

Phosphine Complexes of Lanthanum and Lutetium

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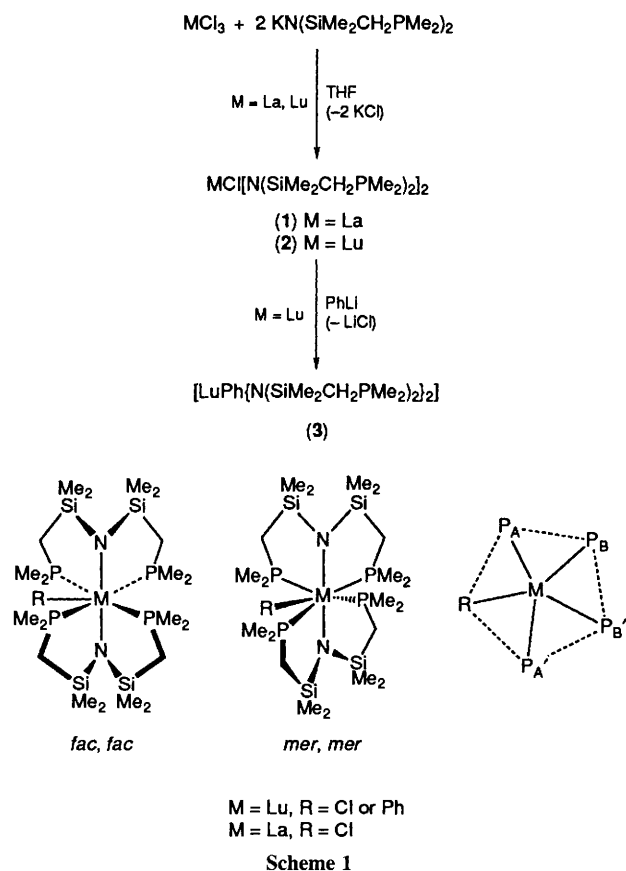
Multinuclear variable temperature NMR studies on $[\text{MCl}\{\text{N}(\text{SiMe}_2\text{CH}_2\text{PMe}_2)_2\}_2]$, $\text{M} = \text{La}$ or Lu , and $[\text{LuPh}\{\text{N}(\text{SiMe}_2\text{CH}_2\text{PMe}_2)_2\}_2]$ conclusively show phosphine co-ordination to these hard metal centres; in the case of lanthanum, this is the first reported phosphine complex.

The co-ordination of soft, neutral phosphorus donors to the hard lanthanoid and group 3 metals has only recently been achieved.¹ To date only a handful of such complexes have been prepared, *e.g.* $[(\eta^5\text{-C}_5\text{H}_4\text{Me})_3\text{Ce}(\text{PMe}_3)]$,² $[(\eta^5\text{-C}_5\text{H}_4\text{Me})_3\text{Ce}\{\text{P}(\text{OCH}_2)_3\text{CEt}\}]$,³ $[\text{M}\{\text{OCBu}^t_2\text{CH}_2\text{PMe}_2\}_3]$ ($\text{M} = \text{Y}$ and Nd),⁴ $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{YbCl}(\text{Me}_2\text{PCH}_2\text{PMe}_2)]$,⁵ and $[\text{Yb}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)]$. It is notable that there are no reported examples of phosphine ligands co-ordinated to lanthanum and only one previous report⁷ of a lutetium phosphine derivative, $[(\eta^5\text{-C}_5\text{H}_5)_2\text{LuCH}_2\text{PMe}_2]$.

Herein we detail the preparation and characterization of the first lanthanum phosphine complex, $[\text{LaCl}\{\text{N}(\text{SiMe}_2\text{-}$

$\text{CH}_2\text{PMe}_2)_2\}_2]$ and two new related lutetium derivatives, $[\text{LuCl}\{\text{N}(\text{SiMe}_2\text{CH}_2\text{PMe}_2)_2\}_2]$ and $[\text{LuPh}\{\text{N}(\text{SiMe}_2\text{-CH}_2\text{PMe}_2)_2\}_2]$. In addition, we establish unequivocally that the phosphine donors are co-ordinated, *via* analysis of low-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra.

Our strategy for obtaining phosphine complexes of typically hard elements is to use the hybrid chelating ligand $\text{N}(\text{SiMe}_2\text{CH}_2\text{PMe}_2)_2^-$. The hard amide donor anchors the ligand to the metal thereby inducing chelation of the pendant phosphine arms by virtue of their close proximity. Using this methodology, we have prepared phosphine complexes of Zr, Hf⁸ and Y.⁹ Thus, the addition of two equivalents of



$\text{K}[\text{N}(\text{SiMe}_2\text{CH}_2\text{PMe}_2)_2]$ (made analogously⁸ to $\text{Li}[\text{N}(\text{SiMe}_2\text{CH}_2\text{PMe}_2)_2]$ except that KCH_2Ph was used instead of BuLi) to a tetrahydrofuran (THF) slurry of LaCl_3 or LuCl_3 yielded the hexanes-soluble bis(amido-diphosphine) derivatives having the general formula $[\text{MCl}\{\text{N}(\text{SiMe}_2\text{CH}_2\text{PMe}_2)_2\}_2]$, (1) $\text{M} = \text{La}$ and (2) $\text{M} = \text{Lu}$ (Scheme 1). These complexes are isolated as very air- and moisture-sensitive white, crystalline solids. Addition of phenyl-lithium to the lutetium derivative generates the phenyl complex $[\text{LuPh}\{\text{N}(\text{SiMe}_2\text{CH}_2\text{PMe}_2)_2\}_2]$ (3). All three complexes were characterized by NMR spectroscopy† and also gave satisfactory microanalyses (C, H, and N).

† NMR data in C_7D_8 : ^1H at 300 MHz referenced to PhCD_2H at 2.09 ppm, ^{31}P at 121.4 MHz referenced to external $\text{P}(\text{OMe})_3$ in C_7D_8 at +141.0 ppm, and ^{13}C at 75.4 MHz referenced to PhCD_3 at 20.4 ppm; J in Hz. (1): ^1H δ 1.09 (24H, s, PMe), 0.79 (8H, s, PCH_2Si), and 0.27 (24H, s, SiMe); $^{31}\text{P}\{^1\text{H}\}$ at 20°C δ -43.5 (s); at -60°C δ -40.4 (br, s) and -42.5 (br, s); $^{13}\text{C}\{^1\text{H}\}$ [$^1J_{\text{C-H}}$] δ 20.05 (s, PCH_2Si) [t, 118.4], 16.05 (s, PMe) [q, 127.7], and 6.81 (s, SiMe) [q, 117.1]. (2): ^1H δ 1.06 (24H, s, PMe), 0.80 (8H, s, PCH_2Si), and 0.34 (24H, s, SiMe); $^{31}\text{P}\{^1\text{H}\}$ at 20°C δ -42.9 (s); at -80°C δ -40.8 (br, s) and -42.8 (br, s); $^{13}\text{C}\{^1\text{H}\}$ [$^1J_{\text{C-H}}$] δ 20.48 (s, PCH_2Si) [t, 120.8], 16.13 (s, PMe) [q, 128.3], and 7.11 (s, SiMe) [q, 117.3]. (3): ^1H at 20°C δ 8.24 (2H, d, J 6.6, H_α), 7.28 (2H, t, J 7.2, H_m), 7.11 (1H, t, J 7.2 H_β), 0.94 (24H, s, PMe), 0.68 (8H, s, PCH_2Si), and 0.37 (24H, s, SiMe); at -70°C δ 8.52 (H_α), 7.50 (H_m), 7.28 (H_β), 0.98, 0.95, 0.76, and 0.76 (PMe), 1.39, 0.80, 0.39, and -0.73 (PCH_2Si), and 0.71, 0.65, 0.49, and 0.20 (SiMe); $^{31}\text{P}\{^1\text{H}\}$ at 20°C δ -43.6 (s); at -60°C δ -39.7 (m) and -46.4 (m); $^{13}\text{C}\{^1\text{H}\}$ at 20°C δ 195 (s, C_i), 142.77 (s, C_o), 125.96 (s, C_m), 124.98 (s, C_p), 20.10 (s, PCH_2Si), 16.99 (s, PMe), and 7.35 (s, SiMe); at -49°C δ 195.5 (C_i), 143.83 (C_o), 125.73 (C_m), 124.73 (C_p), 20.05 and 19.56 (PCH_2Si), 17.68, 16.61, 16.34, and 16.21 (PMe), and 8.20, 7.78, 7.16, and 6.68 (SiMe).

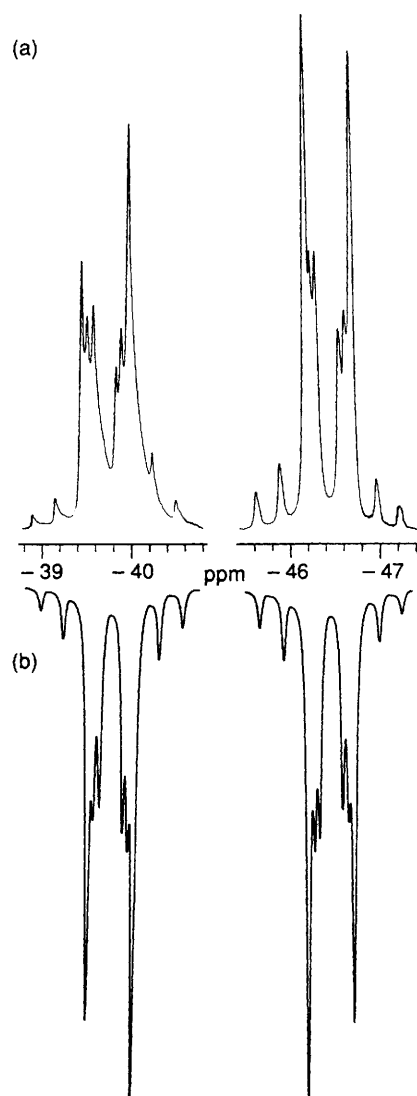


Figure 1. (a) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex (3) at -60°C . (b) Simulated $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum using Bruker PANIC software with the following coupling constants (Hz): $^2J_{\text{AA}'}$ = ± 62.1 ; $^2J_{\text{BB}'}$ = ± 19.6 ; $^2J_{\text{AB}'}$ = $^2J_{\text{A'B}}$ = 70.8; $^2J_{\text{AB}}$ = $^2J_{\text{A'B}}$ = -7.9.

These complexes display highly fluxional behaviour as expected for seven-co-ordinate species.¹⁰ Thus, at room temperature each complex displays three resonances for the amido-diphosphine ligands in each of the $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR spectra (*i.e.* the phosphorus methyl hydrogens and carbons, the methylene protons and carbons, and the silyl methyl hydrogens and carbons, respectively). At low temperatures, the ^1H NMR spectra of the chloro derivatives (1) and (2) are uninformative as broad signals are observed down to -95°C . However, the low-temperature ^1H NMR spectrum of the phenyl complex (3) displays proton resonances for four different silyl methyls, four phosphorus methyls, and four methylene groups, while the low-temperature $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows four silyl methyl, four phosphorus methyl, and two methylene carbon resonances.

At room temperature, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of complexes (1)–(3) consist of singlets at -43.5 , -42.9 , and -43.6 ppm respectively, considerably shifted from the uncoordinated ligand signal at -56.2 ppm. At lower temperatures, the chloro complexes (1)–(2) again show broadened and

uninformative spectra even down to -95°C (two unresolved signals in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra are observed). However, the phenyl complex (**3**) is well behaved in that at -60°C , a resolved AA'BB' pattern is found; this is reproduced in Figure 1 along with the simulation.

The only co-ordination geometry consistent with these spectral data is a pentagonal bipyramid having C_2 symmetry. Two possible stereoisomers of this structural type are shown in Scheme 1, one in which the amido-diphosphine ligands are *fac-fac* (phosphine donors of each ligand are *cisoid*) and in the other they are *mer-mer* (phosphine donors of each ligand are *transoid*). At this point, we are unable to distinguish between these two possibilities. However, it is noteworthy that the magnitude of the two-bond phosphorus-phosphorus couplings ($^2J_{\text{PP}}$) correlates with the assumed positions in the equatorial pentagonal plane in that *transoid* couplings are greater than *cisoid* ones (see Figure 1 caption for actual values).

Despite the difference in ionic radii¹¹ for La^{3+} (1.17 Å) and Lu^{3+} (1.00 Å), phosphine complexes for both these metals are isolable using the same tridentate chelating system. This illustrates the versatility of this mixed-donor, amido-diphosphine ligand and bodes well for access to complexes of any lanthanoid metal.¹²

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- 12 This work is in progress.