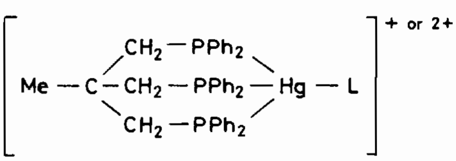
Mixed Mercury(II)–Tetraphosphine Complexes of the Type $[Hg(tripod)L]^{+}$ and $^{2+}$ (tripod = $MeC(CH_2PPh_2)_3$, L = Anionic or Neutral Phosphorus Ligand)

PAUL PERINGER* and MARIA LUSSER

Institut für Anorganische und Analytische Chemie der Universität Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria

(Received August 2, 1985; revised April 2, 1986)

A series of the new title compounds **1** is formed according to the reactions (1) and (2).



1

$$[Hg(Me_2SO)_6](O_3SCF_3)_2 + \text{tripod} + L \longrightarrow [Hg(\text{tripod})L](O_3SCF_3)_2 + 6Me_2SO \quad (1)$$

L = PPh_3, PBu_3, PCy_3 (Cy = cyclohexyl), $CH_2(PPh_2)_2$, $P(OEt)_3$ and 2,8,9-trioxa-1-phosphatricyclo[3.3.1.1.^{3,7}]-decane (**2**)

$$[HgLCl] + \text{tripod} + TlO_3SCF_3 \longrightarrow [Hg(\text{tripod})L]O_3SCF_3 + TlCl \quad (2)$$

L = $(\mu\text{-}PPh_2)Cr(CO)_5$, $P(O)(OEt)_2$

The tripod ligand is η^3-bound in all complexes except for L = PCy_3, for which the temperature dependent equilibrium (3) is observed.

$$[Hg(\eta^3\text{-tripod})PCy_3](O_3SCF_3)_2 \rightleftharpoons [Hg(\eta^2\text{-tripod})PCy_3](O_3SCF_3)_2 \quad (3)$$

The complexes were characterized by ^{31}P and ^{199}Hg NMR spectroscopy. The bonding mode of the ligands is established via the multiplicities of the ^{31}P and ^{199}Hg signals. The parameters are reported in Table I. The coupling constants $^1J(^{199}Hg, ^{31}P)$ involving the tripod ligand are unusually small, whilst those of the η^1 bound phosphorus ligands are unusually large compared with those of other mercury compounds coordinated by 4 phosphorus ligands [1–4]. This was also observed for the d^{10} platinum(0) complexes [5, 6] and was attributed to diminished s character of the tripod–metal bonds as a consequence of the fixed coordination geometry of the tripod ligand differing from the ideal tetrahedral geometry. The metal–P bond involving the η^1 phosphorus ligand will be hybridized correspondingly to include more s character [5, 6].

The coupling constants $^1J(^{199}Hg, ^{31}P)$ for the tripod ligand in the compounds $[Hg(\eta^3\text{-tripod})L]O_3SCF_3$ are especially small, as has been observed for other phosphine addition compounds of mercury complexes involving anionic phosphorus ligands (*e.g.* 143 Hz for $[Hg\{P(O)(OEt)_2\}_2(PPh_3)_2]$ [7]). The coupling $^1J(^{199}Hg, ^{31}P)$ for the tripod ligand in the complex $[Hg(\eta^3\text{-tripod})(\mu\text{-}PPh_2)Cr(CO)_5]O_3SCF_3$ represents the smallest mercury–phosphorus one-bond coupling reported to date (125 Hz).

According to preliminary results, analogous complexes are formed with silver(I) [8].

Acknowledgement

We thank the Fonds zur Förderung der Wissenschaft, Vienna, for making available the NMR spectometer.

*Author to whom correspondence should be addressed.

TABLE I. NMR Parameters of $[Hg(tripod)L]^{+ \text{ or } 2+}$ [a]

P	$\delta(^{31}P)$[b]	$^1J(^{199}Hg, ^{31}P)$[b]	$\delta(^{31}P)$[c]	$^1J(^{199}Hg, ^{31}P)$[c]	$^2J(^{31}P, ^{31}P)$	$\delta(^{199}Hg)$	T (K)
PPh_3	29.1q	4516	3.8d	1278	53	2038	
$CH_2(PPh_2)_2$[d]	27.2q	4811	2.1d	1242	55		233
PBu_3	22.3q	4476	−1.6d	1076	48		193
PCy_3[e]	60.8q	4357	−0.7d	997	48		233
PCy_3[f]	68.3t	4468	27.9d	1698	90		233
$P(OEt)_3$	101.9q	8187	−0.4d	1568	87		253
2	123.2q	7348	1.0d	1632	79		213
$P(O)(OEt)_2$	69.3q	10520	−5.6d	512	105	1899	
$(\mu\text{-}PPh_2)Cr(CO)_5$	28.6q	3085	3.4d	125	36		

[a]Solvent CH_2Cl_2, T = 300 K unless otherwise stated, chemical shifts in ppm to high frequency of 85% H_3PO_4 or aqueous $Hg(ClO_4)_2$ solution (2 mmol HgO/ml 60% $HClO_4$), coupling constants in Hz. [b]L. [c]Tripod. [d]$[Hg(\eta^3\text{-tripod})(\eta^1\text{-}CH_2(PPh_2)_2)]^{2+}$, $\delta(^{31}P_{free})$: −24.9, $J(PPh_2CH_2PPh_2)$: 159 Hz. [e]$[Hg(\eta^3\text{-tripod})(PCy_3)]^{2+}$. [f]$[Hg(\eta^2\text{-tripod})(PCy_3)]^{2+}$.

0020-1693/86/$3.50

References

1 R. Colton and D. Dakternieks, *Aust. J. Chem., 34*, 323 (1981).
2 P. Peringer and M. Lusser, *Inorg. Chem., 24*, 109 (1985).
3 P. P. Winkler and P. Peringer, *Inorg. Chim. Acta, 76*, 259 (1983).
4 D. Obendorf and P. Peringer, *Inorg. Chim. Acta, 77*, 247 (1983).
5 J. Chatt, R. Mason and D. W. Meek, *J. Am. Chem. Soc., 97*, 3826 (1975).
6 A. R. Al-Ohaly and J. F. Nixon, *Inorg. Chim. Acta, 47*, 105 (1980).
7 J. Eichbichler and P. Peringer, *Inorg. Nucl. Chem. Lett., 17*, 305 (1981).
8 D. Obendorf and P. Peringer, unpublished results.