Alkali-metal Complexes with Tris(2-diphenylphosphorylethyl)amine. Crystal Structures of $[Li_2\{N(CH_2CH_2POPh_2)_3\}_2][Li\{N(CH_2CH_2POPh_2)_3\}]_2[BPh_4]_4$ and $[Na\{N(CH_2CH_2POPh_2)_3\}(H_2O)(BuOH)]BPh_4$†

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By oxidation of $N(CH_2CH_2PPh_2)_3$ with H_2O_2 the ligand $N(CH_2CH_2POPh_2)_3{\cdot}3H_2O$ was synthesized. In CH_2Cl_2 with $MBPh_4$ in butanol, where M = Li or Na, the new ligand gives complexes of formula $[Li_2\{N(CH_2CH_2POPh_2)_3\}_2][Li\{N(CH_2CH_2POPh_2)_3\}]_2[BPh_4]_4$, (**1**), and $[Na\{N(CH_2CH_2POPh_2)_3\}(H_2O)(BuOH)]BPh_4$, (**2**). The crystal structures of these compounds have been determined from counter diffraction data: (**1**), triclinic, space group $P\bar{1}$, $a = 19.958(11)$, $b = 17.767(9)$, $c = 17.880(9)$ Å, $\alpha = 87.63(8)$, $\beta = 64.38(8)$, $\gamma = 86.25(8)°$, and $Z = 1$; (**2**), triclinic, space group $P\bar{1}$, $a = 16.958(9)$, $b = 14.341(8)$, $c = 14.200(8)$ Å, $\alpha = 97.39(8)$, $\beta = 109.43(9)$, $\gamma = 94.78(8)°$, and $Z = 2$. The structure of (**1**) consists of two distinct complex cations, in which the lithium atom exhibits different environments, tetrahedral and trigonal respectively. In (**2**) the sodium atom is surrounded in a tetrahedral fashion by two oxygen atoms of the phosphine ligand, and by the oxygen atoms of one water and one butanol molecule.

In the last few years the tripod-like tri(tertiary phosphine) ligand tris(2-diphenylphosphinoethyl)amine, $N(CH_2CH_2PPh_2)_3$, has been found to exhibit interesting characteristics. First, owing to its high geometrical flexibility, it appears able to form metal complexes with different co-ordination numbers (from four to six), and varied geometries (trigonal pyramidal, tetrahedral, square planar, trigonal bipyramidal, octahedral). Secondly, it has shown a very large chemical versatility and the moiety $M\{N(CH_2CH_2PPh_2)_3\}$, M = transition metal, has been found capable of activating several small molecules of general interest and of stabilizing groups which are otherwise very reactive.[1]

Recently, by oxidation of $N(CH_2CH_2PPh_2)_3$ with H_2O_2, we have synthesized the ligand $N(CH_2CH_2POPh_2)_3$, which has the same skeleton but phosphine oxide groups instead of the phosphine ones. We have tested its donor capacity and steric properties with a special class of metal cations, *i.e.* the alkali metals.

Owing to the very weak co-ordinating ability of alkali-metal cations, generally attributed to their relatively large size and low charge, the synthesis of novel complexes is always of great interest. Indeed the ligands able to complex Groups 1 and 2 elements are macrocycles or acyclic polyethers, and are few in number.[2] As regards phosphine ligands, while those acting in an unidentate manner are known to form stable solid adducts,[3] the chelating abilities of the polydentate ones have been little investigated.

Now, by treating $N(CH_2CH_2POPh_2)_3{\cdot}3H_2O$ with $MBPh_4$, M = Li or Na, we have prepared the complexes of formula $[Li_2\{N(CH_2CH_2POPh_2)_3\}_2][Li\{N(CH_2CH_2POPh_2)_3\}]_2[BPh_4]_4$, (1), and $[Na\{N(CH_2CH_2POPh_2)_3\}(H_2O)(BuOH)]BPh_4$, (2), respectively. These compounds were characterized by the usual physical methods and by complete *X*-ray crystal structure determinations.

Experimental

The reactions were carried out in the air. The compound $N(CH_2CH_2PPh_2)_3$ was prepared by a previously described method.[4] The i.r. spectra were recorded on a Perkin-Elmer 283 spectrophotometer, $^{31}P-\{^1H\}$ n.m.r. spectra on a Varian CFT-20 instrument; downfield shifts have positive values.

Preparation of Tris(2-diphenylphosphorylethyl)amine, $N(CH_2CH_2POPh_2)_3{\cdot}3H_2O$.—An excess of hydrogen peroxide was added dropwise and with vigorous stirring to a solution of $N(CH_2CH_2PPh_2)_3$ (3.26 g, 5 mmol) in acetone (100 cm^3), at room temperature. The resulting solution was heated at 50 °C for 2 h with vigorous stirring. **CAUTION**: Care must be used in the temperature control since overheating can cause dangerous explosions; in any case the use of a Teflon beaker and a screen are recommended. The remaining solution was cooled and water (100 cm^3) was added. Colourless crystals immediately crystallized from the solution. They were filtered off, washed with water, ethanol, and light petroleum (b.p. 40—70 °C), recrystallized from methylene chloride and ligroin (b.p. 75—120 °C), and gently dried *in vacuo*. Yield 90% (Found: C, 65.45; H, 6.05; N, 1.90. Calc. for $C_{42}H_{48}NO_6P_3$: C, 66.75; H, 6.40; N, 1.85%). I.r.: 3 500—3 200, 1 660 [$\nu(H_2O)$]; 1 180, 1 150, and 560 cm^{-1} [ν(P=O)]. $^{31}P-\{^1H\}$ N.m.r. (CD_2Cl_2): 31.66 p.p.m.

Preparation of $[Li_2\{N(CH_2CH_2POPh_2)_3\}_2][Li\{N(CH_2CH_2POPh_2)_3\}]_2[BPh_4]_4$, (**1**).—A solution of $LiBPh_4$ (0.33 g, 1 mmol) in butanol (20 cm^3) was added to a solution of $N(CH_2CH_2POPh_2)_3{\cdot}3H_2O$ (0.76 g, 1 mmol) in CH_2Cl_2 (30 cm^3) at room temperature. Evaporation of the solvent yielded colourless crystals. They were filtered off, washed with butanol, and light petroleum, and dried *in vacuo*. Yield 80% (Found: C, 77.05; H, 6.05; Li, 0.65; N, 1.35. Calc. for $C_{66}H_{62}BLiNO_3P_3$: C, 77.1; H, 6.10; Li, 0.65; N, 1.35%). I.r.: 1 210—1 150 and 560 cm^{-1} [ν(P=O)]. $^{31}P-\{^1H\}$ N.m.r. (CD_2Cl_2): 37.70 p.p.m.

The *complex* $[Na\{N(CH_2CH_2POPh_2)_3\}(H_2O)(BuOH)]BPh_4$, (**2**), was prepared by an analogous procedure. Yield 80% (Found: C, 74.7; H, 7.00; N, 1.25. Calc. for $C_{70}H_{74}BNNaO_5P_3$: C, 74.0; H, 6.55; N, 1.25%). I.r.: 3 400, 1 670 [$\nu(H_2O)$]; 1 200—1 150 and 560 cm^{-1} [ν(P=O)]. $^{31}P-\{^1H\}$ N.m.r. (CD_2Cl_2): 37.72 p.p.m.

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† Bis{[tris(2-diphenylphosphorylethyl)amine-μ-*O,O′O″*]lithium}-[tris(2-diphenylphosphorylethyl)amine-*OO′O″*]lithium(1/2) tetrakis-(tetraphenylborate) and aqua(butanol)[tris(2-diphenylphosphorylethyl)amine-*OO′*]sodium tetraphenylborate.

Supplementary data available (No. SUP 56583, 9 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Crystal data and data-collection details *

	Compound (**1**)	Compound (**2**)
Formula	$C_{264}H_{248}B_4Li_4N_4O_{12}P_{12}$	$C_{70}H_{74}BNNaO_5P_3$
M	4 111.62	1 136.90
a/Å	19.958(11)	16.958(9)
b/Å	17.767(9)	14.341(8)
c/Å	17.880(9)	14.200(8)
α/°	87.63(8)	97.39(8)
β/°	64.38(8)	109.43(9)
γ/°	86.25(8)	94.78(8)
U/Å^3	5 703.9	3 200.1
Z	1	2
D_c/g cm^{-3}	1.197	1.179
F(000)	2 168	1 198
Colour	White	Orange
Habit	Parallelepiped	Irregular prism
Dimensions/mm	0.375 × 0.350 × 0.075	0.50 × 0.50 × 0.29
μ(Mo-K_α)/cm^{-1}	1.45	1.43
Scan speed/° s^{-1}	0.07	0.10
Scan width/°	0.70 + 0.3 tanθ	0.80
Max. standard deviation/%	5	3
Total data measured	10 618	8 360
Data [$I \geqslant 3\sigma(I)$] used in refinement	3 533	4 298
Variables	438	256

* Common to both compounds: space group, $P\bar{1}$; diffractometer, Philips PW 1 100; Mo-K_α radiation, λ = 0.7107 Å; graphite-crystal monochromater; ω–2θ scan technique; background time, half the scan time; standards, 3 every 120 readings; 2θ range, 5—40°; data collected, $\pm h$, $\pm k$, $+l$.

X-Ray Crystallography.—Collection and reduction of intensity data. For compound (**1**) a well formed crystal, delimited by the faces of 001, 101, and $\bar{1}$10 and the centrosymmetric ones, was selected and mounted along its crystallographic b axis on a Philips PW 1100 automatic diffractometer. For compound (**2**) a crystal delimited by the faces 100, 001, 010, and $\bar{1}$01 and the centrosymmetric ones was mounted along its crystallographic b axis on the same diffractometer. The crystals of both compounds belong to the triclinic system $P\bar{1}$. The cell dimensions were determined by least-squares refinement of the angular settings of 20 and 22 carefully centred reflections for compounds (**1**) and (**2**) respectively. Details of the crystal data and data collections are given in Table 1. Intensities were rescaled and, after correction for backgrounds, the standard deviations of the intensities, $\sigma(I)$, were calculated as described elsewhere, by using the value of 0.03 for the instability factor k for both compounds.[5] Intensity data were corrected for Lorentz-polarization effects. An absorption correction [μ = 1.45 and 1.43 cm^{-1} for (**1**) and (**2**) respectively] was considered unnecessary since a survey of the transmission factors indicated a maximum variation of 2% for both compounds.

Solution and refinement of the structures. All the calculations were performed by using the SHELX 76,[6] MULTAN 80,[7] and ORTEP[8] crystallographic programs on a SEL32/77 computer. Atomic scattering factors for the non-hydrogen atoms were taken from ref. 9 and those for hydrogen atoms from ref. 10. Both $\Delta f'$ and $\Delta f''$ components of the anomalous dispersion were included for all non-hydrogen atoms.[11] Both structures were solved by direct methods, by using MULTAN 80 and SHELX 76 for (**1**) and (**2**) respectively. All the non-hydrogen atoms were located

Table 2. Fractional positional parameters (× 10^4) for compound (**1**)

Atom	x	y	z
Li(1)	323(16)	301(18)	509(19)
Li(2)	4 801(32)	4 501(37)	3 707(37)
P(1)	−657(3)	371(4)	2 531(4)
P(2)	476(3)	−1 506(4)	333(3)
P(3)	1 829(3)	916(3)	403(3)
P(4)	4 392(3)	6 158(4)	3 347(4)
P(5)	3 403(3)	3 766(4)	4 816(4)
P(6)	5 914(3)	3 801(4)	2 294(4)
O(1)	−302(6)	519(7)	1 630(7)
O(2)	298(5)	−708(7)	118(7)
O(3)	1 333(6)	600(7)	67(7)
O(4)	4 857(7)	5 541(8)	3 547(8)
O(5)	3 987(7)	4 287(8)	4 716(7)
O(6)	5 450(7)	3 724(7)	3 190(7)
N(1)	966(8)	−619(8)	1 726(9)
N(2)	4 095(8)	4 426(10)	2 809(9)
C(1)	516(9)	−494(10)	2 621(10)
C(2)	−316(9)	−473(10)	2 868(11)
C(3)	1 036(10)	−1 425(11)	1 564(11)
C(4)	1 232(9)	−1 609(11)	659(10)
C(5)	1 707(9)	−311(10)	1 467(11)
C(6)	1 679(9)	550(10)	1 413(10)
C(7)	3 910(10)	5 174(11)	2 505(11)
C(8)	3 641(10)	5 786(11)	3 159(11)
C(9)	3 421(11)	4 014(13)	3 261(13)
C(10)	3 500(11)	3 429(11)	3 832(11)
C(11)	4 645(10)	4 007(12)	2 077(12)
C(12)	5 438(10)	4 327(11)	1 748(11)
C(1,1)	−538(7)	1 122(10)	3 086(7)
C(2,1)	−250(7)	1 792(10)	2 670(7)
C(3,1)	−195(7)	2 396(10)	3 110(7)
C(4,1)	−428(7)	2 332(10)	3 966(7)
C(5,1)	−717(7)	1 662(10)	4 381(7)
C(6,1)	−772(7)	1 057(10)	3 941(7)
C(1,2)	−1 647(9)	309(7)	2 921(9)
C(2,2)	−2 127(9)	212(7)	3 758(9)
C(6,8)	3 298(8)	7 299(10)	4 250(14)
C(1,9)	2 512(12)	4 274(8)	5 294(10)
C(2,9)	1 830(12)	3 946(8)	5 547(10)
C(3,9)	1 170(12)	4 393(8)	5 877(10)
C(4,9)	1 191(12)	5 168(8)	5 954(10)
C(5,9)	1 872(12)	5 496(8)	5 701(10)
C(6,9)	2 533(12)	5 050(8)	5 371(10)
C(1,10)	3 439(7)	2 974(12)	5 446(8)
C(2,10)	3 318(7)	2 240(12)	5 303(8)
C(3,10)	3 400(7)	1 644(12)	5 795(8)
C(4,10)	3 603(7)	1 782(12)	6 429(8)
C(5,10)	3 724(7)	2 516(12)	6 572(8)
C(6,10)	3 642(7)	3 112(12)	6 080(8)
C(1,11)	6 201(6)	2 897(7)	1 811(8)
C(2,11)	6 628(6)	2 846(7)	956(8)
C(3,11)	6 768(6)	2 148(7)	571(8)
C(4,11)	6 482(6)	1 501(7)	1 042(8)
C(5,11)	6 055(6)	1 552(7)	1 897(8)
C(6,11)	5 915(6)	2 250(7)	2 281(8)
C(1,12)	6 716(8)	4 356(8)	2 064(7)
C(2,12)	6 871(8)	4 510(8)	2 730(7)
C(3,12)	7 467(8)	4 949(8)	2 606(7)
C(4,12)	7 906(8)	5 232(8)	1 816(7)
C(5,12)	7 751(8)	5 078(8)	1 150(7)
C(6,12)	7 155(8)	4 640(8)	1 274(7)
C(1,13)	1 285(7)	6 144(8)	2 819(7)
C(2,13)	738(7)	6 643(8)	2 767(7)
C(3,13)	468(7)	7 261(8)	3 291(7)
C(4,13)	746(7)	7 380(8)	3 869(7)
C(5,13)	1 294(7)	6 880(8)	3 922(7)
C(6,13)	1 563(7)	6 262(8)	3 397(7)
C(1,14)	1 438(6)	4 631(9)	2 915(6)
C(2,14)	1 901(6)	3 976(9)	2 728(6)
C(3,14)	1 722(6)	3 367(9)	3 286(6)
C(4,14)	1 079(6)	3 414(9)	4 031(6)
C(5,14)	615(6)	4 069(9)	4 218(6)

Table 2 (*continued*)

Atom	x	y	z
C(3,2)	−2 895(9)	265(7)	4 016(9)
C(4,2)	−3 184(9)	416(7)	3 437(9)
C(5,2)	−2 704(9)	513(7)	2 601(9)
C(6,2)	−1 936(9)	460(7)	2 343(9)
C(1,3)	804(7)	−2 124(7)	−545(9)
C(2,3)	1 550(7)	−2 151(7)	−1 118(9)
C(3,3)	1 800(7)	−2 637(7)	−1 789(9)
C(4,3)	1 304(7)	−3 097(7)	−1 887(9)
C(5,3)	558(7)	−3 071(7)	−1 314(9)
C(6,3)	308(7)	−2 584(7)	−643(9)
C(1,4)	−318(8)	−1 899(6)	1 156(8)
C(2,4)	−966(8)	−1 436(6)	1 507(8)
C(3,4)	−1 593(8)	−1 701(6)	2 174(8)
C(4,4)	−1 571(8)	−2 429(6)	2 489(8)
C(5,4)	−922(8)	−2 892(6)	2 138(8)
C(6,4)	−296(8)	−2 627(6)	1 471(8)
C(1,5)	2 806(8)	731(7)	−290(6)
C(2,5)	3 357(8)	707(7)	−7(6)
C(3,5)	4 104(8)	601(7)	−566(6)
C(4,5)	4 299(8)	521(7)	−1 409(6)
C(5,5)	3 748(8)	545(7)	−1 692(6)
C(6,5)	3 001(8)	650(7)	−1 133(6)
C(1,6)	1 720(6)	1 931(8)	486(7)
C(2,6)	1 749(6)	2 324(8)	−219(7)
C(3,6)	1 641(6)	3 108(8)	−206(7)
C(4,6)	1 504(6)	3 499(8)	511(7)
C(5,6)	1 474(6)	3 106(8)	1 215(7)
C(6,6)	1 582(6)	2 322(8)	1 203(7)
C(1,7)	4 944(9)	6 663(7)	2 442(10)
C(2,7)	5 697(9)	6 437(7)	2 047(10)
C(3,7)	6 164(9)	6 797(7)	1 315(10)
C(4,7)	5 878(9)	7 384(7)	978(10)
C(5,7)	5 125(9)	7 611(7)	1 372(10)
C(6,7)	4 658(9)	7 250(7)	2 104(10)
C(1,8)	3 911(8)	6 837(10)	4 190(14)
C(2,8)	4 134(8)	6 816(10)	4 831(14)
C(3,8)	3 743(8)	7 256(10)	5 532(14)
C(4,8)	3 129(8)	7 718(10)	5 591(14)
C(5,8)	2 907(8)	7 739(10)	4 950(14)
C(6,14)	794(6)	4 677(9)	3 660(6)
C(1,15)	1 112(6)	5 318(7)	1 668(9)
C(2,15)	1 341(6)	5 729(7)	925(9)
C(3,15)	902(6)	5 777(7)	491(9)
C(4,15)	234(6)	5 413(7)	801(9)
C(5,15)	5(6)	5 001(7)	1 544(9)
C(6,15)	445(6)	4 954(7)	1 978(9)
C(1,16)	2 517(7)	5 437(6)	1 543(7)
C(2,16)	2 886(7)	4 831(6)	1 025(7)
C(3,16)	3 632(7)	4 872(6)	463(7)
C(4,16)	4 009(7)	5 518(6)	419(7)
C(5,16)	3 640(7)	6 124(6)	936(7)
C(6,16)	2 894(7)	6 084(6)	1 498(7)
C(1,17)	3 544(5)	1 100(8)	2 257(7)
C(2,17)	3 020(5)	1 633(8)	2 203(7)
C(3,17)	3 253(5)	2 240(8)	1 646(7)
C(4,17)	4 009(5)	2 315(8)	1 144(7)
C(5,17)	4 533(5)	1 782(8)	1 198(7)
C(6,17)	4 300(5)	1 175(8)	1 755(7)
C(1,18)	3 198(6)	9 602(7)	2 415(8)
C(2,18)	3 621(6)	9 543(7)	1 560(8)
C(3,18)	3 608(6)	8 894(7)	1 154(8)
C(4,18)	3 171(6)	8 304(7)	1 603(8)
C(5,18)	2 748(6)	8 363(7)	2 458(8)
C(6,18)	2 762(6)	9 012(7)	2 864(8)
C(1,19)	2 411(7)	602(8)	3 682(9)
C(2,19)	2 360(7)	1 001(8)	4 362(9)
C(3,19)	1 666(7)	1 263(8)	4 955(9)
C(4,19)	1 023(7)	1 126(8)	4 868(9)
C(5,19)	1 074(7)	727(8)	4 188(9)
C(6,19)	1 768(7)	465(8)	3 595(9)
C(1,20)	3 858(6)	137(6)	3 331(7)
C(2,20)	4 012(6)	−614(6)	3 490(7)
C(3,20)	4 494(6)	−789(6)	3 859(7)
C(4,20)	4 822(6)	−213(6)	4 068(7)
C(5,20)	4 668(6)	538(6)	3 909(7)
C(6,20)	4 186(6)	713(6)	3 540(7)
B(1)	1 592(11)	5 301(12)	2 250(13)
B(2)	3 270(11)	382(12)	2 881(12)

from successive Fourier and ΔF Fourier maps. Both the. structures were refined by using least-squares techniques, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. A full-matrix least-squares refinement was carried out for the sodium compound; for the lithium derivative, owing to the high number of variables (438), the refinement was performed by least squares in two blocks. For both compounds the phenyl rings were treated as rigid bodies of D_{6h} symmetry (C–C 1.395 Å), their carbon atoms being assigned isotropic thermal factors. Hydrogen atoms, introduced in their calculated positions, were not refined. At convergence final R and R' factors, defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$, were 0.094 and 0.090 for compound (**1**), and 0.084 and 0.095 for compound (**2**) respectively. The rather high value of these indices can be justified by taking into account some disorder detected in the region of some phenyl rings of compound (**1**) and in the vicinity of the butanol in compound (**2**). Tables 2 and 3 report the final positional parameters of (**1**) and (**2**) respectively.

Discussion

The most interesting feature associated with the structure of compound (**1**) is the presence in the lattice of two distinct complex cations, in which the lithium atoms display different environments. The structure consists of dimeric complex cations $[Li_2\{N(CH_2CH_2POPh_2)_3\}_2]^{2+}$, monomeric complex cations $[Li\{N(CH_2CH_2POPh_2)_3\}]^+$, and BPh_4^- anions. Figures 1 and 2 show perspective views of the dimeric and monomeric complex cations respectively. Selected bond distances and angles are reported in Tables 4 and 5.

In the centrosymmetric dimeric cation the two lithium atoms are linked by two bridging oxygen atoms, the Li ··· Li separation being 2.91(5) Å. Each metal centre displays a distorted tetrahedral geometry, being surrounded by three oxygen atoms of one $N(CH_2CH_2POPh_2)_3$ ligand and by a fourth oxygen atom from another. The distortion from the limit geometry can be seen from the values of the O–Li–O angles [range 87.8(16)—117.6(21)°], the smallest angle at lithium being that subtended by the shared edge O(2)–O(2′). The Li–O bond distances, averaging 1.96(4) Å, appear in good agreement with values reported for *trans*-$[PtCl_2(PEt_3)\{CH(PPh_2O)_2Li\}]$ [Li–O 1.97 Å (av.)], in which two tetrahedral lithium atoms are bridged by two oxygens from phosphine oxide ligands.[12] Very similar values were also found for other tetrahedrally co-ordinated lithium-containing compounds, such as $LiCl{\cdot}C_4H_8O_2$ [1.91 Å (av.)],[13] $[LiCl(OH_2)(py)_2]$ (py = pyridine) (1.94 Å),[14] and $[Li(thf)]^+$ (thf = tetrahydrofuran) [1.92 Å (av.)].[15]

In the monomeric cation the lithium atom is trigonally co-ordinated to the three oxygen atoms of the $N(CH_2CH_2POPh_2)_3$ ligand, with the O–Li–O angles averaging 119.6°. The lithium atom is displaced from the oxygen atoms' least-squares plane by 0.11 Å. This type of co-ordination for lithium, although not unique,[16] is uncommon, since its usual co-ordination number is four. However, it is noteworthy that the value of the Li ··· N

Table 3. Fractional positional parameters (× 10^4) for compound (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Na	9 466(2)	3 591(2)	−97(2)	C(3,4)	5 640(3)	3 569(4)	−4 663(5)
P(1)	7 661(1)	1 866(2)	−1 513(2)	C(4,4)	6 161(3)	2 955(4)	−4 917(5)
P(2)	7 299(1)	5 541(2)	−2 423(2)	C(5,4)	7 034(3)	3 146(4)	−4 432(5)
P(3)	8 622(1)	4 501(2)	1 847(2)	C(6,4)	7 386(3)	3 951(4)	−3 694(5)
O(1)	8 481(3)	2 388(4)	−813(4)	C(1,5)	8 245(4)	3 453(5)	2 196(4)
O(2)	8 235(3)	5 709(4)	−2 134(4)	C(2,5)	8 349(4)	2 570(5)	1 745(4)
O(3)	9 138(3)	4 315(4)	1 188(4)	C(3,5)	8 038(4)	1 741(5)	1 995(4)
O(4)	9 448(4)	4 564(5)	−1 272(5)	C(4,5)	7 623(4)	1 794(5)	2 696(4)
O(5)	10 666(4)	2 948(5)	659(6)	C(5,5)	7 519(4)	2 676(5)	3 147(4)
N	7 271(4)	3 877(4)	−343(4)	C(6,5)	7 830(4)	3 505(5)	2 897(4)
C(1)	6 809(5)	2 566(5)	−1 876(6)	C(1,6)	9 265(4)	5 286(4)	2 983(5)
C(2)	6 597(5)	3 140(6)	−1 015(6)	C(2,6)	10 025(4)	5 005(4)	3 546(5)
C(3)	6 987(5)	5 215(6)	−1 409(6)	C(3,6)	10 580(4)	5 612(4)	4 399(5)
C(4)	7 597(5)	4 520(5)	−871(6)	C(4,6)	10 375(4)	6 499(4)	4 691(5)
C(5)	7 681(5)	5 023(6)	1 264(6)	C(5,6)	9 615(4)	6 780(4)	4 128(5)
C(6)	6 991(5)	4 349(5)	445(6)	C(6,6)	9 060(4)	6 173(4)	3 274(5)
C(7)	10 712(11)	1 972(14)	835(15)	C(1,7)	2 664(4)	1 912(4)	7 812(4)
C(8)	10 614(18)	1 976(22)	1 893(24)	C(2,7)	2 380(4)	2 340(4)	8 555(4)
C(9)	10 694(25)	1 141(28)	2 230(34)	C(3,7)	1 553(4)	2 087(4)	8 507(4)
C(10)	10 646(17)	1 348(19)	3 425(24)	C(4,7)	1 011(4)	1 405(4)	7 715(4)
B	3 632(6)	2 294(7)	7 815(7)	C(5,7)	1 295(4)	976(4)	6 972(4)
C(1,1)	7 766(3)	1 382(4)	−2 687(4)	C(6,7)	2 122(4)	1 229(4)	7 020(4)
C(2,1)	8 481(3)	1 738(4)	−2 874(4)	C(1,8)	4 008(4)	1 456(3)	7 218(4)
C(3,1)	8 595(3)	1 401(4)	−3 780(4)	C(2,8)	4 467(4)	1 696(3)	6 610(4)
C(4,1)	7 993(3)	709(4)	−4 499(4)	C(3,8)	4 819(4)	1 000(3)	6 160(4)
C(5,1)	7 278(3)	354(4)	−4 313(4)	C(4,8)	4 711(4)	65(3)	6 318(4)
C(6,1)	7 164(3)	691(4)	−3 406(4)	C(5,8)	4 252(4)	−175(3)	6 925(4)
C(1,2)	7 302(3)	903(4)	−1 009(5)	C(6,8)	3 901(4)	521(3)	7 375(4)
C(2,2)	7 920(3)	405(4)	−456(5)	C(1,9)	4 286(3)	2 606(3)	9 024(4)
C(3,2)	7 695(3)	−342(4)	−17(5)	C(2,9)	4 771(3)	1 953(3)	9 511(4)
C(4,2)	6 852(3)	−593(4)	−131(5)	C(3,9)	5 280(3)	2 198(3)	10 528(4)
C(5,2)	6 233(3)	−96(4)	−685(5)	C(4,9)	5 306(3)	3 095(3)	11 059(4)
C(6,2)	6 459(3)	652(4)	−1 124(5)	C(5.9)	4 821(3)	3 748(3)	10 572(4)
C(1,3)	6 814(4)	6 535(4)	−2 828(4)	C(6,9)	4 311(3)	3 503(3)	9 555(4)
C(2,3)	6 974(4)	6 841(4)	−3 648(4)	C(1,10)	3 543(3)	3 235(4)	7 189(4)
C(3,3)	6 668(4)	7 655(4)	−3 989(4)	C(2,10)	4 216(3)	3 958(4)	7 433(4)
C(4,3)	6 202(4)	8 163(4)	−3 508(4)	C(3,10)	4 133(3)	4 720(4)	6 904(4)
C(5,3)	6 043(4)	7 857(4)	−2 688(4)	C(4,10)	3 376(3)	4 760(4)	6 131(4)
C(6,3)	6 349(4)	7 043(4)	−2 347(4)	C(5,10)	2 702(3)	4 037(4)	5 888(4)
C(1,4)	6 865(3)	4 565(4)	−3 440(5)	C(6,10)	2 786(3)	3 275(4)	6 416(4)
C(2,4)	5 992(3)	4 374(4)	−3 924(5)				

Table 4. Selected bond distances (Å) and angles (°) for the $[Li_2\{N(CH_2CH_2POPh_2)_3\}_2]^{2+}$ cation

Li(1)–O(1)	1.89(3)	P(1)–C(2)	1.79(2)	P(2)–C(1,4)	1.79(1)	N(1)–C(3)	1.46(2)
Li(1)–O(2)	1.96(4)	P(1)–C(1,1)	1.78(2)	P(3)–O(3)	1.51(2)	N(1)–C(5)	1.48(2)
Li(1)–O(3)	1.92(3)	P(1)–C(1,2)	1.80(2)	P(3)–C(6)	1.80(2)	C(1)–C(2)	1.52(2)
Li(1)–O(2′)	2.08(4)	P(2)–O(2)	1.51(1)	P(3)–C(1,5)	1.82(1)	C(3)–C(4)	1.54(3)
Li(1) • • • N(1)	3.30(5)	P(2)–C(4)	1.83(2)	P(3)–C(1,6)	1.81(2)	C(5)–C(6)	1.53(3)
P(1)–O(1)	1.47(1)	P(2)–C(1,3)	1.80(2)	N(1)–C(1)	1.48(2)		

O(1)–Li(1)–O(2)	117.6(15)	C(2)–P(1)–C(1,1)	106.0(9)	O(3)–P(3)–C(6)	113.7(8)	C(1)–N(1)–C(3)	109.2(13)
O(1)–Li(1)–O(3)	117.6(21)	C(2)–P(1)–C(1,2)	106.7(8)	O(3)–P(3)–C(1,5)	111.2(7)	C(1)–N(1)–C(5)	109.3(16)
O(1)–Li(1)–O(2′)	103.8(14)	C(1,1)–P(1)–C(1,2)	105.1(7)	O(3)–P(3)–C(1,6)	112.7(7)	C(3)–N(1)–C(5)	110.8(13)
O(2)–Li(1)–O(3)	110.0(14)	O(2)–P(2)–C(4)	115.1(9)	C(6)–P(3)–C(1,5)	107.6(8)	N(1)–C(1)–C(2)	112.6(17)
O(2)–Li(1)–O(2′)	87.8(16)	O(2)–P(2)–C(1,3)	112.5(7)	C(6)–P(3)–C(1,6)	106.6(8)	P(1)–C(2)–C(1)	113.4(12)
O(3)–Li(1)–O(2′)	116.4(15)	O(2)–P(2)–C(1,4)	111.4(6)	C(1,5)–P(3)–C(1,6)	104.4(6)	N(1)–C(3)–C(4)	113.8(15)
O(1)–P(1)–C(2)	115.3(7)	C(4)–P(2)–C(1,3)	102.5(8)	Li(1)–O(1)–P(1)	155.7(13)	P(2)–C(4)–C(3)	117.1(11)
O(1)–P(1)–C(1,1)	111.3(7)	C(4)–P(2)–C(1,4)	106.3(8)	Li(1)–O(2)–P(2)	135.4(14)	N(1)–C(5)–C(6)	112.5(14)
O(1)–P(1)–C(1,2)	111.8(9)	C(1,3)–P(2)–C(1,4)	108.5(7)	Li(1)–O(3)–P(3)	136.7(13)	P(3)–C(6)–C(5)	113.5(13)

contact [2.57(8) Å] is significantly shorter than the sum of the van der Waals radii (3.34 Å). The fewer ligating atoms around the lithium atom in the monomer accounts for the shortening of the Li–O bond distances [1.85(2) Å (av.)] with respect to the dimer [1.96(4) Å (av.)].

Within the $N(CH_2CH_2POPh_2)_3$ ligand, both in the dimeric and in the monomeric complex, the P=O and P–C bond lengths, which appear normal respectively for double and single bonds, indicate localized bonding.

The structure of (**2**) consists of complex cations [Na-

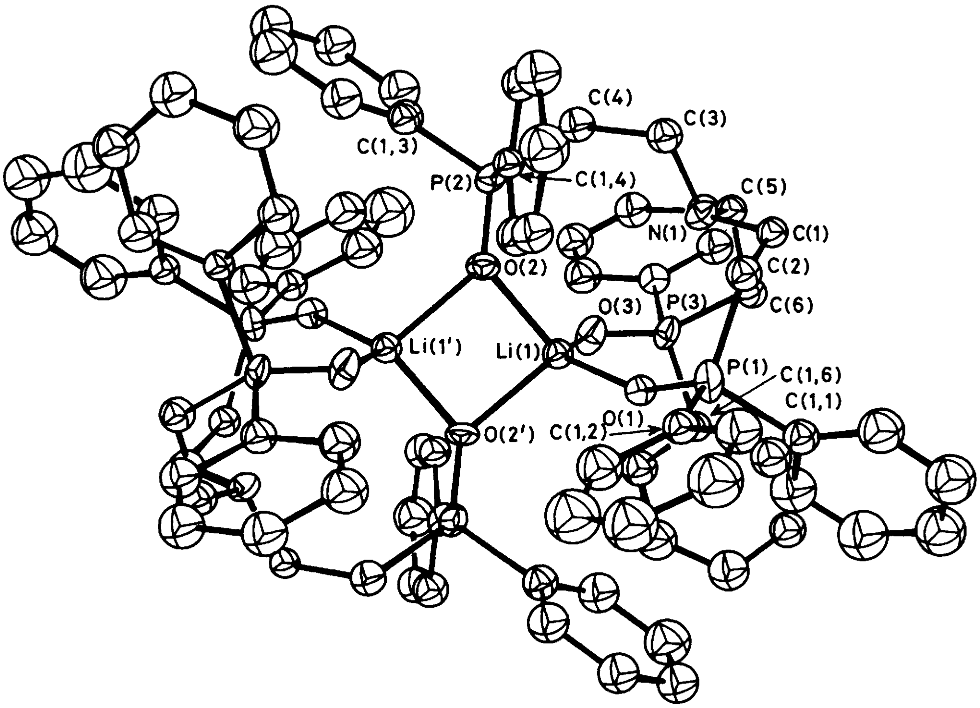

Figure 1. Perspective view of the $[Li_2\{N(CH_2CH_2POPh_2)_3\}_2]^{2+}$ cation. ORTEP drawing with 30% probability ellipsoids

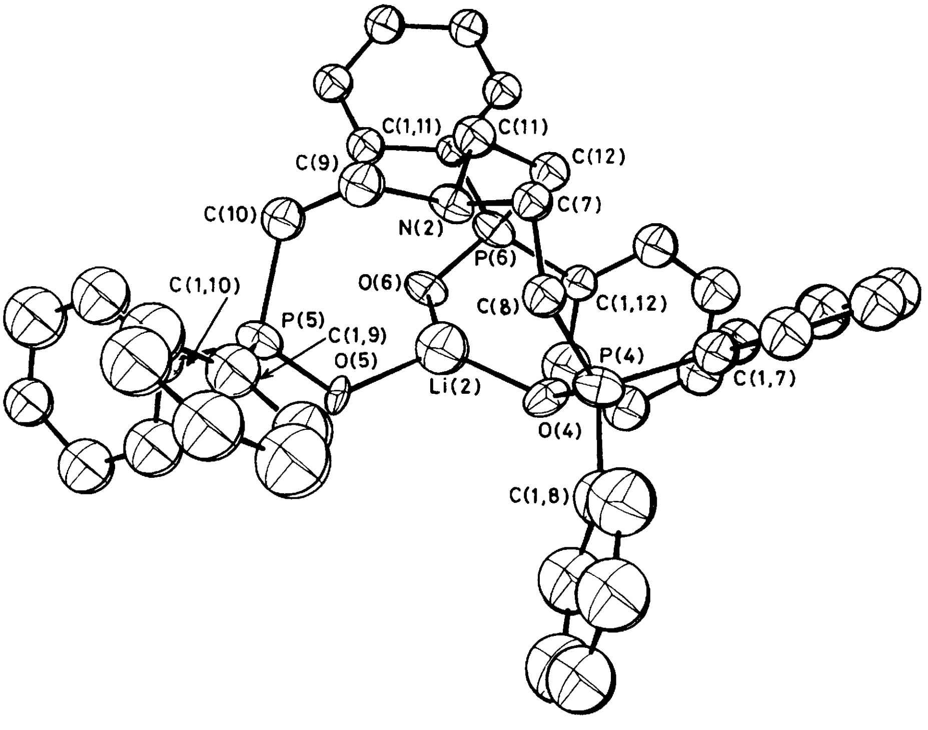

Figure 2. Perspective view of the $[Li\{N(CH_2CH_2POPh_2)_3\}]^+$ cation. ORTEP drawing with 30% probability ellipsoids

$\{N(CH_2CH_2POPh_2)_3\}(H_2O)(BuOH)]^+$ and BPh_4^- anions. Figure 3 shows a perspective view of the cation, and selected bond distances and angles are given in Table 6.

In the cation the sodium is tetrahedrally surrounded by two oxygen atoms from the phosphine oxide groups of the ligand, by a water molecule, and by a butanol molecule. The third phosphine oxide group remains unco-ordinated. The arrangement of the ligands around the sodium is only slightly distorted from regularity; the O–Na–O angles range from 105.3(2) to 119.9(3)°. The Na–O bond distances involving the phosphine ligand appear somewhat shorter than the others. It is noteworthy that the water molecule as well as the butanol ligand are

Table 5. Selected bond distances (Å) and angles (°) for the $[Li\{N(CH_2CH_2POPh_2)_3\}]^+$ cation

Li(2)–O(4)	1.86(7)	P(4)–C(1,7)	1.76(2)	P(6)–O(6)	1.47(1)	N(2)–C(9)	1.46(3)
Li(2)–O(5)	1.88(5)	P(4)–C(1,8)	1.84(2)	P(6)–C(12)	1.83(2)	N(2)–C(11)	1.48(2)
Li(2)–O(6)	1.81(6)	P(5)–O(5)	1.48(2)	P(6)–C(1,11)	1.80(1)	C(7)–C(8)	1.52(3)
Li(2) ··· N(2)	2.57(8)	P(5)–C(10)	1.81(2)	P(6)–C(1,12)	1.82(2)	C(9)–C(10)	1.48(3)
P(4)–O(4)	1.52(2)	P(5)–C(1,9)	1.80(2)	N(2)–C(7)	1.50(3)	C(11)–C(12)	1.57(3)
P(4)–C(8)	1.84(2)	P(5)–C(1,10)	1.78(2)				

O(4)–Li(2)–O(5)	109.5(30)	O(5)–P(5)–C(10)	112.2(8)	O(6)–P(6)–C(1,12)	112.2(8)	C(7)–N(2)–C(11)	107.7(14)
O(4)–Li(2)–O(6)	132.0(30)	O(5)–P(5)–C(1,9)	108.2(9)	C(12)–P(6)–C(1,11)	106.4(9)	C(9)–N(2)–C(11)	112.1(17)
O(5)–Li(2)–O(6)	117.4(35)	O(5)–P(5)–C(1,10)	110.1(9)	C(12)–P(6)–C(1,12)	102.6(8)	N(2)–C(7)–C(8)	113.6(17)
O(4)–P(4)–C(8)	112.7(9)	C(10)–P(5)–C(1,9)	107.3(10)	C(1,11)–P(6)–C(1,12)	110.6(6)	P(4)–C(8)–C(7)	113.5(13)
O(4)–P(4)–C(1,7)	110.9(8)	C(10)–P(5)–C(1,10)	108.6(9)	Li(2)–O(4)–P(4)	134.4(25)	N(2)–C(9)–C(10)	113.4(20)
O(4)–P(4)–C(1,8)	113.7(10)	C(1,9)–P(5)–C(1,10)	110.3(7)	Li(2)–O(5)–P(5)	124.8(24)	P(5)–C(10)–C(9)	115.4(15)
C(8)–P(4)–C(1,7)	106.4(10)	O(6)–P(6)–C(12)	113.2(8)	Li(2)–O(6)–P(6)	117.8(21)	N(2)–C(11)–C(12)	111.7(18)
C(8)–P(4)–C(1,8)	104.4(9)	O(6)–P(6)–C(1,11)	111.4(7)	C(7)–N(2)–C(9)	110.5(16)	P(6)–C(12)–C(11)	106.4(13)
C(1,7)–P(4)–C(1,8)	108.2(8)						

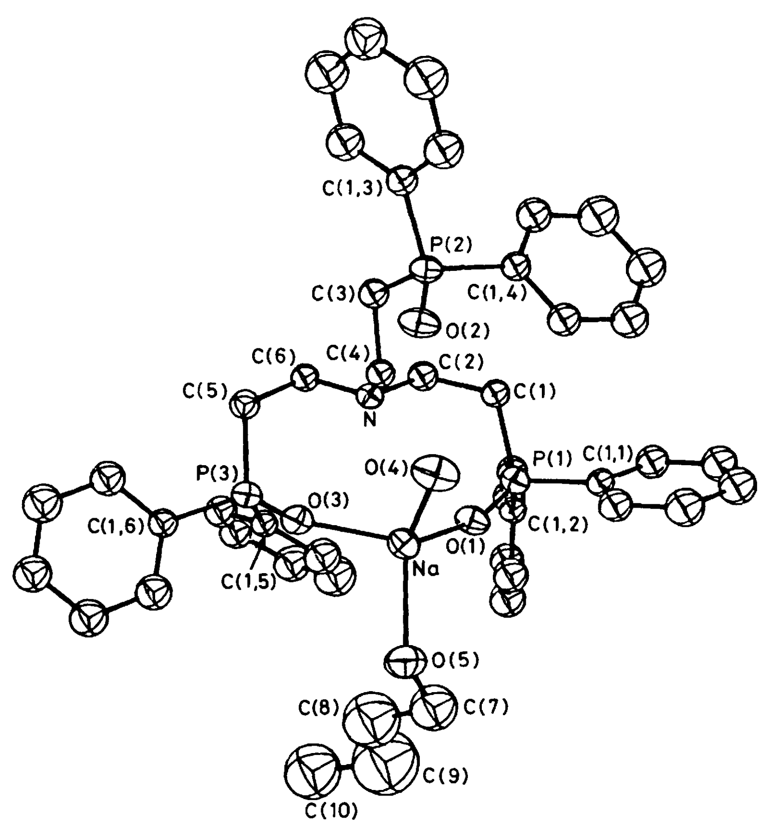

Figure 3. Perspective view of $[Na\{N(CH_2CH_2POPh_2)_3\}(H_2O)(BuOH)]^+$. ORTEP drawing with 30% probability ellipsoids

involved in hydrogen-bonding interactions. The intermolecular separations $O(4)(H_2O) \cdots O(3)^*$ and $O(5)(BuOH) \cdots O(2)^*$ are 2.73 and 2.71 Å respectively [shorter than twice the van der Waals radius of oxygen as reported by Pauling (2.84 Å)[17] and by Bondi (3.04 Å)].[18]

The i.r. spectra of both compounds (Nujol mulls) show two bands in the region 1 210—1 150 cm^{-1} and another one at *ca.* 560 cm^{-1}, characteristic of the phosphine oxide group. Moreover, the sodium derivative shows a broad band centred at 3 400 cm^{-1} and a band centred at 1 670 cm^{-1}, attributable to the OH stretching and H–O–H bending vibrations respectively.

Compounds (**1**) and (**2**) are soluble in the common organic polar solvents. The $^{31}P-\{^1H\}$ n.m.r. spectra of the sodium and lithium complexes in CD_2Cl_2 solution, at room temperature, are similar, showing singlets at 37.70 (**1**) and 37.72 p.p.m. (**2**), attributable to the ligand phosphorus atoms. The shift downfield with respect to the free ligand (31.66 p.p.m.), similar to that found for $Ph_2P(O)CH_2P(O)Ph_2$ in *trans*-$[PtCl_2(PEt_3)\{CH(PPh_2O)_2Li\}]$[12] (116 *vs.* 100 p.p.m.), indicates

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* The equivalent position referred to is 2 − *x*, 1 − *y*, −*z*.

Table 6. Selected bond distances (Å) and angles (°) for the $[Na\{N(CH_2CH_2POPh_2)_3\}(H_2O)(BuOH)]^+$ cation

Na–O(1)	2.177(6)	P(1)–C(1,2)	1.787(6)	P(3)–C(1,5)	1.778(7)	C(3)–C(4)	1.58(1)
Na–O(3)	2.237(6)	P(2)–O(2)	1.491(6)	P(3)–C(1,6)	1.793(6)	C(5)–C(6)	1.51(1)
Na–O(4)	2.302(7)	P(2)–C(3)	1.792(8)	N–C(2)	1.466(9)	C(7)–O(5)	1.46(2)
Na–O(5)	2.293(7)	P(2)–C(1,3)	1.769(7)	N–C(4)	1.445(9)	C(7)–C(8)	1.56(3)
P(1)–O(1)	1.482(5)	P(2)–C(1,4)	1.786(7)	N–C(6)	1.465(9)	C(8)–C(9)	1.35(4)
P(1)–C(1)	1.800(8)	P(3)–O(3)	1.494(5)	C(1)–C(2)	1.54(1)	C(9)–C(10)	1.71(4)
P(1)–C(1,1)	1.793(6)	P(3)–C(5)	1.809(8)				

O(1)–Na–O(3)	105.3(2)	C(1)–P(1)–C(1,2)	106.9(3)	O(3)–P(3)–C(1,6)	108.6(3)	P(1)–C(1)–C(2)	117.1(6)
O(1)–Na–O(4)	108.6(3)	C(1,1)–P(1)–C(1,2)	107.6(3)	C(5)–P(3)–C(1,5)	104.3(3)	N–C(2)–C(1)	115.2(6)
O(1)–Na–O(5)	105.5(3)	O(2)–P(2)–C(3)	111.9(4)	C(5)–P(3)–C(1,6)	108.5(3)	P(2)–C(3)–C(4)	108.2(5)
O(3)–Na–O(4)	111.7(3)	O(2)–P(2)–C(1,3)	112.5(3)	C(1,5)–P(3)–C(1,6)	108.1(3)	N–C(4)–C(3)	116.7(6)
O(3)–Na–O(5)	104.8(3)	O(2)–P(2)–C(1,4)	110.2(3)	Na–O(1)–P(1)	157.4(4)	P(3)–C(5)–C(6)	114.3(6)
O(4)–Na–O(5)	119.9(3)	C(3)–P(2)–C(1,3)	109.0(3)	Na–O(3)–P(3)	157.0(3)	N–C(6)–C(5)	113.5(6)
O(1)–P(1)–C(1)	115.7(4)	C(3)–P(2)–C(1,4)	105.5(3)	Na–O(5)–C(7)	126.5(8)	O(5)–C(7)–C(8)	104.8(18)
O(1)–P(1)–C(1,1)	109.8(3)	C(1,3)–P(2)–C(1,4)	107.4(3)	C(2)–N–C(4)	113.7(6)	C(7)–C(8)–C(9)	114.2(32)
O(1)–P(1)–C(1,2)	112.0(3)	O(3)–P(3)–C(5)	114.1(4)	C(2)–N–C(6)	109.3(6)	C(8)–C(9)–C(10)	105.4(33)
C(1)–P(1)–C(1,1)	104.2(3)	O(3)–P(3)–C(1,5)	113.0(3)	C(4)–N–C(6)	114.1(6)		

phosphine oxide–alkali metal interaction.* The interaction between chelating phosphine oxide and Li^+ in solution has already been demonstrated by ^{31}P n.m.r. spectroscopy.[19] In the case of CH_2Cl_2 solutions of the adduct $LiI\cdot5PPh_3O$,[3] such interaction was not observed.[20]

Acknowledgements

Thanks are due to Mr. F. Cecconi for technical assistance and to Mr. F. Nuzzi for microanalyses.

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20 P. Innocenti and S. Midollini, unpublished work.

Received 14th October 1985; Paper 5/1776

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* The difficulty in assigning the OH bands in the ^1H n.m.r. spectrum of compound (**2**) does not allow us to determine with certainty whether the water and butanol molecules remain co-ordinated to the metal atom in solution.