Diphenylphosphido Complexes of the Lanthanides: Reactions of Compounds $[\mathrm{Ln\{N(SiMe_3)_2\}_3}]$ (Ln = La or Eu) or $[\mathrm{Ln\{N(SiMe_3)_2\}_3(Ph_3PO)}]$ (Ln = La, Eu, or Y) with $\mathrm{Ph_2PH}$ to give $[\mathrm{Ln\{N(SiMe_3)_2\}_2(PPh_2)}]$ or $[\mathrm{Ln\{N(SiMe_3)_2\}_2(PPh_2)(Ph_3PO)}]$

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$[\mathrm{LnL_3}]$ [*Ln* = La or Eu, L = $\mathrm{N(SiMe_3)_2}$] reacts with $\mathrm{Ph_2PH}$ to give $[\mathrm{LnL_2(PPh_2)}]$ with elimination of HL. The reaction is most rapid for Eu, slower for La, and immeasurably slow for Y. Reaction of $[\mathrm{LnL_3(Ph_3PO)}]$ (Ln = La, Eu, or Y) with $\mathrm{Ph_2PH}$ gives $[\mathrm{LnL_2(PPh_2)(Ph_3PO)}]$, and is more rapid than the reaction between $[\mathrm{LnL_3}]$ and $\mathrm{Ph_2PH}$. These extremely air-sensitive products have been characterized by n.m.r. spectroscopy (^{1}H or ^{31}P).

The lanthanides have generally been considered to be hard acceptors, bonding predominantly to oxygen or nitrogen donor ligands with substantial ionic character. In recent years a considerable organometallic chemistry has developed, especially with cyclopentadienyl ligands, and here again, photoelectron spectroscopy and molecular orbital calculations indicate that the bonding is predominantly ionic.[1] If covalent bonding in lanthanide complexes is possible, the most likely complexes are those containing soft ligands such as P or S donors. There are few reports in the literature of lanthanide complexes with phosphorus ligands: tertiary phosphine adducts include $[\mathrm{Yb(\eta\text{-}C_5H_5)_3(PR_3)}]$ (R = Me, Ph, or $\mathrm{C_6H_{11}}$),[2] $[\mathrm{Yb\{N(SiMe_3)_2\}_2(Me_2PCH_2CH_2PMe_2)}]$,[3] and $[\mathrm{Yb(\eta\text{-}C_5Me_5)_2Cl(Me_2PCH_2PMe_2)}]$;[4] a small number of dialkyl- or diaryl-phosphido complexes have also been described, for example $[\mathrm{Ln(\eta\text{-}C_5H_5)_2(PBu^t{}_2)}]$,[5] $[\mathrm{Ln(\eta\text{-}C_5H_5)_2(PPhBu^t)}]$,[5] and $[\mathrm{Sm(\eta\text{-}C_5H_4Me)_2(PPh_2)}]$.[6] We have already reported the reactions of $[\mathrm{LnL_3}]$ [Ln = La, Eu, or Gd; L = $\mathrm{N(SiMe_3)_2}$] with $\mathrm{Bu^tSH}$ to give the dimeric thiolate complexes $[\{\mathrm{LnL_2(SBu^t)}\}_2]$[7] and we now report the synthesis of phosphido complexes by the analogous reaction between $[\mathrm{LnL_3}]$ and $\mathrm{Ph_2PH}$.

Table 1. ^{1}H N.m.r. data (solvent $\mathrm{C_6D_6}$)

Complex	δ/p.p.m. L	δ/p.p.m. Aromatics
$[\mathrm{LaL_2(PPh_2)}]$	0.29 (s)	6.9—8 (m)
$[\mathrm{EuL_2(PPh_2)}]$	0.25 (broad)	7.1 (broad)
$[\mathrm{YL_2(PPh_2)(Ph_3PO)}]$	0.38 (s)	6.8—7.9 (m)
$[\mathrm{LaL_2(PPh_2)(Ph_3PO)}]$	0.37 (s)	6.5—7.8 (m)
$[\mathrm{EuL_2(PPh_2)(Ph_3PO)}]$	0.1 (broad)	6.5—7.8 (broad)

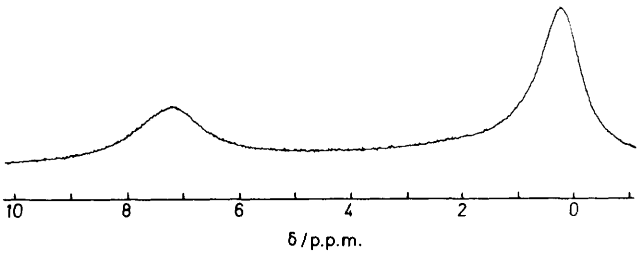

Figure 1. ^{1}H N.m.r. spectrum of $[\mathrm{EuL_3}]$ + $\mathrm{Ph_2PH}$

Results and Discussion

Reactions of $[\mathrm{LnL_3}]$ *with* $\mathrm{Ph_2PH}$.—We began our investigations with the orange $[\mathrm{EuL_3}]$, since most $\mathrm{Eu^{3+}}$ compounds are coloured and any colour change accompanying the reaction would easily be seen. Addition of one equivalent of $\mathrm{Ph_2PH}$ to a toluene solution of $[\mathrm{EuL_3}]$ resulted in a colour change to yellow after *ca.* 2 h at room temperature. Removal of solvent *in vacuo* gave yellow needles which could be recrystallized from pentane. These needles were exceedingly air sensitive, rapidly decomposing to give a white powder and we were unable to isolate them. Because of these difficulties we decided to study the reactions in sealed n.m.r. tubes.

The ^{1}H n.m.r. spectrum of the yellow solution resulting from the addition of one equivalent of $\mathrm{Ph_2PH}$ to a $\mathrm{C_6D_6}$ solution of $[\mathrm{EuL_3}]$ is shown in Figure 1. The spectrum is consistent with the reaction (1), with HL and co-ordinated L in the product

$$[\mathrm{EuL_3}] + \mathrm{Ph_2PH} \longrightarrow [\mathrm{EuL_2(PPh_2)}] + \mathrm{HL} \qquad (1)$$

appearing at the same chemical shift. Complete reaction is indicated as $[\mathrm{EuL_3}]$ shows a fairly sharp singlet in the ^{1}H n.m.r. spectrum at 6.5 p.p.m. $\mathrm{Eu^{3+}}$ ($4f^6$) has a diamagnetic $J = 0$ ground state. However, the $J = 1$ and $J = 2$ excited states are generally appreciably populated at room temperature, making $\mathrm{Eu^{3+}}$ paramagnetic, and thus n.m.r. spectra of its compounds are expected to show considerable shifts compared with those of an analogous diamagnetic compound, due to the pseudo-contact or dipolar mechanism. The magnitude of the pseudo-contact shift is given by $K(3\cos^2\theta - 1)r^{-3}$, where r is the distance of the nucleus under investigation from the paramagnetic centre, and θ is the angle between the radius vector and the principal axis of the magnetic susceptibility tensor; K contains terms dependent on the anisotropy of the magnetic susceptibility.

We were surprised to find that the chemical shifts for $[\mathrm{EuL_2(PPh_2)}]$ were in the regions expected for a diamagnetic compound, although the peaks were considerably broadened (Table 1). No change in chemical shift was observed on varying the temperature between 303 K and 243 K. Possible explanations for these results would be: (*i*) all the protons are at an average value $\theta = 54.73°$ ($3\cos^2\theta - 1 = 0$) to the principal axis of the magnetic susceptibility tensor, (*ii*) the magnetic susceptibility tensor is isotropic, (*iii*) only the $J = 0$ ground state of $\mathrm{Eu^{3+}}$ is populated, leading to a diamagnetic complex, and (*iv*) $\mathrm{Eu^{3+}}$ has been reduced to $\mathrm{Eu^{2+}}$ (F^7) which has an isotropic tensor and would therefore not give rise to n.m.r. shifts by the pseudo-contact mechanism. Possibility (*i*) is discounted as it is a geometrical impossibility with the ligands present. Similarly (*ii*) is rejected on geometrical grounds as an isotropic magnetic susceptibility tensor would require a ligand field of cubic symmetry, which seems to be impossible for $[\mathrm{EuL_2(PPh_2)}]$. (*iv*) Is discounted on the grounds that the electronic

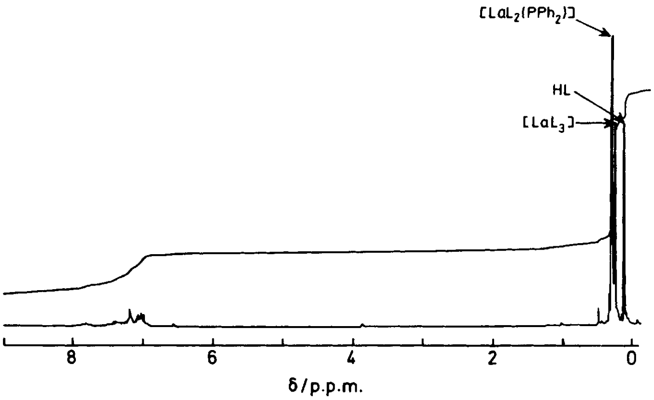

Figure 2. ^1H N.m.r. spectrum of $[LaL_3]$ + Ph_2PH

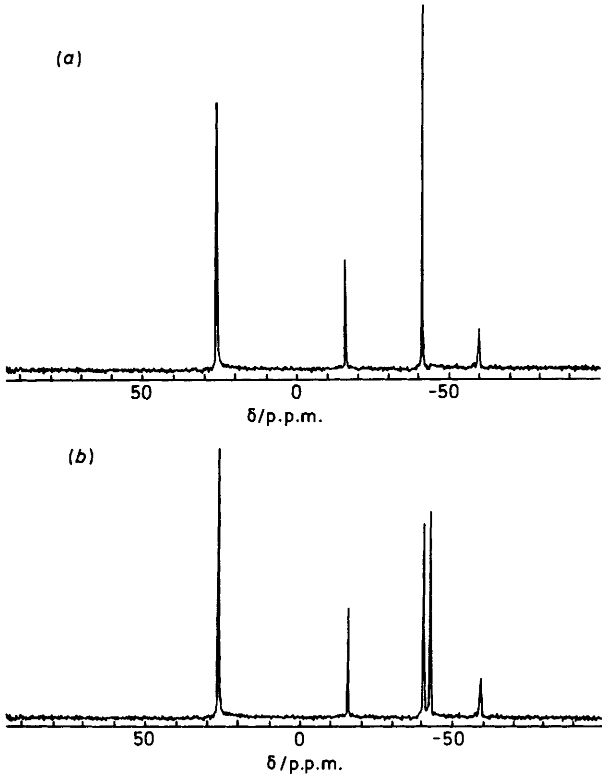

Figure 3. ^{31}P N.m.r. spectrum of $[LaL_3]$ + Ph_2PH with (*a*) ^1H decoupling and (*b*) without ^1H decoupling

Table 2. ^{31}P N.m.r. data[a] (solvent C_7H_8–C_6D_6, 1:1)

Complex	δ/p.p.m.
$[LaL_2(PPh_2)]$[b]	26.5 (s)
$[LaL_3(Ph_3PO)]$[c]	39 (s)
$[YL_3(Ph_3PO)]$[c]	38 (d, $^2J_{Y-P}$ 12 Hz)
$[LaL_2(PPh_2)(Ph_3PO)]$[b]	39.8 (s), 40.8 (s)
$[YL_2(PPh_2)(Ph_3PO)]$	40.3 (t, $^1J_{Y-P}$ 10.9 Hz), 42.1 (d, $^2J_{Y-P}$ 12.4 Hz)

[a] Positive shifts downfield relative to 85% phosphoric acid. [b] Recorded at 233 K. [c] Recorded at 253 K.

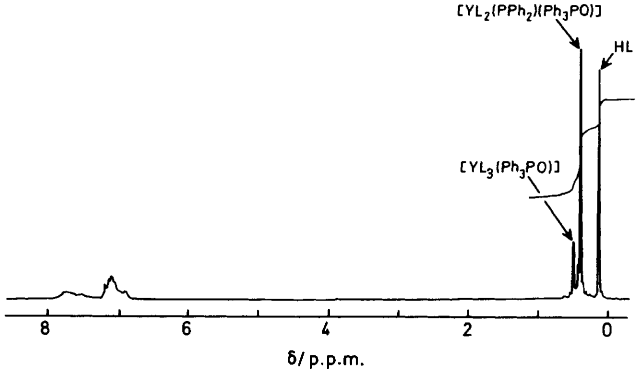

Figure 4. ^1H N.m.r. spectrum of $[YL_3(Ph_3PO)]$ + Ph_2PH

relaxation of Eu^{2+} would be slow at room temperature and one would therefore not expect to see an n.m.r. signal at all. Thus (*iii*) appears to be the most reasonable explanation although, to our knowledge, there are no reported examples of diamagnetic Eu^{3+} compounds at room temperature. The broadness of the lines in the spectrum suggests that there is some residual paramagnetism in the solution.

In investigating the reactions of $[LnL_3]$ with Bu^tSH we found that the reaction was faster for the larger Ln.[7] This seemed reasonable if the reaction involved prior co-ordination of Bu^tSH before elimination of HL, and we expected a similar trend in the reaction with Ph_2PH. We therefore next investigated the reaction between $[LaL_3]$ and Ph_2PH, expecting it to be more rapid than that of $[EuL_3]$.

Addition of one equivalent of Ph_2PH to a solution of $[LaL_3]$ gave a primrose yellow colour within 5 min. However, the ^1H n.m.r. spectrum of the solution, shown in Figure 2, showed incomplete reaction even after 24 h at room temperature, and resonances due to $[LaL_3]$, $[LaL_2(PPh_2)]$, and HL can clearly be seen. We found that there was no detectable reaction between $[YL_3]$ and Ph_2PH, even after heating to 78 °C for 24 h. Thus, there is a size effect on the rate of reaction between $[LnL_3]$ and Ph_2PH, although $[EuL_3]$ shows anomalously high reactivity.

The reaction of $[LaL_3]$ with Ph_2PH was also studied by ^{31}P n.m.r. spectroscopy. At room temperature there is a broad resonance at 26.5 p.p.m. which we have assigned to $[LaL_2(PPh_2)]$ (Table 2). The broadness is presumably due to interaction between ^{31}P and the quadrupolar La nucleus (100% abundant, $I = \frac{7}{2}$). On lowering the temperature to 233 K this peak sharpens and the spectrum shown in Figure 3(*a*) is obtained. The singlet at −42 p.p.m. is due to unreacted Ph_2PH, and the singlet at −15 p.p.m. to Ph_2PPPh_2 formed in small quantities during the reaction. In order to establish that the signal at 26.5 p.p.m. is due to $[LaL_2(PPh_2)]$ rather than to a phosphine adduct $[LaL_3(Ph_2PH)]$ the spectrum was recorded without ^1H decoupling. This spectrum, shown in Figure 3(*b*) still shows a singlet at 26.5 p.p.m., ruling out the possibility that this resonance is due to co-ordinated Ph_2PH. The peak at −42 p.p.m. became a doublet confirming that it is due to Ph_2PH.

Reactions of $[LnL_3(Ph_3PO)]$ *with* Ph_2PH.—As $[LnL_2(PPh_2)]$ are too air sensitive to be isolable, we attempted to prepare more tractable four-co-ordinate complexes by addition of Ph_3PO. In the course of these experiments we found, to our surprise, that the known four-co-ordinate complexes $[LnL_3(Ph_3PO)]$[8] react more rapidly with Ph_2PH than do the three-co-ordinate, and thus less sterically hindered, $[LnL_3]$. Addition of one equivalent of Ph_2PH to colourless solutions of $[LnL_3(Ph_3PO)]$ (Ln = La, Eu, or Y) resulted in an immediate deep orange colouration. ^1H N.m.r. of the reaction mixtures for La and Y showed the reaction to be that shown in equation (2).

$$[LnL_3(Ph_3PO)] + Ph_2PH \longrightarrow [LnL_2(PPh_2)(Ph_3PO)] + HL \quad (2)$$

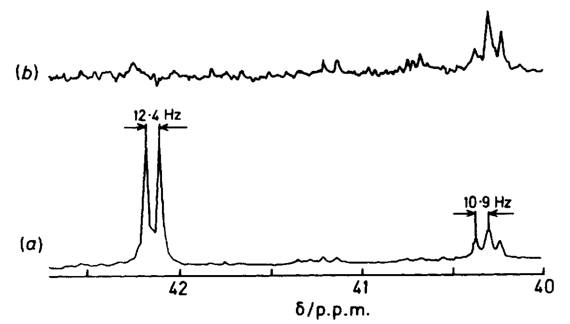

Figure 5. (*a*) ^{31}P N.m.r. spectrum of [$YL_3(Ph_3PO)$] + Ph_2PH. (*b*) ^{31}P N.m.r. spectrum of [$YL_3(Ph_3PO)$] + Ph_2PH with ^{31}P decoupling

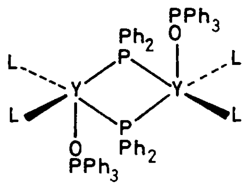

Figure 6. Possible structure of [$YL_2(PPh_2)(Ph_3PO)$]

The ^1H n.m.r. spectrum of the mixture of [$YL_3(Ph_3PO)$] with Ph_2PH is shown in Figure 4. The same reaction is seen for [$EuL_3(Ph_3PO)$], giving a deep orange solution, and as in the case of [$EuL_2(PPh_2)$], the ^1H n.m.r. spectrum of the product shows broad peaks at diamagnetic shifts, and these shifts do not change with temperature. ^{89}Y is 100% abundant and has $I = \frac{1}{2}$, and therefore, much information should be available from ^{31}P n.m.r. studies of the reaction between [$YL_3(Ph_3PO)$] and Ph_2PH. The ^{31}P n.m.r. spectrum of [$YL_3(Ph_3PO)$] at room temperature shows two rather broad resonances due to exchange between free and co-ordinated Ph_3PO. However, on lowering the temperature to 253 K this exchange is slowed down, and a sharp doublet ($J_{P\text{-}Y}$ = 12 Hz) appears at 38 p.p.m. due to co-ordinated Ph_3PO. On addition of one equivalent of Ph_2PH to a solution of [$YL_3(Ph_3PO)$], the spectrum shown in Figure 5(*a*) is obtained, which shows a triplet (J = 10.9 Hz) at 40.3 p.p.m. and a doublet (J = 12.4 Hz) of equal intensity at 42.1 p.p.m. Due to the closeness of the coupling constants it was important to establish whether coupling was due to P–Y or P–P interactions. We therefore saturated the doublet signal, and found that the triplet signal remained as shown in Figure 5(*b*), thus demonstrating that the coupling is due to ^{89}Y rather than ^{31}P. These are the largest values of $J(^{89}Y\text{-}^{31}P)$ yet reported, the previous largest being 6.5 Hz for [$Y\{C[P(O)Ph_2]_3\}_2$].[9] The ^{31}P n.m.r. spectrum could be explained either by a dimeric structure as shown in Figure 6, with the terminal Ph_3PO ligands giving rise to the doublet and the bridging PPh_2 ligands giving rise to the triplet, or by a rapid intermolecular exchange of PPh_2 *via* a dimeric intermediate. On steric grounds the dimeric structure seems rather unlikely, and we therefore favour a monomeric structure with rapid exchange of PPh_2.

We have been able to isolate deep orange crystals from toluene solutions of [$LnL_2(PPh_2)(Ph_3PO)$] for Ln = La, Eu, Gd, or Y. However, they are totally insoluble in toluene or Et_2O, suggesting that some further reaction has occurred, and they are too air sensitive to survive more than an hour in a Lindeman capillary sealed under Ar, thus preventing *X*-ray structure determination.

The phosphido lanthanide complexes described in this paper have several intriguing properties. They are all intensely coloured, which is unusual for compounds of La, Y, and Gd, and they are all extremely air sensitive. We have found that their reactions with oxygen are chemiluminescent; in the case of Eu compounds a bright orange glow is emitted, and in the case of La and Y a less intense blue-white emission is seen. To our knowledge the only other example of chemiluminescence for a lanthanide complex in solution is the reaction of [$Yb(\eta\text{-}C_5Me_5)_2$] with O_2.[10]

Experimental

^1H N.m.r. spectra were recorded on a Bruker WP80 spectrometer at QMC, and ^{31}P n.m.r. spectra on a Bruker WH400 spectrometer at QMC or a 250 MHz spectrometer at Kings College under the University of London Intercollegiate Research Service.

Preparative scale reactions were performed under dry, oxygen free nitrogen using standard Schlenk techniques. Solvents were distilled from sodium benzophenone ketyl and stored over 4 Å molecular sieves prior to use. For the n.m.r. tube reactions, solvents (C_6D_6 or C_7D_8) were distilled from $LiAlH_4$ and degassed by four freeze–pump–thaw cycles prior to use. In a typical experiment a Pyrex n.m.r. tube (5 mm for ^1H, 10 mm for ^{31}P) was attached to a Youngs tap *via* a short length of 5 mm outside diameter medium wall Pyrex tubing, and weighed empty. A solution of [LnL_3] or [$LnL_3(Ph_3PO)$] (*ca.* 50 mg for ^1H, *ca.* 150 mg for ^{31}P) in pentane was transferred to the n.m.r. tube under N_2, the solvent removed under vacuum, and the tube reweighed. Solvent (C_6D_6 or C_7D_8 for ^1H, a mixture of C_6D_6 and C_7H_8 for ^{31}P) was transferred to the n.m.r. tube. A stoicheiometric amount of Ph_2PH was added by microsyringe, the resulting solution degassed by three freeze–pump–thaw cycles, and the tube sealed under vacuum.

Acknowledgements

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References

1 R. A. Andersen, J. M. Boncella, C. J. Burns, J. C. Green, D. Hohl, and N. Rosch, *J. Chem. Soc., Chem. Commun.*, 1986, 405.
2 G. Bielang and R. D. Fischer, *J. Organomet. Chem.*, 1978, **161**, 335.
3 T. D. Tilley, R. A. Andersen, and A. Zalkin, *J. Am. Chem. Soc.*, 1982, **104**, 3725.
4 T. D. Tilley, R. A. Andersen, and Z. Zalkin, *Inorg. Chem.*, 1983, **22**, 856.
5 H. Schumann and G. M. Frisch, *Z. Naturforsch., Teil B*, 1981, **36**, 1244.
6 W. J. Evans, I. Bloom, W. E. Hunter, and J. L. Atwood, *Organometallics*, 1983, **2**, 709.
7 H. C. Aspinall, D. C. Bradley, M. B. Hursthouse, K. D. Sales, and N. P. C. Walker, *J. Chem. Soc., Chem. Commun.*, 1985, 1585.
8 D. C. Bradley, J. S. Ghotra, F. A. Hart, M. B. Hursthouse, and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1977, 1166.
9 S. O. Grim and S. A. Sangokoya, *J. Chem. Soc., Chem. Commun.*, 1984, 1599.
10 A. C. Thomas and A. B. Ellis, *J. Chem. Soc., Chem. Commun.*, 1984, 1270.

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