Low Co-ordination Numbers in Lanthanoid and Actinoid Compounds. Part 2.[1] Syntheses, Properties, and Crystal and Molecular Structures of Triphenylphosphine Oxide and Peroxo-derivatives of [Bis(trimethylsilyl)amido]lanthanoids

By **Donald C. Bradley, Joginder S. Ghotra, F. Alan Hart, Michael B. Hursthouse,*** and **Paul R. Raithby,** Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS

The preparation, properties, and n.m.r. spectra of 1 : 1 triphenylphosphine oxide adducts of $[M\{N(SiMe_3)_2\}_3]$ (M = La, Eu, or Lu) and dimeric peroxo-species $[M_2\{N(SiMe_3)_2\}_4(O_2)(PPh_3O)_2]$ (M = La, Pr, Sm, Eu, or Lu) are described. The crystal and molecular structures of $[La\{N(SiMe_3)_2\}_3(PPh_3O)]$ (1) and $[La_2\{N(SiMe_3)_2\}_4(O_2)(PPh_3O)_2]$ (2) have been determined by single-crystal *X*-ray diffraction methods from data measured on a manual diffractometer and refined by least-squares to *R* 0.116 for 2 770 observed reflections for (1) and to *R* 0.113 for 2 153 data for (2). Both species crystallise in space group $P\bar{1}$ with cell parameters: (1); a = 19.92, b = 12.64, c = 12.48 Å, α = 120.5, β = 87.3, γ = 102.7°, Z = 2; (2); a = 13.55, b = 18.54, c = 12.54 Å, α = 90.8, β = 121.7, γ = 115.3°, Z = 1. Complex (1) is monomeric and the lanthanum atom has slightly distorted LaN_3O tetrahedral geometry. The La–O–P unit is almost linear, with La–O 2.39(2) Å; La–N distances are 2.38(2)—2.41(2) Å. Complex (2) is a peroxo-bridged centrosymmetric dimer in which the peroxo-function acts as a symmetrical doubly bidentate bridge linking two $La\{N(SiMe_3)_2\}_2(PPh_3O)$ units. The metal atom can again be considered to have distorted tetrahedral co-ordination if the O_2 function is assumed to occupy one co-ordination site. The La–O(O_2) distances are both 2.33(3) Å, whilst La–O(PPh_3O) is 2.42(2) and La–N 2.37(2) and 2.49(3) Å. The O–O separation is 1.65(4) Å, but this may be artificially lengthened by the effects of crystal decomposition.

WE have reported [1,2] the synthesis, structure, and properties of monomeric three-co-ordinate tris[bis(trimethylsilyl)amido]lanthanoids, which have a pyramidal structure. Because of their low co-ordination number and unusual conformation, these complexes should form adducts rather readily, although the large size of the silylamido-ligands might reduce this tendency to some extent. These adducts would be of interest because four-[3] and five-co-ordinate[4] lanthanoid complexes are extremely rare, and the adducts would furnish information as to the stability and preferred stereochemistry of such complexes. Triphenylphosphine oxide was selected as the ligand to be added as it is known to complex very strongly with lanthanoid ions.[5]

The exceedingly air-sensitive silylamides $[M\{N(SiMe_3)_2\}_3]$ (M = La, Eu, or Lu) were treated in benzene solution, under anaerobic conditions, with one molecular proportion of PPh_3O. The products were the adducts $[M\{N(SiMe_3)_2\}_3(PPh_3O)]$. These complexes are well crystalline with m.p.s of 185—187, 141—144, and 165—166 °C respectively. The PPh_3O ligand is moderately firmly bound, dissociating and subliming away at 85—100 °C and 10^{-4} mmHg.† The complexes of La and Lu are colourless, while that of Eu is orange-yellow. As in the similarly coloured $[Eu\{N(SiMe_3)_2\}_3]$, the colour probably arises from a charge transfer from the amido-ligand to the easily reducible Eu^{3+} ion.

A number of experiments intended to synthesise the diadduct $[M\{N(SiMe_3)_2\}_3(PPh_3O)_2]$ failed to give this product. Instead, a peroxo-complex $[M_2\{N(SiMe_3)_2\}_4(O_2)(PPh_3O)_2]$ was isolated, either alone or, on the evidence of analytical results, mixed with $[M\{N(SiMe_3)_2\}_3(PPh_3O)]$. In order to synthesise the peroxide directly, $[Lu\{N(SiMe_3)_2\}_3]$ was treated with a half-molar proportion of $(Ph_3PO)_2{\cdot}H_2O_2$. Prepared either way, the resulting $[M_2\{N(SiMe_3)_2\}_4(O_2)(PPh_3O)_2]$ complexes were obtained as crystalline solids, yields being typically in the region of 60%. These peroxo-complexes are colourless for M = La, Lu and, surprisingly, Pr, pale yellow for M = Sm, and orange-red for M = Eu, the colouration of the last two correlating with the relative ease of reduction of their central ion. Heated under nitrogen, they all decompose at 120—140 °C; PPh_3O sublimes off at *ca.* 100 °C at 10^{-4} mmHg pressure.

The origin of the peroxo-group remains obscure in those experiments where the peroxo-complex was obtained by the action of excess of PPh_3O on the tris(silylamide). The triphenylphosphine oxide was prepared by the bromination of the phosphine followed by hydrolysis and sublimation. The solvents were purified as described in the Experimental section, and quantities of air of the order of 100 cm³ would have been required to provide the weight of O_2 necessary for conversion at the scale of our strictly anaerobic experiments.

EXPERIMENTAL

Synthesis.—Since all the complexes are decomposed by trace amounts of moisture, all the preparations and manipulations were carried out using a vacuum-line system and a glove-box filled with purified nitrogen. Benzene, tetrahydrofuran, and n-pentane were distilled over calcium hydride and redistilled from a blue solution of sodium diphenylketyl as required for use. The preparation of the tris[bis(trimethylsilyl)amido]lanthanoids and the analytical procedures used were as previously described.[1]

Tris[bis(trimethylsilyl)amido](triphenylphosphine oxide)-lanthanum(III), $[La\{N(SiMe_3)_2\}_3(PPh_3O)]$. The complex

---

† Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

[1] D. C. Bradley, J. S. Ghotra, and F. A. Hart, *J.C.S. Chem. Comm.*, 1972, 349; *J.C.S. Dalton*, 1973, 1021.

[2] J. S. Ghotra, M. B. Hursthouse, and A. J. Welch, *J.C.S. Chem. Comm.*, 1973, 669.

[3] S. A. Cotton, F. A. Hart, M. B. Hursthouse, and A. J. Welch, *J.C.S. Chem. Comm.*, 1972, 1225.

[4] D. C. Bradley, J. S. Ghotra, F. A. Hart, M. B. Hursthouse, and P. R. Raithby, *J.C.S. Chem. Comm.*, 1974, 40.

[5] G. A. Catton, F. A. Hart, and G. P. Moss, *J.C.S. Dalton*, 1976, 208.

$[La\{N(SiMe_3)_2\}_3]$ (4.7 g) and PPh_3O (3.1 g, 1.5 mol) were stirred in benzene at 25 °C (50 cm^3) for 3 h. The solvent was removed under reduced pressure and the residue was extracted with n-pentane, leaving an insoluble portion (PPh_3O). On removal of the n-pentane under reduced pressure, the *adduct* remained as colourless crystals [Found: La, 16.1; $N(SiMe_3)_2$, 53.1. Calc. for $C_{36}H_{69}LaN_3OPSi_6$: La, 15.45; $N(SiMe_3)_2$, 53.5%]. Similarly prepared were the corresponding europium [Found: Eu, 16.35; $N(SiMe_3)_2$, 52.5. Calc. for $C_{36}H_{69}EuN_3OPSi_6$: Eu, 16.7; $N(SiMe_3)_2$, 52.8%] and lutetium *complexes* [Found: Lu, 18.6; $N(SiMe_3)_2$, 49.8. Calc. for $C_{36}H_{69}LuN_3OPSi_6$: Lu, 18.7; $N(SiMe_3)_2$, 51.5%].

Tetrakis[bis(trimethylsilyl)amido]peroxobis(triphenylphosphine oxide)dilutetium(III), $[Lu_2\{N(SiMe_3)_2\}_4(O_2)(PPh_3O)_2]$. The complex $[Lu\{N(SiMe_3)_2\}_3]$ (0.82 g) and $(Ph_3PO)_2 \cdot H_2O_2$ (0.37 g, 2 mol) were stirred in benzene (10 cm^3) for 16 h. The solvent was removed under reduced pressure and the residue was extracted with n-pentane. After filtration and concentration, the *peroxo-complex* was deposited as colourless crystals which were collected and dried *in vacuo* (Found: C, 45.2; H, 6.7; Lu, 22.3; N, 3.7. Calc. for $C_{60}H_{102}Lu_2N_4O_4P_2Si_8$: C, 45.6; H, 6.45; Lu, 22.15; N, 3.5%).

Tetrakis[bis(trimethylsilyl)amido]peroxobis(triphenylphosphine oxide)dieuropium(III), $[Eu_2\{N(SiMe_3)_2\}_4(O_2)(PPh_3O)_2]$. The complex $[Eu\{N(SiMe_3)_2\}_3]$ (3.00 g) and PPh_3O (3.00 g, 2.28 mol) were stirred in benzene (50 cm^3) for 2 h. The solvent was removed under reduced pressure and the residue was extracted from residual PPh_3O with n-pentane (50 cm^3). On concentration, the pentane solution deposited the *peroxo-complex* as orange-red crystals (Found: C, 46.5; H, 6.65; Eu, 19.6; N, 3.8; P, 4.3. Calc. for $C_{60}H_{102}Eu_2N_4O_4P_2Si_8$: C, 46.9; H, 6.65; Eu, 19.8; N, 3.65; P, 4.0%).

By similar treatment of $[M\{N(SiMe_3)_2\}_3]$ with PPh_3O (2—5 mol), the analogous *peroxo-complexes* of the following metals were obtained: lanthanum [Found: La, 18.1; $N(SiMe_3)_2$, 42.3. Calc. for $C_{60}H_{102}La_2N_4O_4P_2Si_8$: La, 18.4; $N(SiMe_3)_2$, 42.5%], praseodymium (Found: C, 45.3; H, 6.4; N, 3.7; P, 4.3; Pr, 18.1. Calc. for $C_{60}H_{102}N_4O_4P_2Pr_2Si_8$: C, 47.6; H, 6.7; N, 3.6; P, 4.1; Pr, 18.65%), samarium (Found: C, 45.6; H, 6.5; N, 3.6; P, 4.0; Sm, 20.8. Calc. for $C_{60}H_{102}N_4O_4P_2Si_8Sm_2$: C, 47.0; H, 6.7; N, 3.7; P, 4.05; Sm, 19.65%), and europium (Found: C, 46.5; H, 6.65; Eu, 19.6; N, 3.8; P, 4.3. Calc. for $C_{60}H_{102}Eu_2N_4O_4P_2Si_8$: C, 46.9; H, 6.65; Eu, 19.8; N, 3.65; P, 4.0%).

N.m.r. Spectra.—Resonances were as follows in deuteriated benzene solutions: $[M\{N(SiMe_3)_2\}_3(PPh_3O)]$ (M = La) Me 9.93, Ph 2.43; (M = Eu) Me 10.43, Ph 5.10; (M = Lu) Me 9.90, Ph 2.50; $[M_2\{N(SiMe_3)_2\}_4(O_2)(PPh_3O)_2]$ (M = La) Me 9.93, Ph 2.50; (M = Pr) Me 9.83, Ph 5.97; (M = Sm) Me 10.00, Ph 2.70; (M = Eu) Me 10.86, Ph 0.14; (M = Lu) Me 9.90, Ph 2.50 p.p.m. The paramagnetic shifts were in the range 0.1—3.5 p.p.m. and are evidently mainly dipolar in origin because the relative magnitudes for Pr, Sm, and Eu are approximately as expected for that mechanism.[6] However, owing to the uncertain averaged location of the hydrogen atoms in solution, it is difficult to correlate shifts with molecular structure in a detailed way. It is noteworthy that the shifts observed for $[Eu\{N(SiMe_3)_2\}_3(PPh_3O)]$ imply a departure from a tetrahedral ligand field, which would be isotropic and give no shifts.

Infrared Spectra.—These were obtained from Nujol mulls. They include resonances in the ranges 1 132—1 139 cm^{-1}, probably the P–O stretching mode (compared with 1 195 cm^{-1} in free PPh_3O), and 374—384 cm^{-1}, probably the M–N stretching mode. Both these resonances lie in the expected regions.

X-*Ray Crystallography*.—In order to effect complete characterisation of the two species, we subjected the lanthanum derivative of each type of complex to single-crystal *X*-ray study.

(*a*) $[La\{N(SiMe_3)_2\}_3(PPh_3O)]$. Crystals were obtained from toluene and mounted under nitrogen in Lindemann capillaries. During this process some surface decomposition occurred, making proper measurement of the crystal and face indexing impossible. Approximate cell dimensions and space group were determined photographically; improved cell dimensions were obtained by accurate 2θ, ϕ, and χ angle measurements of axial reflections on a G.E. XRD6 manual diffractometer.

Crystal data. $C_{36}H_{69}LaN_3OPSi_6$, $M = 898.25$, Triclinic, space group $P\bar{1}$, $a = 19.920(5)$, $b = 12.644(6)$, $c = 12.482(2)$ Å, $\alpha = 120.53(3)$, $\beta = 87.33(2)$, $\gamma = 102.66(4)°$, $U = 2\,634$ Å^3, $Z = 2$, $D_c = 1.09$ g cm^{-3}, Cu-K_α radiation [$\lambda = 1.541\,8$ Å, $\mu(\text{Cu-}K_\alpha) = 75.5$ cm^{-1}].

Intensity data were collected on a manual diffractometer using Cu-K_α radiation, and the stationary-crystal–stationary-counter technique with a counting time of 10 s. Backgrounds were measured at $(2\theta + 1)°$ for each peak and the 200, 400, 030, and 002 reflections measured every 100 reflections; variations in their values indicated a decay of *ca.* 10% over the period (8 d) of data collection. Of the 3 340 reflections measured up to a θ limit of 40°, 2 770 had significant $[I > 2\sigma(I)]$ intensities. These data were corrected for Lorentz and polarisation effects but not for absorption. The structure was solved by standard Patterson and successive electron-density synthesis techniques and refined by full-matrix least-squares methods. After inclusion of all the atoms in the molecule, the difference map showed a number of residual peaks, close to the centre of symmetry at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$, which were assumed to arise from disordered solvent since the arrangement of peaks did not correspond to any possible molecule. Attempts were made to allow for this by inclusion of partial carbon atoms at the site of the heavier peaks but the results were not satisfactory. The final R was 0.116 with La, O, N, P, and Si atoms assigned anisotropic thermal parameters and C atoms isotropic. A Hughes-type weighting scheme was used with $w^{\frac{1}{2}} = 1$ for $F_o < F^*$ and $w^{\frac{1}{2}} = F^*/F_o$ for $F_o > F^*$ and $F^* = 70$ giving the best agreement analysis. The final atomic co-ordinates and thermal parameters are given in Table 1.

(*b*) $[La_2\{N(SiMe_3)_2\}_4(O_2)(PPh_3O)_2]$. Crystals were obtained and mounted in capillaries in a manner similar to that described in (*a*); cell dimensions were also determined as described earlier.

Crystal data. $C_{60}H_{102}La_2N_4O_4P_2Si_8$, $M = 1\,457.97$, Triclinic, space group $P\bar{1}$, $a = 13.548(1)$, $b = 18.537(3)$, $c = 12.536(1)$ Å, $\alpha = 90.80(1)$, $\beta = 121.74(1)$, $\gamma = 115.32(2)°$, $U = 2\,300$ Å^3, $Z = 1$, $D_c = 1.06$ g cm^3. Cu-K_α radiation [$\lambda = 1.541\,8$ Å, $\mu(\text{Cu-}K_\alpha) = 84.7$ cm^{-1}].

Intensity data were recorded as described in (*a*). The 020, 040, and 002 reflections were used as references; intensity variations again indicated a slow deterioration of the crystal, amounting to *ca.* 15%. Of the 2 887 reflections measured ($2\theta < 80°$), 2 153 had significant intensities, and

---

[6] B. Bleaney, *J. Magnetic Resonance*, 1972, **8**, 91.

these were corrected for Lorentz and polarisation effects. The structure analysis and refinement proceeded along the lines described in (*a*). Again the presence of disordered solvent molecules was detected, this time in pockets centred on the *a* axis, but again no allowance was made for these. The final *R* was 0.113 with $F^* = 70$ for the optimum weighting scheme. The final atomic co-ordinates and thermal parameters are listed in Table 2.

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$), and temperature factors ($\text{Å} \times 10^3$) for $[La\{N(SiMe_3)_2\}_3(PPh_3O)]$

	x/*a*	*y*/*b*	*z*/*c*	*U*
La(1)	2 394(1)	4 045(1)	1 488(2)	*
N(1)	1 325(10)	3 293(17)	2 146(19)	*
N(2)	3 332(12)	4 434(20)	2 864(20)	*
N(3)	2 593(10)	2 822(18)	−654(22)	*
O(1)	2 367(7)	6 077(14)	1 804(14)	*
P(1)	2 283(4)	7 307(7)	1 959(6)	*
Si(1)	1 287(5)	2 701(8)	3 133(8)	*
Si(2)	579(4)	3 444(8)	1 640(9)	*
Si(3)	3 923(5)	3 452(9)	2 305(9)	*
Si(4)	3 452(5)	5 675(8)	4 291(8)	*
Si(5)	3 292(5)	3 526(8)	−1 190(8)	*
Si(6)	2 102(5)	1 432(9)	−1 644(9)	*
C(11)	455(18)	1 539(32)	2 929(32)	117(12)
C(12)	2 023(16)	1 949(29)	2 933(29)	100(10)
C(13)	1 324(16)	3 949(29)	4 837(29)	99(10)
C(21)	826(16)	4 086(28)	600(29)	97(10)
C(22)	−59(17)	1 908(30)	546(30)	108(11)
C(23)	96(21)	4 518(38)	2 944(38)	147(15)
C(31)	4 765(18)	4 117(32)	1 746(32)	117(12)
C(32)	3 494(15)	1 856(27)	881(28)	92(10)
C(33)	4 228(20)	3 129(35)	3 491(36)	135(13)
C(41)	3 416(20)	5 354(35)	5 645(35)	132(13)
C(42)	4 275(18)	6 912(32)	4 558(32)	116(12)
C(43)	2 670(16)	6 483(28)	4 549(29)	95(10)
C(51)	3 083(20)	3 713(35)	−2 556(36)	136(13)
C(52)	4 003(19)	2 635(34)	−1 722(35)	129(13)
C(53)	3 701(15)	5 156(27)	95(27)	89(9)
C(61)	1 467(24)	1 494(44)	−2 817(44)	175(17)
C(62)	2 551(16)	124(30)	−2 775(30)	104(10)
C(63)	1 596(17)	741(31)	−779(31)	113(11)
C(101)	1 523(13)	7 729(22)	2 699(24)	62(7)
C(102)	1 033(19)	8 014(32)	2 151(33)	117(12)
C(103)	466(19)	8 363(32)	2 738(34)	116(12)
C(104)	261(18)	8 293(32)	3 806(34)	116(12)
C(105)	744(18)	8 049(31)	4 426(31)	108(11)
C(106)	1 369(17)	7 769(29)	3 793(31)	102(10)
C(201)	3 006(13)	8 552(24)	2 947(24)	67(8)
C(202)	3 638(16)	8 286(28)	2 829(28)	92(10)
C(203)	4 227(21)	9 275(40)	3 621(38)	137(13)
C(204)	4 082(20)	10 420(37)	4 356(35)	124(12)
C(205)	3 509(21)	10 765(36)	4 462(35)	130(13)
C(206)	2 886(18)	9 726(34)	3 713(33)	113(11)
C(301)	2 258(16)	7 263(31)	568(30)	101(10)
C(302)	1 907(16)	6 184(30)	−535(32)	102(10)
C(303)	1 885(18)	6 113(33)	−1 684(33)	114(11)
C(304)	2 132(19)	7 183(38)	−1 709(36)	126(12)
C(305)	2 494(19)	8 307(36)	−704(38)	125(12)
C(306)	2 559(17)	8 332(31)	385(32)	107(11)

* Anisotropic temperature factors for these atoms are in SUP 22010.

Observed and calculated structure factors for the two complexes are in Supplementary Publication No. SUP 22010 (24 pp.).* Computations for the two structure analyses were made using the ' *X*-Ray '72 ' programs [7] on the University of London CDC 7600 computer. Atomic scattering factors for all the atoms were taken from ref. 8, with those for La, P, and Si corrected for anomalous dispersion. Both structure analyses are characterised by high *R* factors and low accuracy in atomic positions. We feel this is due, in the main, to our inability to obtain crystals of the quality preferred for *X*-ray work, to the presence of disordered solvent molecules, and to the slow deterioration of both samples. Although allowance was made for the average decay in each case, the variations in the reference reflections indicate possible anisotropic decomposition, but no attempt was made to allow for this.

TABLE 2

Fractional atomic co-ordinates ($\times 10^4$), and temperature factors ($\text{Å} \times 10^3$) for $[La_2\{N(SiMe_3)_2\}_4(O_2)(PPh_3O)_2]$

	x/*a*	*y*/*b*	*z*/*c*	*U*
La(1)	252(2)	1 166(1)	807(2)	*
N(1)	1 836(22)	1 643(14)	3 130(23)	*
N(2)	−1 863(19)	1 207(13)	−205(19)	*
O(1)	1 036(17)	2 167(9)	−174(18)	*
O(2)	505(22)	264(11)	−210(21)	*
P(1)	1 350(7)	2 782(5)	−879(8)	*
Si(1)	1 206(11)	1 107(7)	3 946(9)	*
Si(2)	3 513(9)	2 396(6)	3 933(9)	*
Si(3)	−3 331(9)	342(6)	−1 394(9)	*
Si(4)	−1 691(9)	2 047(6)	507(9)	*
C(11)	1 812(41)	373(26)	4 687(40)	151(15)
C(12)	−745(37)	377(23)	2 686(36)	134(13)
C(13)	1 493(48)	1 861(30)	5 274(47)	182(18)
C(21)	3 971(32)	2 447(20)	2 762(31)	104(10)
C(22)	4 750(41)	2 204(25)	5 467(39)	150(14)
C(23)	3 838(45)	3 528(28)	4 398(43)	171(17)
C(31)	−4 750(51)	511(32)	−2 418(49)	195(19)
C(32)	−3 946(34)	−528(21)	−690(33)	118(12)
C(33)	−3 307(39)	−98(24)	−2 739(38)	141(14)
C(41)	−2 681(37)	1 830(23)	1 164(36)	134(13)
C(42)	−2 221(39)	2 717(24)	−549(38)	139(13)
C(43)	154(35)	2 806(22)	2 005(34)	119(12)
C(101)	2 709(29)	2 869(20)	−892(28)	88(9)
C(102)	3 680(38)	3 668(23)	−775(34)	123(12)
C(103)	4 646(44)	3 711(28)	−976(41)	152(12)
C(104)	4 807(44)	3 020(31)	−911(41)	150(14)
C(105)	3 981(40)	2 295(24)	−940(35)	126(12)
C(106)	3 947(34)	2 254(21)	−907(31)	106(11)
C(201)	1 827(29)	3 804(18)	−97(29)	83(8)
C(202)	1 096(32)	4 193(21)	−751(31)	102(10)
C(203)	1 449(36)	4 976(23)	−72(37)	120(12)
C(204)	2 458(33)	5 300(20)	1 312(33)	102(10)
C(205)	3 195(37)	4 962(25)	1 949(36)	126(12)
C(206)	2 838(37)	4 161(24)	1 245(37)	122(12)
C(301)	−36(28)	2 429(17)	−2 536(26)	75(8)
C(302)	115(37)	2 631(23)	−3 501(38)	125(12)
C(303)	−1 074(52)	2 362(30)	−4 877(47)	167(16)
C(304)	−2 360(47)	1 895(28)	−5 197(44)	156(15)
C(305)	−2 489(41)	1 752(24)	−4 210(43)	140(14)
C(306)	−1 323(39)	2 035(22)	−2 815(37)	132(12)

* Anisotropic temperature factors for these atoms are in SUP 22010.

DISCUSSION

(*a*) $[La\{N(SiMe_3)_2\}_3(PPh_3O)]$.—Some of the more important bond lengths and angles computed from the data of Table 1 are given in Table 3; a complete list is given in SUP 22010. The complex is monomeric and molecular with pseudo-tetrahedral geometry around the lanthanum atom (Figure 1). Significant features of this geometry are the relative sizes of the O–La–N and N–La–N angles, which range from 105—108° for the former and 109—116° for the latter. It is probable that the greater bulk of the amido-ligand is responsible

---

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

[7] The ' *X*-Ray System,' Technical Report TR-192, The Computer Science Center, University of Maryland, June 1972.

[8] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 3, pp. 202 and 211.

for the small differences between the average values for the two groups and that non-bonded interactions, both intra- and inter-molecular, are responsible for the variations within each group.

Such interactions are also probably significant in the choice of ligand orientations. Table 4 lists the results of some mean-plane calculations and two points of particular interest are: (*i*) the orientations of the three NSi_2 planes relative to the N_3 plane vary from 39 to 48°; and (*ii*) the lanthanum ion lies 0.06—0.16 Å off the NSi_2 planes. The latter result, taken in conjunction with the inequality of the La–N–Si angles for two of the amido-ligands, indicates that the lanthanum ion generally does not lie along the bisectors of the Si–N–Si angles. The deviations, however, are not as large as in the parent $[M\{N(SiMe_3)_2\}_3]$ complexes,[2] but again seem to reflect a reduction in the stereochemical rigidity arising out of a significant ionic component in the metal–ligand bonding. A third point of interest is the orientation and conformation of the PPh_3O ligand. The P–O–La unit is almost linear, the angle at O being 174°, and the O–La bond is almost perpendicular to the N_3 basal plane. In view of the potential three-fold symmetries of the ligand and the $La\{N(SiMe_3)_2\}_3$ moiety, it might be expected that the complex as a whole would adopt a conformation approaching this symmetry. Apart from the three differing N_3/NSi_2 dihedral angles, the main distortion from such a conformation lies in the relative orientations of the three phenyl rings. The angles between their planes and the N_3 reference plane are 38.2, 60.0, and 60.4° (Table 4). Again, this result can probably be ascribed to the packing requirements of the ligands, and the overall picture of this packing is best given by the intramolecular interligand contacts (Table 5).

TABLE 3

Some important bond lengths (Å) and angles (°) for $[La\{N(SiMe_3)_2\}_3(PPh_3O)]$

(*a*) Lengths			
La(1)–N(1)	2.41(2)	La(1)–N(2)	2.40(3)
La(1)–N(3)	2.38(2)	La(1)–O(1)	2.40(2)
N(1)–Si(1)	1.73(3)	N(2)–Si(3)	1.76(3)
N(1)–Si(2)	1.74(3)	N(2)–Si(4)	1.65(2)
N(3)–Si(5)	1.78(3)	N(3)–Si(6)	1.65(2)
O(1)–P(1)	1.52(2)		
(*b*) Angles			
O(1)–La(1)–N(1)	107.8(7)	La(1)–N(2)–Si(3)	119.3(10)
O(1)–La(1)–N(2)	105.2(7)	La(1)–N(2)–Si(4)	119.7(14)
O(1)–La(1)–N(3)	104.8(8)	La(1)–N(3)–Si(5)	116.1(8)
N(1)–La(1)–N(2)	109.2(9)	La(1)–N(3)–Si(6)	124.1(14)
N(1)–La(1)–N(3)	116.4(6)	Si(1)–N(1)–Si(2)	119.6(13)
N(2)–La(1)–N(3)	112.7(8)	Si(3)–N(2)–Si(4)	120.9(16)
La(1)–N(1)–Si(1)	123.7(12)	Si(5)–N(3)–Si(6)	119.8(15)
La(1)–N(1)–Si(2)	116.6(14)	La(1)–O(1)–P(1)	174.6(9)

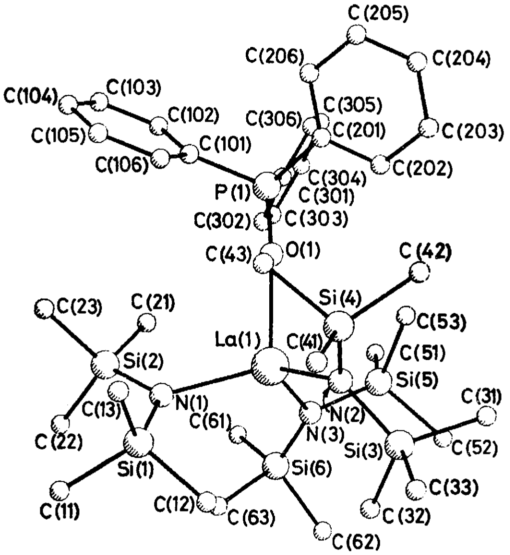


FIGURE 1 One molecule of $[La\{N(SiMe_3)_2\}_2(PPh_3O)]$ showing atomic-numbering scheme

TABLE 4

Least-squares planes for portions of the molecule $[La\{N(SiMe_3)_2\}_3(PPh_3O)]$. The equation of each plane is given in direct space by $PX + QY + RZ = S$. Deviations (Å) of relevant atoms from the planes are given in square brackets

	P	*Q*	*R*	*S*
Plane (1): N(1), Si(1), Si(2)	−1.535	7.707	4.563	3.314
[La 0.115]				
Plane (2): N(2), Si(3), Si(4)	−7.449	−9.585	8.962	−4.165
[La −0.162]				
Plane (3): N(3), Si(5), Si(6)	14.859	−9.888	6.658	0.613
[La −0.064]				
Plane (4): O, La, N(1)	7.466	−1.517	10.395	2.720
Plane (5): O, La, N(2)	12.685	1.582	−9.094	2.324
Plane (6): O, La, N(3)	18.898	−0.017	1.721	4.773
Plane (7): Ring (1) C(101)–C(106)	4.957	9.333	0.623	8.148
[P(1) −0.075]				
Plane (8): Ring (2) C(201)–C(206)	−1.860	−8.055	12.094	−3.897
[P(1) −0.044]				
Plane (9): Ring (3) C(301)–C(306)	18.891	−5.174	−0.716	0.468
[P(1) −0.077]				
Plane (10): N(1), N(2), N(3)	−5.466	12.467	−4.531	2.408

Angles (°) between planes

(1)–(10)	43.9	(2)–(10)	48.6	(3)–(10)	39.2
(7)–(10)	38.3	(8)–(10)	60.0	(9)–(10)	60.4
(4)–(5)	63.9	(4)–(6)	55.6	(5)–(6)	60.5

In order that a better analysis might be made of these contacts, the positions of the phenyl hydrogen atoms were calculated, each at a distance of 1.08 Å from the relevant carbon atom, and given the same atom number as that carbon atom (see SUP 22010). From the data in Table 5 it can be seen that the phosphine oxide molecule is quite crowded by methyl groups from the silylamido-ligands, with close contacts involving the oxygen atom and the phenyl rings. The Me–Me contacts in the base of the molecule are also fairly short, ⩾3.8 Å.

Bond lengths in the co-ordination sphere seem to be unexceptional. The La–N distances of 2.38—2.41 Å are close to the value (2.37 Å) extrapolated on the basis of comparing ionic radii (from the Eu–N distance [2.259 Å] in [Eu{N(SiMe$_3$)$_2$}$_3$]).[2] Similarly, the La–O distance (2.40 Å) compares well with the Nd–O distances (2.399, 2.433 Å) in [Nd(tfta)$_3$(PPh$_3$O)$_2$] [tfta = trifluoro(thenoyl)acetonate][9] and the mean Pr–O distance (2.354 Å) in [PrCl$_3${P(NMe$_2$)$_3$O}$_3$],[10] and this indicates that, in spite of the molecular crowding, the La–O bond is not lengthened. The P–O distance in the ligand also appears to be normal.

TABLE 5

Non-bonded contacts (Å) less than van der Waals radii for [La{N(SiMe$_3$)$_2$}$_3$(PPh$_3$O)]. van der Waals radii used: Me 2.0, H 1.2, N 1.5, O 1.4 Å

(*a*) Intramolecular			
(*i*) Silylamide–silylamide			
N(3) · · · C(32)	3.47	C(12) · · · C(32)	3.78
C(13) · · · C(43)	3.86	C(21) · · · C(32)	3.78
C(22) · · · C(63)	3.86	C(31) · · · C(52)	3.96
C(31) · · · C(53)	3.85	C(32) · · · C(52)	3.88
(*ii*) Silylamide–phosphine oxide			
O · · · C(21)	3.35	O · · · C(43)	3.26
O · · · C(53)	3.36	C(21) · · · H(302)	2.83
C(43) · · · H(106)	2.69	C(53) · · · H(202)	2.66
(*b*) Intermolecular			
H(205) · · · C(51$^{\rm I}$)	2.97	H(305) · · · C(32$^{\rm II}$)	3.06
H(103) · · · C(11$^{\rm II}$)	3.20	C(13) · · · H(303$^{\rm III}$)	2.87
C(41) · · · C(51$^{\rm III}$)	3.71	H(204) · · · C(42$^{\rm IV}$)	2.86
C(42) · · · C(33$^{\rm V}$)	3.96	C(11) · · · H(105$^{\rm VI}$)	2.99
C(23) · · · C(13$^{\rm VI}$)	3.96	H(103) · · · C(61$^{\rm VII}$)	3.17
H(104) · · · C(61$^{\rm VII}$)	3.09		

Symmetry operations generating second atom from input list:

I	$x, 1 + y, 1 + z$	V	$1 - x, 1 - y, 1 - z$
II	$x, 1 + y, z$	VI	$-x, 1 - y, 1 - z$
III	$x, y, 1 + z$	VII	$-x, 1 - y, -z$
IV	$1 - x, 2 - y, 1 - z$		

The geometries of the silylamide ligands are worthy of comment, although this cannot be detailed in view of the low accuracy of the values. The average N–Si distance is 1.72 Å and the Si–N–Si angle 120°, and these parameters imply that there is a smaller ionic component in the metal–ligand bond than in the [M{N(SiMe$_3$)$_2$}$_3$] species where N–Si is generally shorter and Si–N–Si larger. However, it is possible that the values found here are in fact affected by the steric crowding, which would favour longer bonds and closed-up angles. The intermolecular contacts (Table 5) indicate a fairly compact crystal structure although none of the distances is abnormally short. Figure 2 shows the unit-cell contents viewed down the *c* axis.

TABLE 6

Some important bond lengths (Å) and angles (°) for [La$_2${N(SiMe$_3$)$_2$}$_4$(O$_2$)(PPh$_3$O)$_2$]

La(1)–N(1)	2.37(2)	La(1)–N(2)	2.49(2)
La(1)–O(1)	2.42(2)	O(1)–P(1)	1.51(2)
La(1)–O(2)	2.33(3)	La(1)–O(2′) [a]	2.34(2)
N(1)–Si(1)	1.73(3)	N(1)–Si(2)	1.72(2)
N(2)–Si(3)	1.69(3)	N(2)–Si(4)	1.66(3)
La(1) · · · La(1′)	4.36(1)		
(*b*) Angles			
N(1)–La(1)–N(2)	119.8(11)	N(1)–La(1)–M [b]	109.4(7)
N(1)–La(1)–O(1)	92.1(8)	N(2)–La(1)–M	115.4(8)
N(1)–La(1)–O(2)	124.4(7)	O(1)–La(1)–M	107.0(7)
N(1)–La(1)–O(2′)	103.8(8)	La(1)–N(1)–Si(1)	114.4(9)
N(2)–La(1)–O(1)	111.2(7)	La(1)–N(1)–Si(2)	122.9(17)
N(2)–La(1)–O(2)	111.9(10)	La(1)–N(2)–Si(3)	118.1(15)
N(2)–La(1)–O(2′)	104.4(8)	La(1)–N(2)–Si(4)	115.3(8)
O(1)–La(1)–O(2)	87.4(9)	Si(1)–N(1)–Si(2)	122.5(14)
O(1)–La(1)–O(2′)	126.3(10)	Si(3)–N(2)–Si(4)	126.0(18)
O(2)–La(1)–O(2′)	41.5(10)	La(1)–O(1)–P(1)	172.6(14)
		La(1)–O(2)–La(1′)	138.5(14)

[a] Primed atoms are related to unprimed atoms by $\bar{x}$, $\bar{y}$, $\bar{z}$.
[b] M = Origin, which is the midpoint of the peroxide group.

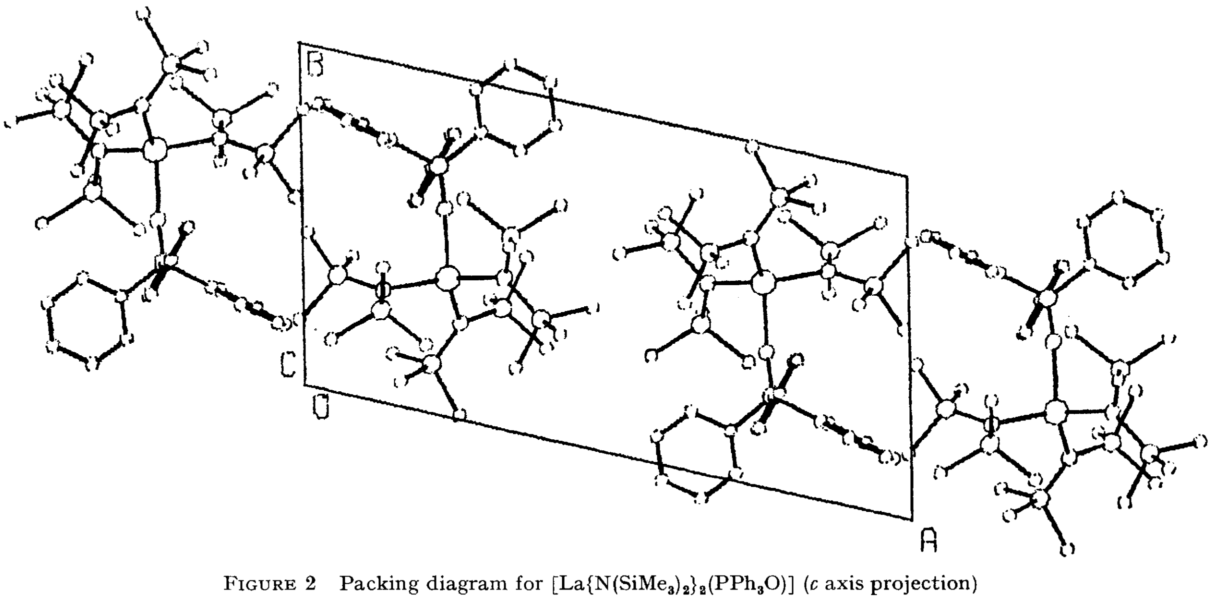


FIGURE 2 Packing diagram for [La{N(SiMe$_3$)$_2$}$_3$(PPh$_3$O)] (*c* axis projection)

(*b*) [La$_2${N(SiMe$_3$)$_2$}$_4$(O$_2$)(PPh$_3$O)$_2$].—Important bond

---

[9] J. G. Leipoldt, L. D. C. Bok, A. E. Laubscher, and S. S. Basson, *J. Inorg. Nuclear Chem.*, 1975, **37**, 2477.

[10] L. D. Radonovich and M. D. Glick, *J. Inorg. Nuclear Chem.*, 1973, **35**, 2745.

lengths and angles for this complex, computed from the data in Table 2, are given in Table 6. The complex exists as centrosymmetric dimeric molecules which comprise a peroxo-group sandwiched between two La$\{N(SiMe_3)_2\}_2(PPh_3O)$ units, as shown in Figures 3 and 4. The lanthanum co-ordination polyhedron is irregular, but if the peroxo-unit is considered to occupy one co-ordination site for each metal ion then the geometry approximates to tetrahedral. This is clearly seen from the angles at lanthanum formed by the two nitrogen atoms, the phosphine oxygen, and the midpoint of the O_2 group (see Table 6). The N(1)–La–N(2) angle (119.8°) is a little larger than corresponding angles in the adduct and is consistent with the idea that this molecule is not as crowded as the adduct molecule. Indeed, the list of intramolecular short contacts (Table 7) is much shorter than for the adduct. In this context, it is very difficult to rationalise the difference between the two independent La–N bond lengths and in particular the La–N(2) value (2.49 Å). However, within the fairly large standard deviations, the difference cannot be considered too significant. The La–N(1) and La–O(PPh_3O) distances are very close to the corresponding values in the adduct. Similarly there does seem to be some disparity between the N–Si distances, but again these are within the limits of experimental error. However, consideration of average values does suggest a tendency to slightly short N–Si bonds and slightly wider Si–N–Si angles than in the crowded adduct, and

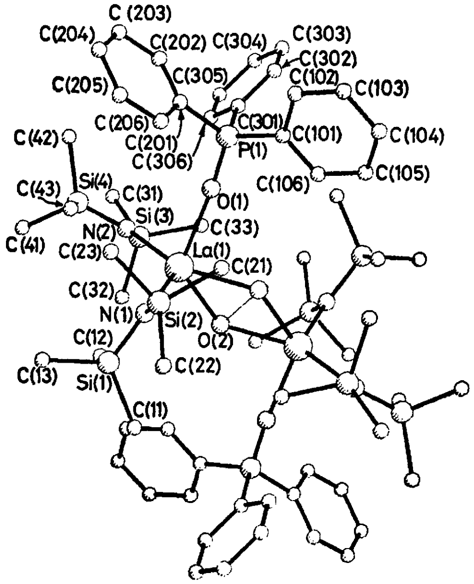


FIGURE 3 One molecule of $[La_2\{N(SiMe_3)_2\}_4(O_2)(PPh_3O)_2]$ showing atomic-numbering scheme

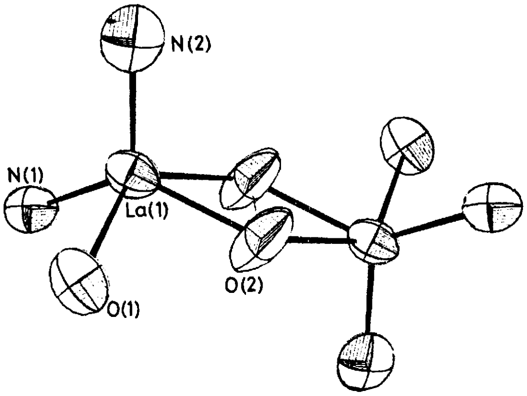


FIGURE 4 Central core of the peroxide molecule (thermal ellipsoids drawn to enclose 50% probabilities)

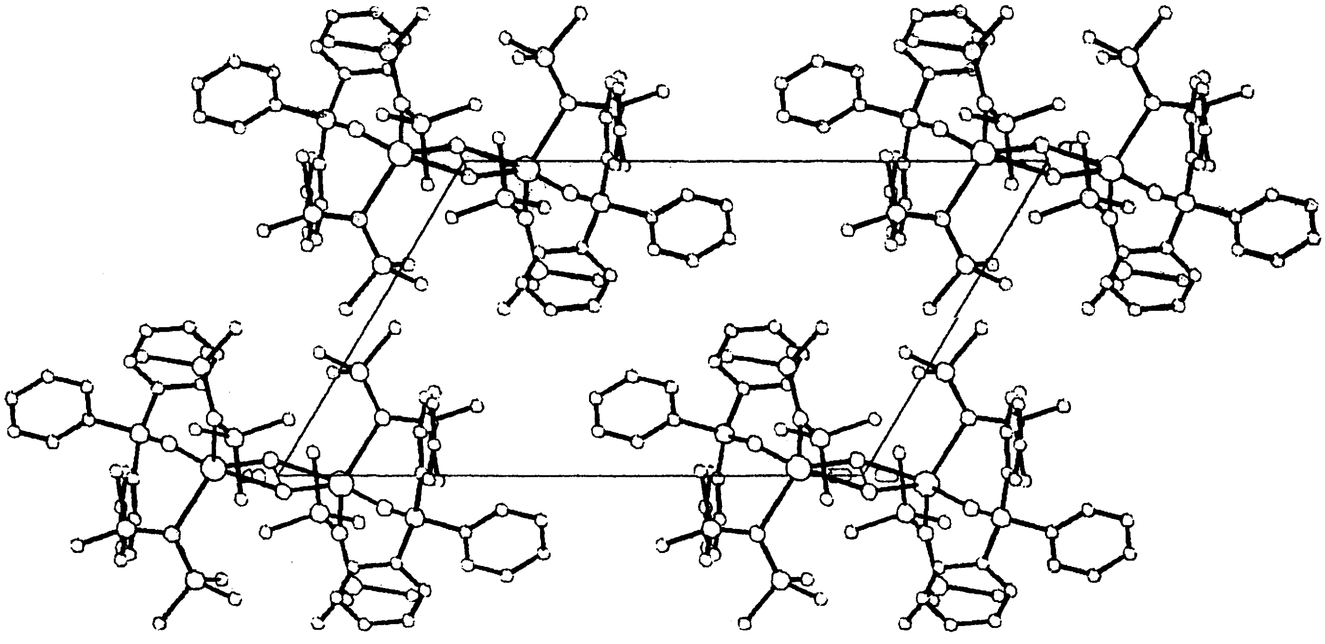


FIGURE 5 Packing diagram for $[La_2\{N(SiMe_3)_2\}_4(O_2)(PPh_3O)_2]$ (*c* axis projection)

this is more in keeping with the situation occurring in the parent $[M\{N(SiMe_3)_2\}_3]$ species.[2]

TABLE 7

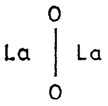
Non-bonded contacts (Å) less than van der Waals radii sums for $[La_2\{N(SiMe_3)_2\}_4(O_2)(PPh_3O)_2]$

(*a*) Intramolecular			
(*i*) Silylamide–silylamide			
C(12) · · · C(32)	3.72	C(23) · · · C(43)	3.76
(*ii*) Silylamide–phosphine oxide			
C(21) · · · H(306)	3.12	C(23) · · · H(206)	3.12
C(42) · · · H(306)	3.14	C(43) · · · H(306)	3.14
C(32) · · · H(105)	3.13		
[H(105) at $-x, -y, -z$]			
(*b*) Intermolecular			
H(104) · · · $C(42^{I})$	3.05	C(13) · · · $H(302^{II})$	3.14
C(23) · · · $H(205^{III})$	2.90	H(203) · · · $C(42^{IV})$	3.19
C(41) · · · $C(42^{V})$	3.84	C(204) · · · $H(103^{VI})$	3.01
C(205) · · · $H(103^{VI})$	2.71		

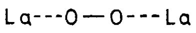
Symmetry operations generating second atom from input list:

I	$1 + x, y, z$	IV	$-x, 1 - y, -z$
II	$x, y, 1 + z$	V	$-1 - x, -y, -z$
III	$1 - x, 1 - y, 1 - z$	VI	$1 - x, 1 - y, -z$

The peroxo-group is in a previously unreported situation, acting as a symmetrical doubly bidentate bridge between the two lanthanum atoms, with the LaO_2La atoms planar by symmetry. Assuming purely electrostatic interactions and point charges, and neglecting polarisability and compressibility, the observed system (A) would be more stable than a linear system (B) by *ca.* 1 200 kJ mol^{-1} and its occurrence is thus not surprising. Where the doubly unidentate M–O–O–M peroxo-systems prevail, as in complexes of first- and second-row transition metals,[11] there is probably a considerable degree of localised covalent bonding. The O–O distance in the peroxo-group is longer than one might expect, even for an $[O_2]^{2-}$ system. The value of 1.65 Å does agree with values found in some dioxygen complexes of iridium,[12] but recent work [13] has shown that these abnormally long bonds are probably due to crystal decomposition and it is quite possible that the same explanation is valid here.



(A)



(B)

The list of close intermolecular contacts (Table 7) shows no abnormal values. A view of the unit-cell contents is given in Figure 5.

We thank the S.R.C. for support.

[6/1719 *Received*, 9*th September*, 1976]

---

[11] W. P. Schaefer, *Inorg. Chem.*, 1968, **7**, 725; L. A. Lindblom, W. P. Schaefer, and R. E. Marsh, *Acta Cryst.*, 1971, **B27**, 1461; J. R. Fritch, G. C. Christopher, and W. P. Schaefer, *Inorg. Chem.*, 1973, **12**, 2170; T. Shibahara, S. Kodas, and M. Mori, *Bull. Chem. Soc. Japan*, 1973, **46**, 2070; F. R. Fronczek, W. P. Schaefer, and R. E. Marsh, *Acta Cryst.*, 1974, **B30**, 117.

[12] J. A. McGinnety, N. C. Payne, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1969, **91**, 6301; J. A. McGinnety and J. A. Ibers, *Chem. Comm.*, 1968, 235.

[13] M. Laing, M. J. Nolte, and E. Singleton, *J.C.S. Chem. Comm.*, 1975, 660; *J. Amer. Chem. Soc.*, 1975, **97**, 6396.