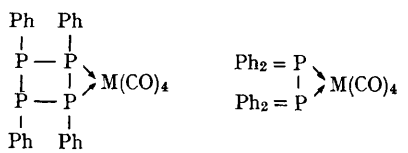
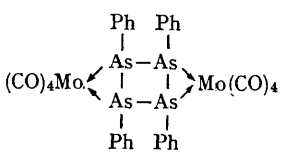
Reactions of Phosphorobenzene and Arsenobenzene with Metal Hexacarbonyls

By G. W. A. FOWLES and D. K. JENKINS
(*Department of Chemistry, University of Southampton*)

ANG *et al.* have recently reported[1] that reaction of molybdenum and tungsten hexacarbonyls with phosphorobenzene results in the expansion of the phosphorus ring system and the formation of complexes $(PhP)_5M(CO)_5$. We have studied the reaction of these two carbonyls and chromium hexacarbonyl with both phosphorobenzene and arsenobenzene in evacuated sealed tubes at 140—150°, but we have not isolated the compounds reported by these workers. The brown non-crystalline products we obtained from the phosphorobenzene reactions were purified chromatographically on silica-gel columns. They had the composition $M(CO)_4(PhP)_4$, were monomeric in benzene solution, and appeared to be simple substituted carbonyls with structure (I); they are analogous to the compounds (II) obtained from the reactions of tetraphenyldiphosphine with the Group VI carbonyls.[2]



(I) (II)



(III)

With arsenobenzene, reaction only occurred readily with $Mo(CO)_6$. Reaction for 5 days in refluxing benzene gave the mononuclear complex $Mo(CO)_4(PhAs)_4$, but a binuclear complex

[1] H. G. Ang, T. S. Shannon, and B. O. West, *Chem. Comm.*, 1965, 10.
[2] G. W. A. Fowles and D. K. Jenkins, unpublished observations.

$[Mo(CO)_4]_2(PhAs)_4$ was obtained when the reaction was carried out in toluene under reflux for 24 hr. Both compounds were monomeric in benzene solution. We suggest that the binuclear complex has the structure (III).

The infrared spectra, of all complexes—which were obtained for $CHCl_3$ or CCl_4 solutions—show CO stretching frequencies typical of *cis*-disubstituted hexacarbonyls.

$Cr(CO)_4(PhP)_4$	2022,	2002,	1951,	1925
$Mo(CO)_4(PhP)_4$	2012,	1988,	1959,	1933
$W(CO)_4(PhP)_4$	2005,	1962,	1920,	1895
$Mo(CO)_4(PhAs)_4$	2090,	2030,	1992,	1960
$[Mo(CO)_4]_2(PhAs)_4$	2081,	2013,	1995,	1960

(*Received, January 28th*, 1965.)