Lanthanum Complexes with the Bis(*o*-methoxyphenyl)-phosphide Ligand†

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Complexes of La and Y with the chelating bis(*o*-methoxyphenyl)phosphide ligand have been prepared. Thus $[\mathrm{Ln(NPr^i_2)_3(thf)}]$ (thf = tetrahydrofuran) or $[\mathrm{Ln\{N(SiMe_3)_2\}_3}]$ react with $\geqslant 1$ equivalent of bis(*o*-methoxyphenyl)phosphine at room temperature to yield $[\mathrm{Ln\{P(C_6H_4OMe\text{-}\mathit{o})_2\}_3}]$ as yellow crystalline solids. The complex $[\mathrm{La(NPr^i_2)\{P(C_6H_4OMe\text{-}\mathit{o})_2\}_2}]$ can be prepared by reaction of $[\mathrm{La(NPr^i_2)_3(thf)}]$ with 2 equivalents of the phosphine at 0 °C. The bimetallic complex $[\mathrm{(Pr^i_2N)_2La\{\mu\text{-}P(C_6H_4OMe\text{-}\mathit{o})_2\}_2Li(thf)}]$ has been prepared by reaction of $\mathrm{Li[La(NPr^i_2)_4]}$ with 2 equivalents of the phosphine, and characterised by X-ray diffraction in the solid state as its toluene solvate. Crystal data: monoclinic, space group *C*2/*c* (no. 15), $a = 17.22(5)$, $b = 14.782(7)$, $c = 21.710(4)$ Å, $\beta = 104.11(2)°$, $Z = 4$, final $R = 0.064$, $R' = 0.079$.

A feature common to much lanthanide chemistry is the high degree of lability in solution of most complexes except those with multidentate ligands. This arises from the ionic nature of the $\mathrm{Ln^{3+}}$–ligand interaction, where the ligand most commonly has first-row donor atoms. The use of more polarisable second-row donor ligands may lead to increased covalent interactions and thus to less-labile complexes: a single-crystal ESR study of $[\mathrm{LaGd(\mu\text{-}SBu^t)_2\{N(SiMe_3)_2\}_4}]$ showed an exceptionally large crystal-field splitting at gadolinium, which is indicative of covalent lanthanide to ligand interaction.[1] There are, however, very few structurally characterised examples of lanthanide complexes with S- or P-donor ligands.[2-5] In this paper we report on the synthesis of lanthanide complexes with the potentially tridentate bis(*o*-methoxyphenyl)phosphide ligand, which combines hard (O) and soft (P) donor sites in a bulky ligand which should give co-ordinatively saturated complexes.

Results and Discussion

The approach we have adopted in the synthesis of the lanthanide complexes has been reaction of lanthanide dialkylamides with secondary phosphine, which gives the lanthanide phosphide with elimination of secondary amine [equation (1); R = alkyl, R′ = aryl].

$$[\mathrm{Ln(NR_2)_3}] + \mathrm{PR'_2H} \longrightarrow [\mathrm{Ln(NR_2)_2(PR'_2)}] + \mathrm{NR_2H} \quad (1)$$

Preparation of $[\mathrm{La\{P(C_6H_4OMe\text{-}\mathit{o})_2\}_3}]$.—Addition of 3 equivalents of $\mathrm{P(C_6H_4OMe\text{-}\mathit{o})_2H}$ to a toluene solution of $[\mathrm{La(NPr^i_2)_3(thf)}]$ (thf = tetrahydrofuran) at room temperature leads to complete reaction within 2 h (as judged by the ^{31}P NMR spectrum of the reaction mixture; see Table 1), to give a bright yellow solution from which bright yellow crystals analysing as $[\mathrm{La\{P(C_6H_4OMe\text{-}\mathit{o})_2\}_3}]\cdot 2\mathrm{C_6H_5Me}$ can be isolated in high yield. The complex $[\mathrm{Y(NPr^i_2)_3(thf)}]$ reacts in a similar manner to the lanthanum complex, rapidly producing $[\mathrm{Y\{P(C_6H_4OMe\text{-}\mathit{o})_2\}_3}]$ on addition of 3 equivalents of $\mathrm{P(C_6H_4OMe\text{-}\mathit{o})_2H}$ at room temperature. We have previously found that $[\mathrm{Ln(NPr^i_2)_3(thf)}]$ reacts far more rapidly with $\mathrm{PPh_2H}$ than do the corresponding $[\mathrm{Ln\{N(SiMe_3)_2\}_3}]$ complexes, due probably both to the higher basicity of $\mathrm{NPr^i_2}^-$, and to the lower steric crowding of its lanthanide complexes; indeed we have found it impossible to replace more than one $\mathrm{N(SiMe_3)_2}^-$ ligand with $\mathrm{PPh_2}^-$.[6] It is therefore noteworthy that ^{31}P NMR studies show formation of the tris(phosphide) complex on reaction of $[\mathrm{Ln\{N(SiMe_3)_2\}_3}]$ with 1 equivalent of $\mathrm{P(C_6H_4OMe\text{-}\mathit{o})_2H}$ even at 0 °C.

The ^{1}H NMR spectrum of $[\mathrm{La\{P(C_6H_4OMe\text{-}\mathit{o})_2\}_3}]$ showed only a single resonance at δ 3.45 due to OMe groups, indicating either that all OMe are co-ordinated to the La resulting in nine-co-ordination or, more likely, that there is rapid exchange between free and co-ordinated OMe. This complex is the first soluble homoleptic lanthanide phosphide, but unfortunately we have so far been unable to prepare suitable crystals for an X-ray structure determination.

Attempts to Prepare Mono- and Bis-(phosphide) Complexes.—If 1 equivalent of $\mathrm{P(C_6H_4OMe\text{-}\mathit{o})_2H}$ is added to a toluene solution of $[\mathrm{La(NPr^i_2)_3(thf)}]$ at room temperature then reaction proceeds to give $[\mathrm{La\{P(C_6H_4OMe\text{-}\mathit{o})_2\}_3}]$ as the only product (as judged by the ^{31}P and ^{1}H NMR spectra of the reaction mixture), along with unreacted lanthanum tris(dialkylamide). If the reaction is carried out at 0 °C then bright yellow crystals analysing as $[\mathrm{La(NPr^i_2)\{P(C_6H_4OMe\text{-}\mathit{o})_2\}_2}]\cdot\mathrm{thf}\cdot\mathrm{C_6H_5Me}$ are precipitated, and virtually none of the tris(phosphide) complex is formed. We have so far been unable to isolate the mono(phosphide) complex. Further reaction of the bis(phosphide) complex with $\mathrm{P(C_6H_4OMe\text{-}\mathit{o})_2H}$ is quite rapid at room temperature and proceeds to give $[\mathrm{La\{P(C_6H_4OMe\text{-}\mathit{o})_2\}_3}]$. A similar reaction, but not quite so fast, is observed with $[\mathrm{Y(NPr^i_2)_3(thf)}]$. Reaction of $[\mathrm{La\{N(SiMe_3)_2\}_3}]$ with $\mathrm{P(C_6H_4OMe\text{-}\mathit{o})_2H}$ also gives the tris(phosphide) complex.

Reaction of $\mathrm{Li[La(NPr^i_2)_4]}$ *with* $\mathrm{P(C_6H_4OMe\text{-}\mathit{o})_2H}$.—In our attempts to prepare crystals suitable for X-ray diffraction studies we found that a toluene solution of $\mathrm{Li[La(NPr^i_2)_4]}$ {prepared by reaction of $\mathrm{Li(NPr^i_2)}$ with 1 equivalent of $[\mathrm{La(NPr^i_2)_3(thf)}]$} reacts readily with 2 equivalents of $\mathrm{P(C_6H_4OMe\text{-}\mathit{o})_2H}$ to give good-quality yellow prisms. The complex crystallised with one molecule of toluene and was shown to be $[\mathrm{(Pr^i_2N)_2La\{\mu\text{-}P(C_6H_4OMe\text{-}\mathit{o})_2\}_2Li(thf)}]$.

Structure of $[\mathrm{(Pr^i_2N)_2La\{\mu\text{-}P(C_6H_4OMe\text{-}\mathit{o})_2\}_2Li(thf)}]\cdot\mathrm{C_6H_5Me}$.—A plot of $[\mathrm{(Pr^i_2N)_2La\{\mu\text{-}P(C_6H_4OMe\text{-}\mathit{o})_2\}_2Li(thf)}]$ is shown in Fig. 1; selected bond distances and angles are given in Table 2 and atomic coordinates in Table 3. The La and Li atoms, and the oxygen atom O(3) of the co-ordinated

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

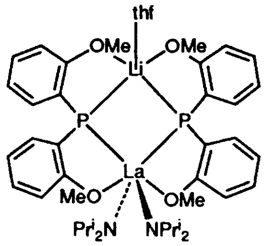
Table 1 Elemental analyses and ^{31}P NMR data for new compounds

Compound	Analysis (%)[a] C	H	N	^{31}P NMR[b]
$[La\{P(C_6H_4OMe\text{-}o)_2\}_3]\cdot 2C_6H_5Me$	63.2	5.7	0.0	−44.6 (s)
	(63.5)	(5.5)	(0.0)	
$[La(NPr^i_2)\{P(C_6H_4OMe\text{-}o)_2\}_2]\cdot thf\cdot C_6H_5Me$	61.8	7.05	1.7	−14.2 (s)
	(60.5)	(6.5)	(1.6)	
$[(Pr^i_2N)_2La\{\mu\text{-}P(C_6H_4OMe\text{-}o)_2\}_2Li(thf)]\cdot C_6H_5Me$	60.95	7.30	2.50	−56.8 (q)
	(61.2)	(7.25)	(2.70)	$[^1J(Li\text{–}P) = 58$ Hz]
$Li[La(NiPr^i_2)_4]\cdot thf$	53.8	10.0	8.7	
	(54.4)	(10.4)	(9.1)	
$[Y\{P(C_6H_4OMe\text{-}o)_2\}_3]$	62.2	6.50	0.00	−45.8 (s)
	(61.2)	(5.1)	(0.00)	
$[LiP(C_6H_4OMe\text{-}o)_2]$	68.6	6.3	0.0	−89.0 (m)
	(66.7)	(5.6)	(0.0)	

[a] Calculated values in parentheses. [b] Recorded in $C_6H_5Me\text{–}C_6D_6$ solution at 193 K. Positive shifts are downfield from 85% H_3PO_4 as external reference.

Table 2 Selected intramolecular bond distances (Å) and angles (°) for $[(Pr^i_2N)La\{\mu\text{-}P(C_6H_4OMe\text{-}o)_2\}_2Li(thf)]\cdot C_6H_5Me$

La–P(1)	3.141(4)	P(1)–C(8)	1.83(1)
La–O(2)	2.787(9)	P(1)–Li	2.53(2)
La–N(1)	2.30(1)	O(1)–Li	2.17(1)
P(1)–C(1)	1.82(1)	O(3)–Li	1.88(4)
P(1)–La–P(1A)	76.2(1)	C(1)–P(1)–Li	100.8(5)
P(1)–La–O(2)	60.9(2)	C(8)–P(1)–Li	152.2(5)
O(2)–La–O(2A)	162.2(4)	P(1)–Li–P(1A)	100(1)
O(2)–La–N(1)	85.1(4)	P(1)–Li–O(1)	74.2(7)
O(2)–La–N(1A)	87.3(3)	P(1)–Li–O(1A)	96.2(9)
N(1)–La–N(1A)	129.4(6)	O(1)–Li–O(1A)	165(2)
La–P(1)–C(1)	108.5(4)	O(1)–Li–O(3)	97(1)
La–P(1)–C(8)	97.1(5)	La–N(1)–C(17)	105.6(9)
La–P(1)–Li	91.9(7)	La–N(1)–C(20)	141(1)
C(1)–P(1)–C(8)	101.1(6)		



thf, lie on a crystallographic two-fold axis. The phosphide ligand bridges La and Li through the P atom and in addition there is chelation through one OMe group to each metal atom.

The La is six-co-ordinate; the La–N bond lengths are normal for a lanthanum dialkylamide. The La–P bond length of 3.141(4) Å is slightly shorter than that in the diphenylphosphide complex $[La\{N(SiMe_3)_2\}_2(PPh_2)(Ph_3PO)_2]$ [3.165(6) Å],[5] and also somewhat shorter than the Nd–P bond length of 3.154 Å in the tertiary phosphine complex $[Nd\{OCBu^t_2(CH_2)_2PMe_2\}_3]$.[7] (The ionic radius of Nd^{3+} is 0.05 Å less than that of La^{3+}.) The La–O(2) bond distances of 2.787(9) Å in $[(Pr^i_2N)_2La\{\mu\text{-}P(C_6H_4OMe\text{-}o)_2\}_2Li(thf)]$ is considerably longer than the Nd–O distance of 2.17 Å in $[Nd\{OCBu^t_2(CH_2)_2PMe_2\}_3]$, but is comparable to the La–O distances of 2.666(2) and 2.775(2) Å found in $[\{La(\eta^5,\kappa^1\text{-}C_5H_4CH_2CH_2OMe)_2(\mu\text{-}Cl)\}_2]$.[8] A shorter La–O distance would result in increased strain in the $LaPC_2O$ ring [the La–P(1)–C(8) angle is 97.1°].

Lithium diarylphosphide complexes have been the subject of numerous structural studies,[9–11] but although there are several examples of the $Ln(\mu\text{-}X)_2Li$ structural unit[12] there is only one structural study of a $Ln(\mu\text{-}PPh_2)_2Li$ complex[4] and only one structural study of a lanthanum diarylphosphide.[5] A selection of structural data for diarylphosphide-bridged complexes containing a lanthanide and/or lithium is given in Table 4.

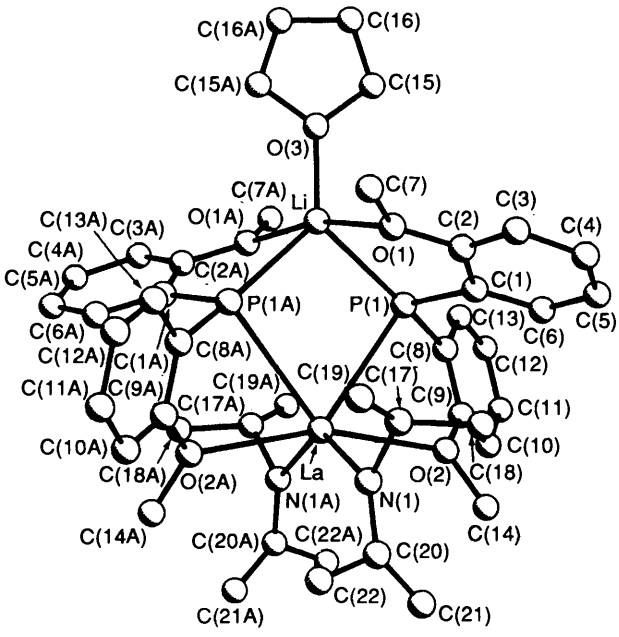


Fig. 1 A plot of $[(Pr^i_2N)_2La\{\mu\text{-}(C_6H_4OMe\text{-}o)_2P\}_2Li(thf)]$

The Li–P bond lengths in lithium diorganophosphides have been found to be related to the co-ordination number of lithium, with low co-ordination numbers giving rise to shorter bonds.[10,11] The Li–P bond length in $[(Pr^i_2N)_2La\{\mu\text{-}P(C_6H_4OMe\text{-}o)_2\}_2Li(thf)]$ is significantly shorter than those in $[(C_5Me_5)_2Lu(\mu\text{-}PPh_2)_2Li(tmen)]$ (tmen = $Me_2NCH_2CH_2NMe_2$) where Li is four-co-ordinate, but compares well with those [2.455(9) and 2.543(9) Å] in the polymer $[\{Li[P(C_6H_{11})_2](thf)\}_n]$ where Li is five-co-ordinate. The Li–O(thf) distance is in the normal range;[13] the Li–OMe distance is somewhat longer, possibly due to crowding at the Li.

^{31}P *NMR Studies of* $[(Pr^i_2N)_2La\{\mu\text{-}P(C_6H_4OMe\text{-}o)_2\}_2Li(thf)]$.—Variable-temperature ^{31}P NMR spectra (Fig. 2) show that the complex is fluxional in solution; at low temperature the solution structure is analogous to that in the solid state, but at room temperature there is a mixture arising from dissociation of the dinuclear species. The sharp resonance at δ −44 is due to a small amount of $[La\{P(C_6H_4OMe\text{-}o)_2\}_3]$ impurity; the resonance at δ −88 is due to $[LiP(C_6H_4OMe\text{-}o)_2]$ (see Table 1), that at δ −56 to $[(Pr^i_2N)_2La\{\mu\text{-}P(C_6H_4OMe\text{-}$

$o)_2\}_2\mathrm{Li(thf)}]$, and we assign the resonance at δ −52 to $[\mathrm{La(NPr^i_2)_2\{P(C_6H_4OMe}\text{-}o)_2\}]$. On lowering the temperature, the resonance at δ −56 sharpens to give a quartet with ^1J(Li–P) = 58 Hz, and those at δ −52 and −88 decrease in intensity until they disappear at 193 K. On raising the temperature all the resonances broaden further except for that due to $[\mathrm{La\{P(C_6H_4OMe}\text{-}o)_2\}_3]$; we have found this effect in other lanthanum phosphides and ascribe it to relaxation effects of the quadrupolar ^{139}La nucleus ($I = \frac{7}{2}$).[5,6]

Conclusion

In conclusion, we have shown that the bis(*o*-methoxyphenyl)-phosphide group can be a useful ligand in lanthanide chemistry, giving soluble, crystallisable complexes. Although these complexes are all very air and moisture sensitive they are significantly less so than those of $\mathrm{PPh_2}^-$, presumably due to the increased size and chelating ability of $\mathrm{P(C_6H_4OMe}\text{-}o)_2^-$. We are now exploring the use of unsymmetrical *o*-methoxyphenylphosphide ligands in lanthanide chemistry with the aim of preparing optically active complexes.

Table 3 Positional parameters for $[\mathrm{(Pr^i_2N)_2La\{\mu\text{-}P(C_6H_4OMe}\text{-}o)_2\}_2\mathrm{Li(thf)]\cdot C_6H_5Me}$

Atom	*x*	*y*	*z*
La*	0	0.556 98(8)	1/4
P(1)	−0.102 4(2)	0.724 1(2)	0.272 2(2)
O(1)	−0.087 1(7)	0.815 6(7)	0.160 1(4)
O(2)	−0.149 8(5)	0.527 8(6)	0.273 9(5)
O(3)*	0	0.961(1)	1/4
N(1)	−0.054 3(6)	0.490 6(7)	0.153 4(5)
C(1)	−0.183 8(8)	0.739 8(8)	0.201 8(6)
C(2)	−0.166(1)	0.788(1)	0.150 3(7)
C(3)	−0.224(1)	0.804(1)	0.095 2(7)
C(4)	−0.301(1)	0.773(1)	0.089 5(8)
C(5)	−0.321(1)	0.728(1)	0.139 5(9)
C(6)	−0.263(1)	0.712(1)	0.193 7(7)
C(7)	−0.061(1)	0.856(1)	0.109 4(8)
C(8)	−0.154 9(8)	0.668(1)	0.325 8(6)
C(9)	−0.172 6(8)	0.576(1)	0.322 6(7)
C(10)	−0.209(1)	0.534(1)	0.365(1)
C(11)	−0.230(1)	0.585(2)	0.411(1)
C(12)	−0.212(2)	0.675(2)	0.417(1)
C(13)	−0.177(1)	0.716(1)	0.375 1(8)
C(14)	−0.195(1)	0.451(1)	0.251(1)
C(15)	−0.068(1)	1.017(2)	0.245(1)
C(16)	−0.042(2)	1.105(2)	0.243(2)
C(17)	−0.088(1)	0.565(1)	0.110 3(8)
C(18)	−0.178(1)	0.560(1)	0.082 1(9)
C(19)	−0.045(1)	0.594(2)	0.061(1)
C(20)	−0.061(2)	0.400(2)	0.120(1)
C(21)	−0.110(3)	0.337(3)	0.127(2)
C(22)	0.003(3)	0.371(3)	0.109(2)
C(23)	0.118(2)	−0.081(2)	0.017(2)
C(24)	−0.037(3)	0.118(3)	0.030(2)
C(25)	−0.106(2)	−0.012(3)	−0.048(2)
C(26)	0.039(3)	−0.036(3)	0.002(2)
C(27)	0.035(2)	0.056(2)	0.035(1)
Li*	0	0.834(3)	1/4

* Occupancy: 0.5.

Experimental

All manipulations were carried out under an atmosphere of dried and deoxygenated nitrogen using standard Schlenk techniques. Solvents were distilled from sodium diphenylketyl and stored over 4 Å molecular sieves under an atmosphere of nitrogen prior to use. Samples for NMR spectroscopy were dissolved in $\mathrm{C_6D_6}$ (^{1}H) or $\mathrm{C_6D_6}$–$\mathrm{C_6H_5Me}$ (^{31}P) and sealed under vacuum as previously described.[6] The spectra were recorded on a Bruker WM 250 spectrometer and chemical shifts are reported downfield from $\mathrm{SiMe_4}$ (^{1}H) or 85% $\mathrm{H_3PO_4}$ (^{31}P) as external reference. The compounds $[\mathrm{Ln\{NPr^i_2\}_3(thf)}]$ (Ln = La or Y),[14] $[\mathrm{La\{N(SiMe_3)_2\}_3}]$,[15] and $(o\text{-}\mathrm{MeOC_6H_4)_2P(O)H}$[16] were prepared by the published methods.

Preparations.—$\mathrm{P(C_6H_4OMe}\text{-}o)_2\mathrm{H}$. The compound $(o\text{-}\mathrm{MeOC_6H_4)_2P(O)H}$ (13.42 g, 51.2 mmol) was added to a mixture of $\mathrm{NEt_3}$ (15.2 cm^3, 127 mmol) and $\mathrm{SiHCl_3}$ (12.5 cm^3, 122 mmol) in toluene (250 cm^3). The mixture was heated to reflux for 15 h, resulting in a colourless solution and a white gelatinous precipitate. It was hydrolysed by careful addition of a degassed solution of NaOH (7.5 g, 187 mmol) in water (70 cm^3), and was stirred for 2 h. The organic layer was decanted off, the aqueous layer extracted with toluene (100 cm^3), and the combined organics dried ($\mathrm{MgSO_4}$). The product was isolated as colourless crystals from the concentrated toluene solution at −10 °C. Yield = 7.3 g, 58%. ^{31}P NMR ($\mathrm{C_6D_6}$): δ 73.3 [d, ^1J(P–H) = 224 Hz].

$[\mathrm{(Pr^i_2N)_2La\{\mu\text{-}P(C_6H_4OMe}\text{-}o)_2\}_2\mathrm{Li(thf)]\cdot C_6H_5Me}$. A solution of $\mathrm{P(C_6H_4OMe}\text{-}o)_2\mathrm{H}$ (0.39 g, 1.6 mmol) in toluene (2 cm^3) was added to a solution of $\mathrm{Li[La(NPr^i_2)_4]\cdot thf}$ (0.49 g, 0.79 mmol) in toluene (5 cm^3). The resulting yellow solution was left at 3 °C for 12 h, after which time yellow crystals of $[\mathrm{(Pr^i_2N)_2La\{\mu\text{-}P(C_6H_4OMe}\text{-}o)_2\}_2\mathrm{Li(thf)]\cdot C_6H_5Me}$ had formed as the only product. The crystals were washed (light petroleum, b.p. 30–40 °C) and dried *in vacuo*.

$[\mathrm{La\{P(C_6H_4OMe}\text{-}o)_2\}_3]\cdot 2\mathrm{C_6H_5Me}$. A solution of $\mathrm{P(C_6H_4OMe}\text{-}o)_2\mathrm{H}$ (0.57 g, 2.3 mmol) in toluene (5 cm^3) was added to a solution of $[\mathrm{La(NPr^i_2)_3(thf)}]$ (0.416 g, 0.77 mmol) in toluene (10 cm^3). The reaction mixture was left at −10 °C for 6 h, after which time yellow crystals of $[\mathrm{La\{P(C_6H_4OMe}\text{-}o)_2\}_3]\cdot 2\mathrm{C_6H_5Me}$ had formed as the only product. These were washed (light petroleum) and dried *in vacuo*. The complex $[\mathrm{Y\{P(C_6H_4OMe}\text{-}o)_2\}_3]$ was prepared similarly.

Structure Determination of $[\mathrm{(Pr^i_2N)_2La\{\mu\text{-}P(C_6H_4OMe}\text{-}o)_2\}_2\mathrm{Li(thf)]\cdot C_6H_5Me}$.—*Crystal data*. $\mathrm{C_{51}H_{72}LaLiN_2O_5P_2}$, M = 1000.93, monoclinic, space group $C2/c$ (no. 15), a = 17.22(5), b = 14.782(7), c = 21.710(4) Å, β = 104.11(2)°, U = 5360(3) Å^3, Z = 4, D_c = 1.240 g cm^{-3}, F(000) = 2088. The cell constants were obtained from 24 carefully centred reflections in the range 20.2 < 2θ < 23.48°. Yellow, air-sensitive prisms; crystal dimensions 0.45 × 0.25 × 0.8 mm; μ(Mo-Kα) = 8.99 cm^{-1}. The crystal was sealed under argon in a Lindeman capillary.

Data collection and processing. Rigaku AFC6S diffractometer, ω–2θ mode with ω scan width = (91.37 + 0.30 tanθ)°, ω scan speed 8.0° min^{-1}, Mo-Kα radiation (λ = 0.710 69 Å); 5115 reflections were measured (1.4 < θ < 25.0°), of which 4934

Table 4 Structural data for $\mathrm{M(\mu\text{-}PR'_2)_2Li}$ systems (M = Ln or Li)

Compound	Ln–P/Å	Li–P/Å	Li–O(ether)/Å	P–Ln–P/°	P–Li–P/°	Ln–P–Li/°	Li–P–Li/°
$[\mathrm{(Pr^i_2N)_2La\{\mu\text{-}(C_6H_4OMe}\text{-}o)_2\}_2\mathrm{Li(thf)}]$	3.141(4)	2.53(2)	1.88(4)	76.2(1)	100(1)	91.9(7)	
$[\mathrm{(C_5Me_5)_2Lu(\mu\text{-}PPh_2)_2Li(tmen)}]$[a]	2.782(1)	2.692(14)		86.8	91.2(4)	87.1(2)	
		2.691(8)				86.5(3)	
$[\{\mathrm{Li(\mu\text{-}PPh_2)(thf)_2}\}_n]$[b]		2.629(22)	1.937(22)		123.1(8)		135.0(5)
		2.634(21)	1.988(22)				
$[\{\mathrm{Li[\mu\text{-}P(C_6H_2Me_3\text{-}2,4,6)_2](OEt)}\}_2]$[c]		2.483(1)	1.926(11)		99.2(4)		81.7(4)
		2.479(11)	1.924(11)		98.2(4)		80.9(4)

[a] Ref. 4. [b] Ref. 10. [c] Ref. 11.

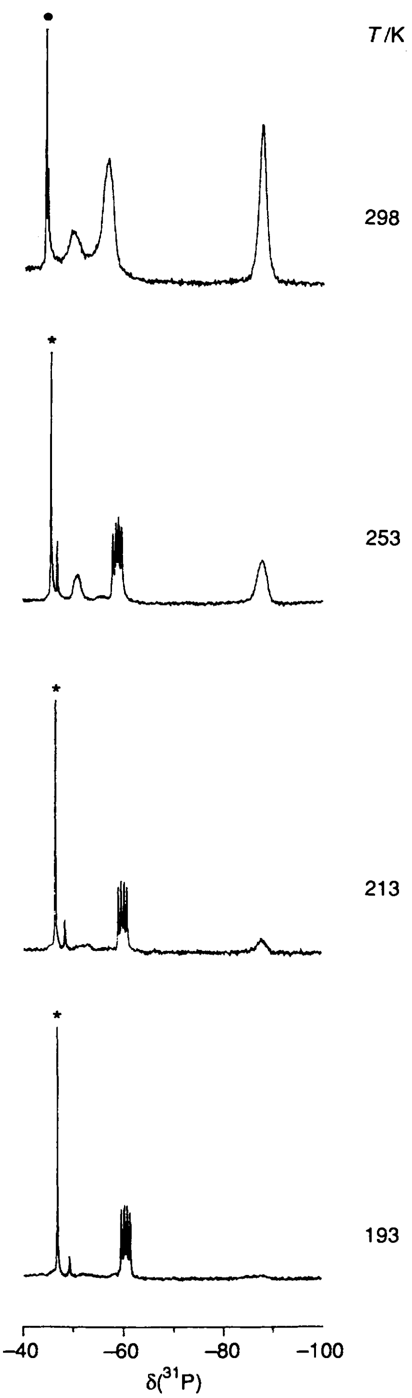


Fig. 2 Variable-temperature ^{31}P NMR spectra of $[(Pr^i_2N)_2La\{\mu\text{-}P(C_6H_4OMe\text{-}o)_2\}_2Li(thf)]$. The resonance marked * is due to a small amount of $[La\{P(C_6H_4OMe\text{-}o)_2\}_3]$ impurity

were unique. Data were collected at 23 °C; there was no crystal decay during data collection. An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.85 to 1.00. The data were corrected for Lorentz and polarisation effects.

Structure analysis and refinement. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 2397 observed reflections $[I > 4.00\sigma(I)]$ and 226 variable parameters, and converged (largest parameter was 0.46 times its e.s.d.) with agreement factors of $R = 0.064$ and $R' = 0.079$. The weighting scheme was based on counting statistics and included a factor to downweight the intense reflections. The maximum and minimum peaks on the final Fourier difference map corresponded to 0.96 and -0.66 e Å^{-3} respectively. The final refinement of the structure was hampered by large thermal motions for the isopropyl groups and disorder of the solvent molecule about a centre of symmetry. However, the most interesting part of the molecule is the LaP_2Li unit and the atoms directly bonded to it, and the thermal parameters for these atoms are all reasonable. Neutral atom scattering factors were taken from Cromer and Waber.[17] Anomalous dispersion effects were included in F_{calc};[18] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[19] All calculations were performed using the TEXSAN crystallographic software package[20] and the figures were plotted using PLUTO.[21] Selected intramolecular bond distances and angles are given in Table 2, atomic coordinates in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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