6)	C806	0.2710(5)	0.5384(10)	−0.1505(7)
C411	−0.0791(5)	0.0696(8)	0.1257(6)	C811	0.2880(7)	0.3294(10)	−0.1109(9)
C412	−0.0597(6)	0.0035(7)	0.0908(6)	C812	0.3119(10)	0.2884(11)	−0.0585(9)
C413	−0.0681(7)	−0.0735(9)	0.1152(8)	C813	0.3548(11)	0.2334(13)	−0.0677(12)
C414	−0.0967(7)	−0.0853(9)	0.1768(8)	C814	0.3762(10)	0.2269(12)	−0.1283(14)
C415	−0.1156(7)	−0.0192(10)	0.2102(8)	C815	0.3560(13)	0.2642(15)	−0.1845(13)
C416	−0.1087(6)	0.0570(8)	0.1854(6)	C816	0.3132(10)	0.3170(12)	−0.1765(11)
C501	−0.0942(5)	0.3777(7)	−0.0529(6)	C1	−0.2863(11)	−0.1363(16)	−0.2670(13)
C502	−0.1245(6)	0.3834(8)	0.0081(7)	C2	−0.8027(12)	0.0030(19)	−0.3147(15)
C503	−0.1442(6)	0.4542(9)	0.0323(8)	C3	−0.3093(12)	−0.0570(19)	−0.2582(15)
				C4	−0.7625(13)	0.1442(20)	−0.3398(16)
				C5	−0.7728(12)	0.0535(18)	−0.3710(15)

[a] E.s.d. less than 0.00005.

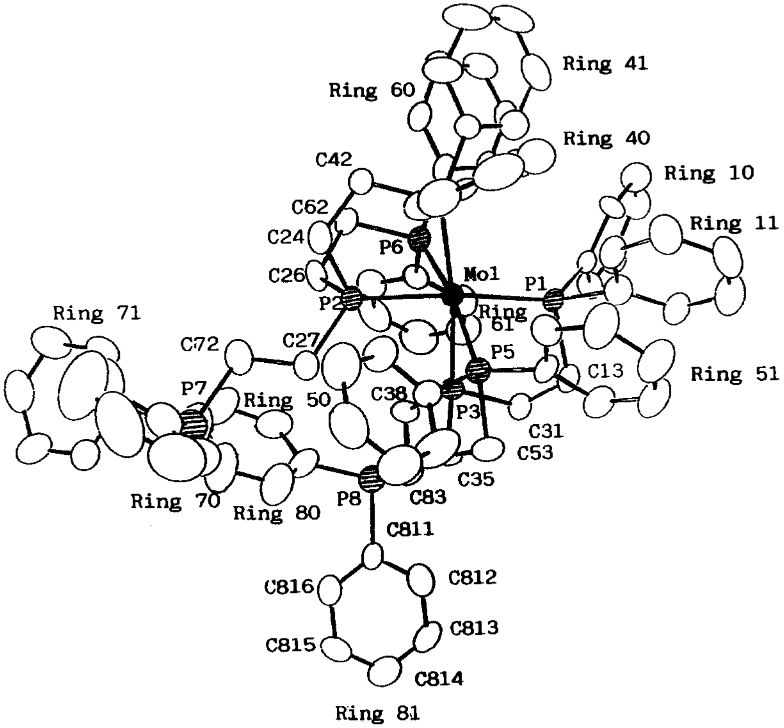


Fig. 1. Molecular structure of [Mo{P(CH$_2$CH$_2$PPh$_2$)$_3$}$_2$] showing the atom numbering scheme.

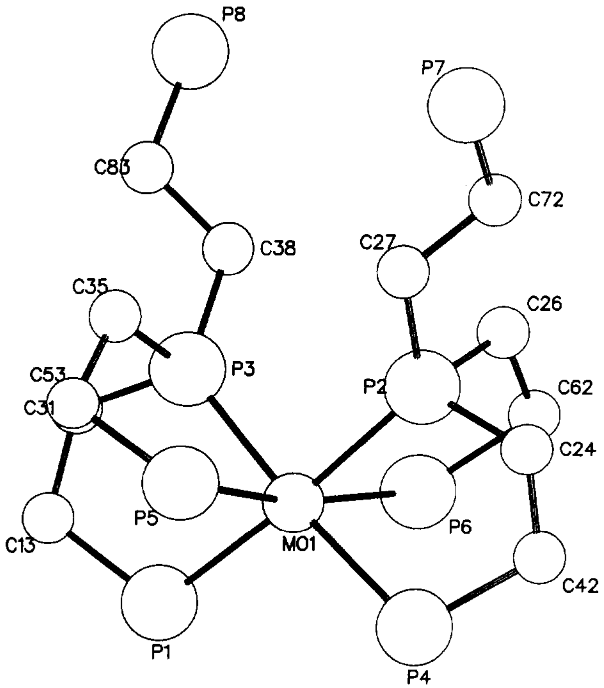


Fig. 2. Molecular structure of [Mo{P(CH$_2$CH$_2$PPh$_2$)$_3$}$_2$] with the phenyl groups omitted for clarity.

Table 2

Selected bond lengths (Å) and angles (°) in $[Mo\{P(CH_2CH_2PPh_2)_3\}_2]\cdot C_5H_{10}$; e.s.d.'s are in parentheses

(a) About the Mo atom			
Mo–P(1)	2.468(3)	Mo–P(4)	2.524(3)
Mo–P(2)	2.427(3)	Mo–P(5)	2.488(3)
Mo–P(3)	2.393(3)	Mo–P(6)	2.525(3)
P(1)–Mo–P(2)	170.6(1)	P(2)–Mo–P(6)	77.8(1)
P(1)–Mo–P(3)	81.3(1)	P(3)–Mo–P(4)	170.2(1)
P(1)–Mo–P(4)	107.3(1)	P(3)–Mo–P(5)	78.8(1)
P(1)–Mo–P(5)	90.4(1)	P(3)–Mo–P(6)	96.0(1)
P(1)–Mo–P(6)	97.3(1)	P(4)–Mo–P(5)	96.1(1)
P(2)–Mo–P(3)	91.2(1)	P(4)–Mo–P(6)	87.7(1)
P(2)–Mo–P(4)	80.7(1)	P(5)–Mo–P(6)	170.0(1)
P(2)–Mo–P(5)	93.6(1)		
(b) Bond lengths in triphosphinophosphine ligands			
P(1)–C(13)	1.880(12)	P(5)–C(53)	1.830(12)
P(1)–C(101)	1.838(12)	P(5)–C(501)	1.843(12)
P(1)–C(111)	1.893(12)	P(5)–C(511)	1.854(12)
P(2)–C(24)	1.887(13)	P(6)–C(62)	1.879(13)
P(2)–C(26)	1.867(12)	P(6)–C(601)	1.872(12)
P(2)–C(27)	1.837(12)	P(6)–C(611)	1.854(13)
P(3)–C(31)	1.861(13)	P(7)–C(72)	1.856(13)
P(3)–C(35)	1.846(12)	P(7)–C(701)	1.854(12)
P(3)–C(38)	1.850(13)	P(7)–C(711)	1.812(14)
P(4)–C(42)	1.889(12)	P(8)–C(83)	1.799(19)
P(4)–C(401)	1.878(11)	P(8)–C(801)	1.792(14)
P(4)–C(411)	1.852(13)	P(8)–C(811)	1.838(17)

The presence of C_5H_{10} was revealed during the crystal structure analysis; it was evidently taken up from the light petroleum used in the recrystallization.

When the substitution reaction was carried out under nitrogen $[Mo(PP_3)_2]$ was again the main product, but small amounts of other unidentified substitution products were formed, as indicated by the NMR spectra of unrecrystallized samples. The existence of compound **2** reveals that the formation of complexes with a MoP_6 core is not restricted to phosphines with less bulky substituents. In addition, compound **2** is easily obtained under very mild conditions even when a stoichiometric deficiency of PP_3 is used, whereas related complexes often require molybdenum vapour co-condensation in the presence of an excess of phosphine [9,11].

Experimental

A solution of equimolar amounts (1 mmol) of **1** and PP_3 in benzene was stirred overnight under argon at room temperature. The resulting solution was taken to dryness. Recrystallization of the residue from benzene–petroleum ether yielded **2** (30% based on molybdenum). Satisfactory analytical data were obtained. (Found: C, 68.82; H, 6.14; P, 16.03. $MoC_{89}H_{94}P_8$ calcd.: C, 70.91; H, 6.29; P, 16.44%.)

A suitably sized crystal was selected and preliminary X-ray photographic examination by the precession method established the crystal system and approximate cell dimensions. Accurate cell dimensions were obtained from the setting angles of 25 accurately centred reflections on the diffractometer.

Crystal data for $[Mo\{P(CH_2CH_2PPh_2)_3\}_2] \cdot C_5H_{10}$

The complex crystallized in the monoclinic system with cell dimensions a = 23.358(1), b = 16.733(1), c = 19.948(1) Å, β = 90.81(1)°, V = 7796.02 Å^3 and Z = 4; space group Ia, M = 1507.5, D_c = 1.284 g/cm^3, μ = 20.19 cm^{-1}, $F(000)$ = 3372, 5810 reflections were collected on a Philips PW1100 diffractometer using graphite monochromator, Cu-K_α radiation (λ = 1.5418 Å) and ω–2θ scan in the range $3° < 2\theta < 120°$. 4923 reflections considered as observed ($I > 3\sigma(I)$) were used in the structural analysis. The structure was solved by a combination of conventional Patterson method and Fourier synthesis and refined on F by full-matrix least-squares calculations.

In the refinements the x and z coordinates of the Mo atom were fixed at the values found from the Patterson analysis. Anisotropic thermal parameters were refined for all non-hydrogen atoms in the complex. In the later stages of the refinement H atoms were included at fixed positions, and with the thermal parameters of the atoms to which they are attached. An appropriate weighting scheme $w = w_1 w_2$ for the refinement was used to give no trends in $\langle w \Delta^2 F \rangle$ vs. $\langle F_0 \rangle$ and vs $\langle \sin\theta/\lambda \rangle$, were $w_1 = 1/(a + b[F_0])^2$, $w_2 = 1/(c + d \sin\theta/\lambda)^2$; and coefficients a = 11.5036, b = −0.3094, c = 0.0030 for $1 < F_0 < 53.5$; a = 3.4788, b = −0.0013 for $53.5 < F_0 < 96$; a = 1.5243, b = 0.0190 for $96 < F_0 < 480$. Final R and R' values were 0.055. All calculations were carried out with DIRDIF [15], PESOS [16], PARST [17] and XRAY80 [18] on a VAX-11750 computer. The absolute structure was not defined.

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