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Phosphorus-31 and Mercury-199 NMR Studies of Some Mercury(II) Complexes Containing Tricyclohexylphosphine and Tributylphosphine

DAINIS DAKTERNIEKS

Department of Inorganic Chemistry, University of Melbourne, Parkville, Vic. 3052, Australia

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Phosphorus-31 and mercury-199 NMR measurements are reported for a series of mercury(II) complexes $HgX_2[P(c\text{-}C_6H_{11})_3][PBu_3]$ *(where X =* O_3SCF_3, ClO_4, NO_3, CF_3COO, CH_3COO, *Cl, Br, I, SCN, CN) in dichloromethane solution. The two bond coupling* $^2J(P'-P)$ *of these asymmetric complexes decrease with increasing coordination ability of the anion and range between 198 Hz and 85 Hz.*

Data are also presented for $Hg(O_3SCF_3)_2[P(c\text{-}C_6H_{11})_3]_2$, $Hg(O_3SCF_3)_2[PBu_3]_n$ *(n = 2, 3, 4) which imply that the perchlorate anion may be more strongly involved in coordination to mercury, in solution, than the trifluoromethylsulphonate anion.*

Introduction

Phosphorus-31 and mercury-199 NMR measurements have been widely used to study phosphine complexes of mercury(II) in solution [1–7]. These studies have shown that one bond mercury–phosphorus couplings, $^1J(Hg-P)$, and mercury-199 chemical shifts, $\delta(^{199}Hg)$ are sensitive to structural changes about mercury caused by variation of the number of coordinated phosphines and by involvement of anions in coordination to mercury. Recently, a correlation between NMR coupling constants and molecular structure has been established for complexes $HgX_2(PPh_3)_2$ (X = NO_3, Cl, Br, SCN, I and CN) and shows that $^1J(Hg-P)$ values are primarily influenced by the P–Hg–P angle, larger angles being associated with larger $^1J(Hg-P)$ values [8, 9]. More recently, phosphorus-31 and mercury-199 NMR measurements of cationic mercury(II) phosphite complexes containing two different phosphite molecules have been reported [10].

Few values for two bond phosphorus–phosphorus coupling through a metal atom have been reported [10–12] although such couplings should also reflect the nature of the phosphorus–metal bond as well as the geometry about the metal atom. Phosphorus-31 and mercury-199 NMR parameters for a series of mixed-phosphine adducts $HgX_2[P(c\text{-}C_6H_{11})_3][PBu_3]$ (where X = O_3SCF_3, ClO_4, NO_3, CF_3COO, CH_3COO, Cl, Br, I, SCN, CN) and for $Hg(O_3SCF_3)_2[P(c\text{-}C_6H_{11})_3]_2$ and $Hg(O_3SCF_3)_2[PBu_3]_n$ (n = 2, 3, 4) are now reported. Tricyclohexylphosphine and tributylphosphine were used in this study because of their similar base strengths [13] and because they form complexes sufficiently soluble in dichloromethane for NMR measurements.

TABLE I. NMR Parameters for $P(c\text{-}C_6H_{11})_3$ and PBu_3 Adducts with $Hg(O_3SCF_3)_2$ and $Hg(ClO_4)_2$.

Compound	$\delta(^{31}P)$ (ppm)	$^1J(Hg-P)$ (Hz)	$\delta(^{199}Hg)$ (ppm)	Temperature (°C)
$Hg(O_3SCF_3)_2[P(c\text{-}C_6H_{11})_3]_2$	75.8	4087	494	30
$Hg(ClO_4)_2[P(c\text{-}C_6H_{11})_3]_2$[a]	78.3	3730	365	30
$Hg(O_3SCF_3)_2[PBu_3]_2$	45.4	4815	365	30
$Hg(O_3SCF_3)_2[PBu_3]_3$	29.3	3144	1075	–60
$Hg(O_3SCF_3)_2[PBu_3]_4$	5.0	1990	1137	–80
$Hg(ClO_4)_2[PBu_3]_2$[a]	49.8	4280	290	30
$Hg(ClO_4)_2[PBu_3]_3$[a]	30.6	3050	1080	–70
$Hg(ClO_4)_2[PBu_3]_4$[a]	4.8	1980	1130	–70

[a] Data from ref. 1.

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TABLE II. NMR Parameters for $HgX_2P'P$ [$P' = P(c\text{-}C_6H_{11})_3$, $P = PBu_3$] in Dichloromethane Solution.

X	$\delta(^{31}P)$ (ppm)		$^2J(P'-P)$ (Hz)	J(Hg–P') (Hz)	J(Hg–P) (Hz)	$\delta(^{199}Hg)$ (ppm)	Temperature (°C)
	P'	P					
O_3SCF_3	72.54	49.65	198	4230	4595	413	30
ClO_4	72.22	52.50	191	3860	4220	376	–80
NO_3	66.36	44.53	190	4755	5170	454	–85
CF_3COO	62.39	37.89	181	4945	5260	667	–70
CH_3COO	58.90	30.71	176	5100	5600	750	–80
Cl	56.72	29.18	156	4960	4940	1055	–100
Br	51.33	23.20	147	4750	4660	1001	–100
I	40.57	8.42	125	4280	4060	895	–105
SCN	61.26	30.31	138	4350	4205	1130	–70
CN	41.85	2.54	85	3730	3110	1135	–105

Results and Discussion

Dichloromethane solutions containing 1:1 stoichiometries of $[Hg(DMSO)_6](O_3SCF_3)_2$ and either tricyclohexylphosphine, $P(c\text{-}C_6H_{11})_3$, or tributylphosphine, PBu_3, have phosphorus-31 and mercury-199 NMR spectra consistent with the formation of 1:2 adducts and unreacted $[Hg(DMSO)_6](O_3SCF_3)_2$. This result is in contrast to the reaction of tertiary phosphites with $[Hg(DMSO)_6](O_3SCF_3)_2$ where 1:1 adducts were observed [10]. The 1:2 adduct $Hg(O_3SCF_3)_2[P(c\text{-}C_6H_{11})_3]_2$ does not react further with tricyclohexylphosphine in solution however $Hg(O_3SCF_3)_2[PBu_3]_2$ does react further with tributylphosphine to product 1:3 and 1:4 adducts in solution at low temperature. NMR data for these adducts are presented in Table I.

A comparison of the NMR parameters for $Hg(O_3SCF_3)_2[P(c\text{-}C_6H_{11})_3]_2$ and $Hg(O_3SCF_3)_2[PBu_3]_2$ with those for the perchlorate analogues $Hg(ClO_4)_2[P(c\text{-}C_6H_{11})_3]_2$ and $Hg(ClO_4)_2[PBu_3]_2$ imply significant differences in the degree of coordination of the two anions ClO_4^- and $O_3SCF_3^-$ in dichloromethane solution. Whilst the $^1J(Hg-P)$ values increase for both phosphine complexes in going from perchlorate to trifluoromethylsulphonate and imply stronger mercury–phosphine bonding, the $\delta(^{31}P)$ chemical shifts on the other hand move to lower frequency and imply more weakly coordinated phosphine molecules. Furthermore the $\delta(^{199}Hg)$ chemical shifts for the trifluoromethylsulphonate derivatives are at higher frequency than for the perchlorate containing compounds and implies greater electron density at mercury for the trifluoromethylsulphonate derivatives. It has previously been reported [8, 9] that $^1J(Hg-P)$ values for phosphine complexes of mercury(II) are largely determined by the P–Hg–P angle. The solid state structure for $Hg(ClO_4)_2[P(c\text{-}C_6H_{11})_3]_2$ [16] shows weakly bonded perchlorate groups which presumably cause the deviation of P–Hg–P angle from linearity (observed P–Hg–P angle is 170.7°). It may be that these weak interactions between perchlorate and mercury persist to some extent in solution. Probably in solution the interaction between the trifluoromethylsulphonate anion and mercury are weaker thus leading to a larger P–Hg–P angle.

Further support for the dominant effect of P–Hg–P angle on $^1J(Hg-P)$ coupling values is given by a comparison of the NMR parameters for $Hg(ClO_4)_2[P(c\text{-}C_6H_{11})_3]_2$ and $Hg(CH_3COO)_2[P(c\text{-}C_6H_{11})_3]_2$ with the solid state structures for these two compounds [16]. Although the acetate groups are more strongly bound to mercury than the perchlorate groups, the mercury–phosphorus distances are virtually identical for both compounds. The most obvious difference in the solid state appears in the P–Hg–P angle, 153° for $Hg(CH_3COO)_2[P(c\text{-}C_6H_{11})_3]_2$ and 170.7° for $Hg(ClO_4)_2[P(c\text{-}C_6H_{11})_3]_2$. Presumably similar differences in P–Hg–P angles also exist in solution and give rise to the quite different NMR parameters ($^1J(Hg-P)$ 3730, $\delta(^{199}Hg)$ 420, $\delta(^{31}P)$ 78.3 for $Hg(ClO_4)_2[P(c\text{-}C_6H_{11})_3]_2$; $^1J(Hg-P)$ 5240, $\delta(^{199}Hg)$ 665, $\delta(^{31}P)$ 53.5 for $Hg(CH_3COO)_2[P(c\text{-}C_6H_{11})_3]_2$) [1].

The differences between perchlorate and trifluoromethylsulphonate are less obvious in the NMR data (Table I) for 1:3 and 1:4 adducts, $HgX_2[PBu_3]_3$ and $HgX_2[PBu_3]_4$ ($X = ClO_4$, O_3SCF_3). In these cases it appears that both perchlorate and trifluoromethylsulphonate are totally uninvolved, in solution, in coordination to mercury.

The phosphorus-31 and mercury-199 spectra of dichloromethane solutions containing equimolar quantities of HgX_2, $P(c\text{-}C_6H_{11})_3$ and PBu_3 (X = Cl, Br, I, SCN, CN) show $HgX_2[P(c\text{-}C_6H_{11})_3]_2$,

$HgX_2[PBu_3]_2$ and $HgX_2[P(c\text{-}C_6H_{11})_3][PBu_3]$ in approximate statistical distributions. Similar distributions were observed in solutions containing equimolar quantities of $HgX_2[P(c\text{-}C_6H_{11})_3]_2$ and $HgX_2[PBu_3]_2$ ($X = NO_3$, CH_3COO, CF_3COO). A solution containing equimolar quantities of $Hg(ClO_4)_2[P(c\text{-}C_6H_{11})_3]_2$ and $Hg(ClO_4)_2[PBu_3]_2$ does not yield mixed-phosphine species unless a small amount (1 drop) of PBu_3 has been added. The addition of a slight excess of PBu_3 is necessary to induce phosphine exchange at mercury via the formation of a small amount of $Hg(ClO_4)_2[PBu_3]_3$. The mixture involving $Hg(O_3SCF_3)_2[P(c\text{-}C_6H_{11})_3][PBu_3]$ was formed by mixing equimolar quantities of $[Hg(DMSO)_6](O_3SCF_3)_2$ [14], $P(c\text{-}C_6H_{11})_3$ and PBu_3. With the exception of the mixture involving the trifluoromethylsulphonate anion, cooling is required to slow phosphine exchange sufficiently to observe mercury-199 satellites in the phosphorus-31 spectra.

The phosphorus-31 spectrum of each of the mixtures studied comprises two singlets (each with mercury-199 satellites) identified as due to $HgX_2[P(c\text{-}C_6H_{11})_3]_2$ and $HgX_2[PBu_3]_2$ as well as an ABX spectrum due to the mixed-phosphine species $HgX_2[P(c\text{-}C_6H_{11})_3][PBu_3]$. The corresponding mercury-199 spectra each contain two triplets due to $HgX_2[P(c\text{-}C_6H_{11})_3]_2$ and $HgX_2[PBu_3]_2$ as well as a doublet of doublets arising from the $HgX_2[P(c\text{-}C_6H_{11})_3][PBu_3]$ species. Analysis of these spectra give the results presented in Table II.

The phosphorus-31 chemical shift of $P(c\text{-}C_6H_{11})_3$ is at higher frequency for $Hg(O_3SCF_3)_2[P(c\text{-}C_6H_{11})_3][PBu_3]$ than for $Hg(O_3SCF_3)_2[PBu_3]_2$ whilst $^1J(Hg\text{–}P)$ is smaller for $Hg(O_3SCF_3)_2[P(c\text{-}C_6H_{11})_3][PBu_3]$ than for $Hg(O_3SCF_3)_2[PBu_3]_2$. The opposite is true when comparing $Hg(O_3SCF_3)_2[P(c\text{-}C_6H_{11})_3][PBu_3]$ with $Hg(O_3SCF_3)_2[P(c\text{-}C_6H_{11})_3]_2$ and these results are consistent with a larger *trans*-influence of $P(c\text{-}C_6H_{11})_3$ in these, presumably, approximately linear complexes. A similar observation is made from the data for the compounds with $X = ClO_4$.

The data in Table II show that the mercury-199 chemical shifts move to higher frequency with increasing donor ability of the anion, X. These shifts are accompanied by decreases in $^1J(Hg\text{–}P')$ values and are consistent with earlier reports [8, 9] correlating decreasing one bond mercury–phosphorus coupling with decreasing P–Hg–P angles. This correlation also appears to hold true for two bond couplings $^2J(P\text{–}P')$ which also decrease as the donor ability of the anion increases. The $^2J(P\text{–}P')$ values cover the narrow range 198 Hz to 83 Hz and are significantly smaller than those determined for $[HgP(OMe_3)P(OEt_3)_3]^{2+}$ (567 Hz) [10] and $Hg[P(O)(Me)_2]_2$ (700 Hz) [15].

Experimental

All NMR spectra were recorded on a JEOL FX100 spectrometer, phosphorus-31 at 40.26 MHz and mercury-199 at 17.82 MHz using external ^7Li lock. Phosphorus-31 spectra were referenced against external 85% H_3PO_4 and mercury-199 against external 1 *M* phenylmercury acetate in DMSO.

Preparation of phosphine complexes of mercury was as previously described [1, 2].

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