Journal of Organometallic Chemistry, 82 (1974) 235—241
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THE REACTION OF PENTAMETHYLCYCLOPENTAPHOSPHINE WITH (Cr, Mo, W) HEXACARBONYLS AND THE CRYSTAL STRUCTURE OF HEXAMETHYLCYCLOHEXAPHOSPHINETUNGSTEN TETRACARBONYL $W(CO)_4(PCH_3)_6$

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(Received July 1st, 1974)

Summary

Complexes of general formulae $(PCH_3)_5M(CO)_4$, $(PCH_3)_6M(CO)_4$, $[(PCH_3)_5]_2M_2(CO)_8$, $(PCH_3)_9M_2(CO)_6$ can be isolated from the reactions of $(PCH_3)_5$ with $M(CO)_6$, (M = Cr, Mo, W). The structure of $(PCH_3)_6W(CO)_4$ has been determined by a single crystal X-ray diffraction study using Patterson and Fourier methods and refined by least-squares techniques to an R of 0.09 for 1091 independent reflections. The crystals are monoclinic, space group $C2/c$, $Z = 4$, $a = 9.29$, $b = 16.88$, $c = 12.92$ (all ± 0.02)Å, $\beta = 96.0(1)°$. The cyclic hexaphosphine which has the 'boat' configuration in the complex with the two *cis* phosphorus atoms coordinating to the metal, has not been detected in the free state. The compound previously reported as $(PCH_3)_5W(CO)_3$ is shown to be $(PCH_3)_9W_2(CO)_6$.

Introduction

Studies of the reactions of cyclic phosphines with the hexacarbonyls of Cr, Mo and W at elevated temperatures (ca. 130-170°) have shown [1, 2] that complexes may be formed in which the phosphine ring is intact and is coordinated to the metal by one or two phosphorus atoms, e.g. $(PR)_5M(CO)_5$ or $(PR)_5M(CO)_4$. The molecular structure of $(PC_2H_5)_5Mo(CO)_4$ has been determined by Bush and Woodward [3] and confirms the bidentate behaviour of the phosphine ring in that compound. Cyclic arsines on the other hand give binuclear complexes under similar reaction conditions [4].

The compounds formed by $(AsCH_3)_5$ have been shown [5] to be correctly formulated as $(AsCH_3)_9M_2(CO)_6$ by an X-ray structural study which established that in $(AsCH_3)_9Cr_2(CO)_6$ the $(AsCH_3)_9$ unit exists as a nine-membered cyclic arsine coordinated to each Cr atom by sets of three As atoms. A second variant of the binuclear species has been identified for the Mo [4] compound formed by reaction of $Mo(CO)_6$ with $(AsR)_5$, R = C_2H_5, n-C_3H_7, having the molecular formula $(AsR)_8Mo_2(CO)_6$. The $(As\text{-}n\text{-}C_3H_7)_8$ complex has been shown by an X-ray study [5] to contain a chain of eight ($As\text{-}n\text{-}C_3H_7$) units, the terminal groups bridging both metal atoms together with one other Mo—As coordinate-link to each Mo and a Mo—Mo distance indicating metal—metal bonding.

The reactions of $(PCH_3)_5$ with Cr, Mo and $W(CO)_6$ have now been re-examined using several different reaction conditions in a search for related binuclear compounds involving phosphine units. Ang and West [1] had previously identified the compounds $(PCH_3)_5M(CO)_4$, M = Cr, Mo, W in reactions conducted for relatively short periods of time at moderate temperatures. A small amount of a complex given the formula $(PCH_3)_5W(CO)_3$ was also reported to be formed in the $W(CO)_6$ reaction, the formula suggesting tridentate behaviour for the phosphine.

Results and discussion

The various compounds prepared in this study are listed in Table 1.

The complex $(PCH_3)_5W(CO)_4$ was formed when $(PCH_3)_5$ was heated with $W(CO)_6$ for a relatively short (7 h) period at 170° and was identical with the product reported by Ang and West [1]. Its mass spectrum showed the parent molecular ion at *m/e* = 526 (based on ^{184}W) as well as the molecular ion for the cyclic phosphine $(PCH_3)_5^+$ indicating the probable existence of the unbroken ring in the compound. In addition, however, a dimeric species $[(PCH_3)_5W(CO)_4]_2$ was isolated and differentiated from the monomer by its mass spectrum which showed a molecular ion $[(PCH_3)_{10}{}^{184}W_2(CO)_8]^+$ at *m/e* = 1052. Other ions formed by successive loss of carbonyl groups were clearly detected together with the molecular ion $[(PCH_3)_5]^+$ and its fragmentation pattern, suggesting that the phosphine rings may still exist in this molecule. The infrared spectrum of the complex is similar in profile to a typical *cis*-disubstituted W carbonyl

TABLE 1

SYNTHETIC AND ANALYTICAL DATA FOR PENTAMETHYLCYCLOPENTAPHOSPHINE COMPLEXES

Reaction conditions	Products	M p. (°C)	Found (calcd.) (%)			Mol wt.[a] Found (calcd.)
			C	H	P	
160°, 30 h	$(PCH_3)_9W_2(CO)_6$	>300	19.0 (19.0)	3.0 (2.9)	29.9 (29.4)	950 (949.8)
	$(PCH_3)_6W(CO)_4$	dec. 180°	20.9 (21.0)	3.2 (3.2)	32.4 (32.5)	572 (571.9)
165°, 16 h	$(PCH_3)_9Mo_2(CO)_6$	>300	23.2 (23.3)	3.5 (3.5)	35.1 (36.0)	778 (774.0)
165°, 17 h	$(PCH_3)_9Cr_2(CO)_6$	>300	26.3 (26.3)	4.0 (4.0)	39.3 (40.6)	686 (686.1)
160°, 6 h	$(PCH_3)_6Cr(CO)_4$	dec. 190°	27.1 (27.3)	4.2 (4.1)	42.4 (42.2)	440 (440.1)

[a] By mass spectrometry. Molecular weight based on most abundant isotope ^{52}Cr, ^{98}Mo and ^{184}W.

TABLE 2

CARBONYL STRETCHING FREQUENCIES FOR PENTAMETHYLCYCLOPENTAPHOSPHINE COMPLEXES IN CHLOROFORM

Complex	Frequencies (cm^{-1})		
$(PCH_3)_6W(CO)_4$	2010s	1920(sh)	1900vs(br)
$(PCH_3)_6Cr(CO)_4$	2008s	1920(sh)	1890vs(br)
$(PCH_3)_9Cr_2(CO)_6$		1932s	1866s(br)
$(PCH_3)_9Mo_2(CO)_6$		1946s	1878s(br)
$(PCH_3)_9W_2(CO)_6$		1940s	1872s(br)
$[(PCH_3)_5W(CO)_4]_2$	2015s	1920(sh)	1905vs(br)
$(PCH_3)_5W(CO)_4$	2010s	1920(sh)	1902vs(br)

complex [6] and was not readily distinguishable from that of the monomer (Table 2).

Heating the phosphine with each hexacarbonyl for substantially longer reaction times (16-30 h) resulted in the formation of the compounds $(PCH_3)_9$-$M_2(CO)_6$, M = Cr, Mo, W. In the case of $W(CO)_6$ a second product, having the empirical formula $(PCH_3)_6W(CO)_4$, was also isolated in rather lower yield than the binuclear compound.

The infrared spectrum of $(PCH_3)_9W_2(CO)_6$ shows two strong bands at 1940 and 1872 cm^{-1} which is consistent with a *fac*-substituted tricarbonyl complex of tungsten [6]. The molecular ion $[(PCH_3)_9{}^{184}W_2(CO)_6]^+$ (m/e = 950), is the most intense peak in the mass spectrum. Two additional peaks of very low intensity (< 1%) were observed at $m/e > 950$ and may indicate an impure sample or recombination ions. The molecular ion and fragmentation pattern associated with the cyclic phosphine were absent. Similar infrared and mass spectral data were obtained for the chromium and molybdenum complexes, $(PCH_3)_9Cr_2(CO)_6$ and $(PCH_3)_9Mo_2(CO)_6$.

These complexes $(PCH_3)_9M_2(CO)_6$ are analogous to the binuclear derivatives [4] obtained by the reactions of pentaalkylcyclicpentaarsines with Cr, Mo and $W(CO)_6$ and may be assumed to have similar structures to that determined [5] for $(AsCH_3)_9Cr_2(CO)_6$ by a single crystal X-ray study. The expected structure of $(PCH_3)_9W_2(CO)_6$ is shown in Fig. 1.

The compound reported by Ang and West [1] having empirical formula $(PCH_3)_5W(CO)_3$ was not isolated in the present work. The close similarity of its infrared spectrum to that of $(PCH_3)_9W_2(CO)_6$, however, suggests that the latter was the complex isolated.

The structure of the second type of complex isolated from the prolonged thermal reaction of $W(CO)_6$, viz. $(PCH_3)_6W(CO)_4$, has been established by a single crystal X-ray diffraction study (Fig. 2). The analogous Cr compound has also been prepared.

The bond lengths and angles with their standard deviations are listed in Table 3. Four carbonyl groups and two phosphorus atoms form a distorted octahedron of ligands about the central tungsten atom. The molecule possesses C_2 symmetry with the tungsten atom situated on the two-fold axis. The phosphorus atoms are arranged as a six-membered ring which has a skew 'boat' conformation. The P—P bond lengths are equal within experimental error, the

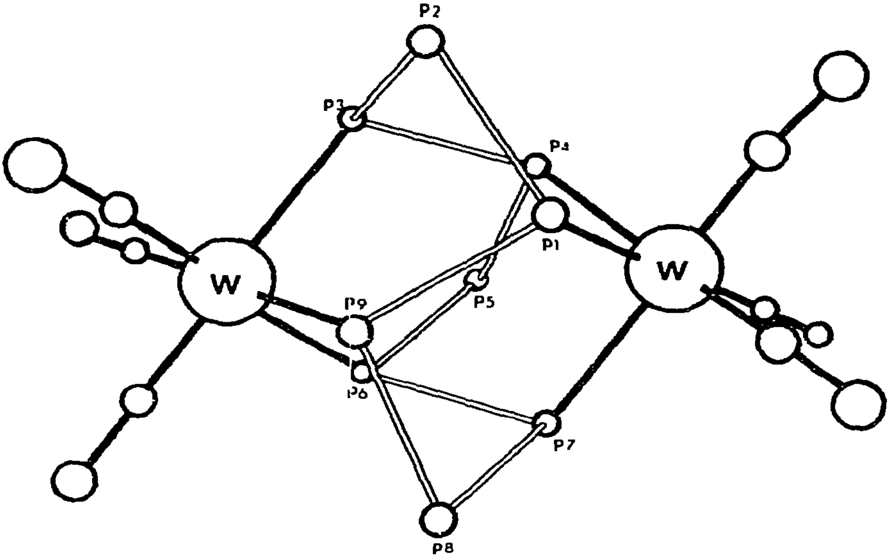

Fig. 1. The expected structure of $(PCH_3)_9W_2(CO)_6$; the methyl groups are not shown.

mean value of 2.235(12) Å being comparable to P—P distances in other six-membered rings of phosphorus atoms, viz., trigonal $(PC_6H_5)_6$ 2.234(2) Å [7]; triclinic $(PC_6H_5)_6$ 2.233(5) Å [8] and orthorhombic black phosphorus 2.234(2) Å [9]. Angles within the phosphorus ring range from 94.9(4)° at P(3) to 104.8(4)° at coordinated P(1) and average 100.9(4)°. The methyl groups on phosphorus atoms P(1) and P(3) occupy pseudo 'equatorial' positions; those on atoms P(2)

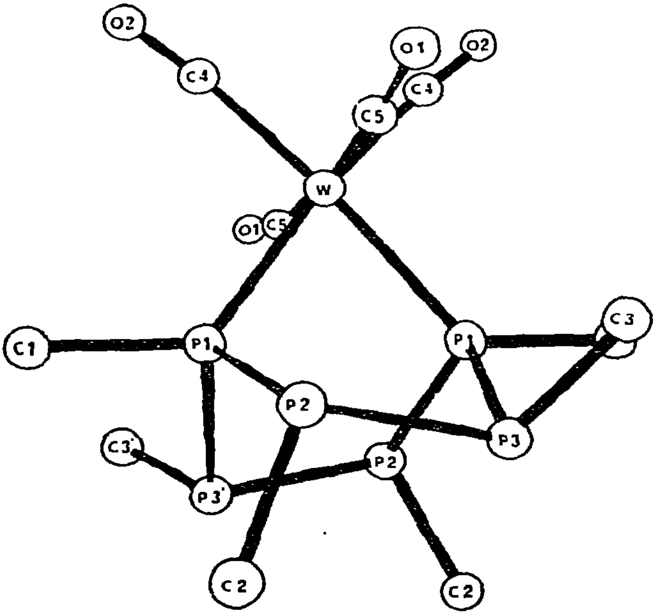

Fig. 2. Molecular geometry of $(PCH_3)_6W(CO)_4$ showing the atom labelling scheme. Primed numbers indicate symmetry related atoms.

TABLE 3

BOND LENGTHS (Å) AND ANGLES (°)[a]

W—P(1)	2.502(7)	P(1)—P(2)	2.221(13)
W—C(4)	2.01(3)	P(2)—P(3)	2.247(11)
W—C(5)	1.99(5)	P(1)—P(3′)	2.237(12)
		P(1)—C(1)	1.88(3)
C(5)—O(1)	1.25(6)	P(2)—C(2)	1.84(3)
C(4)—O(2)	1.09(4)	P(3)—C(3)	1.90(4)
P(1)—W—P(1′)	73.8(2)	P(3′)—P(1)—P(2)	104.8(4)
C(4)—W—C(4′)	89(1)	P(2)—P(3)—P(1′)	97.9(4)
P(1)—W—C(5′)	94(1)	P(1)—P(2)—P(3)	100.1(4)
C(5)—W—C(4)	84(1)	P(2)—P(1)—C(1)	100(1)
P(1)—W—C(4)	98.7(9)	P(3′)—P(1)—C(1)	100(1)
P(1)—W—C(5)	92.6(10)	P(3)—P(2)—C(2)	100(1)
C(5′)—W—C(4)	90(1)	P(1)—P(2)—C(2)	105(1)
W—P(1)—P(3′)	115.3(4)	P(2)—P(3)—C(3)	100(1)
W—P(1)—C(1)	127(1)	P(1′)—P(3)—C(3)	102(1)
W—P(1)—P(2)	106.5(4)		
W—C(5)—O(1)	169(3)		
W—C(4)—O(2)	175(3)		

[a] Estimated standard deviations are given in parentheses.

are pseudo 'axial'. The average P—C bond length of 1.87(3) Å is in agreement with values found for $(PCF_3)_4$ (1.87(1)Å) [10] and $(PC_2H_5)_5Mo(CO)_4$ (1.85(2) Å) [3]. The W—P distance (2.502(7)Å) is less than the sum of the covalent radii of W (1.58 Å) [11] and phosphorus (1.10 Å) [12] but is similar to distances previously reported for these bonds [13].

Deviation from a regular octahedral environment about the tungsten atom is greatest for the P(1)—W—P(1′) inter-ligand angle where a contraction from 90° to 74° occurs. Back donation to carbonyl groups *trans* to the phosphorus atoms is expected to be greater than to *cis* groups. However, the W—C *cis* and *trans* distances are both 2.00(4) Å (cf. 1.96 Å for $(\pi\text{-}C_5H_5)(C_6H_5)(CO)_3W$) [11]. The W—C—O bond angles for *cis* CO groups (169(3)°) deviate more from 180° than do the angles for *trans* groups (175(3)°). A similar result [3] was observed for $(PC_2H_5)_5Mo(CO)_4$.

The formation of such compounds in these reactions involving initially $(PCH_3)_5$ is a most interesting observation since although the hexameric ring compounds $(PC_6H_5)_6$ [8] and $(AsC_6H_5)_6$ [14] are known, $(PCH_3)_6W(CO)_4$ contains the first example of a six-membered, alkyl substituted cyclopolyphosphine or -arsine. A detailed examination of the sample of $(PCH_3)_5$ used in the experiments failed to detect the free species $(PCH_3)_6$ and the question of the mode of formation of hexamethylcyclohexaphosphine has not been resolved.

Thus, the mass spectrum of the pentamethylcyclopentaphosphine sample used in the synthesis showed an intense parent ion at $m/e = 230$ corresponding to $(PCH_3)_5^+$; no peaks were observed at $m/e > 230$. The purity of the phosphine was also inferred from the 40.5 MHz ^{31}P spectrum which showed a single resonance (1.1 hz width at half height) centred at 92.8 ppm with respect to external 85% H_3PO_4. Previous work with ^{31}P spectra of perfluorocyclophosphines [15] has indicated that phosphorus resonances in phosphines of different ring size show very different chemical shifts.

The mass spectrum of a sample of $(PCH_3)_5$ which had been heated in the absence of metal carbonyl under the conditions used for synthesis of $Cr(CO)_4(PCH_3)_6$ (6 h, 160°) was identical with its spectrum before heating [4]. Further prolonged heating increased the viscosity of the phosphine sample possibly indicating the formation of higher PCH_3 polymers, either rings or chains, although these could not be detected by mass spectrometric analysis.

Experimental

Physical measurements were carried out as previously described [4].

Pentamethylcyclopentaphosphine was prepared from methylphosphonous dichloride (Ethyl Corporation) and lithium [16]. Mass spectrum: molecular ion *m/e* 230 $(PCH_3)_5^+$, 50%; other intense peaks include *m/e* 215 $P_5(CH_3)_4^+$, 30%; *m/e* 138 $(PCH_3)_3^+$, 75%; *m/e* 123 $P_3(CH_3)_2^-$, 100%. There were no peaks detected with $m/e > 230$.

Complexes of $(PCH_3)_5$. Equimolar mixtures of the phosphine and the metal carbonyl (5 mmol) were heated with benzene (5-10 ml) in evacuated tubes at temperatures between 120 and 160°C (Table 1). After the reaction the solutions were evaporated and the oily residues crystallized from chloroform or acetone. As the metal complexes are air-sensitive in solution, all operations were carried out in a nitrogen atmosphere.

Crystal and molecular structure of $(PCH_3)_6W(CO)_4$

Crystal data: $C_{10}H_{18}O_4P_6W$, $M = 571.9$, monoclinic, $a = 9.29$, $b = 16.88$, $c = 12.92$ (all ± 0.02) Å, $\beta = 96.0(1)°$, $U = 2015$ Å^3, $D_m = 1.91$ g cm^{-3} (by flotation), $Z = 4$, $D_c = 1.89$ g cm^{-3}. $F(000) = 1096$. Space group $C2/c$ by systematic absences and structure solution. Cu-K_α radiation, $\lambda = 1.5418$ Å; μ(Cu-K_α) = 162.7 cm^{-1}. The intensity data were collected from a crystal of dimensions ca. 0.08 × 0.06 × 0.08 mm.

1091 independent non-zero reflections were collected with a Nonius equi-inclination Weissenberg goniometer for reciprocal lattice levels *Okl* - *7kl* and measured visually. Corrections were made for spot-shape and for Lorentz and polarisation factors but not for absorption or extinction.

A three-dimensional Patterson synthesis revealed the position of the tungsten atom. Successive structure-factor calculations and difference-Fourier syntheses eventually revealed all non-hydrogen atoms. After four cycles of least-squares refinement of the positional and isotropic thermal parameters and eight scales, the R value was 0.096. A difference-Fourier map showed evidence of anisotropic motion around tungsten. A further two cycles of refinement allowing anisotropic temperature factors for tungsten gave $R = 0.093$. In the last two cycles parameter shifts were less than 0.3 σ. A final difference-Fourier synthesis contained no density > 1 e Å^{-3} except close to the tungsten position where values of ca. 3 e Å^{-3} occurred. In all refinements, reflections were assigned unit weight. Atomic scattering factors were taken from Ref. 17.

The final atomic coordinates and thermal parameters together with their estimated standard deviations are given in Table 4. A table of observed and calculated structure factors may be obtained from the authors.

Modified versions of the full-matrix least-squares programme of Busing,

TABLE 4

ATOMIC PARAMETERS (FRACTIONAL) FOR $(PCH_3)_6W(CO)_4$[a]

The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$

Atom	x/a	y/b	z/c	B/A^2
W	0.0	0.2064(1)	0.2500	[b]
P(1)	0.0344(9)	0.3249(4)	0.3663(6)	3.0(1)
P(2)	0.224(1)	0.3904(5)	0.3179(6)	3.8(2)
P(3)	0.147(1)	0.4128(5)	0.1497(6)	3.7(2)
O(1)	0.339(3)	0.179(2)	0.224(2)	5.4(6)
O(2)	0.060(3)	0.079(1)	0.422(2)	5.8(6)
C(1)	0.079(4)	0.326(2)	0.512(2)	4.6(7)
C(2)	0.208(4)	0.491(2)	0.372(2)	4.7(7)
C(3)	0.293(4)	0 359(2)	0.084(2)	4.7(7)
C(4)	0.040(3)	0.121(2)	0.358(2)	3.5(6)
C(5)	0.211(6)	0 198(2)	0.237(2)	3.1(7)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W	0.0108(8)	0.0037(1)	0.0050(1)	0	0.0001(1)	0

[a] Estimated standard deviations are given in parentheses. [b] Anisotropic thermal parameters.

Martin and Levy [18] and the Fourier summation programme of White [19] were used during the refinement. All calculations were performed on the Monash University CDC 3200 computer.

Acknowledgement

This work was supported by the Australian Research Grants Committee.

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