Synthesis and Reactions of Sterically Encumbered, Heteroleptic Lanthanum Phosphides. Structural Characterization of [{(Me₃Si)₂CH}-(C₆H₄-2-CH₂NMe₂)P]₂La(OR) and [{(Me₃Si)₂CH}-(C₆H₄-2-CH₂NMe₂)P]La(THF)[P(C₆H₄-2-CH₂NMe₂)-{CH(SiMe₃)(SiMe₂CH₂)}]] [R = *i*-Pr, *t*-Bu]

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Metathesis between LaI₃ and 2 equiv of {R(C₆H₄-2-CH₂NMe₂)P}K gives the heteroleptic complex {R(C₆H₄-2-CH₂NMe₂)P}₂LaI (**1**), which reacts in situ with 1 equiv of KOR′ to give the corresponding mixed phosphide/alkoxide complexes {R(C₆H₄-2-CH₂NMe₂)P}₂La(OR′) [R = (Me₃Si)₂CH, R′ = *t*-Bu (**2**), *i*-Pr (**3**)]. A similar in situ reaction between **1** and 1 equiv of any of the alkali metal organometallics R′K [R′ = PhCH₂, Me₃SiCH₂, (Me₃Si)₂CH] yields the cyclometalated product {([Me₃Si]₂CH)(C₆H₄-2-CH₂NMe₂)P}La(THF)[P(C₆H₄-2-CH₂NMe₂)-[CH{SiMe₃}{SiMe₂CH₂}]] (**4**) and R′H. Reaction between the homoleptic tris(alkyl) {(Me₃Si)₂-CH}₃La and 2 equiv of the secondary phosphine R(C₆H₄-2-CH₂NMe₂)PH yields **4** as the exclusive product, suggesting that the cyclometalation reaction is intramolecular in nature. Compounds **2**–**4** have been characterized by multielement NMR spectroscopy and X-ray crystallography. Variable-temperature ³¹P and ¹H NMR spectra and 2-D NMR experiments reveal that **4** is subject to dynamic processes in toluene solution, which may be attributed to rapid, reversible inversion at phosphorus, which results in rapid equilibria between stereoisomers; La–C cleavage is slow on the NMR time scale.

Introduction

Cyclopentadienyl-supported lanthanide and group 3 alkyls and hydrides have become well established as catalysts or precatalysts for a range of important organic transformations including the hydrogenation, hydroboration, hydrophosphination, hydroamination/cyclization, and hydrosilylation of olefins.[1–4] In many cases such complexes display enhanced reactivities and/or selectivities in comparison to their transition metal counterparts. Perhaps the greatest interest in these compounds has been in their application as neutral, single-component alternatives to Kaminsky-type transition metal metallocene catalysts for the polymerization of α-olefins and polar monomers such as alkyl acrylates.[5,6]

Although such cyclopentadienyl-supported complexes are often highly efficient, there has recently been a drive to develop more active and varied catalyst systems through the synthesis of lanthanide and group 3 alkyl and hydride complexes which are supported by alternative spectator ligands containing N- and/or O-donor groups,[7] including amidinates,[8] aminotroponiminates,[9] β-diketiminates,[10] diamides,[11] bis(phosphinimino)meth-anides,[12] calix-tetrapyrroles,[13] and Schiff base ligands.[14] These alternative supporting ligands provide excellent

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Chart 1
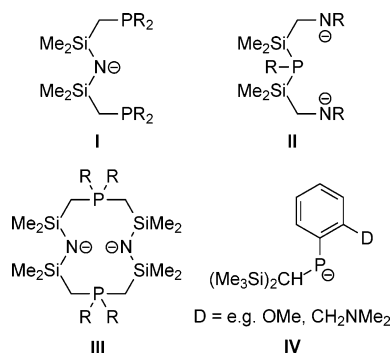
opportunities for tuning the properties of their complexes via substituent modification and may also permit the synthesis of bis(hydrocarbyl) complexes of the form LLnR$_2$, which are typically inaccessible with Cp-based ligands due to facile ligand redistribution equilibria in these systems.
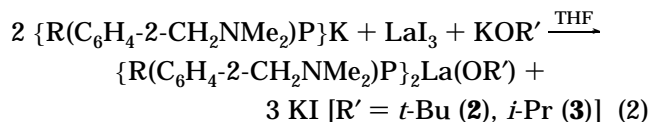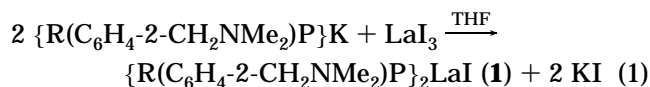
Since the hard lanthanide and group 3 cations favor coordination by hard donors such as amides and alkoxides, investigations into organometallic derivatives of these metals supported by softer P-donor ligands have been limited to only a very few examples. Most significant among these are the tertiary phosphine-substituted amide ligands developed by Fryzuk and co-workers with PNP (**I**), NPN (**II**), and P$_2$N$_2$ (**III**) donor sets (Chart 1).[15] Organolanthanide and group 3 complexes of these ligands undergo highly unusual reactions, including intramolecular C−H activation and the coupling of arenes.[16,17]

As part of an ongoing investigation into the chemistry of bulky P-donor ligands we have recently reported the synthesis of a variety of main group metal and lanthanide(II) complexes containing sterically demanding, donor-functionalized phosphide ligands of type **IV** (Chart 1).[18] The dimethylbenzylamine-substituted phosphide

ligand {(Me$_3$Si)$_2$CH}P(C$_6$H$_4$-2-CH$_2$NMe$_2$)$^-$ is reminiscent of Fryzuk's amide ligands and forms stable complexes with a variety of Ln(II) and main group metal centers, suggesting that this may be an interesting supporting ligand for organolanthanide(III) and group 3 complexes. We herein report the synthesis of several heteroleptic lanthanum(III) complexes of this ligand and their reactions with alkali metal organometallics.

Results and Discussion

Synthesis and Solid State Structures. A straightforward metathesis reaction between lanthanum triiodide and 2 equiv of the potassium phosphide {R(C$_6$H$_4$-2-CH$_2$NMe$_2$)P}K in ether/THF gives the heteroleptic complex {R(C$_6$H$_4$-2-CH$_2$NMe$_2$)P}$_2$LnI (**1**) (eq 1) as a sticky, red solid, which, due to its extremely high solubility, even in hydrocarbon solvents, could not be isolated in pure form [R = (Me$_3$Si)$_2$CH]. However, metathesis between in situ generated **1** and 1 equiv of either KO-*t*-Bu or KO-*i*-Pr in ether/THF cleanly gives the corresponding alkoxide complexes {R(C$_6$H$_4$-2-CH$_2$-NMe$_2$)P}$_2$Ln(OR′) [R′ = *t*-Bu (**2**), *i*-Pr (**3**)] as bright orange solids, which may be recrystallized from cold ether as orange blocks, in good to excellent yields (eq 2). Similar reactions between alternative lanthanide precursors such as LnCl$_3$(THF)$_n$ or Ln(OTf)$_3$ and {R(C$_6$H$_4$-2-CH$_2$NMe$_2$)P}K under the same, or more forcing, conditions did not proceed. We attribute the lack of reaction in these cases to the difficulty in displacing a hard Cl$^-$ or OTf$^-$ anion with a softer phosphide ligand from the hard lanthanum cation.

$$2 \{R(C_6H_4\text{-}2\text{-}CH_2NMe_2)P\}K + LaI_3 \xrightarrow{THF}$$
$$\{R(C_6H_4\text{-}2\text{-}CH_2NMe_2)P\}_2LaI \ (\textbf{1}) + 2 \ KI \ \ (1)$$

$$2 \{R(C_6H_4\text{-}2\text{-}CH_2NMe_2)P\}K + LaI_3 + KOR' \xrightarrow{THF}$$
$$\{R(C_6H_4\text{-}2\text{-}CH_2NMe_2)P\}_2La(OR') +$$
$$3 \ KI \ [R' = t\text{-}Bu \ (\textbf{2}), \ i\text{-}Pr \ (\textbf{3})] \ \ (2)$$

The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of **2** and **3** are as expected; signals in the ^{1}H and ^{13}C spectra are somewhat broadened due to dynamic processes involving conformational changes in the highly flexible phosphide ligands and/or reversible La−P or La−N bond cleavage, which is slow on the NMR time scale. The ^{31}P NMR spectra of **2** and **3** are also rather broad, and this may be attributed both to the dynamic nature of the complexes and to the influence of the quadrupolar La center [^{139}La I = 7/2, 99.91% natural abundance].

Single crystals of **2** and **3** suitable for X-ray crystallography were obtained from cold, concentrated solutions in ether. Compounds **2** and **3** are essentially isostructural, and so only the molecular structure of **2** is shown in Figure 1; details of bond lengths and angles

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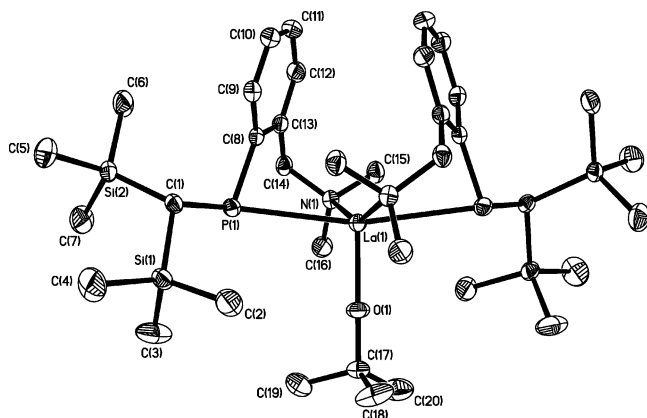
Figure 1. Molecular structure of **2** with 50% probability ellipsoids and with H atoms and disorder component omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2 and 3[a]

			2		
La(1)−O(1)	2.089(2)	La(1)−N(1)	2.6854(17)	La(1)−P(1)	3.0412(6)
P(1)−C(8)	1.827(2)	P(1)−C(1)	1.885(2)	C(1)−Si(1)	1.880(2)
C(1)−Si(2)	1.885(2)	Si(1)−C(2)	1.859(3)	Si(1)−C(3)	1.864(3)
Si(1)−C(4)	1.870(3)	Si(2)−C(5)	1.876(3)	Si(2)−C(6)	1.861(3)
Si(2)−C(7)	1.861(3)				

O(1)−La(1)−N(1)	102.86(4)	N(1A)−La(1)−N(1)	154.29(8)
O(1)−La(1)−P(1)	97.098(11)	N(1A)−La(1)−P(1)	102.57(4)
N(1)−La(1)−P(1)	74.18(4)	P(1A)−La(1)−P(1)	165.80(2)
C(8)−P(1)−C(1)	105.34(9)	C(8)−P(1)−La(1)	78.42(6)
C(1)−P(1)−La(1)	130.64(7)	Si(1)−C(1)−Si(2)	115.18(10)
Si(1)−C(1)−P(1)	109.41(10)	Si(2)−C(1)−P(1)	108.57(10)

			3		
La(1)−O(1)	2.092(5)	La(1)−N(1)	2.680(3)	La(1)−P(1)	3.0354(8)
P(1)−C(8)	1.832(3)	P(1)−C(1)	1.884(3)	C(1)−Si(1)	1.880(3)
C(1)−Si(2)	1.891(3)	Si(1)−C(2)	1.827(5)	Si(1)−C(3)	1.850(6)
Si(1)−C(4)	1.884(6)	Si(2)−C(5)	1.866(4)	Si(2)−C(6)	1.857(5)
Si(2)−C(7)	1.854(5)				

O(1)−La(1)−N(1)	101.72(6)	N(1A)−La(1)−N(1)	156.56(13)
O(1)−La(1)−P(1)	95.475(17)	N(1A)−La(1)−P(1)	103.28(6)
N(1)−La(1)−P(1)	74.43(6)	P(1A)−La(1)−P(1)	169.05(3)
C(8)−P(1)−C(1)	105.03(14)	C(8)−P(1)−La(1)	77.48(9)
C(1)−P(1)−La(1)	130.68(11)	Si(1)−C(1)−P(1)	110.36(17)
Si(1)−C(1)−Si(2)	115.17(16)	P(1)−C(1)−Si(2)	107.76(16)

[a] The suffix A denotes an atom generated by 2-fold rotation.

for **2** and **3** are given in Table 1. Both **2** and **3** crystallize as discrete molecular species which, due to disorder in the alkoxide groups, possess a crystallographic C_2 axis. The metal centers are bound by the P and N centers of the aminophosphide ligands to form two puckered, six-membered chelate rings, and the coordination sphere of each lanthanum center is completed by the oxygen atom of the alkoxide ligand, affording the metal centers a distorted square pyramidal geometry. The bite angles of the ligands are 74.18(4)° and 74.43(6)° for **2** and **3**, respectively. These compare with bite angles for the same ligand of 75.01(6)° in the samarium(II) complex {R(C_6H_4-2-CH_2NMe_2)P}_2Sm(THF),[18e] 75.31(4)° in {R(C_6H_4-2-CH_2NMe_2)P}_2Sr(THF), and 71.13(8)° in {R(C_6H_4-2-CH_2NMe_2)P}_2Ba(THF).[18f]

The La−P distances of 3.0412(6) and 3.0354(8) Å for **2** and **3**, respectively, are within the range of La−P distances in the few reported lanthanum phosphide complexes; for example, the La−P distance in (Ph_2P)-La{N(SiMe_3)_2}_2(OPPh_3)_2 is 3.165(6) Å,[19] while the La−P distances in the ate complex (^{t}Bu_2P)_2La(μ-P^{t}Bu_2)_2Li-(THF) range from 2.857(1) [terminal La−P] to 3.007(1)

Å [bridging La−P].[20] The La−P distance in the ate complex (^{i}Pr_2N)_2La{μ-P(C_6H_4-2-OMe)_2}_2Li(THF), which contains an anisole-functionalized phosphide ligand that is closely related to the phosphide ligand in **2** and **3**, is 3.141(4) Å.[21] The La−O distances in **2** and **3** [2.089(2) and 2.092(5) Å, respectively] are at the lower end of the range of La−O distances reported for lanthanum alkoxides and aryloxides; for example, the terminal La−O distances in La_4(OCH_2^{t}Bu)_{12} are 2.157-(6) and 2.169(7) Å,[22] whereas the La−O distances to the terminal alkoxides in the oxo-centered cluster La_5(μ_5-O)(μ_3-O^{t}Bu)_4(μ_2-O^{t}Bu)_4(O^{t}Bu)_5 range from 2.19(2) to 2.304(13) Å.[23]

While reactions between in situ generated **1** and potassium alkoxides proceed cleanly to the heteroleptic complexes described above, we find that similar reactions between **1** and organometallic reagents do not give the expected bis(phosphido)lanthanum hydrocarbyl complexes {R(C_6H_4-2-CH_2NMe_2)P}_2La(R′). Treatment of in situ generated **1** with 1 equiv of R′Li [R′ = Me, (Me_3Si)_2-CH] results in elimination of {R(C_6H_4-2-CH_2NMe_2)P}Li and the formation of intractable La-containing products, which are presumably heteroleptic species of the form {R(C_6H_4-2-CH_2NMe_2)P}La(R′)(I). Similarly, metathesis reactions between either of the alkoxide complexes **2** or **3** and 1 equiv of R′Li in THF or ether also result in the elimination of {R(C_6H_4-2-CH_2NMe_2)P}Li and the formation of intractable La-containing products. In contrast, treatment of **1** with 1 equiv of any of the organopotassium compounds R′K [R′ = CH(SiMe_3)_2, CH_2SiMe_3, CH_2Ph] leads to the formation of a cyclometalated complex, {R(C_6H_4-2-CH_2NMe_2)P}La(THF)-[P(C_6H_4-2-CH_2NMe_2){CH(SiMe_3)(SiMe_2CH_2)}] (**4**), in high yield, irrespective of the nature of R′ (Scheme 1).

The identity of **4** was confirmed by multielement NMR spectroscopy (see below) and X-ray crystallography; single crystals of **4** suitable for X-ray analysis were obtained from cold ether. The molecular structure of **4** is shown in Figure 2, and details of bond lengths and angles are given in Table 2. Compound **4** crystallizes as discrete molecules in which the lanthanum center is coordinated by the P and N atoms of a chelating aminophosphide ligand and by the P, N, and C atoms of a cyclometalated aminophosphide dianion ligand. The coordination sphere of the lanthanum center is completed by the oxygen atom of a molecule of THF. Thus the La center is six-coordinate, adopting a highly distorted octahedral geometry in which the two sterically encumbered phosphorus atoms are mutually *trans* [P−La−P 165.20(3)°]. The C, P, and N atoms of the cyclometalated ligand adopt a *mer*-configuration about the lanthanum center. The P−La−N bite angles of the ligands are 74.71(7)° and 70.53(7)° for the normal aminophosphide and the cyclometalated ligand, respectively; the C−La−P bite angle in the cyclometalated ligand is 75.20(10)°. The La−P distances of 3.0974(10) (aminophosphide ligand) and 2.9919(10) Å (cyclometa-

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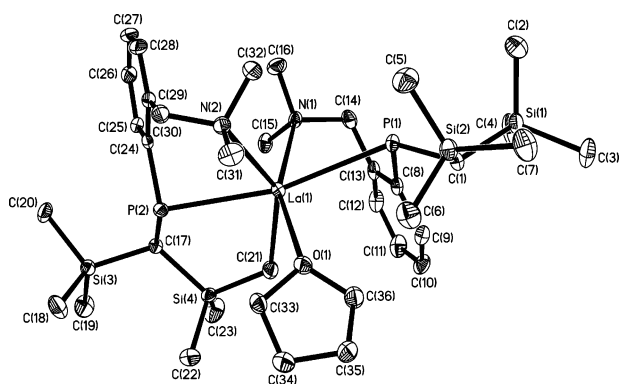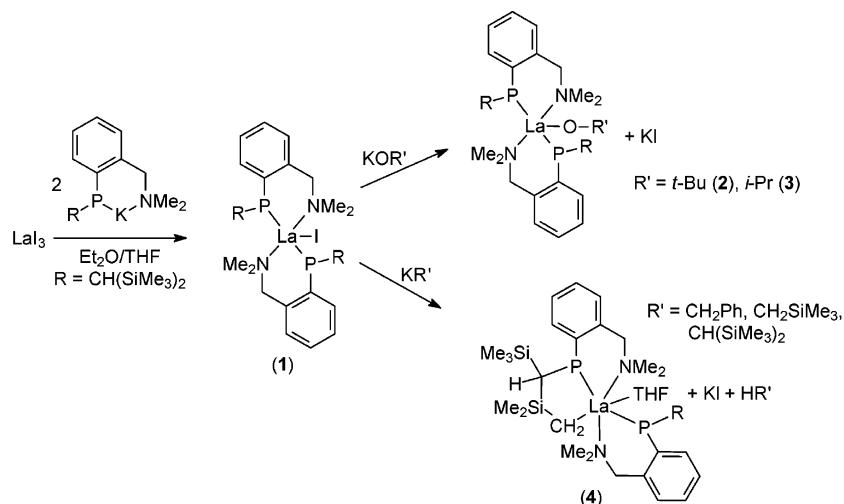
Scheme 1

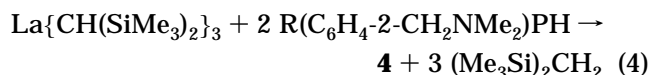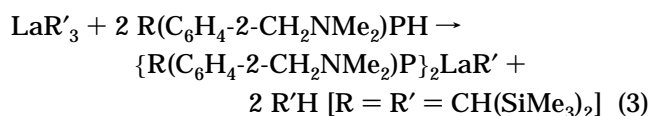**Figure 2.** Molecular structure of **4** with 50% probability ellipsoids and with H atoms omitted for clarity.

lated ligand) are similar to the equivalent distances in **2** and **3** and lie in the range of previously reported La–P distances.[20,21]

The La–C distance of 2.522(4) Å is at the shorter end of the range of previously reported La–C(sp³) distances; for example, the La–C distance in $\{(Me_3Si)_2CH\}_3La$ is 2.515(9),[24] and the La–C distances in $\{(Me_3Si)_2CH\}_3$-LaClLi(pmdeta) range from 2.55(2) to 2.68(4) Å [pmdeta = $N,N,N'N'N''$-pentamethyldiethylenetriamine].[25] The Si(4)–C(21) distance (i.e., that involving the formally anionic carbon center) is somewhat shorter at 1.839(4) Å than the remaining Si–C(Me) distances [average 1.872 Å], consistent with a significant degree of negative hyperconjugation from the carbanion center. Both phosphorus atoms are distinctly pyramidal [sum of angles at P(1) = 315.27°, P(2) = 304.94°].

The formation of **4** closely resembles the reaction of the PNP-ligated amide complex $LaCl\{N(SiMe_2CH_2PMe_2)_2\}_2$ with $LiCH_2SiMe_3$ reported by Fryzuk and co-workers, which gives the cyclometalated complex **5** (Ln = La, Scheme 2a).[16a] It is noteworthy that the syntheses of both **4** and **5** involve the generation of a heteroatom-stabilized carbanion (Si- and P-stabilized in **5** and solely Si-stabilized in **4**). Fryzuk and co-workers have also found that, for Ln = Y or Lu, the organolanthanide(III)

intermediate in this reaction, $RLn\{N(SiMe_2CH_2PMe_2)_2\}_2$ [R = PhCH₂ or Ph], may be isolated and that this intermediate gives the corresponding cyclometalated complex on thermolysis.[16b] These results clearly suggest that the cyclometalated complex **4** is formed via an analogous intramolecular alkane elimination reaction. In this regard, it is also noteworthy that a similar instantaneous alkane elimination has been observed in 5f element chemistry: Scott and co-workers have reported that treatment of the uranium(IV) triamidoamine complex $[\{(t\text{-}BuMe_2Si)NCH_2CH_2\}_3N]UCl$ with an organopotassium compound R′K yields the cyclometalated complex **6** (Scheme 2b), irrespective of the nature of R′.[26]

To gain further insight into the mechanism of formation of **4**, we undertook to prepare the compound $\{R(C_6H_4\text{-}2\text{-}CH_2NMe_2)P\}_2La\{CH(SiMe_3)_2\}$ via an alternative alkane elimination route (eq 3):

$$LaR'_3 + 2\ R(C_6H_4\text{-}2\text{-}CH_2NMe_2)PH \rightarrow$$
$$\{R(C_6H_4\text{-}2\text{-}CH_2NMe_2)P\}_2LaR' +$$
$$2\ R'H\ [R = R' = CH(SiMe_3)_2]\ \ (3)$$

$$La\{CH(SiMe_3)_2\}_3 + 2\ R(C_6H_4\text{-}2\text{-}CH_2NMe_2)PH \rightarrow$$
$$\textbf{4} + 3\ (Me_3Si)_2CH_2\ \ (4)$$

However, treatment of the lanthanum tris(alkyl) $La\{CH(SiMe_3)_2\}_3$ with 2 equiv of the secondary phosphine $\{(Me_3Si)_2CH\}(C_6H_4\text{-}2\text{-}CH_2NMe_2)PH$ in ether gave a sticky red solid, which was shown by NMR spectroscopy to be identical to **4** (eq 4). This strongly suggests that the cyclometalation reaction proceeds via the intramolecular elimination of R′H from transiently formed $\{R(C_6H_4\text{-}2\text{-}CH_2NMe_2)P\}_2La(R')$.

Behavior of 4 in Solution. Compound **4** is chiral at the two phosphorus centers, at the methine carbon in the cyclometalated ring, and at the lanthanum atom and, as such, may exist in several stereoisomeric forms. Multielement NMR spectroscopy reveals that the behavior of **4** in solution is highly solvent-dependent. In d_8-THF the ${}^{31}P\{^1H\}$ NMR spectra of **4** at room temperature and above consist of two broad singlets at −47.8 and 5.4 ppm; these signals sharpen considerably as the temperature is decreased, until at 245 K the spectrum consists of two sharp singlets at −51.5 and 1.2 ppm, which we attribute to the phosphide and cyclometalated

(24) Hitchcock, P. B.; Lappert, M. F.; Smith, R. G.; Bartlett, R. A.; Power, P. P. *Chem. Commun.* **1988**, 1007.
(25) Atwood, J. L.; Lappert, M. F.; Smith, R. G.; Zhang, H. *Chem. Commun.* **1988**, 1308.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 4

La(1)−P(1)	3.0974(10)	La(1)−N(1)	2.668(3)	La(1)−P(2)	2.9919(10)
La(1)−C(21)	2.522(4)	La(1)−N(2)	2.773(3)	La(1)−O(1)	2.555(3)
P(1)−C(1)	1.886(4)	P(1)−C(8)	1.832(4)	C(1)−Si(1)	1.883(4)
C(1)−Si(2)	1.882(4)	Si(1)−C(2)	1.864(5)	Si(1)−C(3)	1.877(5)
Si(1)−C(4)	1.859(5)	Si(2)−C(5)	1.861(5)	Si(2)−C(6)	1.872(5)
Si(2)−C(7)	1.879(5)	C(14)−N(1)	1.484(5)	P(2)−C(17)	1.880(4)
P(2)−C(24)	1.820(4)	C(17)−Si(3)	1.875(4)	C(17)−Si(4)	1.900(4)
Si(3)−C(18)	1.874(5)	Si(3)−C(19)	1.876(5)	Si(3)−C(20)	1.870(4)
Si(4)−C(21)	1.839(4)	Si(4)−C(22)	1.879(5)	Si(4)−C(23)	1.885(5)

P(1)−La(1)−N(1)	74.71(7)	P(1)−La(1)−P(2)	165.20(3)
P(1)−La(1)−C(21)	119.59(10)	P(1)−La(1)−N(2)	95.17(7)
P(1)−La(1)−O(1)	84.90(7)	N(1)−La(1)−P(2)	103.49(7)
N(1)−La(1)−C(21)	100.52(13)	N(1)−La(1)−N(2)	100.48(10)
N(1)−La(1)−O(1)	156.91(9)	P(2)−La(1)−C(21)	75.20(10)
P(2)−La(1)−N(2)	70.53(7)	P(2)−La(1)−O(1)	98.97(7)
C(21)−La(1)−N(2)	143.05(12)	C(21)−La(1)−O(1)	80.03(13)
N(2)−La(1)−O(1)	91.91(10)	La(1)−P(1)−C(1)	136.50(13)
La(1)−P(1)−C(8)	74.64(12)	La(1)−P(2)−C(17)	106.29(12)
La(1)−P(2)−C(24)	93.22	C(1)−P(1)−C(8)	104.13(18)
P(1)−C(1)−Si(1)	107.50(19)	P(1)−C(1)−Si(2)	112.3(2)
Si(1)−C(1)−Si(2)	115.8(2)	C(17)−P(2)−C(24)	105.43(18)
P(2)−C(17)−Si(3)	110.06(19)	P(2)−C(17)−Si(4)	108.73(18)
Si(3)−C(17)−Si(4)	118.4(2)		

Scheme 2
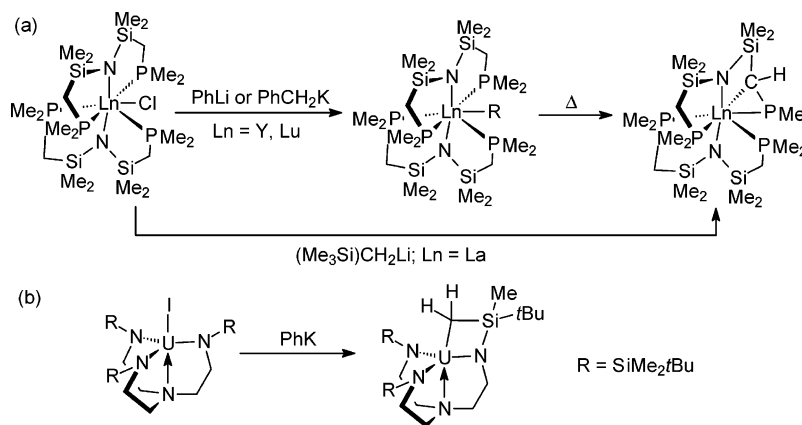
ligands, respectively. This suggests either the presence of only one stereoisomer in THF solution or that inter-conversion between stereoisomers is fast on the NMR time scale. ^{1}H NMR spectra of **4** in d_8-THF are also largely unchanged over the temperature range 217−317 K. At room temperature the diastereotopic protons from the CH$_2$La group are observed as poorly resolved singlets at approximately −1.4 and −1.0 ppm; at 217 K these signals are clearly resolved as two equal intensity doublets ($^2J_{HH} = 12.2$ Hz) at −1.58 and −1.23 ppm. At temperatures up to 317 K there is no evidence for coalescence of these two signals. Over the entire temperature range there are distinct signals for the dia-stereotopic (SiMe$_3$)$_2$ and SiMe$_2$ groups and the unique SiMe$_3$ group; at 217 K these are resolved as five sharp singlets. The diastereotopic benzylic protons are clearly resolved as four double doublets at 217 K, due to additional coupling to the ^{31}P nuclei, and these sig-nals merely broaden and lose resolution at higher temperatures. These data are consistent with the struc-ture observed in the solid state and strongly suggest that **4** exists either as a single species in THF solution or as a rapidly equilibrating mixture of diastereomers and that the La−C bond is not labile on the NMR time scale.

In contrast, multielement, variable-temperature, and 2-D NMR experiments indicate that compound **4** is subject to one or more dynamic processes in toluene
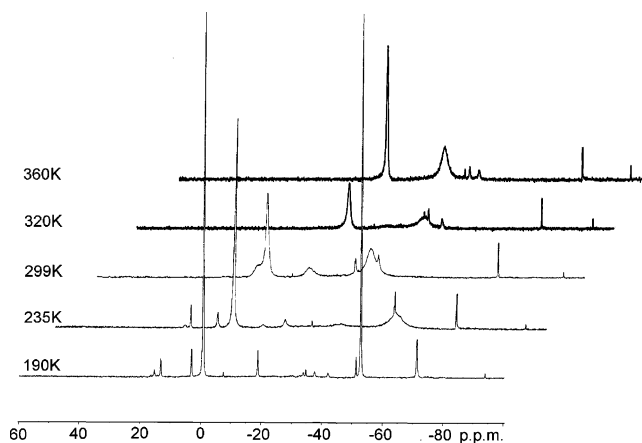

Figure 3. Selected variable-temperature ^{31}P{^{1}H} NMR spectra of **4** in d_8-toluene [small signal at −71 ppm due to free R(C$_6$H$_4$-2-CH$_2$NMe$_2$)PH].

solution. At 360 K the ^{31}P{^{1}H} NMR spectrum of **4** in d_8-toluene consists of two very broad singlets at −11.3 and 13.2 ppm along with significant low-intensity signals at −25.9 and −21.7 ppm (Figure 3). As the temperature is lowered, two new, broad signals begin to appear, until, at room temperature, the spectrum consists of two extremely broad signals centered at −26.7 and 7.9 ppm, assigned to the aminophosphide and
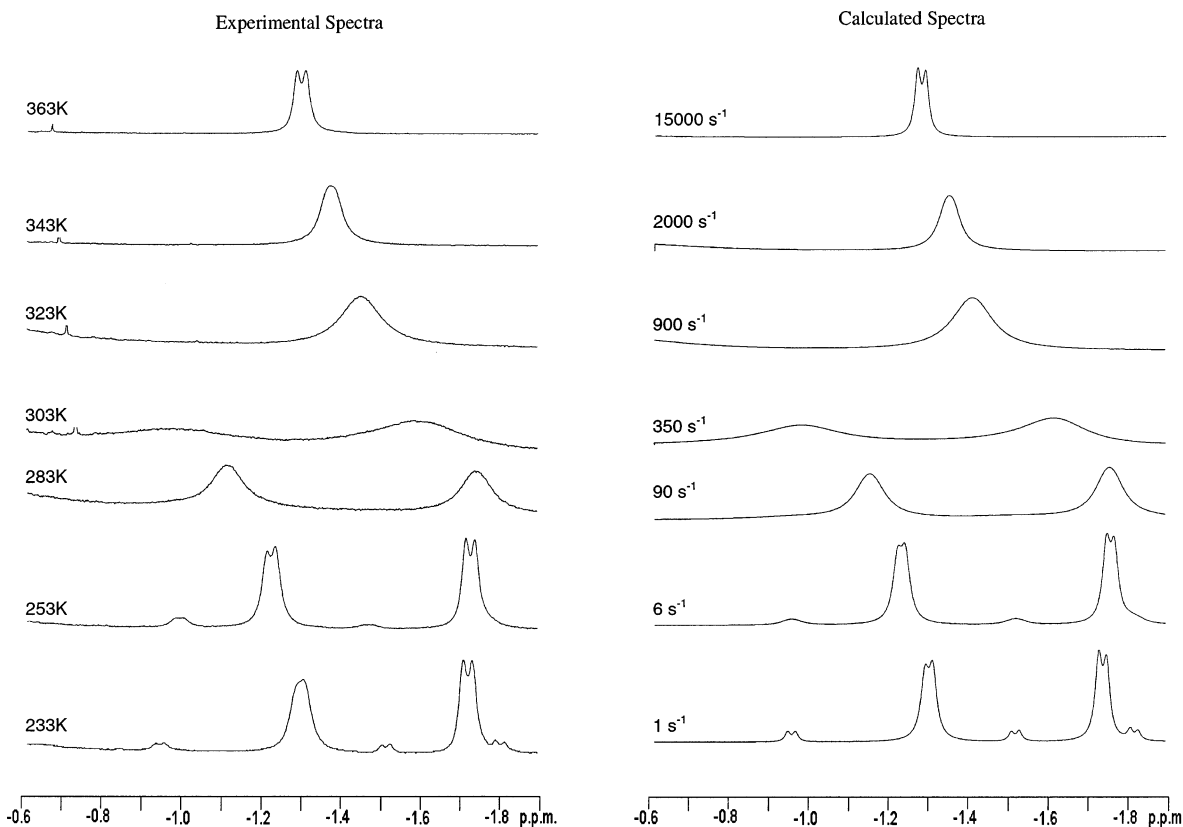
Figure 4. High-field parts of the experimental and simulated 500 MHz LaCH$_2$ proton NMR spectra of **4** in d_8-toluene at different temperatures.[28]

cyclometalated ligands, respectively, along with smaller, broad signals at −6.1 and 11.3 ppm and two sharp, low-intensity signals at −29.2 and −21.6 ppm. As the temperature is lowered, the two broad high-field and the two broad low-field signals sharpen and move considerably, until at 190 K the spectrum consists of two high-intensity, sharp singlets at −53.2 and −0.8 ppm, along with significant low-intensity signals at −51.8, −19.8, 2.8, and 15.4 ppm; in common with the spectra recorded in d_8-THF, coupling between the two ^{31}P nuclei of the major species is not resolved, even at the lowest temperature that we were able to attain (190 K). The ^{31}P NMR spectra of **4** in toluene may be interpreted as arising from the presence of several different stereoisomers in solution; at room temperature one stereoisomer is considerably more favored, and this favored stereoisomer increasingly predominates at low temperature. At higher temperatures there is a dynamic equilibrium between stereoisomers, which is fast on the NMR time scale.

This is confirmed by variable-temperature ^{1}H NMR experiments. Below 253 K the ^{1}H NMR spectrum of **4** in d_8-toluene is essentially consistent with the solid state structure: the spectrum exhibits five signals in the SiMe region due to the diastereotopic nature of the SiMe$_2$ and C(SiMe$_3$)$_2$ groups and separate signals for the four diastereotopic benzylic protons, in addition to signals for the NMe$_2$ and aromatic protons and THF; the diastereotopic protons of the CH$_2$La group give rise to a pair of doublets at −1.75 and −1.25 ppm (J_{HH} = 10.9 Hz) (Figure 4). This assignment was confirmed by low-temperature ^{1}H COSY and ^{1}H−^{13}C correlation experiments; the CH$_2$La group gives rise to a broad

signal at approximately 62 ppm in the ^{13}C{^{1}H} NMR spectrum, the broadness of which is attributed to the quadrupolar nature of the adjacent La center.[27]

In addition to the foregoing signals, the proton spectra at low temperatures have weaker doublets at −1.80 (appearing as a shoulder on the major peak at −1.75), −1.50, and −1.02 ppm, which are attributed to the diastereotopic CH$_2$La protons in minor stereoisomers of **4**. A TOCSY experiment (mixing time 25 ms, equivalent to short-range COSY) at 243 K showed that the signals at −1.80 and −1.50 ppm arise from the protons in the CH$_2$ group of the same stereoisomer and further that the partner of the signal at −1.02 ppm from a third stereoisomer is at +0.97 ppm and is hidden in the 1-D spectrum (see Figure 4). The EXSY spectrum at 253 K shows that protons giving the major signal at −1.75 are exchanging with the minor components at −1.80 and −1.02 and that those giving the major signal at −1.25 are exchanging with the minor components at −1.02 and +0.97 ppm (Figure 5). However, it appears that the two minor components are not exchanging directly. Furthermore, there is no exchange between the diastereotopic protons *within* a CH$_2$La group in any of the three detected isomers.

As the temperature is raised, the two major LaCH$_2$ signals broaden, shift markedly in position, and then

(26) (a) Boaretto, R.; Roussel, P.; Kingsley, A. J.; Munslow, I. J.; Sanders, J. J.; Alcock, N. W.; Scott, P. *Chem. Commun.* **1999**, 1701. (b) Boaretto, R.; Roussel, P.; Alcock, N. W.; Kingsley, A. J.; Munslow, I. J.; Sanders, C. J.; Scott, P. *J. Organomet. Chem.* **1999**, *591*, 174.

(27) The ^{1}H and ^{13}C chemical shifts of the CH$_2$La group of the major stereoisomer of **4** compare with chemical shifts of −0.14 and 75.2 ppm for the corresponding nuclei of the Si$_2$CHLa group in the homoleptic tris(alkyl) complex {(Me$_3$Si)$_2$CH}$_3$La (see ref 24).
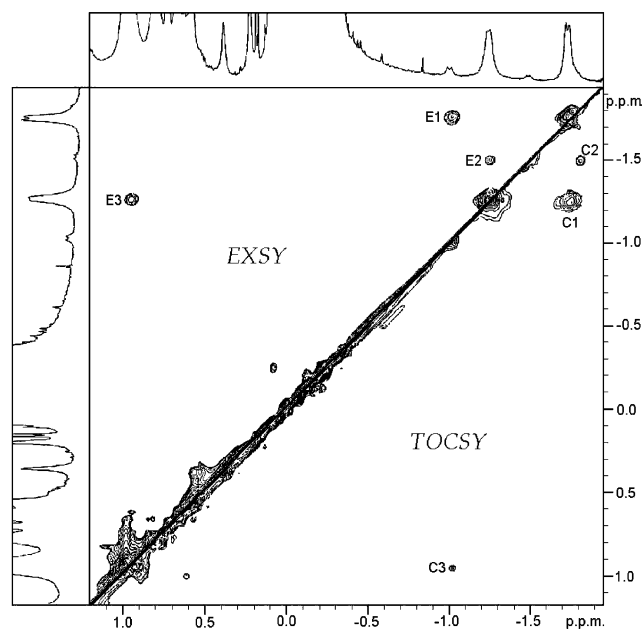
Figure 5. High-field parts of the 500 MHz EXSY (upper left, 253 K, 250 ms mixing time) and TOCSY (lower right, 243 K, 25 ms spin-locking time) of **4** in d_8-toluene. E1: exchange of a $LaCH_2$ proton between the major and one minor stereoisomer; the exchange peaks from the other proton are hidden as shoulders on the diagonal. E2 and E3: exchange of the $LaCH_2$ protons between the major and the other minor stereoisomer. C1: *J*-coupled geminal H—H interaction in the major stereoisomer. C2 and C3: corresponding interactions in the two minor stereoisomers.

regain their sharpness. However, they do not coalesce with one another, and at 363 K the high-field signal appears as a doublet at −1.09 ppm and the low-field signal is hidden by the SiMe signals. Its new position was determined to be at +0.20 ppm by a COSY experiment which showed a cross-peak with −1.09 ppm, and this was confirmed by selective homonuclear decoupling at 0.20 ppm which collapsed the doublet at −1.09 ppm. The foregoing behavior is accompanied by broadening and disappearance of the signals from the minor stereoisomers, and a comparison of experimental and simulated spectra is shown in Figure 4. It should be noted that as the problem is seriously underdetermined (i.e., part of the relevant spectral range is obscured by other signals, and there appears to be a significant temperature dependence of the chemical shifts), it is not realistic to derive thermodynamic parameters from these plots. Nonetheless, it is clear that while the dynamic processes lead to exchange of the stereoisomers, they do not involve interchange of the protons within a CH_2 group.

In the remainder of the proton spectrum in toluene solution the weaker signals from the minor stereoisomers were hidden and only resonances from the major isomer could be identified. At low temperatures these were essentially as found in the THF solution, but at higher temperatures there was coalescence of signals within the following diastereotopic sets of protons: N*Me*$_2$, CH(Si*Me*$_3$)$_2$, and aryl benzylic. However, the Si*Me*$_2$ signals did not behave in this way, and nor (as described above) did the $LaCH_2$ signals.

Compound **4** has four atomic centers of chirality—C(17), P(1), P(2), and La—of which the first may be assumed to be stereochemically rigid. In principle, the inequivalence of a pair of diastereotopic protons can be caused by any one of these centers, but in practice the contribution of a remote center will probably be undetectable. Thus the Si*Me*$_2$ groups will remain diastereotopic irrespective of the dynamics of the remainder of the molecule, and this is also true of the $LaCH_2$ protons *provided that the La−CH$_2$ bond remains intact and inversion at the carbanion center does not occur.* In contrast, chirality at P(1) will contribute to the diastereotopism of the CH(Si*Me*$_3$)$_2$ groups, and hence the coalescence of their signals at higher temperatures requires inversion of this phosphorus. It is similarly to be expected that P(1) and P(2) will contribute to the diastereotopism of the NMe$_2$ groups and the aryl benzylic protons, and their coalescence behavior therefore implies inversion of these two phosphorus atoms at higher temperatures. (In this context it should noted that the benzylic protons of uncoordinated 2-Me$_2$NCH$_2$C$_6$H$_4$PH-{CH(Si*Me*$_3$)$_2$} are diastereotopic, although the NMe$_2$ methyls are not, presumably owing to planarity or rapid inversion at nitrogen.) Rearrangement of the coordination geometry at lanthanum would also affect the observed behavior, but could not *of itself* produce the observed coalescences. Furthermore, if these processes were dominated by events at lanthanum, they would occur at identical rates, which is not the case, and it seems likely that stereochemical rearrangement to generate effective C_s or higher symmetry is facilitated by dissociation of the coordinated THF in toluene solution.

Since P(1) and P(2) each retain a "free" lone pair of electrons, the inversion of either can occur without true La−P bond cleavage. Rather, a simple interchange of the free and coordinating lone pairs will produce the observed effects. However, owing to the geometrical constraints of the remainder of the complex, such inversions will require significant rearrangement, or at least mobility, at lanthanum. As noted above, reversible dissociation of THF to leave the lanthanum effectively five-coordinate could bring this about in toluene solution. In THF solution, however, this dissociation will be inhibited by the vast excess of solvent molecules, and this in turn will prevent the inversions at phosphorus so that no exchange behavior is observed.

For a particular configuration at C(17) the chiral centers at P(1) and P(2) will lead to four NMR-distinguishable isomers of **4**, and the other configuration at C(17) will give the mirror images of these. Inspection of models suggests that potential ring strain and bulky steric interactions will lead to these isomers being of markedly different stabilities, and in fact we have obtained the NMR spectra of only three. Conversion of any one of these isomers into two of the others can be achieved by inversion at a single phosphorus center, whereas conversion to the fourth will need inversion of both phosphorus atoms and should therefore occur less readily. We have observed exchange of the major stereoisomer with each of the minor ones, but it appears that the minor stereoisomers do not mutually exchange. This suggests that the "missing" and the major isomers have opposite configurations at both phosphorus atoms, as do the two observed minor isomers.

Conclusions

Heteroleptic lanthanum(III) phosphides {R(C$_6$H$_4$-2-CH$_2$NMe$_2$)P}$_2$Ln(OR′) [R′ = *t*-Bu (**2**), *i*-Pr (**3**)] are readily accessible through a straightforward metathesis reaction between in situ generated {R(C$_6$H$_4$-2-CH$_2$NMe$_2$)P}$_2$-LaI (**1**) and a potassium alkoxide [R = (Me$_3$Si)$_2$CH]. However, treatment of **1** with 1 equiv of any of the more basic organopotassium reagents R″K [R″ = PhCH$_2$, Me$_3$-SiCH$_2$, or (Me$_3$Si)$_2$CH] results in formation of the cyclometalated compound [{(Me$_3$Si)$_2$CH}(C$_6$H$_4$-2-CH$_2$-NMe$_2$)P]La(THF)[P(C$_6$H$_4$-2-CH$_2$NMe$_2$){CH(SiMe$_3$)(SiMe$_2$-CH$_2$)}]] (**4**), irrespective of the nature of R″. Compound **4** is also isolated as the exclusive phosphorus-containing product from the reaction between {(Me$_3$Si)$_2$CH}$_3$La and 2 equiv of R(C$_6$H$_4$-2-CH$_2$NMe$_2$)PH, suggesting that the cyclometalation reaction proceeds via the intramolecular elimination of R″H from transiently formed {R(C$_6$H$_4$-2-CH$_2$NMe$_2$)P}$_2$LaR″(THF)$_n$. In toluene solution compound **4** is subject to dynamic exchange between a major and two minor stereoisomers, which appears to involve reversible inversion at the P centers, which is rapid on the NMR time scale; the La−C bond appears to be unaffected. In THF solution this dynamic process is not observed due to either the presence of just a single stereoisomer in this solvent or rapid equilibria between stereoisomers.

Experimental Section

General Procedures. All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. Light petroleum (bp 40−60 °C), toluene, ether, and THF were distilled from sodium, potassium, or sodium/potassium alloy and were stored over a potassium film (with the exception of THF, which was stored over activated 4 Å molecular sieves). Hexamethyldisiloxane was distilled from CaH$_2$ and stored over activated 4 Å molecular sieves. Deuterated THF and toluene were distilled from a potassium film, deoxygenated by three freeze−pump−thaw cycles, and stored over activated 4 Å molecular sieves. Anhydrous lanthanum iodide was purchased from Acros and used as supplied; *n*-butyllithium was obtained from Aldrich as a 2.5 M solution in hexanes. Potassium *tert*-butoxide was purchased from Lancaster and heated under vacuum at 100 °C (10^{-3} Torr) for 4 h prior to use. Me$_3$SiCH$_2$I was dried over activated 4 Å molecular sieves prior to use. Benzylpotassium,[29] (Me$_3$Si)$_2$CHLi,[30] {(Me$_3$Si)$_2$CH}-(C$_6$H$_4$-2-CH$_2$NMe$_2$)PH, [{(Me$_3$Si)$_2$CH}(C$_6$H$_4$-2-CH$_2$NMe$_2$)-P]K,[18a] and {(Me$_3$Si)$_2$CH}$_3$La[24] were prepared according to previously published procedures; (Me$_3$Si)$_2$CHK(OEt$_2$) was prepared by a modification of a previously published procedure (see below).[31]

^{1}H, ^{13}C, ^{31}P, and ^{29}Si NMR spectra were recorded on a JEOL Lambda 500 spectrometer operating at 500.1, 125.65, 202.35, and 99.25 MHz, respectively. ^{1}H, ^{13}C,

and ^{29}Si chemical shifts are quoted in ppm relative to tetramethylsilane, and ^{31}P chemical shifts are quoted relative to external 85% H$_3$PO$_4$. 2D proton TOCSY spectra were obtained using a 90°−t_1−$\tau_{spin-lock}$−acquire (t_2) pulse sequence and EXSY spectra using a 90°−t_1−90°−τ_m−90°−acquire (t_2) pulse sequence, each with phase cycling according to the States method. Typically, 16 transients were acquired into a 1024 (t_2) by 512 (t_1) data matrix, which was weighted with a sine-bell function in each dimension prior to Fourier transformation. 2D proton-^{13}C correlation spectra were obtained by indirect detection using the HSQC pulse sequence, and some ^{29}Si spectra were obtained using a refocused INEPT sequence.

Elemental analyses were obtained by the microanalysis service at London Metropolitan University, UK. The low carbon analysis for **2** is typical for this type of compound (see ref 18) and may be due to incomplete combustion.

Preparation of KO-*i*-Pr. Potassium (3.8 g, 97.2 mmol) was freed of encrustations and washed with light petroleum to remove residual mineral oil. The metal was then slurried in THF (30 mL), and dry propan-2-ol (7.2 mL, 94 mmol) was added by syringe. The mixture was stirred for 24 h and filtered, and volatiles were removed in vacuo. The resulting sticky white solid was baked at 75 °C (10^{-3} Torr) for 1 h to afford the product as a free-flowing white powder. Yield: 7.36 g, 80%.

Preparation of Me$_3$SiCH$_2$K. To a cold (−78 °C) solution of Me$_3$SiCH$_2$I (2.55 g, 11.91 mmol) in light petroleum (20 mL) was added *n*-BuLi (4.96 mL, 11.91 mmol). The resulting pale yellow solution was stirred for 1 h at this temperature. Volatiles were removed in vacuo, and the resulting oil was heated under vacuum (ca. 100 °C, 10^{-3} Torr) to afford a colorless crystalline solid. This was dissolved in ether (30 mL) and added to a cold (−10 °C) slurry of KO-*t*-Bu (1.33 g, 11.91 mmol) in ether (5 mL) and stirred for 1 h. Volatiles were removed in vacuo, and the resulting solid was washed with light petroleum (3 × 20 mL) and dried in vacuo to give Me$_3$SiCH$_2$K as a highly pyrophoric light tan powder. Yield: 1.01 g, 67%.

Preparation of (Me$_3$Si)$_2$CHK(OEt$_2$). This was prepared by a modified form of the procedure previously reported by Lappert and co-workers.[29] To a slurry of KO-*t*-Bu (1.29 g, 11.48 mmol) in ether (5 mL) was added a solution of (Me$_3$Si)$_2$CHLi (1.91 g, 11.48 mmol) in ether (25 mL). This mixture was stirred for 15 h. The faintly cloudy solution was filtered, and volatiles were removed in vacuo. The resulting white powder was washed with light petroleum (3 × 30 mL) and dried in vacuo. Yield: 1.8 g, 58%. The product can be further purified by recrystallization from ether/hexane as described by Lappert and co-workers.

Preparation of [{(Me$_3$Si)$_2$CH}(C$_6$H$_4$-2-CH$_2$NMe$_2$)-P]$_2$La(O-*t*-Bu) (2). To a cold (0 °C) slurry of LaI$_3$ (1.06 g, 2.0 mmol) in ether (20 mL) was added, dropwise, a solution of [{(Me$_3$Si)$_2$CH}(C$_6$H$_4$-2-CH$_2$NMe$_2$)P]K (1.45 g, 4.0 mmol) in THF (20 mL). Once the addition was complete, the mixture was allowed to warm to room temperature and was stirred for 24 h. Volatiles were removed in vacuo, and the residue was extracted into ether (3 × 20 mL) and filtered. The resulting deep red solution was added to solid KO-*t*-Bu (0.22 g, 2.0 mmol)

(28) The simulated spectra were calculated using the program GNMR (Cherwell Scientific, Oxford, UK), and a single rate of exchange between the major isomers and each of the two minor ones was assumed.

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Table 3. Crystallographic Data for 2, 3, and 4

	2	**3**	**4**
formula	$C_{36}H_{71}LaN_2OP_2Si_4$	$C_{35}H_{69}LaN_2OP_2Si_4$	$C_{36}H_{69}LaN_2OP_2Si_4$
fw	861.16	847.13	859.14
cryst size, mm	$0.80 \times 0.64 \times 0.52$	$0.38 \times 0.28 \times 0.10$	$0.72 \times 0.28 \times 0.22$
cryst syst	monoclinic	monoclinic	monoclinic
space group	$C2/c$	$C2/c$	$P2_1/c$
a, Å	15.5498(8)	15.3084(9)	11.0397(4)
b, Å	12.7735(7)	12.8699(8)	46.0149(15)
c, Å	24.8213(13)	24.5159(15)	9.6889(3)
β, deg	107.748(2)	106.471(2)	112.354(2)
V, Å^3	4695.5(4)	4631.9(5)	4552.0(3)
Z	4	4	4
ρ_{calcd}, g cm^{-3}	1.218	1.215	1.254
μ, mm^{-1}	1.11	1.12	1.14
no. reflns measd	19 989	19 908	32 246
no. unique reflns, R_{int}	5662, 0.027	5586, 0.045	8026, 0.030
no. reflns with $F^2 > 2\sigma(F^2)$	5187	4361	7472
transmn coeff range	0.471−0.597	0.675−0.896	0.494−0.787
R, $R_w{}^a$ ($F^2 > 2\sigma$)	0.0294, 0.0696	0.0423, 0.1003	0.0447, 0.0811
R, $R_w{}^a$ (all data)	0.0339, 0.0713	0.0648, 0.1121	0.0492, 0.0822
S^a	1.117	1.084	1.377
no. params	234	226	430
max., min. diff map, e Å^{-3}	1.36, −0.75	1.15, −1.33	0.57, −2.04

^{a} Conventional $R = \sum ||F_o| - |F_c||/\sum |F_o|$; $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $S = [\sum w(F_o^2 - F_c^2)^2/(\text{no. data} - \text{no. params})]^{1/2}$ for all data.

and stirred for 18 h. The mixture was filtered, and volatiles were removed in vacuo from the filtrate to afford a bright orange, pyrophoric powder. This was washed with cold (0 °C) hexamethyldisiloxane (3 × 1 mL) and dried in vacuo. Yield: 1.54 g, 95%. Deep orange crystals of **2** suitable for an X-ray diffraction study were grown from ether at 5 °C (a second crop could be obtained by storage of the mother liquor at −30 °C for 24 h). Combined yield of crystalline material: 1.02 g, 62%. Anal. Calcd for $C_{36}H_{71}LaN_2OP_2Si_4$: C, 50.21; H, 8.31; N, 3.25. Found: C, 48.67; H, 8.42; N, 3.13. ^{1}H NMR (d_8-toluene): δ 0.30 (36H, s, SiMe$_3$), 1.03 (2H, s, br, CHP), 1.39 (9H, s, CMe$_3$), 2.22 (12H, s, NMe$_2$), 3.41 (4H, s, br, CH$_2$N), 6.61−7.36 (8H, m, ArH). ^{13}C{^{1}H} NMR (d_8-toluene): δ 2.27 (SiMe$_3$), 10.46 (d, $J_{PC} = 67.2$ Hz, CHP), 34.01 (CMe$_3$), 43.72 (NMe$_2$), 66.85 (d, br, $J_{PC} = 12.4$ Hz, CH$_2$N), 76.75 (OCMe$_3$), 120.68, 131.64 (Ar), 131.76 (d, $J_{PC} = 28.9$ Hz, Ar), 131.87, 137.42 (Ar), 156.05 (d, $J_{PC} = 58.9$ Hz, Ar). ^{31}P{^{1}H} NMR (d_8-toluene): δ −30.8 (s, br). ^{29}Si{^{1}H} NMR (d_8-toluene): δ 1.32 (d, $J_{PSi} = 3.19$ Hz, SiMe$_3$), 1.37 (d, $J_{PSi} = 3.24$ Hz, SiMe$_3$).

Preparation of [{(Me$_3$Si)$_2$CH}(C$_6$H$_4$-2-CH$_2$NMe$_2$)-P]$_2$La(O-i-Pr) (3). To a cold (0 °C) slurry of LaI$_3$ (1.3 g, 2.5 mmol) in ether (20 mL) was added, dropwise, a solution of [{(Me$_3$Si)$_2$CH}(C$_6$H$_4$-2-CH$_2$NMe$_2$)P]K (1.82 g, 5.0 mmol) in THF (20 mL). Once the addition was complete, the mixture was allowed to warm to room temperature and was stirred for 22 h. Volatiles were removed in vacuo, and the residue was extracted into ether (3 × 20 mL) and filtered. The resulting deep red solution was added to solid KO-i-Pr (0.25 g, 2.5 mmol) and stirred for 24 h. The mixture was filtered, and volatiles were removed in vacuo from the filtrate to afford a bright orange, pyrophoric powder. This was washed with cold (0 °C) hexamethyldisiloxane (3 × 1 mL) and dried in vacuo. Yield: 2.03 g, 96%. Deep orange crystals of **3** suitable for an X-ray diffraction study were grown from ether at 5 °C (a second crop could be obtained by storage of the mother liquor at −30 °C for 24 h). Combined yield of crystalline material: 1.35 g, 64%. Anal. Calcd for $C_{35}H_{69}LaN_2OP_2Si_4$: C, 49.62; H, 8.21; N, 3.31. Found: C, 49.70; H, 8.19; N, 3.28. ^{1}H NMR

(d_8-toluene): δ 0.29 (36H, s, SiMe$_3$), 0.93 (2H, d, $J_{PH} = 6.08$ Hz, CHP), 1.25 (6H, d, CHMe$_2$), 2.06 (12H, s, NMe$_2$), 3.47 (4H, s, br, CH$_2$N), 4.33 (2H, septet, CHMe$_2$), 6.56−7.32 (8H, m, ArH). ^{13}C{^{1}H} NMR (d_8-toluene): δ 2.53 (SiMe$_3$), 9.89 (d, $J_{PC} = 66.9$ Hz, CHP), 28.15 (CHMe$_2$), 43.99 (NMe$_2$), 66.77 (d, $J_{PC} = 12.5$ Hz, CH$_2$N), 72.56 (CHMe$_2$), 120.63, 130.14, 131.58, 131.99 (Ar), 133.15 (d, $J_{PC} = 21.8$ Hz, Ar), 157.14 (d, $J_{PC} = 68.5$ Hz, Ar). ^{31}P{^{1}H} NMR (d_8-toluene): δ −29.2 (s, br). ^{29}Si{^{1}H} NMR (d_8-toluene): δ 1.10 (d, $J_{PSi} = 3.37$ Hz, SiMe$_3$), 1.15 (d, $J_{PSi} = 3.28$ Hz, SiMe$_3$).

Preparation of [{(Me$_3$Si)$_2$CH}(C$_6$H$_4$-2-CH$_2$NMe$_2$)-P]La(THF)[P(C$_6$H$_4$-2-CH$_2$NMe$_2$){CH(SiMe$_3$)-(SiMe$_2$CH$_2$)}]] (4). To a cold (0 °C) slurry of LaI$_3$ (1.26 g, 2.42 mmol) in ether (20 mL) was added, dropwise, a solution of [{(Me$_3$Si)$_2$CH}(C$_6$H$_4$-2-CH$_2$NMe$_2$)P]K (1.75 g, 4.8 mmol) in THF (20 mL). Once the addition was complete, the mixture was allowed to warm to room temperature and was stirred for 18 h. Volatiles were removed in vacuo, and the residue was extracted into ether (3 × 20 mL) and filtered. The resulting deep red solution was added to a frozen (−196 °C) slurry of C$_6$H$_5$-CH$_2$K (0.32 g, 2.42 mmol) in ether (10 mL). The mixture was allowed to warm to room temperature and was stirred for 20 h. The mixture was filtered, and volatiles were removed in vacuo from the filtrate to afford a sticky orange solid. This was washed with cold (0 °C) hexamethyldisiloxane (3 × 1 mL) and dried in vacuo. Yield: 1.77 g, 85%. Deep orange crystals of **4** suitable for an X-ray diffraction study were grown from ether at 5 °C (a second crop could be obtained by storage of the mother liquor at −30 °C for 24 h). Combined yield: 1.27 g, 61%. Compound **4** may also be isolated from similar reactions between LaI$_3$, [{(Me$_3$Si)$_2$CH}(C$_6$H$_4$-2-CH$_2$NMe$_2$)P]K, and either (Me$_3$SiCH$_2$)K (91% yield of **4**) or {(Me$_3$Si)$_2$CH}K (99% yield of **4**). Anal. Calcd for $C_{36}H_{69}LaN_2OP_2Si_4$: C, 50.33; H, 8.10; N, 3.26. Found: C, 50.33; H, 8.18; N, 3.27. ^{1}H NMR (d_8-THF, 217 K): δ −1.58 (d, $J_{HH} = 12.2$ Hz, 1H, CH$_2$La), 1.23 (d, $J_{HH} = 12.2$ Hz, 1H, CH$_2$La), −0.22 (s, 9H, SiMe$_3$), −0.09 (s, 9H, SiMe$_3$), −0.03 (s, 3H, SiMe$_2$), 0.08 (s, 3H, SiMe$_2$), 0.15 (s, 9H, SiMe$_3$), 0.82 (s, 1H, CHP), 1.39 (s, 3H, NMe),

1.75 (m, 4H, THF), 2.12 (s, 3H, NMe), 2.59 (s, 3H, NMe), 2.61 (s, 3H, NMe), 2.97 (m, 1H, CH$_2$N), 3.03 (m, 1H, CH$_2$N), 3.59 (m, 4H, THF), 3.85 (m, 1H, CH$_2$N), 4.01 (m, 1H, CH$_2$N), 6.49−7.49 (m, 8H, ArH). ^{31}P{^{1}H} NMR (*d*$_8$-THF, 295 K): δ −47.81 (s, br, aminophosphide ligand), 5.39 (s, br, cyclometalated ligand).

Reaction of {(Me$_3$Si)$_2$CH}(C$_6$H$_4$-2-CH$_2$NMe$_2$)PH with {(Me$_3$Si)$_2$CH}$_3$La. A solution of {(Me$_3$Si)$_2$CH}-(C$_6$H$_4$-2-CH$_2$NMe$_2$)PH (0.24 g, 0.76 mmol) in ether (0.5 mL) was added dropwise to a cold (−20 °C) solution of {(Me$_3$Si)$_2$CH}$_3$La (0.23 g, 0.38 mmol) in ether (5 mL). The resulting red solution was allowed to warm to room temperature and was stirred for 1 h. Volatiles were removed in vacuo to give a slightly sticky, orange crystalline solid. A ^{31}P{^{1}H} NMR spectrum of the product in toluene containing one drop of THF was identical to that recorded for **4**.

X-ray Data Collection, Structure Determination, and Refinement for 2, 3, and 4. Selected crystal data are given in Table 3, and further details of the structure determinations are in the Supporting Information. Crystals were examined on a Bruker AXS SMART CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 150 K. Intensities were integrated from a sphere of data recorded on narrow (0.3°) frames by ω rotation. Cell parameters were refined from the observed positions of all strong reflections in each data set. Semiempirical absorption corrections were applied, based on sym-metry-equivalent and repeat reflections. The structures were solved variously by heavy-atom and direct methods and were refined by least-squares methods on all unique F^2 values, with anisotropic displacement parameters, and with constrained riding hydrogen geometries; U(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} for the parent atom. Disorder for the *tert*-butyl group in **2** over a 2-fold rotation axis is clearly resolved; however, disorder of the isopropyl group in **3** is modeled with only moderate success. The largest features in final difference syntheses were close to heavy atoms. Programs were Bruker AXS SMART (control) and SAINT (integration), and SHELXTL for structure solution, refinement, and molecular graphics.[32]

Supporting Information Available: For **2**, **3**, and **4** details of structure determination, atomic coordinates, bond lengths and angles, and displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org. Observed and calculated structure factor details are available from the authors upon request.

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