Mercury(II) Halide Complexes of Tertiary Phosphines. Part X.* Study of the Triheteroarylphosphine Complexes $HgX_2(PR_3)_2$ [X = Cl, Br, I; R = 2-Furyl or 2-Thienyl]. Crystal Structure of $HgCl_2[P(2\text{-thienyl})_3]_2$. Solid State Vibrational and ^{31}P NMR Solution Studies

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Abstract

The preparation of complexes of the type $HgX_2(PR_3)_2$ [X = Cl, Br or I; R = 2-furyl or 2-thienyl] has been investigated, and a series of compounds has been characterised by analytical and, where possible, solid state vibrational and ^{31}P NMR solution studies. In addition, the X-ray crystal structure of $HgCl_2[P(2\text{-thienyl})_3]_2$ has been determined. Crystals of the complex are monoclinic, space group $P2_1/n$, with $a = 9.556(6)$, $b = 18.280(10)$, $c = 16.609(9)$ Å, $\beta = 102.14(5)°$. The structure was solved using the heavy atom method and refined to a final R-value of 0.049 for 4067 observed diffractometer data. The complex is found to be a distorted tetrahedral monomer, and the geometry about mercury has been compared with that found in $HgCl_2(PR_3)_2$ (R = Et or Ph). These data, and in particular, the relative values of the P–Hg–P angle, indicate the σ-donating ability of tri(2-thienyl)phosphine to be substantially weaker than that of triethylphosphine. Comparison of $^1J(^{199}Hg-^{31}P)$ coupling constants indicates that both triheteroarylphosphines are weaker σ-donors towards mercury(II) halides than is triphenylphosphine, a view given support by the crystallographic data, and also by the solid state vibrational data for certain of the complexes.

Introduction

In our study of the tertiary phosphine complexes $HgX_2(PR_3)_n$ (n = 1 or 2) we have found [1–8] that the structure adopted in the solid state is determined by a number of factors including (i) the nature of the halogen, (ii) the σ-donor strength and steric requirements of the phosphine ligand, and (iii) the tendency of mercury(II) to adopt linear coordination. The extent of interaction between phosphorus and mercury has been monitored using the magnitude of ^1J(Hg–P) [7, 9–12], and, in the bis(phosphine) complexes $HgX_2(PR_3)_2$, by the value of the P–Hg–P angle [6, 7].

The donor properties of tertiary phosphine ligands in which one or more heteroaryl substituents are directly attached to phosphorus are of considerable interest, since the electronic effects of such substituents appear to vary, depending on the nature of the heteroatom, its position with respect to phosphorus, and also on the nature of the interaction of phosphorus with other atoms. From a wide range of studies of the effects of heteroaryl substituents on the rate and course of reactions involving nucleophilic attack at phosphorus in phosphonium salts, phosphine oxides, phosphinate and phosphonate esters [13–15], and also on the rate of quaternization of phosphines [16], we have shown that the 2-furyl and 2-thienyl groups behave as moderately strongly electron-withdrawing substituents, having a substantially greater electron-withdrawing effect than the phenyl group. The following order of apparent electron-withdrawing power applies in many of the systems studied: 2-furyl > 2-thienyl > phenyl, indicating the importance of the σ-electron withdrawing power of the heteroatom. However, a study of the donor properties of a series of (2-thienyl)phosphines towards nickel(II) and cobalt(II) ions showed that these phosphines appear to be better donors than triphenylphosphine, as indicated by band positions in the crystal field spectra of pseudo-tetrahedral complexes of the type $[ML_2X_2]$ (L = phosphine, X = halogen) [17]. The donor properties of 2-furyl- and 2-thienylphosphines towards selenium and platinum(II) acceptors have been investigated by ^{31}P NMR studies of the one bond coupling constants $^1J(^{77}Se-^{31}P)$ and $^1J(^{195}Pt-^{31}P)$, and it has been shown that the respective

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*Part IX: see ref. [8].

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coupling constants increase as the heteroaryl groups become more electron-withdrawing, indicating an increased *s*-character for the phosphorus lone pair, compared to triphenylphosphine [18]. In consequence, it would be expected that the bonds from phosphorus to the acceptor atom should be shorter in the heteroarylphosphine complexes than in the related triphenylphosphine derivatives, and we have recently gained evidence in support of this suggestion from X-ray studies of tri-(2-furyl)-phosphine selenide [19]. We have also observed a similar shortening of the P–Se bond in tri-(*m*-trifluoromethylphenylphosphine)selenide [20]. There are also a number of indications in the literature that an increase in the magnitude of single bond coupling constants *e.g.* between phosphorus and platinum in phosphine or phosphite platinum(II) halides, as a result of the increased electron-withdrawing nature of the phosphorus substituents is paralleled by a shortening of the phosphorus–platinum bond, although it has also been pointed out that such a shortening may not necessarily indicate a strengthening of the bond [21–25].

In view of these results, it was of interest to investigate the donor abilities of such heteroarylphosphines towards other acceptors, and, in view of the earlier correlations observed for phosphine–mercury(II) halide complexes, we chose to investigate the related complexes of tri-(2-furyl)- and tri-(2-thienyl)phosphine. We now present details of a study of the preparation of a series of complexes $HgX_2(PR_3)_2$ (R = 2-furyl- or 2-thienyl; X = Cl, Br, I), together with ^{31}P NMR studies of the single bond coupling constants $^1J(^{199}Hg-^{31}P)$ and also a single crystal X-ray study of the complex $HgCl_2[P(2\text{-thienyl})_3]_2$.

Experimental

All operations involving tertiary phosphines were conducted under nitrogen. Phosphorus-31 NMR spectra were recorded on a JEOL PFT-100 Fourier-transform NMR spectrometer at 40.48 MHz with proton noise decoupling. Chemical shifts are reported on the δ scale with respect to 85% H_3PO_4 and are accurate to ±0.1 ppm. Shifts to high field are negative in sign. Coupling constants are reported in Hz and are accurate to ±1.2 Hz. Far infrared vibrational spectra were recorded at room temperature on a Beckman R11C FS-720 interferometer with the sample dispersed in polyethene.

Preparation of the Complexes

To a hot solution of the mercury(II) halide (1 mol) in ethanol was added a hot solution of the phosphine (2.5 mol) in ethanol. The resulting solution was then allowed to cool, and the resulting complexes filtered off, washed with ethanol and dried. The following complexes were isolated.

Dichlorobis(tri-(2-furyl)phosphine)mercury(II), pale yellow plates, m.p. 192–194 °C. Found: C, 39.50; H, 2.40; $C_{24}H_{18}Cl_2HgO_6P_2$ requires C, 39.20; H, 2.50%.

Dibromobis(tri-(2-furyl)phosphine)mercury(II), pale yellow needles, m.p. 160–162 °C. Found: C, 35.05; H, 2.15. $C_{24}H_{18}Br_2HgO_6P_2$ requires C, 34.95; H, 2.20%.

Di-iodo(tri-(2-furyl)phosphine)mercury(II), pale yellow plates, m.p. 147–150 °C. Found: C, 21.60; H, 1.25; $C_{12}H_9HgI_2O_3P$ requires C, 21.00; H, 1.30%. The corresponding bis(phosphine)mercury(II) iodide complex could not be prepared.

Dichlorobis(tri-(2-thienyl)phosphine)mercury(II), white crystals, m.p. 220–222 °C. Found: C, 34.65; H, 2.10; $C_{24}H_{18}Cl_2HgP_2S_6$ requires C 34.65; H, 2.15%.

Dibromobis(tri-(2-thienyl)phosphine)mercury(II), white crystals, m.p. 197–199 °C. Found: C, 31.45; H, 1.90; $C_{24}H_{18}Br_2HgP_2S_6$ requires C, 31.30; H, 1.95%.

Di-iodobis(tri-(2-thienyl)phosphine)mercury(II), pale yellow crystals, m.p. 173–174 °C. Found: C, 28.60; H, 1.80; $C_{24}H_{18}HgI_2P_2S_6$ requires C, 28.40; H, 1.80%.

Crystallographic Studies

$HgCl_2[P(2\text{-thienyl})_3]_2$ was recrystallised from hot ethanol as colourless needles. A crystal of approximate dimensions 0.30 × 0.23 × 0.40 mm was mounted with its *c*-axis coincident with the ω-axis of a Stoë Stadi 2 two circle diffractometer. Data were collected using the background–ω scan–background technique and with graphite monochromated MoK_α radiation. 4774 unique reflections were measured of which 4067 had $I/\sigma(I) \geq 3.0$ and were used for subsequent analysis. Data were corrected for Lorentz and polarisation effects, but not for absorption.

Crystal data

$C_{24}H_{18}Cl_2HgP_2S_6$, M = 832.2, Monoclinic, a = 9.556(6), b = 18.280(10), c = 16.609(9) Å, β = 102.14(5)°, U = 2836.4 Å^3, $F(000)$ = 1608, space group $P2_1/n$, Z = 4, D_m (by flotation) = 1.93, D_c = 1.95 g cm^{-3}, MoK_α radiation, λ = 0.71069 Å, $\mu(MoK_\alpha)$ = 59.2 cm^{-1}.

The structure was solved using the heavy-atom method and refined by full-matrix least squares. Two of the 2-thienyl units were found to contain rotational disorder such that two thienyl groups (having approximately 50% occupancy) are related to each other by a pseudo two-fold axis about the P2–C(n1) (n = 4, 6) bonds. Each of the disordered 2-thienyl entities were given ideal geometries and included in

TABLE I. Final Fractional Coordinates (Hg × 10^5; other atoms × 10^4) with Estimated Standard Deviations in Parentheses.[a]

Atom	*x*	*y*	*z*
Hg	44386(3)	15488(2)	25479(2)
Cl(1)	2726(3)	498(1)	2070(2)
Cl(2)	3613(3)	2619(1)	1614(2)
P(1)	4303(2)	1891(1)	3969(1)
P(2)	6592(2)	1169(1)	2004(1)
C(11)	5500(9)	1340(5)	4713(6)
S(12)	5150(4)	1115(2)	5635(2)
C(13)	6690(12)	596(6)	5880(8)
C(14)	7429(13)	609(7)	5317(8)
C(15)	6783(10)	1024(7)	4635(8)
C(21)	4783(9)	2821(5)	4209(6)
S(22)	3989(4)	3524(1)	3592(2)
C(23)	4924(13)	4153(6)	4218(8)
C(24)	5875(11)	3868(6)	4890(8)
C(25)	5810(9)	3072(5)	4920(7)
C(31)	2587(8)	1791(4)	4225(5)
S(32)	2027(3)	2290(2)	4948(2)
C(33)	507(12)	1780(7)	4872(7)
C(34)	425(11)	1247(5)	4301(7)
C(35)	1597(10)	1217(5)	3913(7)
C(41)	7385	328	2451
S(42A)	6473	−299	2789
S(42B)	9009	46	2462
C(43A)	7916	−865	3019
C(43B)	8741	−751	2934
C(44A)	9125	−564	2925
C(44B)	7465	−868	3062
C(45A)	8780	80	2453
C(45B)	6576	−230	2717
C(51)	6112(9)	1016(5)	923(5)
S(52)	7229(3)	654(1)	337(2)
C(53)	5943(11)	679(5)	−535(6)
C(54)	4707(12)	970(5)	−418(6)
C(55)	4828(10)	1175(5)	431(6)
C(61)	8001	1836	2212
S(62A)	9401	1822	1763
S(62B)	8056	2439	2936
C(63A)	10153	2562	2308
C(63B)	9690	2748	2835
C(64A)	9333	2794	2804
C(64B)	10294	2327	2345
C(65A)	8004	2411	2783
C(65B)	9112	1868	1779

[a] Two of the 2-thienyl groups are disordered. The first is comprised of C(41), S(42A), C(43A), C(44A), C(45A), and C(41), S(42B), C(43B), C(44B), C(45B) and the second of C(61), S(62A), C(63A), C(64A), C(65A) and C(61), S(62B), C(63B), C(64B), C(65B).

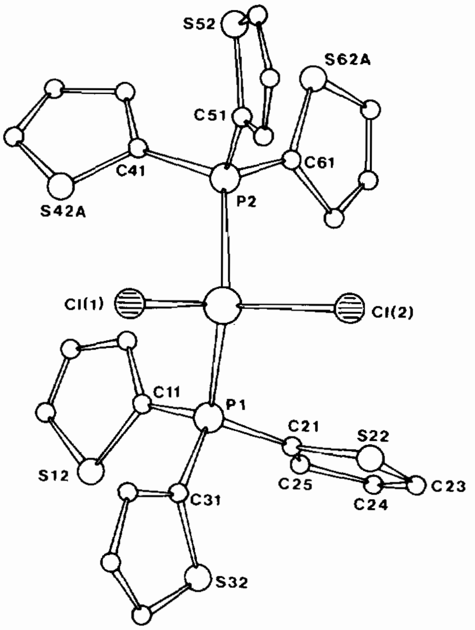

Fig. 1. Molecular structure of $HgCl_2[P(2\text{-thienyl})_3]_2$. For clarity, only one conformation of the two disordered 2-thienyl rings is shown.

the least squares refinement with common isotropic temperature factors applied to atoms related by the pseudo symmetry. The population parameters applied to each pair of thienyl units were refined, the final values corresponding to occupances of 45% [C(41), S(42A)– C(45A)], 55% [C(41), S(42B)–C(45B)], and 50% for each of the disordered units associated with C(61). Hydrogen atoms were located for the ordered 2-thienyl groups and given ideal geometry (C–H 1.08 Å). A common isotropic temperature factor was applied to the hydrogen atoms associated with the ordered thienyl groups, and refined to a final value of 0.059(13) Å^2. Complex neutral-atom scattering factors [26] were employed and in the final cycles of refinement the weighting scheme $w = 1.000/[\sigma^2(F_o) + 0.0078(F_o)^2]$ was adopted. All ordered, non-hydrogen, atoms were given anisotropic temperature factors and refinement converged at $R = 0.049$, $R' = 0.058$. Final positional parameters are given in Table I, bond distances and angles in Table II. Hydrogen positions, thermal parameters, observed and calculated structure factors have been deposited and are available from the Editor.

Results and Discussion

The present X-ray study shows $HgCl_2[P(2\text{-thienyl})_3]_2$ to be a distorted tetrahedral monomer (Fig. 1).

The structural parameters which are most sensitive to the extent of the interactions between mercury and phosphorus, *viz.* Hg–P, Hg–Cl bond distances, P–Hg–P bond angle, closely resemble the values found in $HgCl_2(PPh_3)_2$ (Table III). To a first approximation triphenylphosphine and tri-(2-thienyl)phosphine would appear to have very similar σ-donating

TABLE II. Bond Lengths (Å) and Angles (°) with Estimated Standard Deviations in Parentheses.

Distances (Å)			
Hg–Cl(1)	2.539(2)	Hg–Cl(2)	2.519(2)
Hg–P(1)	2.472(2)	Hg–P(2)	2.513(2)
P(1)–C(11)	1.803(9)	P(2)–C(41)	1.804
P(1)–C(21)	1.785(9)	P(2)–C(51)	1.779(9)
P(1)–C(31)	1.787(9)	P(2)–C(61)	1.795
C(11)–S(12)	1.686(11)	C(41)–S(42A)	1.611
C(11)–C(15)	1.385(14)	C(41)–C(45A)	1.407
S(12)–C(13)	1.726(12)	S(42A)–C(43A)	1.701
C(13)–C(14)	1.285(20)	C(43A)–C(44A)	1.318
C(14)–C(15)	1.395(17)	C(44A)–C(45A)	1.414
C(21)–S(22)	1.717(9)	C(41)–S(42B)	1.631
C(21)–C(25)	1.442(12)	C(41)–C(45B)	1.406
S(22)–C(23)	1.676(12)	S(42B)–C(43B)	1.700
C(23)–C(24)	1.385(16)	C(43B)–C(44B)	1.299
C(24)–C(25)	1.457(13)	C(44B)–C(45B)	1.485
C(31)–S(32)	1.682(10)	C(51)–S(52)	1.720(10)
C(31)–C(35)	1.434(12)	C(51)–C(55)	1.355(12)
S(32)–C(33)	1.708(12)	S(52)–C(53)	1.692(10)
C(33)–C(34)	1.350(17)	C(53)–C(54)	1.346(16)
C(34)–C(35)	1.406(16)	C(54)–C(55)	1.439(15)
C(61)–S(62A)	1.664	C(61)–S(62B)	1.624
C(61)–C(65A)	1.415	C(61)–C(65B)	1.404
S(62A)–C(63A)	1.700	S(62B)–C(63B)	1.701
C(63A)–C(64A)	1.321	C(63B)–C(64B)	1.336
C(64A)–C(65A)	1.444	C(64B)–C(65B)	1.555
Angles (°)			
P(1)–Hg–Cl(1)	109.3(1)	P(2)–Hg–Cl(1)	101.6(1)
P(1)–Hg–Cl(2)	108.6(1)	P(2)–Hg–Cl(2)	99.6(1)
P(1)–Hg–P(2)	128.6(1)	Cl(1)–Hg–Cl(2)	107.3(1)
Hg–P(1)–C(11)	111.1(3)	Hg–P(2)–C(41)	113.1
Hg–P(1)–C(21)	113.0(3)	Hg–P(2)–C(51)	110.4(3)
Hg–P(1)–C(31)	115.8(3)	Hg–P(2)–C(61)	112.4
C(11)–P(1)–C(21)	106.4(4)	C(41)–P(2)–C(51)	106.2
C(11)–P(1)–C(31)	115.8(3)	C(41)–P(2)–C(61)	105.5
C(21)–P(1)–C(31)	104.5(4)	C(51)–P(2)–C(61)	108.9
P(1)–C(11)–S(12)	122.7(6)	P(2)–C(41)–S(42A)	122.6
P(1)–C(11)–C(15)	128.0(9)	P(2)–C(41)–C(45A)	126.2
S(12)–C(11)–C(15)	109.3(8)	S(42A)–C(41)–C(45A)	110.6
C(11)–S(12)–C(13)	91.5(6)	C(41)–S(42A)–C(43A)	92.2
S(12)–C(13)–C(14)	112.9(9)	S(42A)–C(43A)–C(44A)	114.1
C(13)–C(14)–C(15)	112.6(11)	C(43A)–C(44A)–C(45A)	107.8
C(11)–C(15)–C(14)	113.6(12)	C(41)–C(45A)–C(44A)	112.3
P(1)–C(21)–S(22)	121.3(5)	P(2)–C(41)–S(42B)	126.1
P(1)–C(21)–C(25)	125.8(7)	P(2)–C(41)–C(45B)	122.4
S(22)–C(21)–C(25)	112.9(7)	S(42B)–C(41)–C(45B)	110.7
C(21)–S(22)–C(23)	91.8(5)	C(41)–S(42B)–C(43B)	92.3
S(22)–C(23)–C(24)	114.6(8)	S(42B)–C(43B)–C(44B)	117.0
C(23)–C(24)–C(25)	112.2(9)	C(43B)–C(44B)–C(45B)	106.7
C(21)–C(25)–C(24)	108.4(8)	C(41)–C(45B)–C(44B)	112.5
P(1)–C(31)–S(32)	124.0(5)	P(2)–C(51)–S(52)	124.9(5)
P(1)–C(31)–C(35)	123.9(7)	P(2)–C(51)–C(55)	125.7(8)
S(32)–C(31)–C(35)	111.7(7)	S(52)–C(51)–C(55)	109.4(7)
C(31)–S(32)–C(33)	92.6(5)	C(51)–S(52)–C(53)	92.8(5)
S(32)–C(33)–C(34)	111.6(9)	S(52)–C(53)–C(54)	112.8(8)
C(33)–C(34)–C(35)	114.6(10)	C(53)–C(54)–C(55)	110.7(9)
C(31)–C(35)–C(34)	109.5(9)	C(51)–C(55)–C(54)	114.3(9)

(continued on facing page)

TABLE II. *(continued)*

P(2)–C(61)–S(62A)	123.0	P(2)–C(61)–S(62B)	120.7
P(2)–C(61)–C(65A)	122.0	P(2)–C(61)–C(65B)	123.2
S(62A)–C(61)–C(65A)	115.0	S(62B)–C(61)–C(65B)	116.1
C(61)–S(62A)–C(63A)	92.2	C(61)–S(62B)–C(63B)	92.3
S(62A)–C(63A)–C(64A)	110.4	S(62B)–C(63B)–C(64B)	113.1
C(63A)–C(64A)–C(65A)	117.6	C(63B)–C(64B)–C(65B)	109.1
C(61)–C(65A)–C(64A)	104.7	C(61)–C(65B)–B(64B)	104.1

TABLE III. Important Molecular Parameters in $HgCl_2(PR_3)_2$ Complexes.

	$HgCl_2(PEt_3)_2$	$HgCl_2(PPh_3)_2$	$HgCl_2[P(2\text{-thienyl})_3]_2$
Reference	[7]	[6]	Present work
d(Hg–Cl)/Å	2.68(1) 2.68(1)	2.559(2) 2.545(3)	2.539(2) 2.519(2)
d(Hg–P)/Å	2.39(1) 2.39(1)	2.478(2) 2.462(2)	2.513(2) 2.472(2)
Cl–Hg–Cl/°	105.5(5)	110.7(1)	107.3(1)
P–Hg–P/°	158.5(5)	134.1(1)	128.6(1)

TABLE IV. ^{31}P NMR Data for the Complexes $HgX_2(PR_3)_2$ in Dichloromethane Solution.

	$\delta\,^{31}P$/ppm	$^1J(^{199}Hg-^{31}P)$/Hz	Temp. °C	Ref.
R = Ph; X = Cl	28.1	4740	−43	[11]
R = Ph; X = Br	21.7	4178	−43	[11]
R = Ph; X = I	7.3	3073	−43	[11]
R = thienyl; X = I	−26.0	2722	−90	
R-2-furyl; X = Cl	−37.5	4322	−90	
R-2-furyl; X = Br	−44.2	3540	−90	
R = Et; X = Cl	37.1	5067	27	[7]
R = Et; X = Br	30.9	4788	27	[7]
R = Et; X = I	16.8	4004	27	[7]

abilities. Certainly both phosphines are significantly poorer σ-donors than triethylphosphine as evidenced by (i) the shorter Hg–P distances, (ii) the longer Hg–Cl distances, (iii) the larger P–Hg–P angle found in $HgCl_2(PEt_3)_2$. While the low solubility of the 2-thienyl complexes prevents a satisfactory comparison of NMR data with that reported for the complexes $HgX_2(PPh_3)_2$ (X = Cl, Br or I) [11], it can be seen that $^1J(^{199}Hg-^{31}P)$ for $HgI_2[P(2\text{-thienyl})_3]_2$ is significantly lower than that reported for the related triphenylphosphine complex (Table IV). Furthermore, the related data for $HgX_2[P(2\text{-furyl})_3]_2$ (X = Cl or Br) are also significantly smaller than those for the triphenylphosphine complexes. A direct comparison of data for the bis(phosphine) mercury(II) iodide complexes was frustrated by our inability to prepare the complex derived from tri-(2-furyl)phosphine, the preparative procedure yielding instead the 1:1 complex $[R_3PHgI_2]$. A solution of this complex in $CDCl_3$ exhibited no signs of coupling between mercury and phosphorus, even at −90 °C, indicating dissociation, due to the very weak donor properties of tri-(2-furyl) phosphine towards mercury(II) iodide. Such a lowering in $^1J(^{199}Hg-^{31}P)$ has been taken as evidence of a reduction in basicity of the phosphine and in the strength of the σ-interaction between mercury and phosphorus [7, 9–12]. The coupling constant data for the complexes of triethylphosphine, indicate that this phosphine has a much stronger interaction with mercury(II) halides than does triphenylphosphine and the two heteroarylphosphines. Furthermore, it would appear that both heteroarylphosphines are somewhat poorer σ-donors compared with triphenylphosphine. The trends in one-bond coupling constants for this series of tertiary phosphines when complexed to mercury(II) halides are opposite to those observed for the related coupling constants between phosphorus and selenium and between phosphorus and platinum [18, 21]. This apparent anomaly has been noted before [21]. By way of explanation it has recently been pointed out that because substituent effects on $^1J(^{199}Hg-^{31}P)$ are opposite at the Hg and P atoms, it is apparent that substituent effects of mercury are dominant in determining the coupling constant [27, 28].

Careful examination of the crystallographic data offers some support for the above conclusions concerning the donor properties of the heteroaryl phosphines. In the bis(phosphine) complexes $HgCl_2(PR_3)_2$, the stronger the σ-interaction between phosphorus and mercury, then the larger the observed P–Hg–P angle, a consequence of the tendency of mercury(II) to achieve linear coordination. The relative values of the P–Hg–P angle in the complexes $HgCl_2(PR_3)_2$ (R = 2-thienyl, 128.6(1)°; R = phenyl, 134.1(1)°) indicate that the heteroarylphosphine is a somewhat poorer σ-donor towards mercury(II). While differences in the Hg–P and Hg–Cl distances for the two complexes are not wholly consistent it is, nevertheless, interesting to note that in the 2-thienyl complex the average Hg–P distance is longer than that found in the triphenylphosphine complex (2.493(3) Å compared with 2.470(3) Å) while the average Hg–Cl distance is shorter (2.529(3) Å compared with 2.552(4) Å). These differences are consistent with tri-(2-thienyl)phosphine being the poorer σ-donor.

We have also obtained limited solid state vibrational data for some of the above heteroarylphosphine complexes, the assignments of bands for the remaining complexes being made very difficult by the complexity of the spectra of the phosphine ligands. The Hg–X stretching bands in the complex $HgCl_2[P(2\text{-furyl})_3]_2$ occur at 257 (νHgX_2 sym) and 247 (νHgX_2 asym) cm^{-1} respectively, compared with 237 and 223 cm^{-1} for these bands in the related triphenylphosphine complex. Similarly, in the complex $HgBr_2[P(2\text{-furyl})_3]_2$, the Hg–Br stretching bands are observed at 170 and 161 cm^{-1}, compared with 164 and 155 cm^{-1} in the related triphenylphopshine complex. In the light of our earlier studies of vibrational spectra of bis(phosphine)mercury(II) halide complexes [7], these results would indicate that the mercury–halogen bonds in the tri-(2-furyl)phosphine complexes are marginally stronger than in the triphenylphosphine complexes. Conversely, the mercury–phosphorus interaction must therefore be weaker in the tri-(2-furyl)phosphine complexes, a conclusion consistent with the above ^{31}P NMR studies.

While electronic factors appear to be dominant in determining the solid state structure adopted by such $HgX_2(PR_3)_2$ complexes and, in particular the magnitude of the P–Hg–P angle, steric factors cannot be discounted. However, in comparison of triphenylphosphine with tri-(2-thienyl)phosphine, such steric effects are unlikely to play an important role. It is anticipated that the steric requirements of these two ligands will be similar and certainly the C–P–C angles found for the two phosphines are comparable. We are continuing to explore the donor properties of heteroarylphosphines.

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