Oxidation and Reduction Chemistry of Bis(η-arene)niobium Compounds; The *X*-Ray Crystal Structure of Bis(η-toluene)(trimethylphosphine)niobium Tetrafluoroborate†

Judith A. Bandy and Keith Prout
Chemical Crystallography Laboratory, 9 Parks Road, Oxford OX1 3PD
F. Geoffrey N. Cloke* and Helen C. de Lemos
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ
Julian M. Wallis
Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR

Cyclic voltammetry shows that [Nb(η-$C_6H_5Me)_2$] undergoes both one-electron reversible reduction and oxidation; chemical oxidation with $AgBF_4$ in the presence of PR_3 (R = Me, R_3 = Me_2Ph) yields [Nb(η-$C_6H_5Me)_2(PR_3)]BF_4$. The *X*-ray crystal structure of [Nb(η-$C_6H_5Me)_2(PMe_3)]BF_4$ has been determined and shows the molecule to have the bent bis(η-arene) structure. Reduction of [Nb(η-$C_6H_3Me_3$-2,4,6$)_2$] with potassium and treatment with carbon monoxide yields $[Nb(CO)_6]^-$; reduction in the presence of 18-crown-6 (1,4,7,10,13,16-hexaoxacyclo-octadecane,L) gives [KL][Nb(η-$C_6H_3Me_3$-2,4,6$)_2$].

Metal vapour synthesis provides unique access to a wide range of bis(η-arene)metal(0) complexes of the early transition elements.[1] Whilst considerable studies have been made on the bis(η-arene)tungsten system,[2] the analogous niobium compounds have not been examined. We therefore set out to explore, in particular, the oxidation and reduction chemistry of the paramagnetic, 17-electron bis(η-arene)niobium complexes.[3]

Results and Discussion

Cyclic voltammetry of [Nb(η-$C_6H_5Me)_2$] in tetrahydrofuran gave two fully reversible one-electron waves at chemically accessible potentials: an oxidation at −0.90 V and a reduction at −2.46 V (*vs.* the saturated calomel electrode). Treatment of the deep red-brown tetrahydrofuran solution of [Nb(η-$C_6H_5Me)_2$] with one equivalent of silver tetrafluoroborate at −78 °C gave no tractable product; however, repeating the reaction in the presence of certain tertiary phosphines gave bright red air-sensitive crystals of [Nb(η-$C_6H_5Me)_2(PMe_3)]BF_4$, (**1**), or [Nb(η-$C_6H_5Me)_2(PMe_2Ph)]BF_4$, (**2**). These results parallel the chemistry of the isoelectronic zirconium compounds: [Zr(η-$C_6H_5Me)_2$] decomposes above −100 °C, but the phosphine adduct [Zr(η-$C_6H_5Me)_2(PMe_3)$] is stable.[4]

The compounds (**1**) and (**2**) are sparingly soluble in tetrahydrofuran, and decompose rapidly in other polar solvents. Proton n.m.r. spectra could be obtained from very freshly prepared solutions in CD_2Cl_2, but even then decomposition was evident. The data characterising (**1**) and (**2**) are given in the Experimental section.

Bright red prisms of [Nb(η-$C_6H_5Me)_2(PMe_3)]BF_4$, (**1**), were obtained by slowly cooling a saturated tetrahydrofuran solution. The crystal structure of (**1**) has been determined; the molecular structure and labelling scheme of the cation of (**1**) is shown in the Figure,[5] and the final positional parameters are given in Table 1 and bond lengths and angles in Table 2.

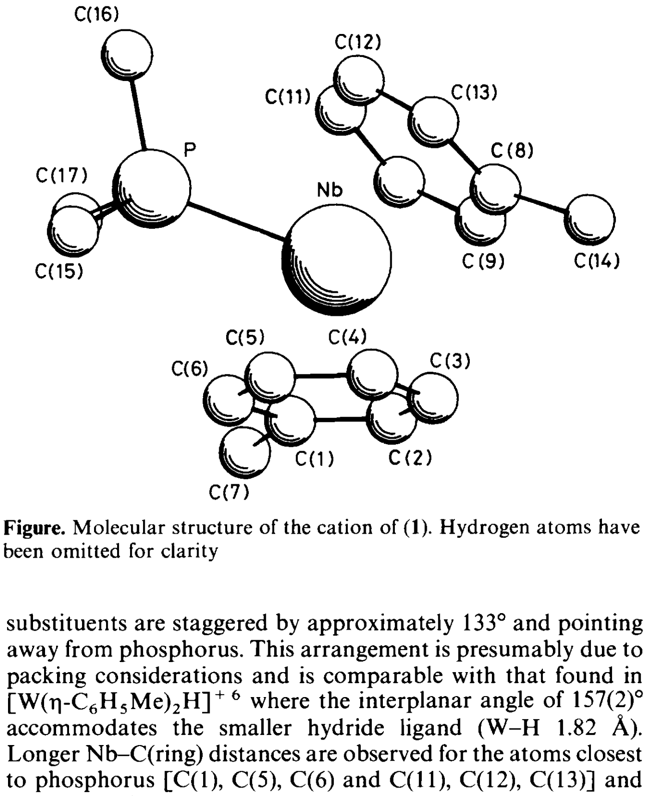

Figure. Molecular structure of the cation of (**1**). Hydrogen atoms have been omitted for clarity

The central niobium atom of the cation is found to exhibit distorted trigonal co-ordination geometry, with the centroids of the phenyl rings and phosphorus lying coplanar with niobium. The toluene ligands are inclined at 142.3° and their methyl substituents are staggered by approximately 133° and pointing away from phosphorus. This arrangement is presumably due to packing considerations and is comparable with that found in $[W(\eta\text{-}C_6H_5Me)_2H]^+$ [6] where the interplanar angle of 157(2)° accommodates the smaller hydride ligand (W–H 1.82 Å). Longer Nb–C(ring) distances are observed for the atoms closest to phosphorus [C(1), C(5), C(6) and C(11), C(12), C(13)] and the perpendicular metal–ring plane separations are 1.904 and 1.914 Å. The methyl groups deviate by 0.10 and 0.23 Å [C(7) and C(14), respectively] from the mean planes of the rings away from the metal. One toluene ring is found to be bent by 3.8° [planes defined as C(10), C(11), C(12), C(13) and C(8), C(9), C(10), C(13)] as observed in other toluene comlexes.[7] The niobium–phosphorus distance, 2.689(2) Å, is comparable with those [2.678(1) and 2.787(1) Å] found in [Nb(η-$C_5H_5)Cl_3(Ph_2PCH_2PPh_2)$].[8] There are a number of anion–cation contacts (H • • • F) of about 2.5 Å, being less than the sum of their van der Waals radii, but otherwise no short intermolecular contacts.

The complexes (**1**) and (**2**), together with [M(η-$C_6H_5Me)_2$-

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Atomic co-ordinates with estimated standard deviations (e.s.d.s) in parentheses for complex (**1**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Nb	0.233 24(5)	0.144 01(4)	0.377 04(3)	C(11)	0.329 7(6)	0.276 8(5)	0.284 0(4)
P	0.421 8(1)	0.232 9(2)	0.481 4(1)	C(12)	0.399 6(6)	0.177 2(7)	0.278 7(4)
C(1)	0.069 4(6)	0.186 4(5)	0.471 0(4)	C(13)	0.342 8(8)	0.075 5(6)	0.256 3(5)
C(2)	0.018 6(6)	0.126 8(7)	0.399 4(4)	C(14)	0.161 1(13)	−0.037 8(9)	0.191 7(9)
C(3)	0.063 3(7)	0.017 6(7)	0.381 2(4)	C(15)	0.478 3(7)	0.156 0(7)	0.579 7(5)
C(4)	0.163 8(7)	−0.028 9(5)	0.431 4(5)	C(16)	0.574 3(8)	0.269 1(9)	0.439 6(5)
C(5)	0.215 0(6)	0.030 3(5)	0.504 0(4)	C(17)	0.379 0(9)	0.370 1(7)	0.524 9(6)
C(6)	0.168 0(6)	0.137 7(5)	0.523 8(3)	B	0.746 3(4)	0.109 0(4)	0.204 0(4)
C(7)	0.012 1(10)	0.300 5(9)	0.496 1(6)	F(1)	0.854 1(5)	0.052 0(5)	0.191 9(5)
C(8)	0.217 2(8)	0.071 7(6)	0.233 3(4)	F(2)	0.652 3(5)	0.065 6(6)	0.151 7(5)
C(9)	0.143 2(6)	0.171 3(8)	0.236 4(4)	F(3)	0.717 6(8)	0.098 7(11)	0.287 3(4)
C(10)	0.200 7(7)	0.274 9(6)	0.265 4(5)	F(4)	0.761 7(8)	0.219 3(5)	0.185 0(8)

Table 2. Bond lengths (Å) and angles (°) with e.s.d.s in parentheses

Nb–P	2.689(2)	C(1)–C(2)	1.381(7)
Nb–C(1)	2.380(6)	C(1)–C(6)	1.402(6)
Nb–C(2)	2.331(7)	C(1)–C(7)	1.529(8)
Nb–C(3)	2.337(6)	C(2)–C(3)	1.401(7)
Nb–C(4)	2.331(6)	C(3)–C(4)	1.385(7)
Nb–C(5)	2.380(5)	C(4)–C(5)	1.393(7)
Nb–C(6)	2.399(5)	C(5)–C(6)	1.396(7)
Nb–C(8)	2.359(6)	C(8)–C(9)	1.410(8)
Nb–C(9)	2.324(6)	C(8)–C(13)	1.355(8)
Nb–C(10)	2.310(7)	C(8)–C(14)	1.536(8)
Nb–C(11)	2.387(5)	C(9)–C(10)	1.419(7)
Nb–C(12)	2.424(6)	C(10)–C(11)	1.378(7)
Nb–C(13)	2.389(7)	C(11)–C(12)	1.388(7)
P–C(15)	1.825(8)	C(12)–C(13)	1.371(7)
P–C(16)	1.827(8)	B–F(1)	1.347(4)
P–C(17)	1.811(8)	B–F(2)	1.337(4)
		B–F(3)	1.338(5)
		B–F(4)	1.340(4)
C(15)–P–Nb	119.5(3)	C(13)–C(8)–C(9)	120.2(3)
C(16)–P–Nb	121.4(3)	C(14)–C(8)–C(9)	120.4(4)
C(16)–P–C(15)	98.9(4)	C(14)–C(8)–C(13)	118.8(4)
C(17)–P–Nb	111.7(3)	C(10)–C(9)–C(8)	119.5(3)
C(17)–P–C(15)	102.2(4)	C(11)–C(10)–C(9)	118.6(4)
C(17)–P–C(16)	99.8(5)	C(12)–C(11)–C(10)	120.0(3)
C(6)–C(1)–C(2)	119.4(3)	C(13)–C(12)–C(11)	121.4(4)
C(7)–C(1)–C(2)	120.2(3)	C(12)–C(13)–C(8)	120.1(4)
C(7)–C(1)–C(6)	120.3(3)	F(2)–B–F(1)	109.51(9)
C(3)–C(2)–C(1)	120.1(3)	F(3)–B–F(1)	109.44(9)
C(4)–C(3)–C(2)	120.5(3)	F(3)–B–F(2)	109.43(9)
C(5)–C(4)–C(3)	119.6(4)	F(4)–B–F(1)	109.48(9)
C(6)–C(5)–C(4)	119.9(3)	F(4)–B–F(2)	109.48(9)
C(5)–C(6)–C(1)	120.4(3)	F(4)–B–F(3)	109.48(9)

$(PMe_3)]$, M = Zr or Hf,[4] and $[W(\eta\text{-}C_6H_5Me)_2H]^+$,[6] complete a series of isoelectronic (d^4) bent bis(η-arene) complexes of the transition-metal groups 4, 5, and 6. No first-row congeners of bent bis(η-arene) complexes are known. This may reflect the smaller size of the first-row transition metals, which would give rise to a destabilising interaction between the η-arene rings. We note that the methyl groups of the η-C_6H_5Me rings in (**1**) show significant deviations from the planes of the aromatic systems, away from the metal atoms.

Anionic bis(η-arene) transition-metal complexes are extremely rare, being confined to $[Ti(\eta\text{-}C_6H_5Me)_2]^-$ [9] and $[V(\eta\text{-}C_6H_6)_2]^-$.[10] Since the cyclic voltammetry results indicated that $[Nb(\eta\text{-arene})_2]^-$ was a stable species in solution on the electrochemical time-scale, we were thus interested in synthesising this anion chemically. Exposure of a tetrahydrofuran solution of $[Nb(\eta\text{-}C_6H_3Me_3\text{-}2,4,6)_2]$ to a potassium mirror led to a rapid disappearance of the characteristic 10-line e.s.r. signal of the starting material, but no tractable product could be isolated from the resultant solution. However, repeating the reaction in the presence of a stoicheiometric amount of 18-crown-6 (1,4,7,10,13,16-hexaoxacyclo-octadecane, L) afforded deep maroon, pyrophoric crystals analysing for $[KL][Nb(\eta\text{-}C_6H_3Me_3\text{-}2,4,6)_2]$, (**3**). Complex (**3**) is insoluble in hydrocarbons, sparingly soluble in tetrahydrofuran, and rapidly decomposed by more polar solvents, thus precluding n.m.r. studies. The i.r. spectrum (Nujol mull) shows bands at 370 and 380 cm^{-1}, assignable to the antisymmetric metal–ring stretch and antisymmetric ring-tilt modes respectively {by analogy with the spectrum of matrix-isolated $[Nb(\eta\text{-}C_6H_3Me_3\text{-}2,4,6)_2]$ in which these bands occur at 275 and 410 cm^{-1} respectively [11]}.

Further evidence for the existence of an unstable anion in solution came from the reaction of $[Nb(\eta\text{-}C_6H_3Me_3\text{-}2,4,6)_2]$ in 1,2-dimethoxyethane with a potassium mirror in the presence of carbon monoxide, which led to a colour change from red-brown to orange. From the solution were isolated yellow crystals whose i.r. spectrum displayed a strong CO stretch at 1 851 cm^{-1}, characteristic of the $[Nb(CO)_6]^-$ ion.[12] Since $[Nb(\eta\text{-}C_6H_3Me_3\text{-}2,4,6)_2]$ is known not to react with carbon monoxide,[11] the presence of its anion as an intermediate is implied. The η-arene rings in the anion are clearly very substitution labile and readily displaced by a better π-acceptor ligand such as carbon monoxide.

Experimental

All manipulations of air- and/or moisture-sensitive materials were carried out in an inert atmosphere achieved by the use of a dual-vacuum nitrogen (or Ar) line using standard Schlenk techniques or in a Miller Howe dry-box under an atmosphere of N_2 (< 5 p.p.m. water, < 1 p.p.m. O_2). Reactions involving neat PMe_3 were carried out in glass ampoules equipped with greaseless taps. Nitrogen, Ar, and CO were purified by passage through a column containing BTS catalyst and 4A molecular sieves. All solvents were thoroughly deoxygenated before use by repeated pumping followed by admission of N_2 (or Ar). Solvents were dried and purified by refluxing over a suitable drying agent, followed by distillation under a nitrogen atmosphere. Toluene was dried over molten sodium; 1,2-dimethoxyethane, tetrahydrofuran, and light petroleum (b.p. 80—100 °C) were dried over molten potassium; light petroleum (b.p. 40—60 °C) was dried over sodium–potassium alloy (1:3 w/w). Trimethylphosphine was prepared by the method of Schmidbauer and Wolfsberger.[13] The bis(η-arene)niobium complexes were prepared on a *ca.* 5-g scale using a large-scale metal-vapour synthesis apparatus, as previously described.[1] Tetra-n-butylammonium tetrafluoroborate was dried under vacuum for 12 h prior to use. All other reagents were used as received.

Cyclic voltammograms were recorded in a two-compartment three-electrode cell at a platinum working electrode. The supporting electrolyte was 0.2 mol dm^{-3} NBu$^n{}_4$BF$_4$ in tetrahydrofuran and all measurements were made under an atmosphere of dinitrogen. Potentiodynamic control was by a Hi-Tek DT-101 potentiostat in conjunction with a Chemical Electronics waveform generator, type 01. The voltammograms were recorded on a type PM 8043 Philips X-Y recorder.

Elemental analyses were obtained from the microanalytical departments of the Inorganic Chemistry Laboratory, Oxford and the School of Chemistry and Molecular Sciences, Brighton, or from Alfred Bernhardt Ltd., Germany. Nuclear magnetic resonance spectra were recorded on a Bruker AM-250 instrument at probe temperature: chemical shifts (δ) are relative to internal solvent. Data are presented as: chemical shift [relative intensity, multiplicity (*J* in Hz), assignment]. Electron spin resonance spectra were recorded on a Varian E-line spectrometer at ambient temperature.

Bis(η-*toluene*)(*trimethylphosphine*)*niobium Tetrafluoroborate*, (**1**).—The compound [Nb(η-$C_6H_5Me)_2$] (0.276 g, 1.0 mmol) in tetrahydrofuran (30 cm^3) was cooled to −78 °C and trimethylphosphine (*ca.* 1 cm^3) was added by distillation *in vacuo*. Silver tetrafluoroborate (0.195 g, 1.0 mmol) in tetrahydrofuran (25 cm^3) was added dropwise with stirring. Over 2 h a silver mirror developed and the solution turned red-brown. The solution was filtered, concentrated under reduced pressure, and cooled to −30 °C. Red needles of [Nb(η-$C_6H_5Me)_2$-(PMe$_3$)]BF$_4$ separated and were collected and dried *in vacuo*. Yield 0.250 g, 0.57 mmol, 57% (Found: C, 46.3; H, 5.6. Calc. for $C_{17}H_{25}BF_4NbP$: C, 46.4; H, 5.7%). ^{1}H N.m.r. data (CD_2Cl_2): 5.76 (2 H, m, *p*-H), 4.54 (8 H, m, *o*- and *m*-H), 2.33 (6 H, s, 2 Me of 2 η-C_6H_5Me), and 1.36 [9 H, d, *J*(PH) 7.6, PMe$_3$].

Bis(*dimethylphenylphosphine*)(η-*toluene*)*niobium Tetrafluoroborate*, (**2**).—The method was essentially identical as for complex (**1**), except that trimethylphosphine was replaced by dimethylphenylphosphine. Yield 0.250 g, 0.56 mmol, 56% (Found: C, 52.4; H, 5.2. Calc. for $C_{22}H_{27}BF_4NbP$: C, 52.6; H, 5.4%). ^{1}H N.m.r. data (CD_2Cl_2): 7.58 (5 H, m, P–C_6H_5), 5.66 (2 H, m, *p*-H), 4.48 (8 H, m, *o*- and *p*-H), 2.34 (6 H, s, 2 Me of 2 η-C_6H_5Me), and 1.61 [6 H, d, *J*(PH) 7.2, PMe$_2$].

(1,4,7,10,13,16-*Hexaoxacyclo-octadecane*)*potassium Bis*(η-*mesitylene*)*niobate*, (**3**).—A solution of [Nb(η-$C_6H_3Me_3$-2,4,6)$_2$] (0.060 g, 0.19 mmol) and 18-crown-6 (0.050 g, 0.18 mmol) in tetrahydrofuran (20 cm^3) was exposed to a freshly prepared potassium mirror. Deep maroon crystals precipitated immediately. The crystals were collected, washed with cold tetrahydrofuran (2 × 5 cm^3), and dried *in vacuo*. Yield 0.090 g, 0.15 mmol, 80% (Found: C, 58.85; H, 7.55. Calc. for $C_{30}H_{48}NbO_6$: C, 56.70; H, 7.60%).

Reaction of Bis(η-*mesitylene*)*niobium with Potassium in the Presence of Carbon Monoxide*.—Purified carbon monoxide was bubbled through a solution of [Nb(η-$C_6H_3Me_3$-2,4,6)$_2$] (0.050 g, 0.18 mmol) in 1,2-dimethoxyethane (20 cm^3) exposed to a potassium mirror for 2 h, resulting in a colour change from red-brown to orange. The solution was filtered and light petroleum (b.p. 80—100 °C, 10 cm^3) added to the filtrate. Concentration of this solution under reduced pressure gave a yellow crystalline precipitate. The crystals were collected, washed with light petroleum (b.p. 40—60 °C, 2 × 5 cm^3), and dried *in vacuo*. Yield 0.025 g, 0.10 mmol, 50%. I.r. (Nujol mull): 1 851vs cm^{-1}, ν(CO).

Crystallography.—*Crystal data*. $C_{17}H_{25}BF_4NbP$, M = 440.07, monoclinic, a = 10.595(1), b = 11.735(1), c = 15.343(4) Å, β = 93.70(2)°, U = 1 903.6 Å^3, space group $P2_1/c$, Z = 4, D_c = 1.54 Mg m^{-3}, λ(Cu-K_α) = 1.5418 Å, μ(Cu-K_α) = 65.38 cm^{-1}, F(000) = 896.

Data collection and processing. A crystal of complex (**1**) was sealed in a glass capillary under argon and mounted on an Enraf-Nonius CAD4 diffractometer. Cell dimensions were obtained by least-squares methods from the positions of 25 carefully centred reflections. Scan mode ω–2θ; 5 525 reflections measured ($2\theta_{max.}$ = 150°), 2 972 unique [$I > 3\sigma(I)$], corrected for absorption,[14] used in structure solution and refinement.

Structure analysis and refinement. Solution by heavy-atom and Fourier difference methods. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic. Phenyl and phosphorus methyl hydrogen atoms were included in calculated positions. Corrections were made for isotropic extinction[15] and anomalous dispersion.[16]

Disorder of the arene rings similar to that found by Prout *et al.*[6] and of the BF$_4$ anion was observed. Attempts to model this disorder satisfactorily by partial occupancies were unsuccessful and these entities were refined anisotropically subject to geometrical constraints.[17] After application of a modified Chebyshev weighting scheme[18] with parameters 9.01, 3.60, and 6.79, refinement converged at R = 0.068, R' = 0.083 $[\Sigma w|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{\frac{1}{2}}$.

Solution and refinement used the Oxford CRYSTALS package[19] on the VAX 11/750 computer of the Chemical Crystallography Laboratory, Oxford University. Scattering factors were taken from ref. 20. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Acknowledgements

We thank the S.E.R.C. for Studentships (to H. C. de L. and J. M. W.), a Fellowship (to J. A. B.), and equipment support. We are grateful to Dr. C. J. Pickett and Mr. K. Ryder for assistance with the electrochemical studies.

References

1 F. G. N. Cloke and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1981, 1938.
2 P. R. Brown, F. G. N. Cloke, M. L. H. Green, and N. J. Hazel, *J. Chem. Soc., Dalton Trans.*, 1983, 1075.
3 F. G. N. Cloke, M. L. H. Green, and D. H. Price, *J. Chem. Soc., Chem. Commun.*, 1978, 431.
4 F. G. N. Cloke, and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 1979, 127.
5 E. K. Davies, CHEMGRAF User Manual, Chemical Crystallography Laboratory, University of Oxford, 1983.
6 K. Prout, A. Gourdon, C. Couldwell, B. Meunier, F. M. Miao, and J. Woolcock, *Acta Crystallogr., Sect. B*, 1982, **38**, 456.
7 J. A. Brandy, V. S. B. Mtetwa, K. Prout, J. C. Green, C. E. Davies, M. L. H. Green, N. J. Hazel, A. Izquierdo, and J. J. Martin-Polo, *J. Chem. Soc., Dalton Trans.*, 1985, 2037.
8 K. Prout and J-C. Daran, *Acta Crystallogr., Sect. B.*, 1979, **35**, 2882.
9 J. A. Bandy, A. Berry, M. L. H. Green, R. N. Perutz, K. Prout, and J. N. Verpeaux, *J. Chem. Soc., Chem. Commun.*, 1984, 729.
10 C. Elschenbroich and F. Gerson, *J. Am. Chem. Soc.*, 1975, **95**, 3556.
11 F. G. N. Cloke, D. Phil. Thesis, University of Oxford, 1978.
12 J. E. Ellis and A. Davison, *Inorg. Synth.*, 1976, **16**, 68.
13 H. Schmidbauer and W. Wolfsberger, *Synth. React. Inorg. Met. Org. Chem.*, 1974, **4**, 149.
14 A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A.*, 1968, **24**, 351.
15 A. C. Larson, *Acta Crystallogr., Sect. A*, 1967, **23**, 664.
16 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, p. 149.

17 J. T. Waser, *Acta Crystallogr., Sect. A*, 1963, **16**, 1091; J. S. Rollett, 'Crystallographic Computing,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1969, p. 169.
18 J. R. Carruthers and D. J. Watkin, *Acta Crystallogr., Sect. A*, 1979, **35**, 698; E. Prince, 'Mathematical Techniques in Crystallography,' Springer, New York, 1982.
19 D. J. Watkin, J. R. Carruthers, and P. W. Betteridge, 'CRYSTALS User Guide,' Chemical Crystallography Laboratory, University of Oxford, 1985.
20 Ref. 16, p. 99.

Received 17*th July* 1987; *Paper* 7/1280