The Expansion of a Phosphorus Ring System by Co-ordination to a Metal

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BURG and Mahler have reported that the cyclic phosphine $(CF_3P)_4$ reacts with $Ni(CO)_4$ to give polymeric products of uncertain composition.[1] We have found that tetraphenylcyclotetraphosphine $(PhP)_4$, "phosphorobenzene," reacts smoothly with $Ni(CO)_4$ at 15° in diethyl ether to give the monomeric product $(PhP)_4Ni(CO)_3$ in which a single phosphorus atom is co-ordinated to the metal. Similarly $Fe(CO)_5$ reacts at 170° with $(PhP)_4$ to give $(PhP)_4[Fe(CO)_4]_2$.

However, the reaction of molybdenum and tungsten hexacarbonyls with $(PhP)_4$ at temperatures greater than 120° yields complexes of the form $(PhP)_5M(Mo,W)(CO)_5$ the four-membered phosphorus ring having been expanded to a five-membered ring. The molecular weights of the complexes determined in benzene showed them to be monomeric. The infrared spectra of the compounds in chloroform provided support for the unidentate nature of the ligand in each case.[2]

	A_1	E_1	B
$(PhP)_5Mo(CO)_5$	2075(vs),	1992(sh),	1950(m).
$(PhP)_5W(CO)_5$	2074(vs),	1985(sh),	1945(m).

The presence of the five-membered phosphorus ring system has been shown by an electron impact study of the tungsten compound.

The mass spectrum of the tungsten compound could only be interpreted in terms of a five-membered phosphorus ring system being bound to tungsten in the complex. A species of $m/e = 834$, $[(PhP)_5W(CO)_4]^+$ and one of $m/e = 540$, $[Ph_5P_5]^+$ were among the ions observed.

An ion of the form $[Ph_4P_4]$ was not observed in the mass spectrum of the complex. The spectrum of the phosphorobenzene sample used in the synthesis agreed with its formulation as a tetramer.[3]

The mechanism of ring expansion is as yet uncertain but may proceed through the formation of the intermediate $PhP{\cdot}Mo(CO)_5$ which can react with a further molecule of $(PhP)_4$. A similar intermediate $CF_3P{\cdot}PMe_3$ was suggested to participate in the ring expansion of $(CF_3P)_4$ to $(CF_3P)_5$ which was aided by the addition of PMe_3 to the system.[4]

Maier and Daly[5] have recently reported the identification of a pentameric form of phosphorobenzene. A sample of phosphorobenzene found to

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[1] A. B. Burg, and W. Mahler, *J. Amer. Chem. Soc.*, 1958, **80**, 2334.
[2] L. E. Orgel, *Inorg. Chem.*, 1962, **1**, 25; F. A. Cotton and C. S. Draihanzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4432.
[3] W. A. Henderson, M. Epstein, and F. S. Seichter, *J. Amer. Chem. Soc.*, 1963, **85**, 2462.
[4] A. B. Burg, and W. Mahler, *J. Amer. Chem. Soc.*, 1961, **83**, 2388.
[5] L. Maier, and J. J. Daly, *Nature*, 1964, **203**, 1167.

be tetrameric in benzene solution by a cryoscopic method, had the molecular weight of a pentamer in the solid state, as determined by *X*-ray diffraction measurements. The compound examined by Maier and Daly had been recrystallised from the co-ordination solvent, acetonitrile, and ring expansion from P_4 to P_5 may have been caused by the formation of a similar type of intermediate to that mentioned above, *viz*, MeCN·PPh.

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