Compounds containing Platinum–Carbon Bonds. Part VII.[1] Crystal and Molecular Structure of *cis*-[Anilino(ethoxy)carbene]dichloro(triethylphosphine)platinum(II) †

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The molecular structure of the platinum(II) carbenoid complex *cis*-$[PtCl_2\{C(OEt)NHPh\}(PEt_3)]$ has been determined by *X*-ray diffraction methods. Crystals are orthorhombic, space group $P2_12_12_1$, with a = 15.063(5), b = 14.102(5), c = 9.306(3) Å, Z = 4. The structure was solved by the heavy-atom method and refined by full-matrix least-squares to R 0.062 for 1 772 diffractometric intensity data. The crystals contain discrete molecules in which the co-ordination of the platinum atom is square planar. Selected bond lengths (Å) are: Pt–P 2.239(8), Pt–C 1.96(2), Pt–Cl(*trans* to carbenoid) 2.361(5), and Pt–Cl(*trans* to PEt_3) 2.367(7).

DURING an investigation of the reactivity of co-ordinated isocyanides it was found that alcohols and amines undergo addition reactions with isocyanide complexes of platinum(II).[2,3] The insolubility of the products of these reactions hampered their characterisation by the usual spectroscopic methods. Accordingly, a crystal-structure

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[1] Part VI, Lj. Manojlović-Muir, K. W. Muir, and R. Walker, *J.C.S. Dalton*, 1976, 1279.

[2] E. M. Badley, J. Chatt, R. L. Richards, and G. A. Sim, *Chem. Comm.*, 1969, 1322.

[3] E. M. Badley, J. Chatt, and R. L. Richards, *J. Chem. Soc.* (*A*), 1971, 21; E. M. Badley, B. J. L. Kilby, and R. L. Richards, *J. Organometallic Chem.*, 1971, **27**, C37.

analysis was undertaken of the title compound, which is formed by addition of ethanol to *cis*-[$PtCl_2(CNPh)(PEt_3)$]. This analysis indicated that ethanol had added 1,2 across the carbon–nitrogen triple bond. The resulting complex, *cis*-[$PtCl_2\{C(OEt)NHPh\}(PEt_3)$], was of a type hitherto unknown, in that it contained a carbenoid ligand attached to platinum(II).[2] Together with spectroscopic studies on related molecules,[3] the structure analysis also established that the reaction between isocyanide complexes and alcohols or amines affords a general synthetic route to carbenoid complexes of platinum(II). Other pathways to these compounds have been discovered more recently.[4-6]

This work also forms part of a systematic investigation of the bonding and *trans*-influence of carbon-donor ligands in platinum(II) complexes.[1,7] A preliminary report has appeared.[2] We now describe the molecular structure in detail.

EXPERIMENTAL

Crystal Data.—$C_{15}H_{26}Cl_2NOPPt$, $M = 533.3$, Orthorhombic, $a = 15.063(5)$, $b = 14.102(5)$, $c = 9.306(3)$ Å, $U = 1\,976.8$ Å^3, $Z = 4$, $D_c = 1.792$ g cm^{-3}, $F(000) = 1\,032$. Space group $P2_12_12_1$. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ (Mo-K_α) = 78.1 cm^{-1}.

TABLE 1

Atomic parameters, with estimated standard deviations in parentheses

Atom	x	y	z	$B \times 10$/Å^2
Pt	0.203 36(4)	0.211 84(5)	−0.001 8(2)	*
Cl(1)	0.339 8(3)	0.129 6(4)	−0.007 8(16)	*
Cl(2)	0.237 3(4)	0.269 0(5)	0.231 1(7)	*
P	0.174 6(5)	0.159 1(6)	−0.223 8(8)	*
O	0.082 7(9)	0.374 2(10)	0.002 1(38)	55(3)
N	0.011 9(13)	0.242 8(14)	0.042 4(20)	41(4)
C(1)	0.090 7(11)	0.281 0(14)	0.014 4(38)	38(4)
C(2)	0.160 3(18)	0.431 7(19)	−0.045 9(27)	50(6)
C(3)	0.129 9(27)	0.518 6(28)	−0.114 4(49)	86(10)
C(4)	−0.005 1(13)	0.147 0(15)	0.081 3(24)	32(4)
C(5)	0.043 8(17)	0.100 3(18)	0.178 9(30)	49(5)
C(6)	0.021 8(21)	0.005 0(23)	0.216 9(40)	66(7)
C(7)	−0.055 4(21)	−0.034 8(21)	0.154 6(37)	61(6)
C(8)	−0.106 6(20)	0.013 6(19)	0.052 7(28)	54(6)
C(9)	−0.081 9(14)	0.108 0(15)	0.023 0(34)	47(5)
C(10)	0.189(4)	0.030(4)	−0.218(7)	145(19)
C(11)	0.121(3)	−0.023(3)	−0.153(5)	96(11)
C(12)	0.080(3)	0.221(3)	−0.311(4)	86(9)
C(13)	0.062(3)	0.187(3)	−0.468(7)	128(15)
C(14)	0.268(3)	0.180(3)	−0.350(5)	89(10)
C(15)	0.286(3)	0.285(3)	−0.370(6)	111(13)

* These atoms were assigned anisotropic temperature factors of the form $\exp(-10^{-4}\sum_{i=1}^{3}\sum_{j=1}^{3}\beta_{ij}h_ih_j)$. The final values of the β_{ij} parameters are:

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	26.8(2)	43.2(3)	107.3(8)	−0.5(3)	3.2(12)	6.3(17)
Cl(1)	30(2)	54(3)	211(10)	6(2)	11(10)	20(12)
Cl(2)	52(3)	72(5)	111(8)	−3(3)	−4(4)	−12(5)
P	68(4)	72(5)	111(9)	−9(4)	−2(5)	−16(6)

TABLE 2

Selected interatomic distances (Å) and angles (°)

(*a*) Bond lengths

Pt–Cl(1)	2.361(5)	C(10)–C(11)	1.40(8)
Pt–Cl(2)	2.367(7)	C(12)–C(13)	1.56(7)
Pt–P	2.239(8)	C(14)–C(15)	1.51(6)
Pt–C(1)	1.962(18)	C(2)–C(3)	1.46(5)
O–C(1)	1.33(2)	C(4)–C(5)	1.34(3)
O–C(2)	1.49(3)	C(5)–C(6)	1.43(4)
N–C(1)	1.33(3)	C(6)–C(7)	1.42(5)
N–C(4)	1.42(3)	C(7)–C(8)	1.40(4)
P–C(10)	1.83(6)	C(8)–C(9)	1.41(3)
P–C(12)	1.86(4)	C(9)–C(4)	1.39(3)
P–C(14)	1.86(4)		

(*b*) Bond angles

Cl(1)–Pt–Cl(2)	90.1(4)	Pt–C(1)–O	124(1)
Cl(1)–Pt–P	89.1(4)	Pt–C(1)–N	126(2)
Cl(2)–Pt–C(1)	87.0(10)	O–C(1)–N	110(2)
P–Pt–C(1)	93.9(10)	C(1)–O–C(2)	120(2)
Cl(1)–Pt–C(1)	176.9(11)	O–C(2)–C(3)	110(3)
Cl(2)–Pt–P	178.6(3)	C(1)–N–C(4)	127(2)
Pt–P–C(10)	106(2)	N–C(4)–C(5)	123(2)
Pt–P–C(12)	113(1)	N–C(4)–C(9)	115(2)
Pt–P–C(14)	113(1)	C(9)–C(4)–C(5)	122(2)
C(10)–P–C(12)	125(2)	C(4)–C(5)–C(6)	120(3)
C(10)–P–C(14)	95(3)	C(5)–C(6)–C(7)	118(3)
C(12)–P–C(14)	103(2)	C(6)–C(7)–C(8)	122(3)
P–C(10)–C(11)	117(4)	C(7)–C(8)–C(9)	117(3)
P–C(12)–C(13)	114(3)	C(8)–C(9)–C(4)	121(2)
P–C(14)–C(15)	112(3)		

(*c*) Mean bond lengths and angles

P–C	1.85(3)	C–P–C	108(9)
C(*sp*^{3})–C(*sp*^{3})	1.48(3)	P–C–C	114(2)
C(*sp*^{2})–(C*sp*^{2})	1.40(1)	C–C–N C–C–C	120(1)
Pt–P–C	111(2)		

(*d*) Intramolecular non-bonded distances

C(1) ··· Cl(2)	2.99	Pt ··· C(2)	3.19
C(1) ··· P	3.08	Pt ··· C(10)	3.27
Cl(1) ··· P	3.23	Pt ··· C(14)	3.42
Cl(1) ··· Cl(2)	3.35	Pt ··· C(12)	3.43
C(1) ··· C(12)	3.15		

(*e*) Intermolecular contacts $\leqslant 4$ Å

Cl(1) ··· N^{I}	3.17	Cl(2) ··· C(15^{II})	3.79
C(5) ··· C(13^{II})	3.52	C(3) ··· C(15^{IV})	3.81
Cl(1) ··· C(10^{III})	3.54	C(3) ··· C(13^{V})	3.82
C(2) ··· C(8^{I})	3.60	Cl(2) ··· C(3^{IV})	3.89
Cl(1) ··· C(11^{III})	3.68	C(11) ··· C(14^{III})	3.96

(*f*) Torsion angles

Pt–P–C(10)–C(11)	76	C(14)–P–C(12)–C(13)	56
C(12)–P–C(10)–C(11)	−58	Pt–P–C(14)–C(15)	−63
C(14)–P–C(10)–C(11)	−168	C(10)–P–C(14)–C(15)	−173
Pt–P–C(12)–C(13)	178	C(12)–P–C(14)–C(15)	60
C(10)–P–C(12)–C(13)	−51		

Roman numerals refer to the following transformations of the co-ordinates in Table 1:

I $\frac{1}{2} + x, \frac{1}{2} - y, -z$

II $x, y, 1 + z$

III $\frac{1}{2} - x, -y, \frac{1}{2} + z$

IV $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$

V $-x, \frac{1}{2} + y, -\frac{1}{2} - z$

TABLE 3

Equations of, and deviations (Å × 10^3) of atoms from, weighted least-squares planes

Plane (1): Pt, Cl(1), Cl(2), P, C(1)

$$6.661x + 11.351y - 3.681z = 3.767$$

[Pt −1, Cl(1) −4, Cl(2) 17, P 26, C(1) −26, C(12) 413, C(13) 487]

Plane (2): Pt, C(1), O, N

$$2.344x + 1.541y + 9.137z = 0.787$$

[Pt 0, C(1) −10, O 3, N 2, C(2) −166, C(3) −729, C(4) 170]

Plane (3): C(4)—(9)

$$8.453x - 4.974y - 6.968z = -1.360$$

[C(4) 20, C(5) −16, C(6) 9, C(7) −13, C(8) 24, C(9) −30, N −42]

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[4] D. J. Cardin, B. Cetinkaya, M. F. Lappert, Lj. Manojlović-Muir, and K. W. Muir, *Chem. Comm.*, 1971, 400.

[5] D. J. Cardin, B. Cetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, 1973, **2**, 99.

[6] F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, 1972, **16**, 487.

[7] Lj. Manojlovic-Muir and K. W. Muir, *Inorg. Chim. Acta*, 1974, **10**, 47.

Measurements.—The space group and preliminary cell dimensions were determined from Weissenberg and precession photographs. Final values of the unit-cell parameters, and the intensities of all reflexions with θ(Mo-K_α) $\leqslant 27°$ in the reciprocal octants hkl, $\bar{h}kl$, and $h\bar{k}l$, were measured on a Hilger and Watts Y 290 diffractometer, by use of zirconium-filtered molybdenum radiation. A symmetrical θ—2θ step scan was employed for all intensity measurements; 1.2 s counts were taken at intervals of 0.01° over a range of 0.50° in θ. Background was measured for 15 s at each end of the scan. The intensities of three strong reflexions, periodically remeasured during the experiment, varied by $< \pm 3\%$ of their mean values.

Intensities were corrected for background and scaled to allow for the variation of the standard reflexions. Those with $I \leqslant 2\sigma(I)$ were excluded from further calculations. Lorentz and polarisation factors were applied and symmetrically-equivalent structure amplitudes averaged, yielding values for 1 772 independent reflexions. No allowance was made for absorption or extinction.

Structure Analysis.—The position of the platinum atom was obtained from a Patterson synthesis. The other atoms, apart from hydrogen, were located in subsequent difference syntheses.

The structure was refined by the method of full-matrix least-squares, the function minimised being $\Sigma w\Delta^2$, where $\Delta = |F_o| - |F_c|$. Atomic scattering factors were taken from ref. 8, with allowance for the anomalous scattering of the platinum, chlorine, and phosphorus atoms.[9]

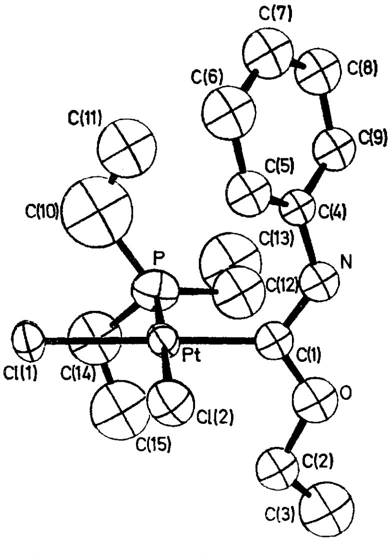

FIGURE 1 A view of the molecule showing the atom numbering scheme; thermal ellipsoids enclose 50% of probability

Refinement of the positional and vibrational parameters of all non-hydrogen atoms gave R 0.075; anisotropic temperature factors were used only for platinum, chlorine, and phosphorus atoms. The configuration of the crystal structure was altered by reversing the z co-ordinates of all atoms, and R decreased to 0.065. The weights were then adjusted so that mean values of $w\Delta^2$ were relatively constant when analysed as a function of $|F_o|$. The final weighting scheme was $w = (52 - 1.19|F_o| + 0.0083|F_o|^2)$. Refinement of the 105 structural parameters converged at R 0.062 and R' 0.063. In the final difference synthesis the extreme values of 1.3 and -1.0 eÅ^{-3} occurred in regions close to the platinum atom.

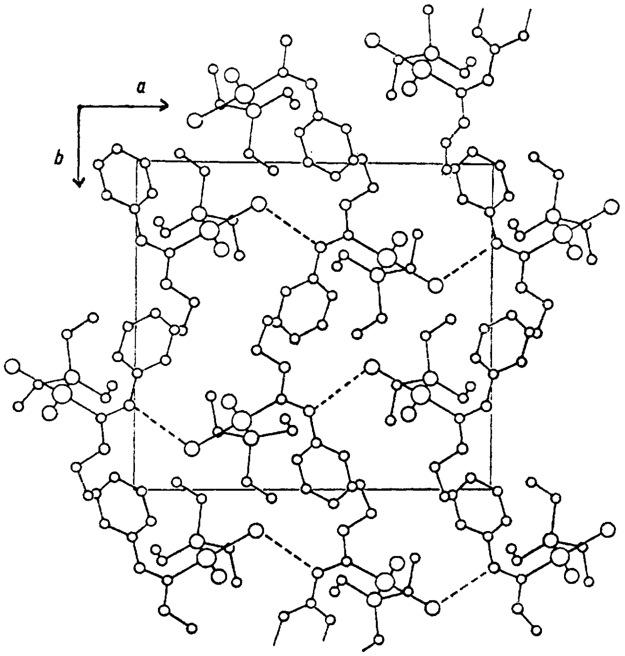

FIGURE 2 The crystal structure viewed down the c axis; dashed lines indicate hydrogen bonds

Final atomic parameters and a selection of functions derived from them are presented in Tables 1—3. Views of the molecule and of the crystal packing are displayed in Figures 1 and 2. Observed and calculated structure amplitudes are listed in Supplementary Publication No. SUP 21693 (11 pp., 1 microfiche).*

The computer programs used were the '*X*-Ray '63' system of Dr. J. M. Stewart, adapted to the ATLAS computer by Dr. J. C. Baldwin, the Hilger and Watts software package for the Y 290 diffractometer, and Dr. C. K. Johnson's ORTEP plotting program.

DISCUSSION

The crystals contain discrete molecules of *cis*-[PtCl$_2$-{C(OEt)NHPh}(PEt$_3$)]. The intermolecular contact of 3.17 Å between Cl(1) and N^{I} (Table 2, Figure 2) is consistent with the presence of an N–H · · · Cl hydrogen bond. On the assumption that the nitrogen atom adopts planar trigonal hybridisation, its attached hydrogen atom lies close to the Cl(1) · · · N^{I} vector, *ca.* 2.2 Å from Cl(1). In linear N–H · · · Cl hydrogen bonds studied by neutron diffraction the H · · · Cl contact is usually close to 2.20 Å.[10] The presence of hydrogen bonds in the solid complex is also supported by the number of N–H stretching bands in the mull spectrum.[3] The molecules are linked into chains parallel with the a axis by the hydrogen

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* See Notice to Authors No. 7, *J.C.S. Dalton*, 1975, Index issue.

[8] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

[9] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

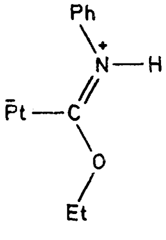
[10] W. C. Hamilton and J. A. Ibers, 'Hydrogen Bonding in Solids,' Benjamin, New York, 1968.

bonds. Between the chains there are only van der Waals contacts.

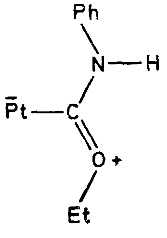
Apart from the unusually large thermal motions of the methylene and methyl carbon atoms the triethylphosphine ligand displays no unusual feature. The torsion angles about the P–CH_2 bonds are close to the values of ± 60 and 180° expected for an exactly staggered conformation. A similar conformation about the P–CH_2 bonds is found in *cis*-[$PtCl_2\{C(NPhCH_2)_2\}(PEt_3)$].[11] The disposition of the P–CH_2 bonds with respect to the co-ordination plane of platinum is such as to cause a rather close approach (3.15 Å) between C(12) and C(1), so that the C(1)–Pt–P–C(12) torsion angle is only 14°. In *cis*-[$PtCl_2\{C(NPhCH_2)_2\}(PEt_3)$] a corresponding torsion angle is exactly zero and the resulting C(methylene) · · · C(carbenoid) non-bonded contact is 3.18 Å.[11]

The small deviations from ideal square-planar geometry at the platinum atom are presumably a consequence of steric interaction between the bulky phosphine and carbenoid ligands. Thus atoms P and C(1) are each displaced by 0.026 Å from the metal co-ordination plane but in opposite directions, and the angle C(1)–Pt–P is 4(1)° greater than 90°, whereas the angle C(1)–Pt–Cl(2) is 3(1)° less than 90°.

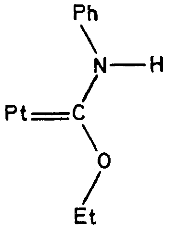
The most interesting question posed by the results concerns the nature of the platinum–carbenoid bonding and specifically, the relative weights which should be given to the three canonical valence-bond structures (Ia)—(Ic).



(Ia)



(Ib)



(Ic)

The Pt–C(1) bond length [1.962(18) Å] is amongst the shortest Pt^{II}–C(carbenoid) distances so far observed; values of 1.95(2)—2.13(2) Å have been found in other square-planar platinum(II)–carbenoid complexes.[11,12] It is 0.05(2) Å shorter than the Pt–C(*trans* to Cl) distance in *cis*-[$PtCl_2\{C(NPhCH_2)_2\}(PEt_3)$],[11] suggesting that (Ic) is more important in the case of an ethoxyaminocarbenoid ligand than it is in the case of a diaminocarbenoid. A similar trend has been found in carbenoid complexes of chromium(0) and has been rationalised in terms of the relative electronegativities of oxygen and nitrogen.[13] The Pt–C(1) distance may also be compared with the σ-Pt–C(*trans* to Cl) bond length [2.03(2) Å] in *trans*-[$PtCl(CH{:}CH_2)(PEt_2Ph)_2$];[14] if it is assumed that the order of a metal–carbon bond 0.1 Å shorter than the single-bond value is *ca.* 1.2,[15] then an order of 1.1—1.2 may tentatively be assigned to the Pt–C bond in *cis*-[$PtCl_2\{C(OEt)NHPh\}(PEt_3)$]. The C(1)–N distance [1.33(3) Å] is within the narrow range typical of amides,[16] while the C(1)–O distance [1.33(2) Å] is comparable with those of the formally single C–O bonds in carboxylic acid dimers; [17] the orders of both bonds are therefore distinctly >1.0. Thus the results suggest that there are significant contributions from each of the structures (Ia)—(Ic), with relative weights very approximately in the order: 0.5 : 0.3 : 0.2.

The Pt–Cl(1) distance [2.361(5) Å] is shorter than the Pt–Cl(*trans* to C) bond length [2.398(4) Å] in *trans*-[$PtCl(CH{:}CH_2)(PEt_2Ph)_2$].[14] The lower *trans*-influence of C(OEt)NHPh, compared with σ-vinyl, on Pt–Cl bond lengths may also be explained in terms of back donation from platinum to the carbenoid ligand, with increased electrostatic attraction between platinum and the *trans*-chlorine atom. This view is consistent with our recent discussion of bond-length trends in square-planar platinum(II) complexes containing an organic ligand *trans* to chlorine.[7]

The Pt–P and Pt–Cl(2) bond lengths are typical of the values found for such bonds in *cis*-[$PtCl_2L(PR_3)$] complexes where R = n-alkyl or phenyl, and L is a weak π-acid such as carbenoid, phosphine, or isocyanide. Weighted mean values (Å) for seven such complexes are: Pt–P 2.242(2) and Pt–Cl 2.375(3).[1]

The Pt,C(1),N,O unit is planar and makes a dihedral angle of 77° with the platinum co-ordination plane. This angle is usually 70—90° in platinum(II)–carbenoid complexes,[11] but values close to zero are found when the carbenoid function is incorporated in a chelate ring.[12] Atoms C(2) and C(4) deviate only slightly from the Pt,C(1),N,O plane. The torsion angles Pt–C(1)–N–C(4) and Pt–C(1)–O–C(2) (respectively 7 and 8°) indicate that the ethyl and phenyl groups are both *cis* with respect to the platinum atom. The multiple character of the C(1)–N and C(1)–O bonds implies that rotation about them is restricted, so that four geometric isomers are capable of existence. It is uncertain whether the *cis,cis*-conformation of the carbenoid ligand in *cis*-[$PtCl_2\{C(OEt)NHPh\}(PEt_3)$] persists in solution, but $CDCl_3$ solutions of the tri-n-propyl analogue have been shown to contain mixtures of geometric isomers.[3]

We thank the S.R.C. for computing facilities and for a studentship (to E. M. B.).

[5/2321 *Received, 28th November,* 1975]

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[11] Lj. Manojlović-Muir and K. W. Muir, *J.C.S. Dalton*, 1974, 2427.

[12] R. F. Stepaniak and N. C. Payne, *J. Organometallic Chem.*, 1973, **57**, 213; *Inorg. Chem.*, 1974, **13**, 797; W. M. Butler and J. H. Enemark, *ibid.*, 1973, **12**, 540; W. M. Butler, J. H. Enemark, J. Parks, and A. L. Balch, *ibid.*, p. 451.

[13] R. J. Hoare and O. S. Mills, *J.C.S. Dalton*, 1972, 653, and refs. therein.

[14] C. J. Cardin, D. J. Cardin, M. F. Lappert, and K. W. Muir, *J. Organometallic Chem.*, 1973, **60**, C70.

[15] M. R. Churchill, *Perspectives in Structural Chem.*, 1970, **3**, 91.

[16] *Chem. Soc. Spec. Publ.*, No. 18, 1965.

[17] B. Beagley, ' Molecular Structure by Diffraction Methods, eds. G. A. Sim and L. E. Sutton, *Chem. Soc. Specialist Periodical Reports*, 1973, **1**, 93.