DALTON

Eight-co-ordination in lanthanide pyrazolylborate chemistry: crystal structures of $[LaTp^{Me,Me}_2(MeCN)(O_3SCF_3)]\cdot MeCN$, $[NdTp^{Me,Me}_2(MeCN)_2][O_3SCF_3]$ and $[LaTp^{Me,Me}_2(NO_3)]\cdot MeCN$ $[Tp^{Me,Me}$ = tris(3,5-dimethylpyrazolyl)hydroborate]

Robin J. H. Clark,[a] **Sung Ying Liu,**[a] **Graham H. Maunder,**[a] **Andrea Sella** *,†,[a] **and Mark R. J. Elsegood**[b]

[a] *Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H 0AJ, UK*

[b] *Department of Chemistry, Bedson Building, The University of Newcastle-upon-Tyne, Newcastle-upon-Tyne NE1 7RU, UK*

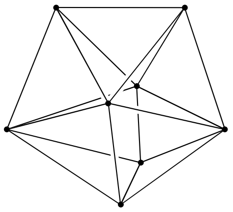
The reaction of $[LnTp^{Me,Me}_2][O_3SCF_3]$ [Ln = La, Ce, Pr or Nd; $Tp^{Me,Me}$ = tris(3,5-dimethylpyrazolyl)hydroborate] in toluene with acetonitrile gave complexes of stoichiometry $LnTp^{Me,Me}_2(MeCN)_2(O_3SCF_3)$ (Ln = La, Ce, Pr or Nd). The structures of those of La and Nd have been determined by X-ray crystallography and found to be ionization isomers of each other: $[LaTp^{Me,Me}_2(MeCN)(O_3SCF_3)]\cdot MeCN$ consists of neutral molecules while $[NdTp^{Me,Me}_2(MeCN)_2][O_3SCF_3]$ adopts an ionic structure. The structure of $[LaTp^{Me,Me}_2(NO_3)]$ has been determined for comparison. The co-ordination environment of the metal centres in all three complexes was shown by polytopal analysis to be dodecahedral in contrast to that (square antiprismatic) commonly adopted by complexes involving unsubstituted hydrotris(pyrazolyl)borate.

The lanthanides are finding increasing use as reagents in organic synthesis and a wide range of sterically demanding ligands, many based upon cyclopentadienyls, has been used both to control the co-ordination sphere and to alter the stereochemistry of these reactions.[1] The poly(pyrazolyl)borates are often viewed as cyclopentadienyl analogues and are increasingly being used as sterically demanding ligands for the f elements.[2] They provide good steric definition and a stable co-ordination environment within which a wide range of chemistry is being developed. Much of the initial work was based upon the unsubstituted hydrotris(pyrazolyl)borate (Tp) ligand. Complexes of the type $[LnTp_2X]$ (X = unidentate ligand) were found to be unstable in solution and to undergo comparatively rapid redistribution reactions.[3] By contrast, when anionic bidentate ligands (X−X) were used in place of X, complexes of the type $[LnTp_2(X{-}X)]$ were obtained. Intermolecular exchange was suppressed to the point that it was only observable on an NMR time-scale and well behaved eight-co-ordinate complexes were isolated.[4] Several possibilities for the co-ordination geometry are possible. Polytopal analysis may be used for the assignment of geometries around the metal centre.[5] In particular it has been used to establish that most complexes based on the ligand Tp are either square antiprismatic (*SAPR*) or bicapped trigonal prismatic (*TPRS*).[2]

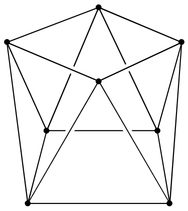
We have recently shown that well defined seven-co-ordinate lanthanide complexes which do not appear to undergo ligand-redistribution reactions can be prepared using the sterically demanding ligand tris(3,5-dimethylpyrazolyl)hydroborate, $Tp^{Me,Me}$.[6] In this paper we show that these complexes may react further with acetonitrile to give eight-co-ordinate complexes in which the co-ordination geometry is close to being dodecahedral (*DD*).

Results

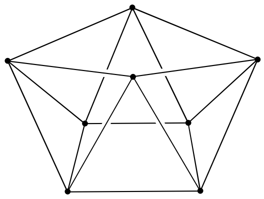
In order to explore the steric control exerted by the pyrazolylborate ligands, we have attempted to explore the ability of the lanthanide ion in the complexes $[LnTp^{Me,Me}_2][O_3SCF_3]$ to accommodate additional neutral ligands and thereby to increase its co-ordination number beyond seven. Initial attempts were carried out using the largest ion in the series, lanthanum. Toluene solutions of an excess of a potential donor ligand were added to solutions of $[LaTp^{Me,Me}_2(O_3SCF_3)]$ in toluene or tetrahydrofuran (thf). The mixtures were stirred for a few hours, concentrated, and crystallized at low temperature. The starting materials were recovered unchanged upon addition of a variety of amines, or of pyridine, benzonitrile, 4-cyanopyridine or triphenylphosphine oxide. Although all of these are known to be good ligands for the f elements, none was found to bind to $[LaTp^{Me,Me}_2(O_3SCF_3)]$, suggesting that the metal centre in this complex is sterically saturated. However, addition of acetonitrile to toluene solutions of $[LnTp^{Me,Me}_2(O_3SCF_3)]$ (Ln = La, Ce, Pr or Nd) in toluene at room temperature resulted in the formation of microcrystalline precipitates of



Dodecahedron (*DD*)



Square antiprism (*SAPR*)



Bicapped trigonal prism (*TPRS*)

---

† E-Mail: ucca245@ucl.ac.uk

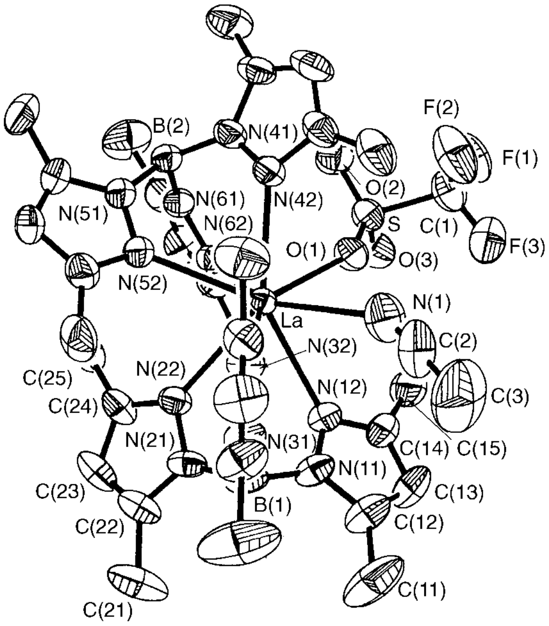


Fig. 1 Molecular structure of complex **1** with the atom numbering scheme. Hydrogen atoms and the acetonitrile molecule of crystallization have been omitted for clarity

complexes **1** (La, white), **2** (Ce, white), **3** (Pr, pale green) and **4** (Nd, lilac) over a few minutes. Although the crystals were found to degrade with time, elemental analyses of freshly prepared samples were consistent in all cases with the presence of two molecules of acetonitrile per $LnTp^{Me,Me}{}_2(O_3SCF_3)$ unit. We presume that the degradation results from loss of acetonitrile from the lattice. In each case appropriate IR bands were observed for the CN stretching vibrations (*ca.* 2300 cm^{-1}), together with bands at around 1205 cm^{-1} consistent with the presence of free, unco-ordinated triflate, as observed previously for $[LnTp^{Me,Me}{}_2][O_3SCF_3]$.[6] All the compounds were found to be moderately soluble in chloroform but not in less-polar solvents such as light petroleum. Proton NMR spectra were recorded in deuteriochloroform solution giving simple spectra with three singlets in the usual 3:3:1 ratio, as expected for two pyrazolylborate ligands undergoing rapid reorientation on the metal centre, together with a single peak integrating for two molecules of acetonitrile.

By contrast, analogous experiments with related smaller ions (Sm, Yb or Y) yielded only the starting material rather than any adducts. This is not surprising since we have previously shown that these starting complexes adopt six-co-ordinate ionic structures of the type $[LnTp^{Me,Me}{}_2][O_3SCF_3]$. Our observations are therefore consistent with the idea that the contraction in ionic radius across the lanthanide series results in steric saturation for these metal centres which cannot therefore accommodate additional ligands within the first co-ordination sphere.[6]

Since the triflate anion is a notoriously poor ligand we have investigated whether nitrate, a potentially chelating ligand, might suppress the formation of adducts. Hydrated lanthanum nitrate was stirred with $KTp^{Me,Me}$ to give, after appropriate work-up, white crystals of $[LaTp^{Me,Me}{}_2(NO_3)]$ **5**, which was characterized by elemental analysis, infrared and NMR spectroscopy. This complex is soluble in a variety of solvents ranging in polarity from toluene to acetonitrile. It may be recovered unchanged from the latter; indeed infrared and ^1H NMR spectra of the material so recovered gave no evidence for adduct formation.

Crystallographic studies

In order to verify the co-ordination mode of the triflate ion we undertook X-ray structural determinations of the compounds **1** and **4**. Although both were crystallized from toluene, each displays very different structural features. In addition the crystal structure of $[LaTp^{Me,Me}{}_2(NO_3)]$ was determined for comparison with the first two. Polytopal analysis was carried out to establish the geometry of the metal co-ordination sphere in each case.

Table 1 Selected bond lengths (Å) and angles (°) for complex **1**

La–N(12)	2.686(4)	La–N(52)	2.708(5)
La–N(22)	2.670(5)	La–N(62)	2.540(5)
La–N(32)	2.613(6)	La–O(1)	2.514(5)
La–N(42)	2.656(5)	La–N(1)	2.756(7)
N(12)–La–N(22)	69.4(2)	N(22)–La–O(1)	135.0(2)
N(12)–La–N(32)	80.9(2)	N(32)–La–O(1)	139.3(2)
N(22)–La–N(32)	72.6(2)	N(42)–La–O(1)	72.3(2)
N(12)–La–N(42)	149.2(2)	N(52)–La–O(1)	130.9(1)
N(22)–La–N(42)	141.4(2)	N(62)–La–O(1)	72.6(2)
N(32)–La–N(42)	104.4(2)	N(12)–La–N(1)	66.4(2)
N(12)–La–N(52)	141.4(2)	N(22)–La–N(1)	123.0(2)
N(22)–La–N(52)	73.0(1)	N(32)–La–N(1)	66.7(2)
N(32)–La–N(52)	79.8(2)	N(42)–La–N(1)	87.5(2)
N(42)–La–N(52)	68.7(2)	N(52)–La–N(1)	132.5(2)
N(12)–La–N(62)	110.2(2)	N(62)–La–N(1)	145.2(2)
N(22)–La–N(62)	83.3(2)	O(1)–La–N(1)	72.6(2)
N(32)–La–N(62)	148.0(2)	La–O(1)–S	148.8(3)
N(42)–La–N(62)	81.6(2)	La–N(1)–C(2)	147.0(8)
N(52)–La–N(62)	73.2(2)	N(1)–C(2)–C(3)	176.6(12)
N(12)–La–O(1)	83.9(2)	C(5)–C(4)–N(2)	159.4(18)

Table 2 Values of δ and φ/° for $[LaTp^{Me,Me}{}_2(MeCN)(O_3SCF_3)]$ **1**, $[NdTp^{Me,Me}{}_2(MeCN)_2][O_3SCF_3]$ **4** and $[LaTp^{Me,Me}{}_2(NO_3)]$ **5**[a]

	Complex			Geometry		
Atoms	**1**[b]	**4**[c]	**5**[d]	*DD*	*SAPR*	*TPRS*
δ [1(57)3]	41.3	35.9	21.2	29.5	0.0	21.8
δ [1(67)4]	23.5	30.4	42.0	29.5	0.0	0.0
δ [2(58)3]	26.5	33.5	52.0	29.5	52.5	48.2
δ [2(68)3]	46.5	27.8	34.9	29.5	52.5	48.2
φ (7 8 1 2)	0.1	6.2	—	0.0	24.5	14.1
φ (5 6 3 4)	7.0	1.7	—	0.0	24.5	14.1
θ_A (1)	36.4	34.1	27.7	34.3–48.6		
θ_A (2)	36.4	34.0	21.8	34.3–48.6		
θ_A (3)	36.5	36.9	36.9	34.3–48.6		
θ_A (4)	36.5	74.7	36.9	34.3–48.6		
θ_B (5)	77.6	74.7	74.0	73.7–88.2		
θ_B (6)	71.8	71.5	82.6	73.7–88.2		
θ_B (7)	75.4	74.3	75.5	73.7–88.2		
θ_B (8)	72.7	76.2	72.6	73.7–88.2		

[a] All data refer to normalized polyhedra. [b] Atoms defined as follows: 1, N(1); 2, O(1); 3, N(52); 4, N(22); 5, N(42); 6, N(12); 7, N(62); 8, N(32). [c] Atoms defined as follows: 1, N(1); 2, N(2); 3, N(12); 4, N(52); 5, N(32); 6, N(62); 7, N(42); 8, N(22). [d] Atoms defined as follows: 1, O(1); 2, O(2); 3, N(22); 4, N(52); 5, N(12); 6, N(62); 7, N(42); 8, N(32).

Complex 1. In contrast to our expectations from the infrared data, the lanthanum complex $[LaTp^{Me,Me}{}_2(MeCN)(O_3SCF_3)]$ **1**, crystallized in the triclinic space group *P*1 as neutral molecules with a second molecule of MeCN contained within the lattice. The molecular structure is shown in Fig. 1 and selected bond lengths and angles are given in Table 1. No significant intermolecular contacts were noted.

The metal centre is eight-co-ordinated by way of two tridentate $Tp^{Me,Me}$ ligands, a molecule of acetonitrile and a unidentate triflate anion, confirming that it is possible to accommodate the narrow acetonitrile molecule within the first co-ordination sphere of the metal atom. Although the metal co-ordination polyhedron is somewhat irregular, polytopal analysis indicates that the geometry is *DD*. The δ and φ angles are listed in Table 2, the trapezia being defined by the atoms N(62), O(1), N(1), N(32) and N(42), N(52), N(22), N(12) respectively. The distortions of the trapezia imply a distortion along the pathway towards *TPRS* in which the trigonal prism is defined

Table 3 Selected bond lengths (Å) and angles (°) for complex **4**

Nd–N(12)	2.593(8)	Nd–N(1)	2.695(13)
Nd–N(22)	2.486(13)	Nd–N(2)	2.643(11)
Nd–N(32)	2.577(11)	N(1)–C(1)	1.161(24)
Nd–N(42)	2.531(10)	C(1)–C(2)	1.440(27)
Nd–N(52)	2.559(10)	N(2)–C(3)	1.141(18)
Nd–N(62)	2.618(10)	C(3)–C(4)	1.453(21)
N(12)–Nd–N(22)	73.5(4)	N(52)–Nd–N(62)	69.1(3)
N(12)–Nd–N(32)	70.8(3)	N(12)–Nd–N(1)	138.9(4)
N(22)–Nd–N(32)	85.5(4)	N(22)–Nd–N(1)	138.2(4)
N(12)–Nd–N(42)	79.9(3)	N(32)–Nd–N(1)	84.7(4)
N(22)–Nd–N(42)	149.9(4)	N(42)–Nd–N(1)	71.8(3)
N(32)–Nd–N(42)	98.9(3)	N(52)–Nd–N(1)	124.1(3)
N(12)–Nd–N(52)	73.7(3)	N(62)–Nd–N(1)	66.3(4)
N(22)–Nd–N(52)	84.3(4)	N(12)–Nd–N(2)	127.7(3)
N(32)–Nd–N(52)	144.5(3)	N(22)–Nd–N(2)	70.3(4)
N(42)–Nd–N(52)	74.9(3)	N(32)–Nd–N(2)	70.0(4)
N(12)–Nd–N(62)	142.7(3)	N(42)–Nd–N(2)	139.2(4)
N(22)–Nd–N(62)	104.6(4)	N(52)–Nd–N(2)	136.1(4)
N(32)–Nd–N(62)	146.4(4)	N(62)–Nd–N(2)	83.1(4)
N(42)–Nd–N(62)	88.2(3)	N(1)–Nd–N(2)	68.2(4)

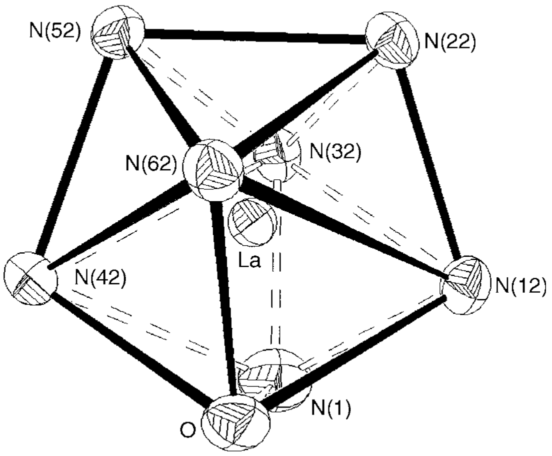


Fig. 2 Inner co-ordination sphere of complex **1**

by N(1), N(12), N(32), N(42), N(52), N(62) and O(1) and N(22) cap the faces.

The average La–N_{pz} distance in complex **1** is 2.645(7) Å, which is similar to that observed by Jones and co-workers[7] for the eight-co-ordinate complex [$CeTp_2$(acac)] (acac = acetylacetonate), 2.63(3) Å, and for complex **5**, [$LaTp^{Me,Me}{}_2(NO_3)$], 2.647(3) Å, all three complexes showing a wide range of M–N bond lengths. A more useful measure of the metal-to-ligand distance is the mean La···B distance, 3.646(7) Å, which is similar to that in **5** (see below). The two pyrazolylborate groups are mutually staggered and bent back with a B–La–B angle of 142.7°. In contrast to a metallocene, however, the 'equatorial plane' defined by the two additional ligands lies at 46.4° to the plane containing the B(1)–La–B(2) unit. In addition the arrangement of the pyrazolyl groups around the two ligands gives an effective C_2 symmetry to the binding site, as shown in Fig. 2. Similar pseudo-C_2 symmetry has been noted in [$SmTp^{Me,Me}{}_2$(PhNNPh)],[8] [$SmTp^{Me,Me}{}_2(O_2)$][9] and [$SmTp^{Me,Me,4\text{-}Et}{}_2(NO_2)$].[10]

Although the angles around the boron atom are tetrahedral to within experimental error both pyrazolylborate groups show considerable distortions from ideal C_3 symmetry resulting from significant twists about one of the B–N bonds as measured by the B–N–N–La torsion angle. For both $Tp^{Me,Me}$ ligands only a single pyrazolyl group shows this twist, while the other two are parallel to the La-B axis to within 10°. In each case the twist appears to result from the need to accommodate the additional ligands in the co-ordination sphere and to maintain a constant angle between the 'extra' ligand and the two arms of the Tp group. Thus pyrazolyl ring 1 [contains N(11) and N(12), ring 2 contains N(21) and N(22), *etc.*] twists by 31.9° away from the acetonitrile ligand. Hence the acetonitrile nitrogen atom lies symmetrically between the pyrazolyl groups 1 and 3, the N_{pz}–La–N(1) angles being 66.4 and 66.7° respectively. Similarly ring 4 twists by 30.7° to accommodate the triflate anion, which lies with N_{pz}–La–O(1) angles of 72.6 and 72.3°, values which presumably reflect the greater size of the triflate group than acetonitrile. The twists in the pyrazolyl rings result in correspondingly uneven bite distances ranging from 3.03 to 3.44 Å.

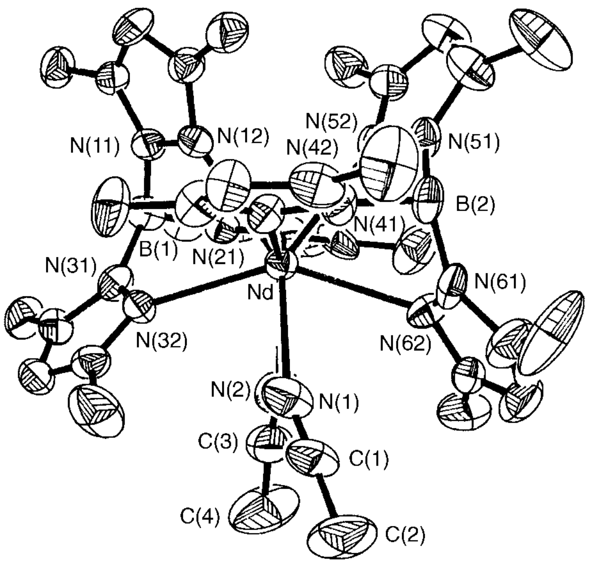


Fig. 3 Molecular structure of the cation of complex **4** with the atom numbering scheme defined. Hydrogen atoms and the triflate anion have been omitted for clarity

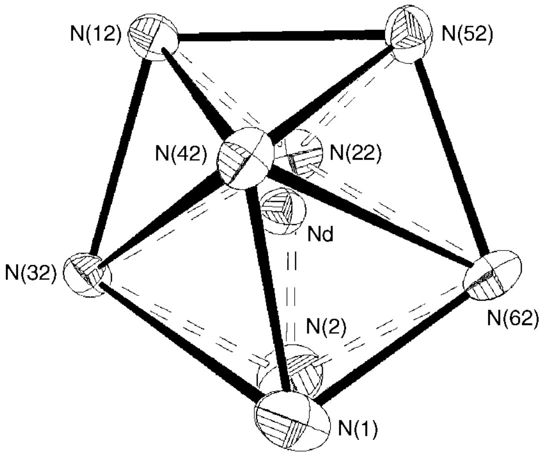


Fig. 4 Inner co-ordination sphere of complex **4**

The La–N(1) distance of 2.756(7) Å is not significantly different from that determined for [$La(C_5H_5)_3$(MeCN)], *viz.* 2.7858(8) Å. The acetonitrile ligand itself shows a considerable distortion away from linearity, the La–N(1)–C(2) angle being 147°, presumably as a result of the need to minimize interactions between the CH_3 and CF_3 groups of the two adjacent ligands. Finally, the La–O(1) distance is 2.514(5) Å, significantly shorter than in the nine-co-ordinate complex ion [$La(en)_4(O_3SCF_3)$]$^{2+}$ (en = ethane-1,2-diamine), 2.598(2) Å, and 10-co-ordinate complex ion [$LaL(O_3SCF_3)$]$^{2+}$, 2.585(3) Å [L = 6,14-bis-(2-aminoethyl)-1,3,6,9,11,14-hexaazacyclohexadecane].[11]

Complex 4. The neodymium complex [$NdTp^{Me,Me}{}_2(MeCN)_2$]-[O_3SCF_3] **4** crystallizes in the space group $P2_12_12_1$ as pale lilac crystals with an ionic structure. The molecular structure of the cation is shown in Fig. 3, and selected interatomic distances and angles in Table 3. The neodymium centre is again eight-co-

Table 4 Selected bond lengths (Å) and angles (°) for complex **5**

La–O(1)	2.5836(13)	La–N(52)	2.6715(14)
La–O(2)	2.5859(13)	La–N(62)	2.7017(14)
La–N(12)	2.6900(14)	La–N(1)	3.013(2)
La–N(22)	2.6724(14)	O(1)–N(1)	1.270(2)
La–N(32)	2.5957(14)	O(2)–N(1)	1.278(2)
La–N(42)	2.5506(14)	O(3)–N(1)	1.221(2)
N(42)–La–O(1)	69.81(5)	N(32)–La–N(12)	77.40(4)
N(42)–La–O(2)	119.02(4)	N(52)–La–N(12)	142.59(4)
O(1)–La–O(2)	49.56(4)	N(22)–La–N(12)	68.99(4)
N(42)–La–N(32)	156.12(5)	N(42)–La–N(62)	79.41(4)
O(1)–La–N(32)	133.74(4)	O(1)–La–N(62)	70.74(4)
O(2)–La–N(32)	84.20(4)	O(2)–La–N(62)	75.83(4)
N(42)–La–N(52)	74.87(4)	N(32)–La–N(62)	103.00(4)
O(1)–La–N(52)	129.92(4)	N(52)–La–N(62)	68.77(4)
O(2)–La–N(52)	138.76(4)	N(22)–La–N(62)	143.86(4)
N(32)–La–N(52)	83.81(4)	N(12)–La–N(62)	146.92(4)
N(42)–La–N(22)	87.85(4)	N(42)–La–N(1)	94.14(5)
O(1)–La–N(22)	135.52(4)	O(1)–La–N(1)	24.74(5)
O(2)–La–N(22)	138.58(4)	O(2)–La–N(1)	24.92(5)
N(32)–La–N(22)	76.26(4)	N(32)–La–N(1)	109.11(5)
N(52)–La–N(22)	75.30(4)	N(52)–La–N(1)	138.54(4)
N(42)–La–N(12)	113.67(4)	N(22)–La–N(1)	145.29(4)
O(1)–La–N(12)	85.08(4)	N(12)–La–N(1)	78.63(4)
O(2)–La–N(12)	71.29(4)	N(62)–La–N(1)	69.94(4)

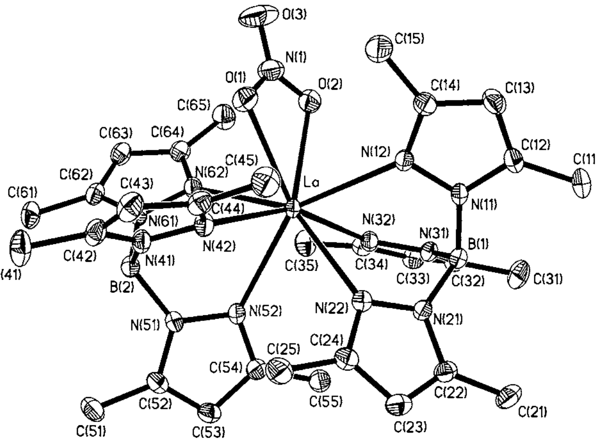


Fig. 5 Molecular structure of complex **5** with the atom numbering scheme. Hydrogen atoms and the acetonitrile molecule of crystallization have been omitted for clarity

ordinated with two tridentate pyrazolylborate groups and two acetonitrile molecules bound to the metal atom. The triflate counter ion is well separated from the metal complex and shows no close interionic contacts. Although the co-ordination sphere is somewhat irregular, it is also best described as a *DD*, with the two trapezia defined by N(32), N(12), N(52), N(62) and N(22), N(2), N(1) N(42) intersecting at an angle of 80.6° rather than the ideal 90°. The inner co-ordination sphere is shown in Fig. 4. Both trapezia are almost planar, as defined by the normalized φ angles, which are 6.2 and 1.7° respectively. These distortions result in an approach towards a *TPRS* geometry in which the trigonal planes defined by N(1), N(32), N(42) and N(62), N(22), N(52) lie at 11.6° and the two capping atoms N(2) and N(12) lie at 132° to each other.

The Nd–N$_{pz}$ distance in complex **4** is 2.561(15) Å, as compared to 2.542(7) Å in the corresponding unsolvated complex [NdTp$^{Me,Me}{}_2$(O$_3$SCF$_3$)].[6] The Nd–N distances lie in the range between 2.486(13) and 2.618(10) Å, as is common among lanthanide complexes of Tp. As always, significant distortions of the pyrazolylborates are apparent from the B–N–N–Nd torsion angles. Particularly noteworthy are rings 6 and 3 which show twists of 39 and 28°, while rings 4 and 2 twist by 17 and 18° respectively. In each case, the deviations from an ideal C_3 arrangement can be seen to relieve the interaction between each acetonitrile ligand and the two pyrazolyl rings closest to it. The bite distances of the Tp^{Me,Me} ligand, which vary between 2.936 and 3.585 Å, mirror this.

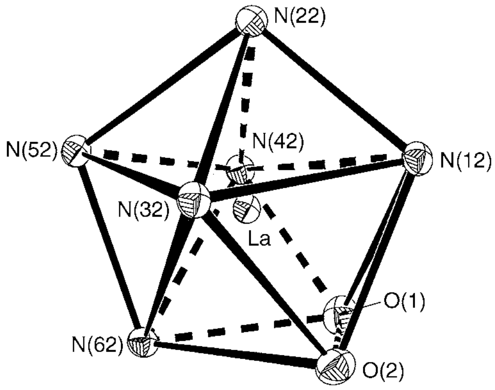


Fig. 6 Inner co-ordination sphere of complex **4**

The metal-to-acetonitrile distances in complex **4** are 2.695(13) and 2.643(13) Å, consistent with the contraction in radius but also with the replacement of the comparatively bulky triflate by an acetonitrile ligand. In addition both nitriles are essentially linear as expected for the two ligands occupying a pocket bounded by planar ligands, thereby contrasting with the situation in **1**.

Complex 5. The complex [LaTp$^{Me,Me}{}_2$(NO$_3$)] **5**, crystallized from acetonitrile as colourless blocks in the space group $P\bar{1}$ with a single molecule of acetonitrile included in the crystal lattice. The molecular structure of the complex is shown in Fig. 5 and selected interatomic distances and angles are listed in Table 4. The molecule contains two tridentate pyrazolylborate groups and a bidentate nitrate anion in the first co-ordination sphere of the eight-co-ordinated metal. The structure is again best described as distorted *DD* (Fig. 6). The two trapezia defined by N(32), O(2), O(1), N(42) and N(62), N(52), N(21), N(12) have normalized φ angles of 8.6 and 6.1°, respectively, and intersect at an angle of 87°. Much of the distortion of the dodecahedron arises from the tight bite angle of the nitrate group (49.6°) which tends to narrow the 'base' of the dodecahedron. A very similar effect is observed for [SmTp$^{Me,Me,4\text{-}Et}{}_2$(NO$_2$)][12] although a crystallographically imposed mirror plane simplifies that structure. The distortion of the co-ordination sphere in **5** tends nevertheless towards *TPRS*.

The pyrazolylborate ligands are mutually staggered as usual, and bent back away from the nitrate anion with a B–La–B angle 143.6°, which is closely comparable to those in complexes **1** and **4**. The average La···B distance is 3.681 Å and the La–N distances, which range from 2.551(1) to 2.724(1) Å, are comparable with those observed for **1**. As in the other two structures, twisting of the pyrazolyl groups occurs, with torsions of between 0 and 21.9°; however in this complex the origin of the distortions is not clear-cut. The planar nitrate anion lies at an angle of 50.6° to the B–La–B plane, and is bound symmetrically within experimental error.

Discussion

While the infrared spectrum of complex **1** suggests that it has an ionic structure, the crystal structure reveals the presence of a neutral lanthanide complex together with an acetonitrile molecule in the lattice. The inconsistency between the solid-state infrared evidence for an ionic structure for **1** and the structure observed by X-ray crystallography is somewhat surprising and may suggest that an unrepresentative crystal had been chosen for the structure determination. Alternatively the material obtained from the initial crystallization differs in structure, in the case of lanthanum, from that grown more slowly and therefore is a kinetic product. Powder X-ray experiments aimed at establishing first the point at which the changeover in structure occurs on moving across the series La–Nd, and secondly whether material obtained by rapid crystallization from solution differs in structure from those described above, were unsuccessful due to the insufficient crystallinity of such material. This latter may be the result of the solvent loss noted above. Furthermore the observed solubility in toluene together with the NMR data suggest that rapid equilibration between the two structures is likely.

The differences between the structures of complexes **1** and **4** are striking in view of the comparatively small reduction in ionic radius on changing from lanthanum to neodymium. They suggest that in this system the neutral acetonitrile molecule is about as good a ligand for the metal centre as the anionic triflate and that the small contraction in the metal co-ordination sphere results in the second acetonitrile being preferred to triflate by neodymium. This suggestion is consistent with the observation that the B–Ln–B angle increases somewhat on moving from **1** to **4**. Indeed all of these structures display among the largest B–Ln–B angles reported to date among Tp_2-type lanthanide complexes, suggesting that the $Tp^{Me,Me}$ ligands may be interpenetrated to their maximum extent.

The distortions in the pyrazolylborates are significant and clearly result from the severe steric congestion of the system. It is noteworthy that significant twists (20.7°) of all three pyrazolyl rings are observed in the structures of the divalent complexes $[LnTp^{Me,Me}{}_2]$ (Ln = Eu or Yb). These distortions are attributed to the need to accommodate the much larger divalent ions into the ligand cavity,[12] and suggest that the energy required to twist the pyrazolyl group around the B–N bond is comparatively low. They may be regarded as initial steps along the path towards the extreme distortion observed in $[UTp^{Me,Me}{}_2I]$ in which the twisting about the B–N bond is such as to bring the N–N π cloud in towards the metal centre and to direct the lone pair on the donor nitrogen atom in the 3 position of the pyrazolyl group away from the metal.[13]

These results provide evidence that eight-co-ordinated lanthanide complexes with the tris(dimethylpyrazolyl)borate ligand are *DD* by contrast to those with the unsubstituted Tp ligands which, with two exceptions, are all *SAPR*. These observations suggest that, although square-antiprismatic geometries may be preferred on inner-sphere electrostatic grounds, secondary (interligand) interactions result in the preference for *DD* geometries when $Tp^{Me,Me}$ is used. Indeed previous work with Tp complexes suggests that the less sterically congested Tp complexes tend to adopt *TPRS/SAPR* geometries whereas the more sterically congested centres prefer the *DD* structure[2] and only two clear-cut examples of *DD* complexes have been observed with Tp as the ancillary, $[EuTp_2(mosal)]$[14] (Hmosal = 5-methoxysalicylaldehyde) and Sm(2) in $[\{SmTp_2(O_2CPh)\}_2]$.[15] Molecular modelling studies may be able to give further insight into these matters.

The structure of complex **5** confirms that, in the case of a complex in which the third anionic ligand is chelating, it is not possible to accommodate an acetonitrile group within the metal co-ordination sphere. In spite of the apparent saturation of the metal co-ordination sphere, the ligand set remains fluxional and significant twisting of the pyrazolyl groups occurs. This suggests that the steric definition provided by these bis(pyrazolyl)borate systems may be insufficient to control chemical reactions occurring at ligands bound to the lanthanide centre.

Experimental

All preparations and manipulations were carried out using standard Schlenk-line and dry-box techniques in an atmosphere of dinitrogen.[16] Oxygen-free nitrogen was purified by passage over columns containing 3 Å molecular sieves and MnO.[17] All solvents were pre-dried over 5 Å molecular sieves or sodium wire and distilled under nitrogen from appropriate drying agents [Na (toluene), K (benzene or tetrahydrofuran) or Na/K alloy (light petroleum, b.p. 40–60 °C; pentane or diethyl ether)], before use.

The complexes $[LnTp^{Me,Me}{}_2][O_3SCF_3]$ were prepared from lanthanide trifluoromethanesulfonates and potassium hydrotris(pyrazolyl)borate[18] as previously described.[6]

Infrared spectra were recorded as KBr pellets or in solution using 0.1 mm CaF_2 solution cells on a Nicolet 205 FTIR spectrometer, ^1H spectra in solution on Varian XL-200 and VXR-400 spectrometers at 200 and 400 MHz respectively. Spectra were calibrated using residual proton resonances and are reported relative to tetramethylsilane. Elemental analyses were determined by Mr. Alan Stones of the University College London Analytical Services.

Preparations

$[LaTp^{Me,Me}{}_2(MeCN)(O_3SCF_3)]$ 1. The complex $[LaTp^{Me,Me}{}_2O_3SCF_3]$ (0.31 g, 0.34 mmol) was dissolved in toluene (20 cm^3) in a Schlenk flask under nitrogen. The solution was gently concentrated under reduced pressure to about 10 cm^3 at which point the compound began to precipitate. Acetonitrile (1 cm^3) was added and the solution warmed in hot water until all the solids had dissolved. The solution was then cooled slowly to 0 °C to give colourless crystals of the product. Yield: 0.24 g (73%) (Found: C, 43.3; H, 5.25; N, 19.95. $C_{35}H_{50}B_2F_3LaN_{14}O_3S$ requires C, 43.55; H, 5.25; N, 20.35%). δ_H($CDCl_3$, 298 K) 1.83 (s, 18 H, 3-Me), 1.97 (s, 6 H, MeCN), 2.40 (s, 18 H, 5-Me) and 5.70 (s, 6 H, CH). δ_C($CDCl_3$, 298 K) 2.01 (q, MeCN), 12.9 (q, 3- or 5-Me), 13.5 (q, 5- or 3-Me), 106.3 (d, CH), 145.7 (s, 2- or 4-C) and 150.2 (s, 4- or 2-C). IR (KBr): $\tilde{\nu}_{max}/cm^{-1}$ 2557 (BH), 2295, 2267, 2252 (C≡N) and 1202 (CF_3SO_3).

$[CeTp^{Me,Me}{}_2(MeCN)_2(O_3SCF_3)]$ 2. The complex $[CeTp^{Me,Me}{}_2(O_3SCF_3)]$ (0.31 g, 0.34 mmol) was dissolved in acetonitrile (20 cm^3) in a Schlenk flask under nitrogen. The solution was concentrated under reduced pressure to 10 cm^3 and layered with light petroleum. The solution was then cooled slowly to −10 °C to give colourless crystals of the product. Yield: 0.23 g (70%) (Found: C, 43.25; H, 5.05; N, 20.1. $C_{35}H_{50}B_2CeF_3N_{14}O_3S$ requires C, 43.55; H, 5.2; N, 20.3%). δ_H($CDCl_3$, 298 K) −13.84 (s, 18 H, 3-Me), 1.98 (s, 6 H, MeCN), 6.13 (s, 6 H, CH) and 7.19 (s, 18 H, 5-Me). δ_C($CDCl_3$, 298 K) 12.3 (q, MeCN), 19.6 (q, 3- or 5-Me), 13.5 (q, 5- or 3-Me), 113.1 (d, CH), 144.2 (s, 2- or 4-C) and 158.8 (s, 4- or 2-C). IR (KBr): $\tilde{\nu}_{max}/cm^{-1}$ 2562 (BH), 2294, 2265, 2252 (C≡N) and 1202 (CF_3SO_3).

$[PrTp^{Me,Me}{}_2(MeCN)_2(O_3SCF_3)]$ 3. The complex $[PrTp^{Me,Me}{}_2(O_3SCF_3)]$ (0.31 g, 0.34 mmol) was dissolved in acetonitrile (20 cm^3) in a Schlenk flask under nitrogen. The solution was concentrated under reduced pressure to 10 cm^3 and layered with light petroleum. The solution was then cooled slowly to −10 °C to give pale green crystals of the product. Yield: 0.25 g (76%) (Found: C, 43.55; H, 5.05; N, 19.95. $C_{35}H_{50}B_2F_3N_{14}O_3PrS$ requires C, 43.5; H, 5.2; N, 20.3%). δ_H($CDCl_3$, 298 K) −11.97 (s, 18 H, 3-Me), 1.78 (s, 6 H, MeCN), 5.58 (s, 18 H, 5-Me) and 7.08 (s, 6 H, CH). δ_c($CDCl_3$, 298 K) 12.5 (q, MeCN), 19.4 (q, 3- or 5-Me), 20.2 (q, 5- or 3-Me), 125.6 (d, CH), 152.6 (s, 2- or 4-C) and 164.1 (s, 4- or 2-C). IR (KBr): $\tilde{\nu}_{max}/cm^{-1}$ 2559 (BH), 2302, 2276 (C≡N) and 1202 (CF_3SO_3).

$[NdTp^{Me,Me}{}_2(MeCN)_2][O_3SCF_3]$ 4. The complex $[NdTp^{Me,Me}{}_2(O_3SCF_3)]$ (0.31 g, 0.34 mmol) was dissolved in acetonitrile (20 cm^3) in a Schlenk flask under nitrogen. The solution was concentrated under reduced pressure to 10 cm^3 and layered with light petroleum. The solution was then cooled slowly to −10 °C to give lilac crystals of the product. Yield: 0.20 g (63%) (Found: C, 43.15; H, 5.0; N, 20.1. $C_{35}H_{50}B_2F_3N_{14}NdO_3S$ requires C, 43.4; H, 5.2; N, 20.25%). δ_H($CDCl_3$, 298 K) −9.70 (s, 18 H, 3-Me), 1.88 (s, 6 H, MeCN), 5.16 (s, 18 H, 5-Me) and

Table 5 Crystal data, structure solution and refinement for [LaTp$^{Me,Me}{}_2$(MeCN)(O$_3$SCF$_3$)]·MeCN **1**, [NdTp$^{Me,Me}{}_2$(MeCN)$_2$][O$_3$SCF$_3$] **4** and [LaTp$^{Me,Me}{}_2$(NO$_3$)]·MeCN **5**

	1	**4**	**5**
Chemical formula	$C_{35}H_{50}B_2F_3LaN_{14}O_3S$	$C_{35}H_{50}B_2F_3N_{14}NdO_3S$	$C_{32}H_{47}B_2LaN_{14}O_3$
M	964.46	969.91	836.37
T/K	298	298	160
Crystal system, space group	Triclinic, $P\bar{1}$	Orthorhombic, $P2_12_12_1$	Triclinic, $P\bar{1}$
a/Å	10.513(3)	13.713(4)	11.2042(9)
b/Å	13.757(3)	13.988(6)	11.1982(9)
c/Å	17.530(2)	23.120(10)	16.1533(13)
α/°	109.30(1)		80.006(2)
β/°	98.00(2)		76.953(2)
γ/°	102.81(2)		82.924(2)
U/Å^3	2275(1)	4441(3)	1937.0(3)
Z	2	4	2
D_c/g cm^{-3}	1.41	1.45	1.434
μ/cm^{-1}	10.47	12.89	11.55
F(000)	984	1980	856
Reflections for cell refinement	29 ($15.61 \leqslant 2\theta \leqslant 28.32$)	23 ($15.21 \leqslant 2\theta \leqslant 25.45$)	11 876 ($5.00 \leqslant 2\theta \leqslant 56.60$)
Crystal colour	Colourless	Pale lilac	Colourless
Crystal size/mm	0.40 × 0.25 × 0.35	0.60 × 0.35 × 0.22	0.56 × 0.46 × 0.36
Data-collection method	ω–2θ	ω	ω, with 0.3° frames
2θ range for data collection	5–50	5–50	3.70–56.74
Index ranges (maximum)	$0 \leqslant h \leqslant 13$, $-17 \leqslant k \leqslant 17$, $-21 \leqslant l \leqslant 21$	$0 \leqslant h \leqslant 18$, $0 \leqslant k \leqslant 19$, $0 \leqslant l \leqslant 31$	$-12 \leqslant h \leqslant 14$, $-14 \leqslant k \leqslant 13$, $-21 \leqslant l \leqslant 13$
Reflections collected	8488	5620	13 412
Independent reflections	8014	5593	8387
R_{int}	0.0249	0.0000	0.0186
Observed reflections	6080 [$I > 3\sigma(I)$]	3493 [$I > 3\sigma(I)$]	8062 [$I > 4\sigma(I)$]
Maximum, minimum transmission	0.965, 0.827	0.965, 0.723	0.701, 0.577
Structure solution	Patterson	Patterson	Direct methods
Refinement method (see text)	F	F	F^2
Weighting parameters	0.000 640[a]	0.002 0681[a]	$a = 0.0188$, $b = 1.3242$[b]
Parameters	517	527	489
Final R indices (defined below)	0.0481,[c] 0.0492[d]	0.0472,[c] 0.0520[d]	0.0201,[c] 0.0519[e]
Largest shift/e.s.d.	0.009	0.007	0.004
Largest difference peak	+0.745, −0.716	+0.461, −0.761	+0.420, −0.564

[a] $w^{-1} = \sigma(F^2) + w(F)^2$. [b] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + (bP)$, where $P = (2F_c^2 + F_o^2)/3$. [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. [e] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$.

8.00 (s, 6 H, CH). δ_C(CDCl$_3$, 298 K) 1.9 (q, 3- or 5-Me), 12.5 (q, MeCN), 18.6 (q, 5- or 3-Me), 132.9 (d, CH), 159.7 (s, 2- or 4-C) and 169.1 (s, 4- or 2-C). IR (KBr): $\tilde{\nu}_{max}$/cm^{-1} 2560 (BH), 2277, 2229 (C≡N) and 1203 (CF$_3$SO$_3$).

[LaTp$^{Me,Me}{}_2$(NO$_3$)] 5. The complex [LaTp$^{Me,Me}{}_2$(O$_3$SCF$_3$)] (0.5 g, 0.56 mmol) and NaNO$_3$ (0.048 g, 0.56 mmol) were placed in a Schlenk flask. Tetrahydrofuran (50 cm^3) was added to the flask by means of a cannula and the mixture stirred for 16 h. A fine, translucent precipitate appeared in the solution as the reaction proceeded. The solvent was removed under reduced pressure and the white residue extracted with toluene (2 × 30 cm^3). Removal of solvent under reduced pressure yielded a white solid which was recrystallized from acetonitrile. Yield: 0.35 g (79%) (Found: C, 45.3; H, 5.55; N, 22.9. $C_{30}H_{44}B_2LaN_{13}O_3$ requires C, 45.3; H, 5.6; N, 22.9%). δ_H(CDCl$_3$, 298 K) 1.83 (s, 18 H, 3-Me), 2.38 (s, 18 H, 5-Me) and 5.69 (s, 6 H, CH). δ_C(CDCl$_3$, 298 K) 12.5 (q, 3- or 5-Me), 13.5 (q, 5- or 3-Me), 106.3 (d, CH), 145.5 (s, 2- or 4-C) and 150.0 (s, 4- or 2-C). IR: $\tilde{\nu}_{max}$/cm^{-1} 2556 (BH) and 1507 (NO$_3$). Electron impact mass spectrum: *m/z* 795 (M^+), 733 {[LaTp$^{Me,Me}{}_2$]$^+$} and 531 {[LaTp^{Me,Me}(dmpz)]$^+$} (dmpz = 3,5-dimethylpyrazolyl).

X-Ray crystallography

Complexes 1 and 4. *Data collection and processing.* All data were collected on a Nicolet R3mV four-circle diffractometer using graphite-monochromated Mo-Kα (λ = 0.710 73 Å) radiation. Data were corrected for Lorentz-polarization effects, and for absorption by a semiempirical method based on ψ-scan data. The intensity of three check reflections measured every 97 showed no decay over the course of the data collection. Crystallographic details are summarized in Table 5.

Structure solution and refinement. Crystallographic calculations were carried out with the SHELXTL PLUS[19] suite of programs on a MicroVAX II computer. The structures were solved by Patterson methods and developed by alternating cycles of full-matrix least-squares refinement and Fourier-difference techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions with one overall, refined thermal parameter U_{iso} = 0.08(2) Å^2.

Complex 5. *Data collection and processing.* All data were collected on a Siemens SMART CCD area-detector diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Data were corrected for Lorentz-polarization effects, and for absorption by a semiempirical method from redundant and symmetry-equivalent reflections. Frames measured early in the data collection were remeasured at the end to reveal no crystal decay by analysis of the repeated data.

Structure solution and refinement. Crystallographic calculations were carried out with SHELXTL version 5[20] suite of programs. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 with statistical weighting. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were constrained using riding models with methyl groups allowed torsional freedom. For H(1) and H(2) the coordinates were freely refined. All hydrogen atoms were refined with isotropic displacement parameters set to be 120% of those of the carrier atoms (150% for methyl H).

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/475.

Acknowledgements

We are grateful to the Royal Society for support, to the EPSRC for a studentship (to G. H. M.) (GR/H31943) and for grants of the diffractometers, and to the Formosa Chemical Company for study leave to S. Y. L. We also thank Dr. C. J. Jones, Professor Josef Takats and Professor V. W. Day for their discussions and helpful advice, and Professor W. Clegg for use of the crystallographic facilities at Newcastle.

References

1 T. Imamoto, *Lanthanides in Organic Synthesis*, Academic Press, London, 1994.
2 I. Santos and N. Marques, *New J. Chem.*, 1995, **19**, 551.
3 K. W. Bagnall, A. C. Tempest, J. Takats and A. P. Masino, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 555.
4 M. A. J. Moss and C. J. Jones, *Polyhedron*, 1990, **9**, 697.
5 M. G. B. Drew, *Coord. Chem. Rev.*, 1977, **24**, 179.
6 S. Y. Liu, G. H. Maunder, A. Sella, M. Stevenson and D. A. Tocher, *Inorg. Chem.*, 1996, **35**, 76.
7 M. A. Moss, C. J. Jones and A. J. Edwards, *J. Chem. Soc., Dalton Trans.*, 1989, 1393.
8 J. Takats, X. W. Zhang, V. W. Day and T. A. Eberspacher, *Organometallics*, 1993, **12**, 4286.
9 X. W. Zhang, G. R. Loppnow, R. MacDonald and J. Takats, *J. Am. Chem. Soc.*, 1995, **117**, 7828.
10 G. H. Maunder and A. Sella, unpublished work.
11 P. H. Smith and K. N. Raymond, *Inorg. Chem.*, 1985, **24**, 3469.
12 G. H. Maunder, A. Sella and D. A. Tocher, *J. Chem. Soc., Chem. Commun.*, 1994, 558; G. H. Maunder, Ph.D. Thesis, University College London, 1996.
13 Y. Sun, R. McDonald, J. Takats, V. W. Day and T. A. Eberspacher, *Inorg. Chem.*, 1994, **33**, 4433.
14 R. G. Lawrence, C. J. Jones and R. A. Kresinski, *J. Chem. Soc., Dalton Trans.*, 1996, 501.
15 D. L. Reger, S. J. Knox, J. A. Lindeman, and L. Lebioda, *Inorg. Chem.*, 1990, **29**, 416.
16 S. McNally and N. J. Cooper, *ACS Symp. Ser.*, 1987, **357**.
17 D. F. Shriver and M. A. Drezdzon, *The Manipulation of Air-Sensitive Compounds*, Wiley, New York, 2nd edn., 1986.
18 S. Trofimenko, *J. Am. Chem. Soc.*, 1967, **89**, 6288.
19 G. M. Sheldrick, SHELXTL PLUS, Siemens Analytical X-Ray Instruments, Madison, WI, 1990.
20 SHELXTL version 5, Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1995.

Received 24th December 1996; *Paper* 6/08620I