Structural Studies of Steric Effects in Phosphine Complexes. The Crystal and Molecular Structure of Dithiocyanato(tricyclohexylphosphine)mercury(II)

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The title complex crystallizes in space group $P2_1/c$ with unit-cell parameters $a = 10.850(1)$, $b = 9.825(2)$, $c = 21.977(3)$ Å, $\beta = 94.34(1)°$, and $Z = 4$. The structure has been refined anisotropically to R 0.030 and R' 0.033 for 1 995 independent reflections. The mercury atom forms three normal covalent bonds [Hg–P 2.411(3), Hg–S 2.471(4) (terminal thiocyanato), and 2.553(3) Å (bridging thiocyanato)] in a distorted trigonal-planar arrangement. A nitrogen atom from a neighbouring molecule is situated above the 'trigonal plane' [Hg–N 2.516(10) Å] and the mercury is effectively four-co-ordinate with a distorted trigonal-pyramidal configuration. The crystal structure thus contains infinite chains of mercury atoms linked by bridging thiocyanato-groups. The cone angle θ for the bulky tricyclohexylphosphine ligand is 177(3)°.

COMPLEXES of the general form HgX_2L (L = unidentate ligand) are thought to exist as dimers with bridging X groups and *trans* ligands.[1-3] Although little crystallographic information is available for complexes of this type, $[HgCl_2(PPh_3Se)]$ is known to be dimeric with the mercury atoms having a distorted tetrahedral geometry.[4] *X*-Ray analysis of $[Hg(NO_3)_2(PPh_3)]$ shows that one nitrato-group is unsymmetrically co-ordinated while the other bridges in a *syn–anti* arrangement to link mercury atoms into an infinite chain.[5] We have established a distorted square-pyramidal geometry for mercury in what we have shown [6] to be dimeric $[\{Hg(NO_3)_2[P(C_6H_{11})_3]\}_2]$. Although i.r.-spectral data [7] were interpreted in favour of a dimeric thiocyanato-bridged structure for $[Hg(SCN)_2(AsPh_3)]$, a crystal-structure determination [8] showed clearly that this was false: the crystal structure could either be described as containing a monomer with 'characteristic' three-co-ordination for the mercury, or alternatively as containing a polymeric system with trigonal-bipyramidal geometry at mercury (by considering two weak intermolecular interactions with thiocyanato-nitrogens of neighbouring molecules). On the basis of a vibrational study a structure similar to that found for $[Hg(SCN)_2(AsPh_3)]$ was postulated for $[Hg(SCN)_2\{P(C_6H_{11})_3\}]$.[9] As part of our structural investigations [6] of complexes of sterically demanding phosphine ligands [*e.g.* $P(C_6H_{11})_3$, PBu^t_3, and $P(C_6H_4\text{-}Me\text{-}o)_3$],[10] we have determined that the crystal structure is quite different from that found in $[\{Hg(NO_3)_2[P(C_6H_{11})_3]\}_2]$ and in $[Hg(SCN)_2(AsPh_3)]$. Of particular interest in the present structure is the effect of the bulky tricyclohexylphosphine ligand on the geometry adopted by the mercury atom, the possible steric meshing of the cyclohexyl rings, and the cone angle θ for the $P(C_6H_{11})_3$ group in this structure.

EXPERIMENTAL

The $[Hg(SCN)_2\{P(C_6H_{11})_3\}]$ complex was prepared as previously reported [9] and recrystallized from n-propanol. The colourless crystals, which gave satisfactory analyses and m.p. of 214—215 °C (decomp.), had virtually identical i.r. and Raman spectral bands to those previously reported. The complex is stable in air but is too insoluble in common solvents for a molecular-weight determination.

Crystal Data.—$C_{20}H_{33}HgN_2PS_2$, $M = 597.2$, Monoclinic, $a = 10.850(1)$, $b = 9.825(2)$, $c = 21.977(3)$ Å, $\beta = 94.34(1)°$, $U = 2\,336.1$ Å^3, $D_m = 1.70$, $Z = 4$, $D_c = 1.70$ g cm^{-3}, $F(000) = 1\,176$. Space group $P2_1/c$ (C^5_{2h}, no. 14) from systematic absences; $h0l$ when $l = 2n + 1$, $0k0$ when $k = 2n + 1$. Mo-K_α radiation [λ 0.710 69 Å; μ(Mo-K_α) 69.7 cm^{-1}].

The cell parameters were obtained from a least-squares refinement of the setting angles of 12 general reflections measured on a Hilger and Watts Y290 computer-controlled diffractometer. The θ—2θ scan technique and graphite-monochromatized molybdenum radiation were used to record the intensities of a unique quadrant of data within the limits $2 < 2\theta < 46°$. A symmetric scan was composed of 60 steps of 0.01° with a 1-s count at each step. Stationary-crystal–stationary-counter background counts were measured for 15 s at the beginning and end of the scan range. The intensities of two standard reflections, monitored every 100 reflections, decreased by 6% during data collection and the transparent crystal became slightly dark during exposure to the *X*-ray beam.

Data were corrected for Lorentz and polarization factors and for absorption.† Maximum and minimum values of

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† Calculations were performed on the University of Guelph IBM 370/155 computer. Data processing was done using a locally modified version of DATCO5 from the crystallographic package of programs contained in the *X*-Ray System (1972). (J. M. Stewart, Technical Report TR–192, Computer Science Center, University of Maryland, College Park, Maryland, U.S.A.). Numerical absorption corrections were applied using a locally modified version of DABS (R. F. Dellaca, University of Canterbury, Christchurch, New Zealand) which has been inserted into the '*X*-Ray '72' system. Mathematical methods are described in 'Crystallographic Computing,' Munksgaard, Copenhagen, 1970.

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the transmission coefficients are 0.727 and 0.582 respectively. Of the 3 472 measured reflections, 1 995 with $I > 3\sigma(I)$ were used in the final refinement of the structure parameters.

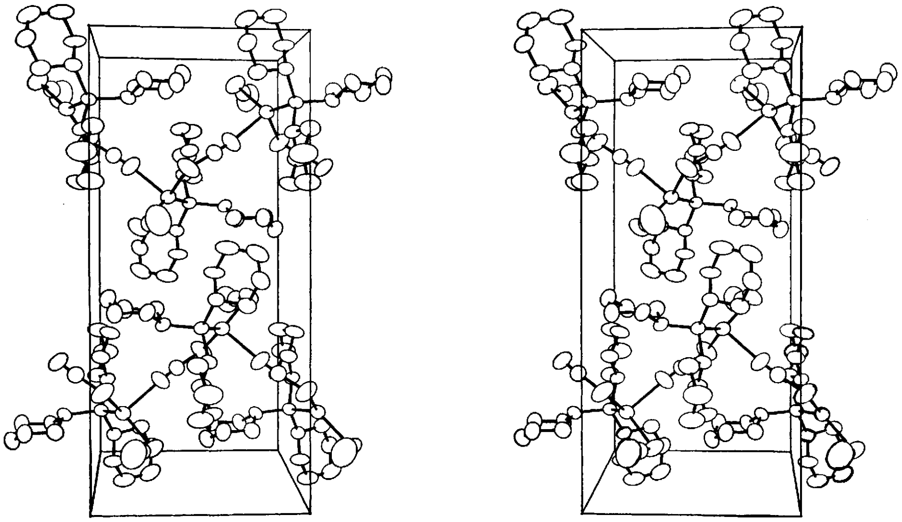

FIGURE 1 Stereoview of the molecular packing diagram for $[Hg(SCN)_2\{P(C_6H_{11})_3\}]$

Structure Solution and Refinement.—An estimate of the overall scale factor was obtained using Wilson's method and fractional co-ordinates for the unique mercury atom were readily obtained from a sharpened three-dimensional Patterson map. A Fourier synthesis based on the mercury phases revealed all the 27 non-hydrogen atoms. Using anisotropic temperature factors for Hg, P, and S and isotropic parameters for the other non-hydrogen atoms and unit weights, full-matrix least-squares refinement resulted in R (= $\Sigma||F_o| - |F_c|/\Sigma|F_o|$) being lowered to 0.049. The scattering functions of Cromer and Mann [11] were used for all the non-hydrogen atoms treated as neutral species, and the curve for the mercury atom was corrected for the real and imaginary part of the anomalous dispersion.[12] Two further cycles of refinement with anisotropic thermal parameters for all the non-hydrogen atoms reduced R to 0.043 and R' $\{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$, the function minimized, to 0.049. The weighting scheme which was employed is defined as $w^{\frac{1}{2}} = 1/[\sigma^2(F) + pF^2]^{\frac{1}{2}}$ with $p = 5 \times 10^{-4}$, a factor introduced to avoid over-weighting strong reflections.[13] This appears satisfactory in that the average values of the minimized functions are independent of $|F_o|$.

A difference-Fourier synthesis computed when R 0.043 showed maxima consistent with the expected positions of the hydrogen atoms; these were then allowed for (in chemically expected positions with C–H 0.95 Å, isotropic U values of 0.063 Å^2, and scattering factors from ref. 14) but not refined in subsequent calculations. Convergence was achieved in two more cycles with R 0.030 and R' 0.033. The error in an observation of unit weight is 1.05 and a final difference Fourier showed no significant features.

Final positional parameters for the non-hydrogen atoms, together with their standard deviations as estimated from the inverse matrix, are listed in Table 1. The calculated positions of the hydrogen atoms, with numbering corresponding to the attached carbon atom, are in Table 2, and interatomic distances and angles in Table 3. A view of the crystal structure is given in Figure 1 and the co-ordination about the unique mercury atom and our numbering scheme are shown in Figure 2. Final thermal parameters and observed and calculated structure factors are given in Supplementary Publication No. SUP 22060 (29 pp.).*

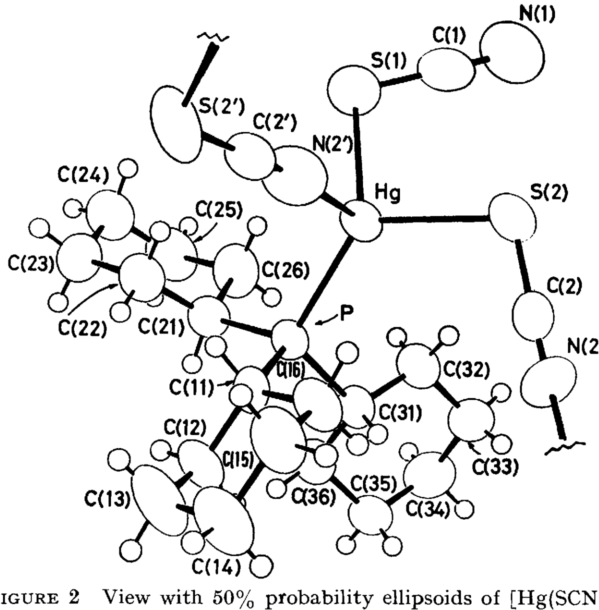

FIGURE 2 View with 50% probability ellipsoids of $[Hg(SCN)_2\{P(C_6H_{11})_3\}]$ showing molecular geometry and details of the numbering scheme. The co-ordinates of the atoms marked with a prime are obtained from the unprimed atoms by the transformation $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$ (symmetry operation I in Table 3)

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

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DISCUSSION

It is clear from the molecular-packing diagram (Figure 1) that the prediction[9] of a trigonal-bipyramidal geometry for [Hg(SCN)$_2${P(C$_6$H$_{11}$)$_3$}] similar to that found in [Hg(SCN)$_2$(AsPh$_3$)] is not borne out. The mercury atom forms three normal covalent bonds (to phosphorus and sulphur, see below) in a distorted trigonal-planar arrangement with the mercury atom 0.335 Å from the plane of S(1), S(2), and P. A nitrogen atom of one of the thiocyanato-groups from a neighbouring molecule is situated above the trigonal plane [Hg–N 2.516(10) Å] so that the co-ordination about the mercury can be described as distorted trigonal pyramidal. The other thiocyanato-nitrogen, N(1), only makes normal van der Waals contacts with cyclohexyl rings of adjacent molecules, and the fifth co-ordination site, which would correspond to a trigonal-bipyramidal geometry at mercury, is unoccupied. The crystal structure thus contains a polymer system with mercury atoms linked by one bridging thiocyanato-ligand.

TABLE 1

Final positional * parameters for [Hg(SCN)$_2${P(C$_6$H$_{11}$)$_3$}]

Atom	*x*	*y*	*z*
Hg	0.484 02(3)	0.134 67(4)	0.151 50(2)
P	0.288 6(2)	0.017 7(3)	0.136 9(10)
S(1)	0.594 9(3)	0.284 6(4)	0.083 7(15)
S(2)	0.668 8(3)	0.041 3(4)	0.217 4(15)
N(1)	0.837 0(11)	0.191 3(15)	0.103 4(7)
N(2)	0.569 9(10)	−0.176 2(10)	0.278 0(4)
C(1)	0.735 2(11)	0.228 7(12)	0.096 0(5)
C(2)	0.608 3(9)	−0.089 9(11)	0.252 6(4)
C(11)	0.200 1(8)	0.046 7(10)	0.203 7(4)
C(12)	0.072 4(9)	−0.013 3(12)	0.201 1(4)
C(13)	0.003 8(11)	0.030 7(18)	0.254 7(6)
C(14)	0.073 2(11)	−0.000 9(15)	0.314 3(5)
C(15)	0.202 0(10)	0.060 3(13)	0.317 4(4)
C(16)	0.272 0(9)	0.015 0(12)	0.263 4(4)
C(21)	0.198 6(9)	0.081 8(10)	0.068 2(4)
C(22)	0.148 5(10)	0.224 0(12)	0.079 2(4)
C(23)	0.078 4(10)	0.279 9(12)	0.022 2(5)
C(24)	0.153 1(11)	0.275 7(14)	−0.032 6(5)
C(25)	0.198 6(11)	0.135 6(15)	−0.043 6(4)
C(26)	0.275 5(10)	0.078 6(13)	0.012 8(4)
C(31)	0.314 5(8)	−0.167 3(9)	0.130 4(4)
C(32)	0.437 3(10)	−0.202 1(11)	0.103 6(5)
C(33)	0.460 1(10)	−0.354 4(12)	0.103 8(5)
C(34)	0.351 8(12)	−0.432 8(12)	0.074 2(5)
C(35)	0.231 8(10)	−0.397 8(11)	0.099 8(5)
C(36)	0.206 7(10)	−0.245 1(11)	0.096 3(4)

* Estimated standard deviations of the last digit are in parentheses.

TABLE 2

Positional parameters for the hydrogen atoms of [Hg(SCN)$_2${P(C$_6$H$_{11}$)$_3$}]

Atom	*x*	*y*	*z*
H(11)	0.193	0.143	0.199
H(121)	0.028	0.015	0.164
H(122)	0.079	−0.110	0.201
H(131)	−0.009	0.127	0.252
H(132)	−0.074	−0.013	0.253
H(141)	0.029	0.035	0.347
H(142)	0.080	−0.097	0.319
H(151)	0.195	0.157	0.317
H(152)	0.246	0.032	0.355
H(161)	0.350	0.062	0.265
H(162)	0.287	−0.080	0.266
H(21)	0.131	0.020	0.061
H(221)	0.094	0.220	0.111
H(222)	0.215	0.283	0.091
H(231)	0.006	0.227	0.013
H(232)	0.056	0.372	0.029
H(241)	0.104	0.306	−0.068
H(242)	0.223	0.335	−0.026
H(251)	0.129	0.078	−0.053
H(252)	0.248	0.138	−0.077
H(261)	0.300	−0.012	0.005
H(262)	0.348	0.133	0.021
H(31)	0.319	−0.190	0.172
H(321)	0.437	−0.170	0.064
H(322)	0.503	−0.161	0.128
H(331)	0.530	−0.370	0.081
H(332)	0.476	−0.383	0.144
H(341)	0.345	−0.415	0.032
H(342)	0.368	−0.528	0.081
H(351)	0.167	−0.445	0.077
H(352)	0.235	−0.426	0.141
H(361)	0.199	−0.217	0.055
H(362)	0.132	−0.225	0.114

TABLE 3

Interatomic distances (Å) and angles (°) for [Hg(SCN)$_2${P(C$_6$H$_{11}$)$_3$}]

(*a*) Distances			
Hg–S(1)	2.471 (4)	C(21)–C(22)	1.525 (15)
Hg–S(2)	2.553 (3)	C(22)–C(23)	1.518 (14)
Hg–N(2^{I})	2.516 (10)	C(23)–C(24)	1.501 (16)
Hg–P	2.411 (3)	C(24)–C(25)	1.488 (20)
		C(25)–C(26)	1.546 (14)
P–C(11)	1.836 (9)	C(21)–C(26)	1.527 (13)
P–C(21)	1.845 (9)		
P–C(31)	1.846 (9)	C(31)–C(32)	1.535 (14)
		C(32)–C(33)	1.516 (16)
S(1)–C(1)	1.622 (12)	C(33)–C(34)	1.510 (16)
S(2)–C(2)	1.663 (11)	C(34)–C(35)	1.497 (17)
		C(35)–C(36)	1.526 (15)
C(1)–N(1)	1.163 (17)	C(31)–C(36)	1.542 (13)
C(2)–N(2)	1.113 (14)		
C(11)–C(12)	1.503 (14)	N(1) · · · C(22^{II})	3.48(2)
C(12)–C(13)	1.504 (17)	N(1) · · · C(23^{II})	3.39(2)
C(13)–C(14)	1.492 (16)	N(1) · · · C(25^{III})	3.48(2)
C(14)–C(15)	1.518 (17)		
C(15)–C(16)	1.523 (15)		
C(11)–C(16)	1.505 (12)		
(*b*) Angles			
S(1)–Hg–S(2)	99.1(1)	Hg–P–C(11)	109.1(3)
P–Hg–S(1)	131.8(1)	Hg–P–C(21)	110.6(3)
P–Hg–S(2)	123.3(1)	Hg–P–C(31)	110.0(3)
P–Hg–N(2^{I})	101.0(2)	C(11)–P–C(21)	108.9(4)
S(1)–Hg–N(2^{I})	94.4(2)	C(11)–P–C(31)	107.8(4)
S(2)–Hg–N(2^{I})	97.2(2)	C(21)–P–C(31)	110.3(4)
Hg–S(1)–C(1)	101.0(4)	C(11)–C(12)–C(13)	111.5(9)
Hg–S(2)–C(2)	102.8(4)	C(12)–C(13)–C(14)	112.4(10)
		C(13)–C(14)–C(15)	111.0(10)
S(1)–C(1)–N(1)	177.8(9)	C(14)–C(15)–C(16)	111.2(9)
S(2)–C(2)–N(2)	177.5(9)	C(15)–C(16)–C(11)	111.2(8)
Hg–N(2^{I})–C(2^{I})	169.9(9)	C(16)–C(11)–C(12)	111.6(8)
C(21)–C(22)–C(23)	111.3(8)	C(31)–C(32)–C(33)	111.4(9)
C(22)–C(23)–C(24)	112.6(9)	C(32)–C(33)–C(34)	112.4(9)
C(23)–C(24)–C(25)	111.2(10)	C(33)–C(34)–C(35)	113.0(9)
C(24)–C(25)–C(26)	111.7(9)	C(34)–C(35)–C(36)	111.4(9)
C(25)–C(26)–C(21)	109.7(9)	C(35)–C(36)–C(31)	109.7(8)
C(26)–C(21)–C(22)	111.6(8)	C(36)–C(31)–C(32)	110.6(7)

The superscripts refer to the following equivalent positions: I $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; II $1 + x, y, z$; III $1 - x, -y, -z$.

The Hg–N(2) distance [2.516(10) Å] is intermediate in length between the weak interactions found in [Hg(SCN)$_2$(AsPh$_3$)] [Hg–N 2.673(7) and 2.736(9) Å][8] and in Hg[SCN]$_2$ [Hg–N 2.81(1) Å],[15] and the much stronger Hg–N interaction [Hg–N 2.40(1) Å] found for the bridg-

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[15] A. L. Beauchamp and D. Goutier, *Canad. J. Chem.*, 1972, **59**, 977.

ing thiocyanato-group in $[PPh_4][Hg(SCN)_3]$.[16] For comparison, the Hg–N distance predicted [2] for a pure covalent bond is 2.2 Å. The considerable distortion of bond angles at the mercury atom [S–Hg–S 99.1(1), P–Hg–S 123.3(1) and 131.8(1)°] presumably arises because of a combination of the bulkiness of the tricyclohexylphosphine ligand and crystal-packing effects. In contrast, with the less bulky triphenylarsine ligand, in $[Hg(SCN)_2(AsPh_3)]$,[8] the S–Hg–S angle is 'normal' [123.4(1)°] but the As–Hg–S angles are quite different [108.9(1) and 126.9(1)°]. The angles at mercury in tetrahedral systems also vary widely; in monomeric $[Hg(SCN)_2(PPh_3)_2]$ [17] S–Hg–S 96.7(1)° with P–Hg–S 104.3—116.2(1)°, and in $[Hg(SCN)_4]^{2-}$ the S–Hg–S angles are in the range 105.3—117.3(1)°.[18]

The Hg–S bond length of the terminal thiocyanato-group [2.471(4) Å] is significantly shorter than the Hg–S distance [2.553(3) Å] of the bridging thiocyanato-group. Both distances are within the range expected for four-co-ordinate compounds, *e.g.* $[Hg(SCN)_4]^{2-}$ [2.491(3)—2.575(4) Å] [18] and $[Hg(SCN)_2(PPh_3)_2]$ [2.565(4)—2.577(3) Å],[17] and intermediate between those reported for two-co-ordinate [15] {Hg[SCN]$_2$, 2.381(6) Å} and six-co-ordinate [19] {$[Hg(SCN)_2(phen)_2]$ (phen = 1,10-phenanthroline) 2.582(8)—2.622(8) Å} complexes. A similar weakening of the Hg–S bond for the bridging group [2.591(4) Å] was observed in the infinite chains of $[Hg(SCN)_3]^-$ ions [16] as compared to the Hg–S bonds of the two non-bridging thiocyanato-groups [2.460(4) and 2.462(4) Å].

The thiocyanato-groups have their normal bonding parameters: the SCN groups are essentially linear [mean S–C–N 177.7(1)°], the mean S–C and C–N distances are 1.64(1) and 1.14(2) Å respectively, and the mean Hg–S–C angle is 101.4(9)°. Comparison of these data with those reported [8,15-20] for other derivatives of mercury thiocyanate indicate that these bonding characteristics are independent of whether the thiocyanato-group is terminal or bridging. The presence of both types of thiocyanato-bonding in the case of $[Hg(SCN)_2\{P(C_6H_{11})_3\}]$, as established by this *X*-ray analysis, is consistent with the observed i.r. and Raman bands.

The co-ordination about phosphorus is essentially tetrahedral [mean Hg–P–C 109.8(4)°, C–P–C 109.0(7)]. The Hg–P bond length [2.411(3) Å] is significantly longer than the distance [2.359(2) Å] found in $[\{Hg(NO_3)_2[P(C_6H_{11})_3]\}_2]$ but is nevertheless shorter than the Hg–P distances [2.489(3) and 2.487(3) Å] [17] in pseudo-tetrahedral $[Hg(SCN)_2(PPh_3)_2]$ where *two* bulky PPh_3 ligands are attached to mercury. The changes in co-ordination geometry and donor atoms around mercury, however, preclude any detailed assessment of the influence of the bulkiness of the phosphorus ligand on the Hg–P bond length. The mean P–C bond length [1.842(3) Å], the average C–C bond length [1.515(4) Å], and the average C–C–C angle [111.4(2)°] for the cyclohexyl rings are in agreement with previous determinations.[6,20,21]

The cyclohexyl rings all adopt chair conformations but the orientation with respect to the appropriate P–C bond is quite different for each ring; thus the Hg–P–C(*i*1)–H torsion angles are 63, 170, and 87° for i = 1—3 respectively. Very similar orientations were found [6] for the cyclohexyl rings in $[\{Hg(NO_3)_2[P(C_6H_{11})_3]\}_2]$ where the Hg–P–C(*i*1)–H torsion angles are 65, 172, and 95°.

The steric effect of the tricyclohexylphosphine ligand can be described in terms of the concept of a ligand cone angle; [10a] the original estimate of 179(10)° has recently been revised to 170° on the basis of n.m.r.[22] and exchange studies.[10c] The co-ordinates of Table 1 were used, in conjunction with an assumed van der Waals radius for hydrogen of 1.2 Å and a C–H distance of 1.08 Å, to calculate the maximum values of the semi-cone angle,[10b,c] $\frac{\theta}{2}$, for each cyclohexyl ring (Figure 3). Values of 87.4, 86.7, and 91.9 were found for rings C(11)—C(16), C(21)—C(26), and C(31)—C(36) respectively. Thus the effective mean cone angle θ is 177(3)°, in accord with predictions.

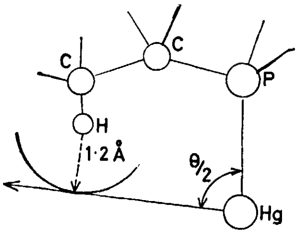

FIGURE 3 The semi-cone angle, $\frac{\theta}{2}$ for a cyclohexyl ring of the $Hg\{P(C_6H_{11})_3\}$ moiety in $[Hg(SCN)_2\{P(C_6H_{11})_3\}]$. The point of contact of the cone-generating vector from the mercury with the van der Waals sphere of hydrogen is coplanar with the mercury, phosphorus, and hydrogen atoms

Further *X*-ray studies are in progress to provide additional quantitative data on steric effects in other bulky phosphine complexes.

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