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THE COORDINATING PROPERTIES OF PENTAMETHYLCYCLOPENTA-ARSINE

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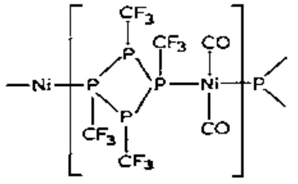
Double bond formation between pairs of atoms of phosphorus, arsenic or antimony does not occur, hence compounds analogous to azo derivatives are unknown for these elements. Instead cyclic compounds can be formed in which the Group V element is exerting a covalency of three; compounds containing 4, 5 and 6 numbered rings are known[1].

The coordinating properties of such ring compounds with transition metals were first examined by Burg and Mahler[2] who reacted tetraperfluoromethylcyclotetraphosphine with nickel carbonyl and obtained a solid product of indefinite composition believed to be a polymer of the form (I).



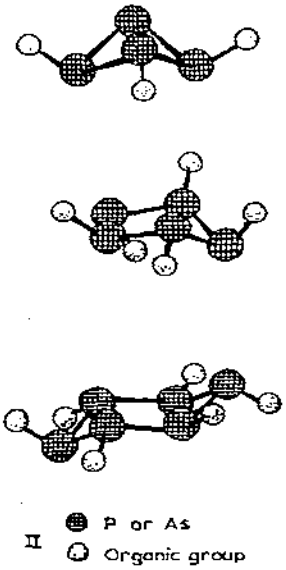
I

Isslieb and Mitcherling[3] also obtained ill-defined products from the reaction of tetraethylcyclotetraphosphine with nickel bromide.

More recent attempts at examining the coordinating properties of cyclic phosphines have been successful, and compounds in which a five-membered cyclic phosphine has been observed to act as a uni-, bi- or tridentate ligand have been reported[4,5]. Ang, Shannon and West[6] reported that a ring expansion from four to five members accompanied reaction of "phosphoro-benzene" with metal carbonyls. The product believed to be tetraphenylcyclotetraphosphine reacted with tungsten hexacarbonyl to give the five-membered ring compound $W(CO)_5(C_6H_5P_5)$, the cyclic phosphine showing in the mass spectrum of the complex. However, Maier and Daly[7,8] have shown that the phenylcyclophosphine long believed to be a tetramer and indeed giving solution molecular weights corresponding to the tetrameric form, is actually pentameric in the solid state. Continued investigation of the anomalous molecular weight problem has caused Maier[9] to conclude that the pentamer can occlude sufficient traces of the reagents from which it is commonly synthesised, particularly $C_6H_5PH_2$, to effect the molecular weight determination adversely.

The ring expansion reported by Ang, Shannon and West[6] appears therefore, to have been due to an impurity in the cyclic phosphine used. However, Stone, Forster, Cundy and Green[4] have reported a similar change in ring size in the reaction of cyclopentamethylphosphine with cuprous halides. Copper(I) bromide reacts to form $[(CH_3P)_5CuBr]_x$ while copper(I) chloride gives $[(CH_3P)_4CuCl]_x$. The existence of a ring in the latter compound has not been proven other than by inference from analytical data, and it may be that a bridged compound of the type formed with $Fe(CO)_5$ and cyclic phosphines (see later) exists in this molecule.

The structures of a number of cyclic phosphines and arsines have been determined[1] and indicate that a puckered ring form exists for each type of ring as shown in (II). This would allow phosphorus or arsenic atoms having their lone pairs oriented in similar directions to act as coordination sites. The crystal structure of the complex $Mo(CO)_4(C_2H_5P)_5$ described by Bush, Cook and Woodward[10] has established this type of coordination for a cyclic phosphine acting as a bidentate ligand.



II

The reaction of an arsenic derivative, pentamethylcyclopenta-arsine with some metal carbonyls has now been examined. The arsine in its liquid modification is known to have a puckered ring conformation with one arsenic atom displaced from the plane of other four[11].

The methyl substituted cyclic arsine has only been reported in the form of a five membered arsenic ring compound and indeed the mass spectrum of the compound failed to show the existence of any $(CH_3As)_6$ molecular ions or of $(CH_3As)_4$

TABLE 1

MASS SPECTRUM OF $(AsCH_3)_5$

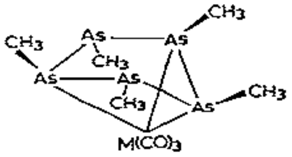
Ion$^+$	*m/e*	%	*Ion*$^+$	*m/e*	%	*Ion*$^+$	*m/e*	%
$(CH_3As)_5$	450	32	$(CH_3As)_4$	360	4	$(CH_3As)_3$	270	80
$(CH_3)_4As_5$	435	22	$(CH_3)_3As_4$	345	8	$(CH_3)_2As_3$	255	79
			$(CH_3)_2As_4$	330	4	CH_3As_3	240	7
$(CH_3)_2As_5$	405	4	CH_3As_4	315	9	$(CH_3)_2As_3$	105	100
						$AsCH_3$	90	23
As_5	375	5	As_4	300	27	As_3	225	49

species other than could be accounted for by disintegration of the pentameric parent ion $[(CH_3As)_5]^+$. The main species detected are listed in Table 1.

The n.m.r. spectrum of the arsine shows three proton resonances at τ values of 8.33, 8.36 and 8.37 relative to T.M.S. in the ratio of 2:2:1. The separation between the peaks is virtually unchanged between $-60°$ and $+180°$. A similar distribution of ^{19}F resonances has been reported by Wells[12] for $(CF_3P)_5$ in the intensity ratio of 3:2 with a notable merging of the peaks above 183 °C. This has been explained by the assumption of a cyclic interchange of the positions of the phosphorus atoms around the ring at high temperatures.

A model of the five membered arsenic ring system suggests that only if the molecule becomes planar by ring vibration can there be groups of CH_3 groups which could be distinguished by n.m.r. signals in the ratio 2:2:1. In all other configurations five resonances should be observed. It is considered therefore, that a very rapid rotation of the puckering in the arsenic ring, even at low temperatures can lead to the methyls experiencing a time average field comparable to that of a planar configuration for the ring, thus giving rise to the observed n.m.r. spectrum.

The direct reaction of $(CH_3As)_5$ with Cr(Mo, W) $(CO)_6$ at 170° in benzene solution yielded red crystalline products having the formula $M(CO)_3(CH_3As)_5$, the arsine acting as a tridentate ligand. This is supported by the infra-red spectra of the complexes which show two strong C–O stretching frequencies in the region expected for carbonyl complexes substituted by three groups in the *cis* position (Table 2). This suggests a structure of the type shown in (III).



III

since three of the five arsenic atoms in the ring have their lone pairs of electrons similarly oriented. The n.m.r. spectra of the complexes are much more complex than that of the free ligand but groups of resonances having intensities in the

TABLE 2

CO STRETCHING FREQUENCIES FOR COMPLEXES $M(CO)_3(CH_3As)_5$

	cm^{-1}	cm^{-1}
Cr	1926(s)	1862(s)
Mo	1930(s)	1855(s)
W	1930(s)	1858(s)

ratio 3:1:1 can be identified. The Cr complex, for example, has resonances centred at $\tau = 7.92(3)$, 8.48(1) and 8.58(1). At this stage of the analysis the peak centering at 7.92 is taken to indicate the methyls attached to the three coordinated arsenic atoms.

The reaction of the arsine at room temperature with the ethanol-substituted pentacarbonyl complexes, $M(CO)_5C_2H_5OH$ ($M = Cr$, Mo, W) has produced the yellow, binuclear complexes $[M(CO)_5]_2(AsCH_3)_5$. The infrared spectra of these compounds show the three-band carbonyl pattern expected for mono-substituted Group VI A carbonyls (Table 3).

The n.m.r. spectra of the compounds are complex, but bands can be identified with intensities in the ratio 1:1:3 *e.g.* the Cr complex shows resonances at $\tau = 8.02(1)$, 8.10(1) and 8.24(3), the two resonances having experienced shifts to low field relate to the metal atoms coordinated to separate arsenic atoms.

TABLE 3

CO STRETCHING FREQUENCIES FOR COMPLEXES $[M(CO)_5]_2(CH_3As)_5$

	cm^{-1}	cm^{-1}	cm^{-1}
Cr	2055(w)	1936(s)	1926(sh)
Mo	2066(w)	1944(s)	1922(s)
W	2066(w)	1936(s)	1925(sh)

Preliminary experiments in which the cyclo-octadiene derivatives, $M(CO)_4$-C_8H_{12} ($M = Cr$, Mo, W) have been reacted with the arsine at room temperature have shown infra-red evidence for the existence of di-substituted derivatives in solution, but crystallization of the products has so far proved exceedingly difficult.

Thus the cyclic arsine appears sufficiently flexible to act as either a uni, bi or tri-dentate ligand.

The reaction of cyclic pentaphosphines with $Fe(CO)_5$ produced binuclear compounds of the form $[Fe(CO)_3]_2(RP)_4$. The mass spectra of these compounds did not show the existence of a cyclic phosphine as a separate species in the fragmentation pattern and it has been concluded that the ring is broken during reaction to give a phosphido bridged derivative[5]. Pentamethylcyclopenta-arsine reacts similarly with $Fe(CO)_5$ to yield the dark-orange crystalline material $[Fe(CO)_3]_2$-

$(CH_3As)_4$. The chief ions detected in the spectrum of the complex are listed in Table 4. It can be seen that the molecular ion decomposes by the successive loss of CO groups to yield $Fe_2(CH_3As)_4^+$ followed by the loss of CH_3 groups to form $Fe_2As_4^+$ and subsequently Fe_2^+. The absence of any peak assignable to the species $(CH_3As)_4{}^+$ is evidence against the existence of an arsine ring in the parent compound, while the existence of Fe_2^+ species supports the existence of an Fe–Fe bond in the parent molecule.

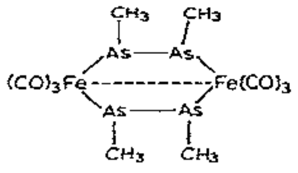
TABLE 4

THE MASS SPECTRUM OF $[Fe(CO)_3]_2(CH_3As)_4$

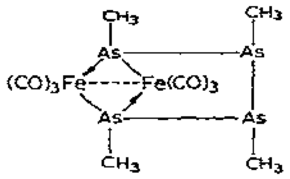
Ion⁺	*m/e*	*Relative* %
$Fe_2(CO)_6(CH_3As)_4$	640	22
$Fe_2(CO)_5(CH_3As)_4$	612	8
etc ↓		
$Fe_2(CH_3As)_4$	472	100
$Fe_2(CH_3)_3As_4$	457	31
etc ↓		
Fe_2As_4	412	44
Fe_2As_3	337	44
etc ↓		
Fe_2	112	100

The infra-red spectrum of the complex shows bands at 2044(s), 2008(s), 1978(s), 1967(s) and 1955(w) cm^{-1}.

The n.m.r. spectrum shows only two bands at high resolution at $\tau = 7.68$ and 8.50 of equal intensity. The evidence at this stage suggests two possible bridged structures for the complex, (IV) and (V).



IV



V

Structure V is slightly favoured because it allows each Fe atom to achieve a rare-gas configuration, whereas structure IV does not. A structural study is in progress to decide the issue.

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