Organometallic Bases as Mono-, Di-, and Tri-dentate Ligands in Metal Carbonyls

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DESPITE the large range of phosphine- and arsine-substituted metal carbonyls,[1] little effort has been made to investigate the ligand properties of the corresponding organometallic phosphines and arsines, though complexes involving the phosphines $(Me_3Si)_3P$,[2] $(Me_3Ge)_3P$,[2] $(Me_3Sn)_3P$,[2] and $(Ph_2P)_4Sn$ [3] have been reported.

In addition to the possible variations of the ligand properties of the phosphorus and arsenic atoms by attachment of metals and metalloids, the stereochemical possibilities are of interest. Thus (I), (II), and (III), represent mono-, di-, and tri-dentate ligands specifically synthesised for this work.

The Table comprises a representative set of substituted metal carbonyls incorporating this type of ligand. Complexes such as (IV) and (V) may be looked upon as phosphorus and arsenic bridged mixed-metal derivatives.

The virtual identity, in the carbonyl stretching region of the spectra of pairs of compounds $Me_2Si(AsMe_2)_2Ni(CO)_2$ and $Me_2Sn(AsMe_2)_2Ni(CO)_2$; $Me_2Si(AsMe_2)_2Cr(CO)_4$ and $Me_2Sn(AsMe_2)_2Cr(CO)_4$ is noteworthy. It shows that a considerable change in the size and electronic character of the metal atom separating the two arsenic atoms of the bidentate ligands appears to have no overall effect upon the arsenic to transitional metal bonding.

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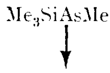
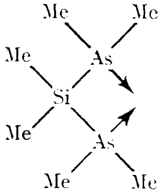
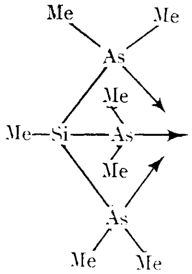


$Me_3SiAsMe_2 \downarrow$

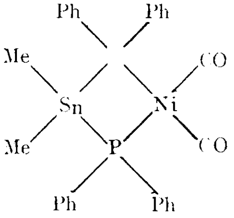
(I)



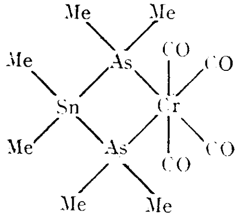
(II)



(III)



(IV)



(V)

Organometallic base substituted metal carbonyls

Compound[†]	Colour	Carbonyl i.r. stretching frequencies in cm.$^{-1}$.[‡]
$(Me_3SnPPh_2)_2Ni(CO)_2$	Orange	1993 (10), 1927 (10)
$Me_2Sn(PPh_2)_2Ni(CO)_2$	Orange	2001 (10), 1947 (10)
$Me_3SnAsMe_2Ni(CO)_3$	Yellow	2062 (9), 1981 (10)
$Me_2Si(AsMe_2)_2Ni(CO)_2$	Pale yellow	1993 (10), 1925 (10)
$Me_2Sn(AsMe_2)_2Ni(CO)_2$	Yellow	1990 (10), 1916 (10)
$Me_2Si(AsMe_2)_2Cr(CO)_4$	Yellow	1998 (5), 1883 (10), 1871 (10), 1855 (8)
$Me_2Sn(AsMe_2)_2Cr(CO)_4$	Yellow	1998 (5), 1884 (10), 1873 (10), 1855 (8)
$Me_2Si(AsMe_2)_2Mo(CO)_4$	Yellow	2015 (5), 1896 (10), 1882 (10), 1856 (8)
$MeSi(AsMe_2)_3Cr(CO)_3$	Orange–yellow	1905 (10), 1805 (10)
$MeSi(AsMe_2)_3Mo(CO)_3$	Orange–yellow	1920 (10), 1815 (10)

† Analytical data are good for each compound.
‡ Integers in brackets refer to the relative peak heights, with the strongest absorption as 10 units.

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