Carbon-13 Nuclear Magnetic Resonance of the Group V Triphenyls and of Triphenylphosphinemolybdenum Pentacarbonyl

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Summary Carbon-13 n.m.r. spectra of triphenylphosphorus, -antimony, -arsenic, and -bismuth and of $Ph_3PMo(CO)_5$ are reported and factors determining chemical shift parameters are discussed.

WHILE carbon-13 n.m.r. studies of complex organic molecules are now becoming routine, little interest has been focussed on the use of ^{13}C n.m.r. for investigating structure and bonding in organometallic and metal carbonyl compounds. We have obtained ^{13}C n.m.r. spectra of the aromatic carbons of triphenyl-phosphorus, -arsenic, -antimony, and -bismuth and of all carbons of one metal carbonyl complex, $Ph_3PMo(CO)_5$, in which triphenylphosphine is thought to act as a σ-electron-donor, π-electron-acceptor ligand. Separate resonances with the expected 4:1 ratio of intensity are observed for the *cis*- and *trans*-carbonyls. The spectra provide good evidence that there is little or no delocalization of electron density from the metal into the π-aromatic system of the ligand whereas the σ-bond to the phenyl group is strengthened upon complex formation.

Except for the two phosphorus-containing molecules, each chemically distinct aromatic carbon, under conditions of complete proton irradiation[1] gives a single resonance. The carbons directly bonded to antimony or bismuth show broad resonances due to internuclear spin coupling. Every aromatic carbon in Ph_3P and in the metal complex shows up in the spectrum as a doublet (Figure; Table). Resonances were assigned by comparing magnitudes of ^{31}P–^{13}C coupling constants and relative peak heights. All resonances are concentration-independent and accurate to ±0·2 p.p.m.

The linear plot (not shown) of the chemical shift of C-1 in the triphenyls (free in solution) against electronegativity for the Group V elements indicates that the inductive effect of the ligand is dominating the paramagnetic term of the Saika–Slichter equation which describes screening in carbon chemical shifts.[2,3] Similar observations have been reported for a series of substituted benzenes.[4] Numerous factors could affect the chemical shifts of C-2 and C-3. These will be discussed in detail elsewhere. However, it is generally accepted that the chemical shift of C-4 is principally determined by the π-electron density in the phenyl ring.[3–5] We note that the C-4 shifts are detected between −128·3 and −129·3 p.p.m., and conclude that electron π-density varies little within this series of compounds.

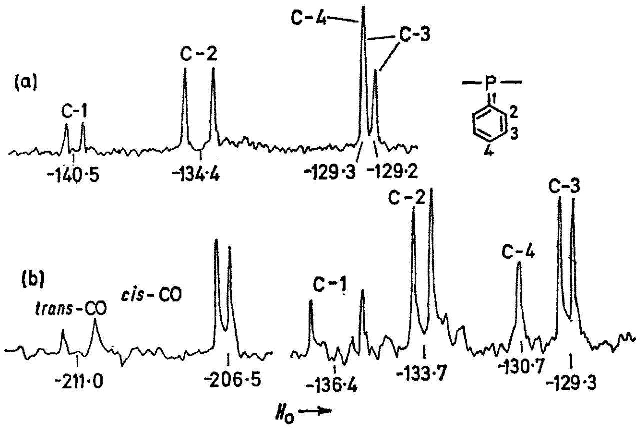

FIGURE. *The carbon-13 n.m.r. spectra of* (a) *triphenylphosphine and* (b) *triphenylphosphinemolybdenum pentacarbonyl, relative to* Me_4Si.

Upon co-ordination, the C-1 resonance of Ph_3P moves upfield, whereas that of C-4 is shifted downfield. Accompanying this is a 72% increase in the magnitude of the P–C-1 coupling constant. The coupling constant change and the increased C-1 shielding can both be attributed to an increase in the C–P σ-bond order and decreased anisotropy of the phosphorus atom.[4] That there is no significant *d*-π bonding between metal and aromatic orbitals is indicated by the small *downfield* shift of the C-4 resonance. Increased electron density in aromatic rings is known to effect an *upfield* shift in carbons *para* to the substituted position.[4,5] The chemical shift separation of 4·5 p.p.m. between the *cis*- and *trans*-carbonyls indicates that ^{13}C resonances are quite sensitive probes of geometry in metal carbonyls.

^{13}C *n.m.r. shift parameters* (*relative to* Me_4Si) *for the Group V triphenyls and for* $Ph_3PMo(CO)_5$

Compounds	C-1	C-2	C-3	C-4	J_{P-C-1}	J_{P-C-2}	J_{P-C-3}	J_{P-C-4}	*cis* (CO)	*trans* (CO)
$Ph_3PMo(CO)_5$ ..	−136·4	−133·7	−129·3	−130·7	36	13	9	<2	−206·5	−211·0
Ph_3P	−138·3	−134·4	−129·2	−129·3	21	20	7	<1		
Ph_3As	−140·5	−134·3	−129·3	−129·0						
Ph_3Sb	−139·3	−136·8	−129·4	−129·2						
Ph_3Bi	−131·1	−138·1	−131·0	−128·3						

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