Mercury-199–Phosphorus-31 Nuclear Spin–Spin Coupling in Tertiary Phosphine Complexes of Mercury(II) Bromide

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HEAVY-ATOM nuclear spin–spin coupling has received considerable attention recently in phosphorus co-ordination compounds.[1–4] It had been shown previously that J_{M-P} increases as the number of phenyl groups increases from $n = 0$ to $n = 2$ or 3 in the tertiary phosphines, $Ph_nBu^n_{3-n}P$, for compounds of the type *cis*- and *trans*-L_2PtCl_2[3] and $LW(CO)_5$.[4] Thus, the less basic ligand with more phenyl groups has the larger coupling constant. It is concluded that the π-acceptor character of the ligand is an important factor in the bonding in these compounds, and this is reflected in the magnitude of J_{M-P}.

In the present work we have examined complexes in which π-bonding is less likely to occur, *i.e.* in bivalent tetrahedral complexes of mercury. This stereochemistry is contrasted to the favourable π-bonding situations previously examined, *viz.* divalent square-planar platinum and zero-valent octahedral tungsten.

The coupling of mercury-199 (nuclear spin, $\frac{1}{2}$; natural abundance, 16·9%) with phosphorus is manifest as a widely-spaced triplet (*ca.* 2 : 21 : 2) in the ^{31}P n.m.r. spectrum of a mercury complex in methylene chloride solution. No coupling was observed with mercury-201 (nuclear spin, $\frac{3}{2}$; natural abundance, 13·2%). The results are given in the Table and show that the most basic of the tertiary phosphines examined has the largest J_{Hg-P} coupling. The triphenylphosphine complex was too insoluble to permit measurement of the spectrum. We conclude that the strength of the σ-bond is therefore the determining influence in the magnitude of J_{M-P} in this case, since π-bonding would not be expected to be important in these mercury complexes. These conclusions are consistent with our earlier results with platinum and tungsten if it is assumed that the signs of the coupling constants do not vary. To date there is no experimental information on the latter point.

^{31}P *Nuclear magnetic resonance data for some complexes of mercury*(II) *bromide*

Compound	Chemical shift (p.p.m. *vs.* H_3PO_4)	J_{Hg-P} (Hz)
$[Bu_3P]_2HgBr_2$	$-56·9 \pm 0·8$	4777 ± 13
$(Bu_2PhP)_2HgBr_2$	$-48·3 \pm 0·8$	4629 ± 14
$BuPh_2PHgBr_2$	$-36·4 \pm 0·8$	4216 ± 7

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