Organosilicon and Organotin Phosphines and Arsines as Mono- and Poly-dentate Ligands to Metal Carbonyls

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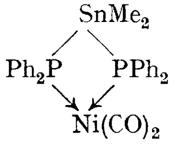
The organometallic phosphines and arsines Me_3SnPPh_2, $Me_2Sn(PPh_2)_2$, $Me_3SiAsMe_2$, $Me_2Si(AsMe_2)_2$, $MeSi(AsMe_2)_3$, $Me_3SnAsMe_2$, and $Me_2Sn(AsMe_2)_2$ react with nickel, chromium, and molybdenum carbonyls, behaving as mono-, bi-, and tri-dentate ligands as appropriate. The i.r. and ^1H n.m.r. spectra of the products are reported and discussed.

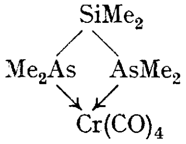
A VERY wide range of organic phosphines and arsines are known to form stable co-ordination complexes with many metal carbonyls.[1] Recently some organometallic phosphines of silicon,[2] germanium,[2] and tin [2,3] have been shown to act as ligands. The difference in size and electronic properties of silicon and tin made it of interest to prepare and contrast the properties of the organometallic phosphines and arsines of silicon and tin as ligands.

The monophosphine Me_3SnPPh_2 and monoarsines $Me_3SiAsMe_2$ and $Me_3SnAsMe_2$ displace one carbonyl group from tetracarbonylnickel to produce the products $LNi(CO)_3$. In the presence of an excess of ligand and with a longer reaction time, the organotin phosphine also forms the disubstitution product $[Me_3SnPPh_2]_2Ni(CO)_2$.

The diphosphine $Me_2Sn(PPh_2)_2$ and the diarsines $Me_2Si(AsMe_2)_2$ and $Me_2Sn(AsMe_2)_2$ behave towards metal carbonyls as bidentate ligands and take the place of two carbonyl groups in tetracarbonylnickel and chromium and molybdenum carbonyls. These complexes, as exemplified by (I) and (II), may be regarded as phosphorus and arsenic bridged mixed-metal and metalloid derivatives.

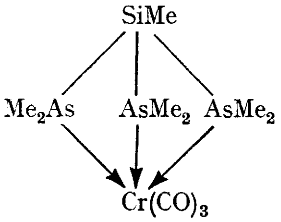


(I)



(II)

The triarsine $MeSi(AsMe_2)_3$ displaces cycloheptatriene instantly from cycloheptatrienetricarbonylmolybdenum to produce $MeSi(AsMe_2)_3Mo(CO)_3$ (III); the corresponding reaction to produce $MeSi(AsMe_2)_3Cr(CO)_3$ required heat, to displace the cycloheptatriene from $C_7H_8Cr(CO)_3$.



(III)

TABLE 1

I.r. spectra of organometallic base substituted metal carbonyls

Compound	Colour	Carbonyl i.r. stretching frequencies (cm.) *	
$Me_3SnPPh_2Ni(CO)_3$	Colourless	2064(6), 1993(10)	(Cyclohexane)
$(Me_3SnPPh_2)_2Ni(CO)_2$	Orange	1993(10), 1927(10)	(Mull)
$Me_2Sn(PPh_2)_2Ni(CO)_2$	Orange	2001(10), 1947(10)	(Mull)
$Me_3SiAsMe_2Ni(CO)_3$	Colourless	2065(6), 1994(10)	(Cyclohexane)
$Me_3SnAsMe_2Ni(CO)_3$	Yellow	2064(6), 1989(10) †	(Cyclohexane)
$Me_2Si(AsMe_2)_2Ni(CO)_2$	Pale yellow	1993(10), 1925(10)	(Mull)
$Me_2Sn(AsMe_2)_2Ni(CO)_2$	Yellow	1990(10), 1916(10)	(Mull)
$Me_2Si(AsMe_2)_2Cr(CO)_4$	Yellow	1998(5), 1883(10), 1871(10), 1855(18)	(Mull)
$Me_2Sn(AsMe_2)_2Cr(CO)_4$	Yellow	1998(5), 1884(10), 1873(10), 1855(8)	(Mull)
$Me_2Si(AsMe_2)_2Mo(CO)_4$	Yellow	2015(5), 1896(10), 1882(10), 1856(8)	(Mull)
$MeSi(AsMe_2)_3Cr(CO)_3$	Orange-yellow	1905(10), 1805(10)	(Mull)
$MeSi(AsMe_2)_3Mo(CO)_3$	Orange-yellow	1920(10), 1815(10)	(Mull)

* Integers in brackets refer to relative peak heights, with the strongest absorption as ten units. † These values are marginally different from our earlier report (*Chem. Comm.*, 1968, 1817), due to a change of solvent.

The carbonyl i.r. stretching frequencies of all of these new compounds are recorded in Table 1. It is notable that for all the organosilicon and organotin phosphine and arsine metal carbonyls, the i.r. frequencies of the metal carbonyl stretching modes are lower than those for the comparable complexes of purely organic phosphines and arsines. It would therefore appear that, compared with carbon, the lowered electronegativity of silicon and tin allows more pronounced electron donation from phosphorus and arsenic to the transition-metal. It must be further observed that for the individual pairs of compounds $Me_3SiAsMe_2Ni(CO)_3$ and $Me_3SnAsMe_2Ni(CO)_3$, $Me_2Si(AsMe_2)_2Ni(CO)_2$ and $Me_2Sn(AsMe_2)_2Ni(CO)_2$, and $Me_2Si(AsMe_2)_2Cr(CO)_4$ and $Me_2Sn(AsMe_2)_2Cr(CO)_4$, the metal carbonyl regions of the spectra are virtually identical. Thus, the considerable difference in size between silicon and tin does not

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[1] T. A. Manuel, *Adv. Organometallic Chem.*, 1965, **3**, 181.

[2] H. Schumann and O. Stelzer, *Angew. Chem., Internat. Edn.*, 1967, **6**, 701; *ibid.*, 1968, **7**, 300.

[3] J. Ellermann and K. Dorn, *Z. Naturforsch.*, 1968, **23b**, 420.

appear to effect the complexes overall. Further, it would appear that there is no difference in the electronic behaviour of silicon and tin in these complexes. It is tempting to believe that these donor properties of arsenic might even be expected to be similar in organosilicon and organotin arsines due to the negligible differences between the electronegativities of silicon and tin on both the Pauling and Allred-Rochow scales.[4,5]

The very low solubility of many of our products suggests that they may be polymeric, a possibility cannot be completely eliminated. It should be recalled, however, that the majority of phosphine and arsine substituted carbonyls are of very low solubility. With the exception of the three compounds listed in Table 2, our products were too insoluble for solution n.m.r. measurements.

As might be expected, the shielding of all protons decreases slightly from the unco-ordinated ligand to its metal carbonyl derivative. Similarly, the small increase in J(Sn–C–H) for the methyltin protons may be rationalized with increased *s*-character of the Sn–As and Sn–P bonds in the complex. In this light the increase of $J(P^{31}$–Sn–C–H) from 1·95 to 3·50 is as expected and also as observed [2] in the complex formation of $(Me_3Sn)_3P$. A problem, however, arises with the arsine where J(Sn–As–C–H) drops markedly from *ca.* 53 in the unco-ordinated ligand to *ca.* 33 in the complex. This would be in the opposite direction predicted by an increase in *s*-character of the Sn–As bond upon co-ordination.

TABLE 2

^{1}H N.m.r. spectra of the $LNi(CO)_3$ complexes and the unco-ordinated ligands

Compound	τ Values of protons		J (c./sec.)	
$Me_3SiAsMe_2Ni(CO)_3$	H in Me_3Si	9·70		
	H in Me_2As	8·80		
$Me_3SnAsMe_2Ni(CO)_3$	H in Me_3Sn	9·64	H–C–Sn^{117}	52
			H–C–Sn^{119}	54
	H in Me_2As	8·68	H–C–As–Sn^{117}	33
			H–C–As–Sn^{119}	34
$Me_3SnPPh_2Ni(CO)_3$	H in Me_3Sn	9·75	H–C–Sn^{117}	52
			H–C–Sn^{119}	54
	H in Ph_2P	2·6—3·5	H–C–Sn–P^{31}	3·50
$Me_3SiAsMe_2$	H in Me_3Si	9·81		
	H in Me_2As	9·11		
$Me_3SnAsMe_2$	H in Me_3Sn	9·79	H–C–Sn^{117}	47·0
			H–C–Sn^{119}	49·5
	H in Me_2As	8·89	H–C–As–Sn^{117}	51·0
			H–C–As–Sn^{119}	53·5
Me_3SnPPh_2	H in Me_2Sn	9·87	H–C–Sn^{117}	49·0
			H–C–Sn^{119}	51·0
	H in Ph_2P	2·5—3·1	H–C–Sn–P^{31}	1·95

It is believed[6] that the J(Sn–As–C–H) coupling-constant is anomalously high in unco-ordinated $Me_3SnAsMe_2$, an effect analogous to many other β-couplings with tin. This may involve opposite signs for the α- and β-coupling constants, and the effect of co-ordination upon the relative values of α and β may control the value of J(Sn–As–C–H) in both ligand and complex, and simple *s*-character arguments would be inapplicable.

The co-ordinated organometallic ligands were generally more stable to attack than the free ligand. Thus, whereas $Me_2Si(AsMe_2)_2Cr(CO)_4$ was stable in the air and in boiling methanol, uncomplexed dimethylsilylenebis(dimethylarsine) is rapidly oxidised in the air, and undergoes rapid and complete methanolysis at room temperature.[7]

EXPERIMENTAL

All reactions were carried out under dry nitrogen, and solvents were distilled off sodium–benzophenone. Infrared spectra were determined on a Perkin-Elmer 257 instrument and n.m.r. spectra were obtained on a Varian A60 instrument. The ligands were all prepared by literature methods, with the exception of dimethylstannylenebis(dimethylarsine) which is reported below.

Preparation of Dimethylstannylenebis(dimethylarsine).—Dimethyl(trimethylsilyl)arsine (7·4 ml., 2 mol.) was slowly added to dichlorodimethylstannane (3·0 g., 1 mol.) at −80°.

$$Me_2SnCl_2 + Me_3SiAsMe_2 \longrightarrow Me_2Sn(AsMe_2)_2 + 2Me_3SiCl$$

The mixture was allowed to warm to room temperature with stirring. After being set aside for 1 hr. chlorotrimethylsilane was pumped off to leave dimethylstannylenebis(dimethylarsine), d_4^{20} 1·67 (Found: C, 20·7; H, 5·5. $C_6H_{18}As_2Sn$ requires C, 21·1; H, 5·3%). The product distils at 55°/0·01 mm., but due to the extensive decomposition that takes place during distillation, the ligand was not normally distilled before use in the reactions below. The ^{1}H n.m.r. spectrum showed two peaks: one due to Me_2As at τ 8·80, $J(^{117}$Sn–As–C–H) 51·5 c./sec., $J(^{119}$Sn–As–C–H) 54·0 c./sec.), and the other due to Me_2Sn at τ 9·68, $J(^{117}$Sn–C–H) 42·5 c./sec., $J(^{119}$Sn–C– H) 45·0 c./sec.): relative intensities 2 : 1.

Diphenyl(trimethylstannyl)phosphinetricarbonylnickel.—Diphenyl(trimethylstannyl)phosphine (1 ml.) was added to tetracarbonylnickel (0·6 ml., excess) and the mixture stirred for 1 hr. at 30°, during which time carbon monoxide was evolved. Excess of tetracarbonylnickel was removed (0·005 mm./15 min.) to leave the liquid *product* (Found: C, 43·5; H, 3·7. $C_{18}H_{19}NiO_3Sn$ requires C, 44·1; H, 3·9%).

Under identical conditions the other two substituted nickel tricarbonyls were prepared as colourless or pale yellow liquids. Dimethyl(trimethylsilyl)arsinetricarbonylnickel (Found: C, 29·8; H, 4·7. $C_8H_{15}AsNiO_3Si$ requires C, 30·0; H, 4·7%) and dimethyl(trimethylstannyl)arsinetricarbonylnickel (Found: C, 23·8; H, 3·9. $C_8H_{15}AsNiO_3Sn$ requires C, 23·8; H, 3·9%).

Bis[diphenyl(trimethylstannyl)phosphine]dicarbonylnickel.—Diphenyl(trimethylstannyl)phosphine (2·5 g.) was added to tetracarbonylnickel (0·5 ml.) and the mixture was stirred until it solidified. The crystals were washed with dry nitrogen-purged methylcyclohexane, and dried (25°/0·05 mm.), to yield bis[diphenyl(trimethylstannyl)phosphine]dicarbonylnickel (70%) as orange crystals (Found: C, 47·8; H, 4·8. $C_{32}H_{38}NiO_2P_2Sn_2$ requires C, 47·3; H, 4·7%).

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[4] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Interscience–John Wiley, 1966, 2nd edn., p. 103.

[5] E. W. Abel, D. A. Armitage, and D. B. Brady, *Trans. Faraday Soc.*, 1966, **62**, 3459, and references therein.

[6] E. W. Abel and D. B. Brady, *J. Organometallic Chem.*, 1968, **11**, 145.

[7] E. W. Abel and S. M. Illingworth, *J. Chem. Soc. (A)*, 1969, 1094.

Dimethylsilylenebis(*dimethylarsine*)*dicarbonylnickel*.—Tetracarbonylnickel (0·6 ml.) and dimethylsilylenebis(dimethylarsine) (1·5 ml., excess), were stirred for 3 days at 30°. Subsequent washing with dry nitrogen-purged cyclohexane yielded the yellow crystalline *product* (50%) (Found: C, 25·2; H, 4·7; As, 39·4; Ni, 15·3. $C_8H_{18}As_2NiO_2Si$ requires C, 25·1; H, 4·7; As, 39·3, Ni, 15·2%).

Dimethylstannylenebis(*dimethylarsine*)*dicarbonylnickel*.—Tetracarbonylnickel (1·0 ml.) and dimethylstannylenebis(dimethylarsine) (2·0 ml., excess) were stirred together for 4 days at 20°. Subsequent washing and drying as above yielded the yellow crystalline *product* (50%) (Found: C, 20·1; H, 3·8. $C_8H_{18}As_2NiO_2Sn$ requires C, 20·4; H, 3·6%).

Dimethylstannylenebis(*diphenylphosphine*)*dicarbonylnickel* (I).—Dimethylstannylenebis(diphenylphosphine) (2·5 g.) in ether was made *in situ* by the method of Schumann,[8] and tetracarbonylnickel (0·7 ml.) was added. The orange-red *product* (*ca.* 50% yield) was rapidly precipitated, and washed and dried as above (Found: C, 55·0; H, 4·1. $C_{28}H_{26}NiO_2P_2Sn$ requires C, 53·4; H, 4·1%).

Dimethylsilylenebis(*dimethylarsine*)*tetracarbonylmolybdenum*.—To hexacarbonylmolybdenum (0·7 g.) in acetonitrile (25 ml.) was added dimethylsilylenebis(dimethylarsine); the resulting solution was heated under reflux for 6 hr. The mixture was cooled and a yellow solid crystallised out; it was washed and dried as above to yield the *product* (*ca.* 70%) (Found: C, 25·2; H, 3·4; As, 31·6; Mo, 19·9. $C_{10}H_{18}As_2MoO_4Si$ requires C, 25·2; H, 3·8; As, 31·5; Mo, 20·2%).

Dimethylsilylenebis(*dimethylarsine*)*tetracarbonylchromium* (II).—To norbornadienetetracarbonylchromium (0·4 g.) in methylcyclohexane (20 ml.) was added dimethylsilylenebis(dimethylarsine); the solution heated under reflux for *ca.* 1 hr. During this time a bright yellow solid was precipitated which was filtered off, washed, and dried to give the *product* (*ca.* 90%) (Found: C, 27·8; H, 3·9; As, 34·9; Cr, 12·0. $C_{10}H_{18}As_2CrO_4Si$ requires C, 27·8; H, 4·2; As, 34·7; Cr, 12·0%).

In an analogous manner, but with a heating time of only 10 min. was prepared *dimethylstannylenebis*(*dimethylarsine*)*tetracarbonylchromium* (*ca.* 70% yield) (Found: C, 21·1; H, 3·5; As, 29·2; Cr, 9·9. $C_{10}H_{18}As_2CrO_4Sn$ requires C, 23·0; H, 3·5; As, 28·7; Cr, 10·0%). Despite repetition, the carbon analysis was persistently low, possibly due to carbide formation. In the light of the excellent analyses of the other elements, we regard the compound as well characterised.

Methylsilylidynetris(*dimethylarsine*)*tricarbonylchromium*.—To cycloheptatrienetricarbonylchromium (0·7 g.) in cyclohexane (20 ml.) was added methylsilylidynetris(dimethylarsine (1·10 ml.). The mixture was heated under reflux for 15 min. during which time the bright red colour of the cycloheptatrienetricarbonylchromium was completely discharged and a yellow precipitate was obtained. This was filtered off, washed, and dried to yield the *product* (*ca.* 80%) (Found: C, 23·6; H, 4·2; As, 45·5; Cr, 10·2 $C_{10}H_{21}As_3CrO_3Si$ requires C, 24·3; H, 4·3; As, 45·5; Cr, 10·5%).

Methylsilylidynetris(*dimethylarsine*)*tricarbonylmolybdenum* (III).—To cycloheptatrienetricarbonylmolybdenum (0·5 g.) in benzene (20 ml.) was added methylsilylidynetris(dimethylarsine) (0·65 ml.). The bright scarlet colour of the cycloheptatrienetricarbonylmolybdenum was instantly discharged in the cold, and upon addition of cyclohexane an orange-yellow solid was deposited. This was filtered off, washed, and dried to yield the *product* (*ca.* 60%) (Found: C, 23·8; H, 4·7; As, 41·8; Mo, 17·8. $C_{10}H_{21}As_3MoO_3Si$ requires C, 22·3; H, 3·9; As, 41·8; Mo, 17·8%).

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[8] H. Schumann, H. Kopf, and M. Schmidt, *J. Organometallic Chem.*, 1964, **2**, 159.