Izod K, Jones CF, Wildman EP, Harrington RW, Waddell PG.

[A Suite of Sterically-Demanding Hybrid Alkyl/Cyclopentadienyl Ligands.](#)

Organometallics 2017

DOI: <https://doi.org/10.1021/acs.organomet.7b00662>

Copyright:

This document is the Accepted Manuscript version of a Published Work that appeared in final form in *Organometallics*, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see

<https://doi.org/10.1021/acs.organomet.7b00662>

DOI link to article:

<https://doi.org/10.1021/acs.organomet.7b00662>

Date deposited:

27/10/2017

Embargo release date:

30 October 2018

A Suite of Sterically-Demanding Hybrid Alkyl/Cyclopentadienyl Ligands

Keith Izod,* Claire F. Jones, Elizabeth P. Wildman, Ross W. Harrington, Paul G. Waddell

Main Group Chemistry Laboratories, School of Chemistry, Bedson Building, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK, e-mail: keith.izod@ncl.ac.uk

Supporting Information Placeholder

ABSTRACT: The hybrid alkyl/cyclopentadienyl “constrained-geometry” proligands $(\text{Me}_3\text{Si})_2\text{CH}\{\text{SiMe}_2(\text{C}_5\text{H}_5)\}$, $(\text{Me}_3\text{Si})_2\text{CH}\{\text{SiMe}_2(\text{C}_5\text{Me}_4\text{H})\}$ and $(\text{Me}_3\text{Si})_2\text{CH}\{\text{SiMe}_2(\text{C}_5\text{H}_4\text{-}3\text{-SiMe}_3)\}$ are synthesized by the reaction of the bromosilane $(\text{Me}_3\text{Si})_2\text{CH}(\text{SiMe}_2\text{Br})$ with the corresponding lithium cyclopentadienide. Metalation of these proligands with an excess of MeK gives access to the corresponding dipotassium salts $[(\text{Me}_3\text{Si})_2\text{C}\{\text{SiMe}_2(\text{C}_5\text{H}_4)\}]\text{K}_2(\text{OEt})_{0.5}$, $[(\text{Me}_3\text{Si})_2\text{C}\{\text{SiMe}_2(\text{C}_5\text{Me}_4)\}]\text{K}_2(\text{OEt})_2$ and $[(\text{Me}_3\text{Si})_2\text{C}\{\text{SiMe}_2(\text{C}_5\text{H}_3\text{-}3\text{-SiMe}_3)\}]\text{K}_2(\text{C}_6\text{H}_6)]_2 \cdot 2\text{C}_6\text{H}_6$, after recrystallization. Similarly, the reaction between the phosphine-borane-substituted chlorosilane $(\text{Me}_3\text{Si})\text{CH}\{\text{PMe}_2(\text{BH}_3)\}(\text{SiMe}_2\text{Cl})$ and $[\text{C}_5\text{Me}_4\text{H}]\text{Li}$ gives the proligand $(\text{Me}_3\text{Si})\text{CH}\{\text{PMe}_2(\text{BH}_3)\}\{\text{SiMe}_2(\text{C}_5\text{Me}_4\text{H})\}$, which reacts with two equivalents of PhCH_2K to give the dipotassium salt $[(\text{Me}_3\text{Si})\text{C}\{\text{PMe}_2(\text{BH}_3)\}\{\text{SiMe}_2(\text{C}_5\text{Me}_4)\}]\text{K}_2(\text{THF})$. X-ray crystallography reveals that the dipotassium salts of these hybrid ligands crystallize as zig-zag polymers or three-dimensional networks. The suitability of the dipotassium salts as ligand transfer reagents for the synthesis of lanthanide complexes was probed through the synthesis of the lanthanum(III) complex $[(\text{Me}_3\text{Si})_2\text{C}\{\text{SiMe}_2(\text{C}_5\text{Me}_4)\}]\text{La}(\text{I})(\text{THF})_2$, in which the dianionic ligand chelates the lanthanum center.

INTRODUCTION

Ligands in which a cyclopentadienyl moiety and an anionic donor fragment, such as an amide or phosphide group, are linked via a spacer group (e.g. SiMe_2 , CH_2) into a single, dianionic unit (**I**), often referred to as “constrained geometry” ligands, are versatile supporting scaffolds in early transition metal and lanthanide chemistry.¹ Complexes of these ligands are well established as highly active catalysts for olefin polymerization and co-polymerization.² However, constrained geometry ligands in which a cyclopentadienyl group and a carbanion are linked into a single unit (**II**) are rather scarce.³ This is particularly true for lanthanide complexes, where the few reported examples arise from C-H activation of the *t*Bu or SiMe_3 substituents of a cyclopentadienyl ligand,⁴ or else the “carbanion” center forms part of a carborane cluster which is linked to the cyclopentadienyl ring.⁵

Sterically-hindered ligand systems of this type are even more uncommon. The sole example of a sterically-demanding cyclopentadienyl/carbanion constrained geometry ligand, initially isolated as its di-lithium salt, $[(\text{C}_5\text{H}_4)\text{SiMe}_2\text{CH}(\text{SiMe}_3)]\text{Li}_2(\text{tmeda})_2$, was reported by Lappert and co-workers

in 1998.⁶ The potential utility of this class of bulky hybrid alkyl/cyclopentadienyl ligand was illustrated through the isolation of a small number of zirconium(IV) complexes and its use as a precursor to an aza-allyl ligand system. No further complexes or reactivity of this, or closely related systems have been reported, in spite of the potential for tuning their steric and electronic properties through substitution at both the cyclopentadienyl ring and carbanion centers.

In an effort to expand this range of ligands for the synthesis of coordinatively unsaturated lanthanide complexes we have begun to investigate more fully this class of sterically-demanding, hybrid alkyl/cyclopentadienyl ligands. We report herein the synthesis of several new examples of these ligand systems as their di-potassium salts and present their solid state structures.

RESULTS AND DISCUSSION

The reaction between the bromosilane $(\text{Me}_3\text{Si})_2\text{CH}(\text{SiMe}_2\text{Br})$ ⁷ and any of CpLi , $[\text{C}_5\text{Me}_4\text{H}]\text{Li}$ or $[(\text{Me}_3\text{Si})\text{C}_5\text{H}_4]\text{Li}$ in THF under reflux yields the corresponding substituted cyclopentadienes $(\text{Me}_3\text{Si})_2\text{CH}\{\text{SiMe}_2(\text{C}_5\text{H}_5)\}$ (**1a**) $(\text{Me}_3\text{Si})_2\text{CH}\{\text{SiMe}_2(\text{C}_5\text{Me}_4\text{H})\}$ (**1b**) and $(\text{Me}_3\text{Si})_2\text{CH}\{\text{SiMe}_2(\text{C}_5\text{H}_4\text{-}3\text{-SiMe}_3)\}$ (**1c**) (Scheme 1). Due to the poor nucleophilicity of the cyclopentadienyl anions, these reactions require several hours to reach completion.

Compounds **1a-c** are isolated as colorless, viscous oils, although a single regioisomer of **1b** may be crystallized from cold light petroleum as colorless plates. For **1c** there is no evidence for the formation of the positional isomer $(\text{Me}_3\text{Si})_2\text{CH}\{\text{SiMe}_2(\text{C}_5\text{H}_4\text{-}2\text{-SiMe}_3)\}$, presumably as a result of the increased steric congestion that would arise in this compound.

Nonetheless, the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **1a-c** are complicated due to the presence of the three possible regioisomers in each case (four regioisomers in the case of **1c**), due to the different possible positions of the double bonds in the cyclopentadiene moiety; this results in complex spectra with multiple, overlapping signals which are difficult to interpret. These spectra simplify considerably on metalation of the cyclopentadienyl ring and consequent removal of this isomerism.

Scheme 1.

In order that the impact of metalation on the core of the ligand might be determined, the X-ray crystal structure of **1b** was obtained (Figure 1).

Figure 1. Molecular structure of **1b** with 40% probability ellipsoids and with H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–Si(1) 1.8909(19), C(1)–Si(2) 1.8909(18), C(1)–Si(3) 1.8872(19), C(10)–Si(1) 1.926(2), Si(1)–C(1)–Si(2) 114.84(10), Si(1)–C(1)–Si(3) 113.61(9), Si(2)–C(1)–Si(3) 114.45(10), C(1)–Si(1)–C(10) 110.35(8).

Attempted metalation of **1a-c** with two equivalents of $n\text{BuLi}$, $i\text{Pr}_2\text{NLi}$ or PhCH_2K resulted in deprotonation only of the cyclopentadienyl rings in each case, as judged by NMR spectroscopy, leaving the central methine protons untouched, even when the reactions were heated under reflux for extended periods. However, use of the much more reactive MeK in large excess led to complete double deprotonation to give the corresponding dipotassium salts $[(\text{Me}_3\text{Si})_2\text{C}\{\text{SiMe}_2(\text{C}_5\text{H}_4)\}]\text{K}_2(\text{OEt}_2)_{0.5}$ (**2a**), $[(\text{Me}_3\text{Si})_2\text{C}\{\text{SiMe}_2(\text{C}_5\text{Me}_4)\}]\text{K}_2(\text{OEt}_2)_{0.5}$ (**2b**) and $[(\text{Me}_3\text{Si})_2\text{C}\{\text{SiMe}_2(\text{C}_5\text{H}_3-3-\text{SiMe}_3)\}]\text{K}_2(\text{C}_6\text{H}_6)_{0.5}$ (**2c**) as colorless to pale yellow sticky solids (Scheme 2). The use of a large excess of MeK is necessary in these reactions due to their rather sluggish nature and the competing reaction between MeK and the diethyl ether solvent.

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **2a-c** are consistent with the above formulations. Compounds **2a** and **2b** have limited solubility in benzene, but are soluble in THF, whereas **2b** is soluble in both benzene and ethereal solvents. All three compounds **2a-c** react rapidly with toluene to give benzylpotassium;

similar reactivity was observed for the closely related $[(\text{Me}_3\text{Si})_3\text{C}]\text{K}]_\infty$ (**3**).⁸

We were unable to obtain single crystals of **2a** suitable for X-ray crystallography, but the solvates $[(\text{Me}_3\text{Si})_2\text{C}\{\text{SiMe}_2(\text{C}_5\text{Me}_4)\}]\text{K}_2(\text{OEt}_2)$ (**2b.OEt**₂) and $[(\text{Me}_3\text{Si})_2\text{C}\{\text{SiMe}_2(\text{C}_5\text{H}_3-3-\text{SiMe}_3)\}]\text{K}_2(\text{C}_6\text{H}_6)]_2 \cdot 2\text{C}_6\text{H}_6$ (**2c.C**₆**H**₆) were obtained as colorless crystals in moderate yield on crystallization of **2b** and **2c** from diethyl ether and benzene, respectively.

Scheme 2.

Compound **2b.OEt**₂ crystallizes as zig-zag chains which contain two distinct potassium environments (Figure 2): K(1) is coordinated by the central carbanion and an η^5 -cyclopentadienyl group of the ligand, to give a pseudo-four-membered chelate ring [C(12)–K(1)–ring centroid angle 87.43(4)°], along with a molecule of diethyl ether. The second potassium ion connects these units and is coordinated by the central carbanion of one ligand and an η^5 -cyclopentadienyl group of a second ligand. Thus, both the central carbanion and the cyclopentadienyl groups bridge the two distinct potassium centers to form the polymer. In addition, there are short K...Me contacts between K(1) and C(14), C(15), C(16) and C(20), and between K(2) and C(13A) and C(18A). The K(1)–C(12) distance [3.1909(18) Å] is significantly longer than the K(2)–C(12A) distance [3.0140(18) Å], and the K(1)–ring centroid distance [2.7274(4) Å] is longer than the K(2)–ring centroid distance [2.6687(4) Å], due to the constraints of the small C(12)–K(1)–ring centroid chelate ring.

Figure 2. Extended solid-state structure of **2b.OEt**₂ with 40% probability ellipsoids and with H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): K(1)–O(1) 2.6673(14), K(1)–C(1) 3.0781(19), K(1)–C(2) 3.148(2), K(1)–C(3) 2.993(2), K(1)–C(4) 2.8128(18), K(1)–C(5) 2.8711(18), K(1)–ring centroid 2.7274(4), K(1)–C(12) 3.1909(18), K(1)...C(14) 3.428(2), K(1)...C(15) 3.539(3), K(1)...C(16) 3.346(2), K(1)...C(20) 3.406(3), K(2)–C(1) 2.9293(19), K(2)–C(2) 2.951(2), K(2)–C(3) 2.937(2), K(2)–C(4) 2.9043(18), K(2)–C(5) 2.9272(18), K(2)–ring centroid 2.6687(4), K(2)–C(12A) 3.0140(18), K(2)...C(13A) 3.183(2), K(2)...C(18A) 3.419(3), K(1A)–C(12)–K(2) 175.03(7), K(1)–ring centroid–K(2) 169.60(4), C(12)–K(1)–ring centroid 87.43(4).

The CSi_3 skeleton of the ligand is essentially planar (sum of Si-C-Si angles at C(12) = 359.75°) and the K(1A)-C(12)-K(2) angle is $175.03(7)^\circ$. This is reminiscent of the CSi_3 skeleton and K-C-K angle in the linear polymeric **3** [sum of angles at C(1) = 360° , K-C(1)-K' angle $179.2(3)^\circ$].⁸ The K(2)-C(12A) and K(1)-C(12) distances in **2b.OEt₂** [3.0140(18) and 3.1909(18) Å, respectively] lie to either side of the K-C(1) distance in **3** [3.090(11) Å], but are similar to the K(2)-C(1) and K(1)-C(1) distances in $[(\text{Me}_3\text{Si})_2\text{C}(\text{Me}_2\text{Si})_2\text{O}]\text{K}_2(\text{OEt}_2)_\infty$ (**4**) [3.0132(18) and 3.2302(18) Å, respectively];⁹ compound **4** also consists of a zig-zag polymer in which the potassium ions are alternately chelated by the dicarbanion ligand, or else bridge dialkylpotassate anions in the chain. The K(1)-ring centroid and K(2)-ring centroid distances [2.7274(4) and 2.6687(4), respectively] lie in the range of previously reported K-ring centroid distances in potassium cyclopentadienyls; for example, the K-ring centroid distances in $[\{1,2,4\text{-(SiMe}_3)_3\text{C}_5\text{H}_2\}\text{K}]_\infty$ range from 2.710 to 2.772 Å.¹⁰

The solid-state structure of **2c.C₆H₆** consists of two slightly different polymeric chains, which are connected by a short K...Me(Si) contact between K(4) in one chain and C(17) in the other (Figure 3). The polymeric chain involving K(1) is similar to that in **2b.OEt₂**: K(1) is coordinated by the carbanion center and an η^5 -cyclopentadienyl group of one dicarbanion ligand to generate a pseudo-four-membered chelate ring [C(1)-K(1)-ring centroid angle $88.325(4)^\circ$], along with an η^6 -benzene molecule and two short K...Me contacts. In comparison, K(2) is coordinated by the carbanion center of one ligand and an η^5 -cyclopentadienyl group of a second ligand, along with two short K...Me contacts. Thus, the central carbanion and cyclopentadienyl groups of each ligand bridge the two distinct potassium ions to form the polymer chain. In the second chain, K(3) is coordinated by an η^5 -cyclopentadienyl group of one ligand, an η^4 -benzene molecule, and a single short K...Me contact, but has no significant interaction with the carbanion center [K(3)...C(24) 3.7392(12) Å], i.e., this ligand does not chelate K(3). In contrast, K(4) is coordinated in a similar manner to K(2) in the first chain: by the carbanion center of one ligand and an η^5 -cyclopentadienyl group of a second ligand, along with two short K...Me contacts. The reason for the different coordination of K(3) is unclear, but may be due to crystal packing effects.

Figure 3. Extended solid-state structure of **2c.C₆H₆** with 40% probability ellipsoids and with H atoms omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): K(1)-C(1) 3.226(5), K(1)-ring centroid 2.7483(1), K(1)-ring centroid(PhH) 3.0074(1), K(1)...C(3) 3.224(7), K(1)...C(7) 3.4401(1), K(2)-C(1) 2.983(5), K(2)-ring centroid 2.7151(1), K(2)...C(4A) 3.367(7), K(2)...C(5A) 3.103(6), K(1A)-C(1)-K(2) 176.04(19), K(1)-ring centroid-K(2) 162.2375(5), K(3)-ring centroid 2.7269(1), K(3)-C(42) 3.464(8), K(3)-C(43) 3.329(8), K(3)-C(44) 3.317(9), K(3)-C(45) 3.456(9), K(3)...C(30) 3.353(8), K(4)-C(24A) 3.031(6), K(4)-ring centroid 2.7667(1), K(4)...C(29A) 3.467(7), K(4)...C(31A) 3.499(7), K(4)...C(17) 3.6031(2), K(4)-C(24A)...K(3A) 160.702(1), K(3)-ring centroid-K(4) 173.246(1).

The K-C(carbanion) distances in **2c.C₆H₆** [3.226(5), 2.983(5) and 3.031(6) Å] are similar to those in **2b.OEt₂** and other potassium complexes of silicon-stabilized carbanions (see above). In both chains the CSi_3 skeletons of the ligands are close to planar [sum of angles at C(1) = 359.7° , C(24) 357.9°], even though the K(3)...C(24) distance is long. The K(1A)-C(1)-K(2) angle [$176.04(19)^\circ$] in **2c.C₆H₆** is close to linear, but the K(3A)...C(24A)-K(4) angle is $160.702(1)^\circ$, reflecting the weaker K(3)...C(24) interaction in this chain.

Given the difficulty of removing the methine protons from **1a-c**, we sought an alternative ligand system that would undergo double deprotonation under milder conditions. Over the last decade we and others have developed phosphine-borane-stabilized carbanions as a new class of ligand for s-, p- and f-block metal centers.¹¹⁻¹³ The precursor phosphine-boranes $\text{R}_2\text{CHPR}_2(\text{BH}_3)$ typically undergo α -deprotonation readily, usually upon treatment with *n*BuLi or PhCH₂K. We therefore posited that a ligand containing linked cyclopentadienyl and phosphine-borane units would undergo facile deprotonation to the corresponding dianion, and so sought to prepare such a precursor.

The reaction between in situ-prepared $[(\text{Me}_3\text{Si})\text{CH}\{\text{PMe}_2(\text{BH}_3)\}]\text{Li}^{12d}$ and excess Me_2SiCl_2 in cold (0°C) diethyl ether gives the chlorosilane $(\text{Me}_3\text{Si})\text{CH}\{\text{PMe}_2(\text{BH}_3)\}(\text{SiMe}_2\text{Cl})$ (**5**) as moisture-sensitive colorless crystals in good yield, after crystallization from cold diethyl ether (Scheme 3). The identity of **5** was confirmed by ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{11}\text{B}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy and X-ray crystallography (see supporting information).

Scheme 3

Treatment of **5** with $[\text{C}_5\text{Me}_4\text{H}]\text{Li}$ in refluxing THF for 16 h gives the cyclopentadienyl-substituted phosphine-borane $(\text{Me}_3\text{Si})\text{CH}\{\text{PMe}_2(\text{BH}_3)\}\{\text{SiMe}_2(\text{C}_5\text{Me}_4\text{H})\}$ (**6**) as a colorless, sticky solid (Scheme 3). The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **6** are again rather complex due to the presence of regioisomers and the diastereotopic nature of the SiMe_2 and PMe_2 groups. However, **6** may be crystallized from cold diethyl ether to give colorless blocks of a single regioisomer in moderate yield, in which the cyclopentadiene proton is adjacent to the silicon atom of the proligand (**6'**). The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **6'** are consistent with this formulation, while the $^{11}\text{B}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **6'** consist of broad singlets at -15.4 and -0.5 ppm. Single crystals of **6'** were studied by X-ray crystallography (Figure 4); the structure of **6'** is very similar to that of **1b**, with which it is isoelectronic.

Figure 4. Molecular structure of **6'** with 40% probability ellipsoids and with C-bound H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–Si(1) 1.9156(19), C(1)–Si(2) 1.9046(18), C(1)–P(1) 1.8342(19), C(9)–Si(1) 1.926(2), P(1)–B(1) 1.914(3), Si(1)–C(1)–Si(2) 113.92(9), Si(1)–C(1)–P(1) 113.02(10), Si(2)–C(1)–P(1) 114.16(9), C(1)–Si(1)–C(9) 107.83(9).

In contrast to **1a–c**, compound **6** undergoes rapid double deprotonation on treatment with two equivalents of PhCH_2K to give the dipotassium salt $[(\text{Me}_3\text{Si})\text{C}\{\text{PMe}_2(\text{BH}_3)\}\{\text{SiMe}_2(\text{C}_5\text{Me}_4)\}]\text{K}_2(\text{THF})_{0.5}$ (**7**) as a pale red foam. Colorless blocks of the alternative solvate $[(\text{Me}_3\text{Si})\text{C}\{\text{PMe}_2(\text{BH}_3)\}\{\text{SiMe}_2(\text{C}_5\text{Me}_4)\}]\text{K}_2(\text{THF})$ (**7.THF**) were obtained by crystallization at room temperature from a 10:1 mixture of benzene and THF. The $^{11}\text{B}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **7** consist of a broad doublet at -29.7 and a broad quartet at -7.5 ppm, respectively, with a ^{11}B – ^{31}P coupling constant of 93.8 Hz. The large ^{11}B – ^{31}P coupling constant is consistent with metalation of the central carbon; we have previously found that alpha-metalation

of phosphine-boranes leads to an increase of between 30 and 50 Hz in the ^{11}B – ^{31}P coupling constant compared to the neutral phosphine-borane precursor.¹¹

Compound **7.THF** crystallizes as a three-dimensional network material containing two distinct potassium environments (Figure 5). K(1) is coordinated by an η^5 -cyclopentadienyl group and an η^2 - BH_3 group of one ligand, generating a pseudo-five-membered chelate ring, a molecule of THF, and an η^2 - BH_3 group from a second adjacent ligand, along with a short $\text{K}\cdots\text{Me}(\text{P})$ contact; K(1) has no short contact with the carbanion center. In contrast, K(2) is coordinated by an η^5 -cyclopentadienyl group of one ligand, the central carbanion C(1B) of a second ligand, and an η^1 - BH_3 group from the second ligand, along with two short $\text{K}\cdots\text{Me}(\text{Si})$ contacts. Thus, each ligand bridges the two potassium ions via the cyclopentadienyl ring fragment, while the borane hydrogens bridge between symmetry equivalent K(1) ions and between K(1) and K(2).

The carbanion center C(1) has an essentially planar CSi_2P skeleton [sum of angles about C(1) = 359.0°] and only one contact with a potassium ion. The closest approach on the “vacant” side of C(1) is by the methyl group of a cyclopentadienyl ring within the same ligand [C(1)⋯C(17) 3.764(3) Å], while the closest potassium ion K(1) lies over 4.7 Å from C(1). The carbanion center C(1) therefore adopts a highly unusual trigonal pyramidal coordination geometry.

Figure 5. Extended solid-state structure of **7.THF** with 40% probability ellipsoids and with C-bound H atoms and minor disorder component omitted for clarity. Selected bond lengths (Å) and angles (°): K(1)–ring centroid 2.751(1), K(1)–O(1) 2.6718(16), K(1)⋯B(1) 3.184(3), K(1)⋯B(1A) 3.015(2), K(1)⋯C(2) 3.425(2), K(2)–ring centroid 2.6919(10), K(2)–C(1B) 3.049(2), K(2)⋯C(8) 3.361(3), K(2)⋯C(4b) 3.429(3), K(2)⋯B(1B) 3.519(3), P(1)–B(1) 1.936(2), K(1)–ring centroid–K(2) 164.62(4), ring centroid–K(2)–C(1B) 143.39(5).

The K(2)–C(1B) distance [3.049(2) Å] and the K–ring centroid distances [2.751(1) and 2.6919(10) Å] are similar to the corresponding distances in **2b.Et₂O** and **2c.C₆H₆** and to the K–C distances in other potassium complexes of phosphine-borane-stabilized carbanions,¹¹ in spite of the unusual coordination geometry of C(1).

Comparison of the structures of the neutral precursors **1b** and **6'** with those of the corresponding dipotassium salts **2b.OEt₂** and **7.THF** reveals that metalation leads to a decrease in the Si-C(H/K) distances from an average of 1.890 and 1.910 Å in **1b** and **6'**, respectively, to an average of 1.825 and 1.839 Å for **2b.OEt₂** and **7.THF**, respectively. Similarly, the P-C(K) distance in **7.THF** [1.725(2) Å] is shorter than the P-C(H) distance in **6'** [1.8342(19) Å]. This is consistent with the change in hybridization of the central carbon from sp³ to sp² on metalation and with stabilization of the carbanion center through hyperconjugation between the carbanion lone pair and the vacant Si-C(Me) and P-C(Me) σ* orbitals. Metalation also leads to a widening of the C(carbanion)-Si(1)-C(cyclopentadienyl) angles from 110.35(8)° in **1b** to 115.22(8)° in **2b.OEt₂** and from 107.83(9)° in **6'** to 118.66(9)° in **7.THF**.

In order to demonstrate the efficacy of this new class of ligand for the preparation of lanthanide complexes, we have prepared a representative complex of lanthanum(III). The reaction between **2b** and one equivalent of LaI₃(THF)₄ in THF gives [(Me₃Si)₂C{SiMe₂(C₅Me₄)}]La(I)(THF)₂ (**8.THF**) as colorless crystals in moderate yield after recrystallization from toluene/THF. Exposure of these crystals to vacuum for a few minutes leads to partial solvent loss, leaving the alternative solvate [(Me₃Si)₂C{SiMe₂(C₅Me₄)}]La(I)(THF) (**8**) as a colorless powder.

The ¹H and ¹³C{¹H} NMR spectra of **8** are consistent with a lanthanum complex containing a dianionic hybrid alkyl/cyclopentadienyl ligand. This was confirmed by an X-ray crystallographic study of **8.THF** (Figure 6). Compound **8.THF** crystallizes as discrete molecules in which the lanthanum center is bound by the cyclopentadienyl group and the central carbanion of the dianionic ligand, generating a pseudo-four-membered chelate ring [C(12)-La(1)-ring centroid angle 94.14(7)°]. The coordination sphere of the lanthanum ion is completed by two molecules of THF and an iodide ligand, giving the lanthanum ion a distorted trigonal bipyramidal geometry.

Figure 6. Molecular structure of **8.THF** with 40% probability ellipsoids and with H atoms and minor disorder component omitted for clarity. Selected bond lengths (Å) and angles (°): La(1)-C(12) 2.710(3), La(1)-I(1) 3.1520(3), La(1)-O(1) 2.717(2), La(1)-O(2) 2.5640(19), La(1)-ring centroid 2.5080(14), C(12)-Si(1) 1.859(3), C(12)-Si(2) 1.854(3), C(12)-Si(3) 1.866(3), C(12)-La(1)-ring centroid 94.14(7), Si(1)-C(12)-Si(2) 115.29(15), Si(1)-C(12)-Si(3) 118.91(16), Si(2)-C(12)-Si(3) 109.00(15).

The La(1)-C(12) distance [2.710(3) Å] is at the longer end of the range of previously reported sigma bonds between lanthanum(III) and carbon, possibly due to the highly strained chelate ring in **8.THF**. For example, the La-C distances in {(Me₃Si)₂CH}₃La are 2.515(9) Å,¹⁴ whereas the La-C distances in {2-(Me₂N)C₆H₄CH₂}₃La are 2.635(3), 2.661(3) and 2.638(3) Å.¹⁵ The La(1)-ring centroid distance [2.5080(14) Å] is typical of La-Cp* distances; for example, the La-ring centroid distances in [Cp*₂La(μ-SPh)]₂ are 2.525 and 2.560 Å.¹⁶ In contrast to the potassium salts described above, the CSi₃ skeleton of the ligand deviates significantly from planarity [sum of C-Si-C angles at C(12) = 342.48°].

CONCLUSIONS

While the series of sterically-demanding, silicon-substituted hybrid alkyl/cyclopentadienyl proligands **1a-1c** is readily accessible, they undergo only single deprotonation of the cyclopentadiene ring on treatment with strong bases such as *n*BuLi or PhCH₂K. Complete double deprotonation of these proligands (i.e. at the cyclopentadiene ring and the methine carbon) may only be achieved using an excess of highly reactive MeK. In contrast, the phosphine-borane-substituted proligand **6**, which is isoelectronic and isosteric with **1b**, undergoes double deprotonation on treatment with two equivalents of PhCH₂K. In the solid state the dipotassium complexes **2b**, **2c** and **7.THF** crystallize as extended polymers or three-dimensional networks, in which the hybrid alkyl/cyclopentadienyl ligands chelate one potassium center. The suitability of these dipotassium salts as reagents for the synthesis of novel lanthanide complexes has been established with the synthesis of a representative La(III) complex. We are currently further exploring these ligands as supporting scaffolds in lanthanide and main group chemistry.

EXPERIMENTAL SECTION

All manipulations were carried out using standard Schlenk or dry-box techniques under an atmosphere of dry nitrogen or argon. THF, light petroleum (b.p. 40–60°C), diethyl ether, toluene, and *n*-hexane were dried prior to use by distillation under nitrogen from sodium, potassium, or sodium/potassium alloy, as appropriate; dichloromethane was distilled under nitrogen from CaH₂. THF and CH₂Cl₂ and were stored over activated 4A molecular sieves; all other solvents were stored over a potassium film. Deuterated THF and C₆D₆ were distilled from potassium and CDCl₃ was distilled from CaH₂ under nitrogen; all NMR solvents were deoxygenated by three freeze-pump-thaw cycles and were stored over activated 4A molecular sieves. Benzylpotassium,¹⁷ MeK,¹⁸ (Me₃Si)₂CH(SiMe₂Br),⁷ C₅H₅SiMe₃,¹⁹ and (Me₃Si)CH₂{PMe₂(BH₃)}₂^{12d} were prepared by previously published procedures; *n*-butyllithium was purchased from Aldrich as a 2.5 M solution in hexanes. All other compounds were used as supplied by the manufacturer unless otherwise stated.

¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker Avance300 spectrometer operating at 300.13 and 75.48 MHz, respectively, or a Bruker Avance400 spectrometer operating at 399.78 and 100.54 MHz, respectively; ¹¹B{¹H} and ³¹P{¹H} NMR spectra were recorded on a Bruker Avance400 spectrometer operating at 128.27 and 161.83 MHz, respectively. ¹H and ¹³C chemical shifts are quoted in ppm relative to tetramethylsilane, ³¹P and ¹¹B chemical shifts are quoted in ppm relative to external 85% H₃PO₄ and BF₃·Et₂O, respectively. Due to the air- and moisture-sensitive nature of the potassium and lanthanum derivatives and the oily nature of the precursors it was not possible to obtain elemental analyses to assess bulk purity and so the purity of all compounds has been established by multi-element NMR spectroscopy.

Preparation of (Me₃Si)₂CH{SiMe₂(C₅H₅)} (1a**):** To a cold (–10 °C) solution of freshly cracked cyclopentadiene monomer (1.21 g, 18.29 mmol) in THF (20 mL) was added *n*BuLi (7.62 mL, 18.29 mmol). This

mixture was stirred for 30 mins and then added, dropwise, to a cold (-10 °C) solution of (Me₃Si)₂CH(SiMe₂Br) (5.44 g, 18.29 mmol) in THF (15 mL). The reaction mixture was allowed to stir for 30 mins and then heated under reflux for 16 h. Water (50 mL) was added and the product was extracted into diethyl ether (3 x 50 mL). The solvent was removed *in vacuo* from the combined organic extracts to give a yellow oil which was dissolved in light petroleum (50 mL) and dried over activated 4 Å molecular sieves. The solution was filtered and the solvent was removed *in vacuo* from the filtrate to give **1a** (mixture of regioisomers) as a yellow oil. Yield 3.58 g, 69%. ¹H NMR of the mixture of regioisomers (CDCl₃, 24 °C): δ -0.75, -0.48, -0.43 (s, Si₃CH), -0.04, 0.11, 0.13, 0.18, 0.26 (s, SiMe₃/SiMe₂), 2.99, 3.03 (s, C₅H₅), 6.36, 6.50, 6.61, 6.79 (m, C₅H₅).

Preparation of (Me₃Si)₂CH{SiMe₂(C₅Me₄H)} (1b): To a cold (-10 °C) solution of C₅Me₄H₂ (1.89 g, 15.47 mmol) in THF (20 mL) was added *n*BuLi (6.21 mL, 15.46 mmol). The reaction mixture was stirred for 30 min and the suspension was then added, dropwise, to a cold (-10 °C) solution of (Me₃Si)₂CH(SiMe₂Br) (4.60 g, 15.47 mmol) in THF (20 mL). The reaction mixture was allowed to stir for 30 min and then heated under reflux for 16 h. Water (40 mL) was added and the product was extracted into diethyl ether (3 x 50 mL). The solvent was removed *in vacuo* from the combined organic extracts to give a yellow oil, which was dissolved in light petroleum (40 mL) and dried over activated 4 Å molecular sieves. The solution was filtered and the solvent was removed *in vacuo* from the filtrate to give **1b** as a mixture of regioisomers as a yellow oil. Yield 4.28 g, 82%. Crystals of a single regioisomer were grown from cold (-24 °C) light petroleum as large colorless plates suitable for X-ray crystallography. Yield of crystalline material 1.16 g, 27%. ¹H NMR of crystalline material (CDCl₃, 23 °C): δ -0.23 (s, 1H, Si₃CH), -0.08 (s, 6H, SiMe₂), 0.16 (s, 18H, SiMe₃), 1.80 (s, 6H, C₅Me₄), 1.94 (s, 6H, C₅Me₄), 3.00 (s, br, 1H, C₅Me₄H). ¹³C{¹H} NMR of crystalline material (CDCl₃, 24 °C): δ -0.31 (SiMe₂), 2.57 (Si₃C), 3.68 (SiMe₃), 11.27 (C₅Me₄), 15.17 (C₅Me₄), 55.92 ((CMe)₄CHSiMe₃), 133.62, 135.93 (C₅Me₄).

Preparation of (Me₃Si)₂CH{SiMe₂(C₅H₄-3-SiMe₃)} (1c): To a cold (-10 °C) solution of C₅H₃SiMe₃ (0.76 g, 5.48 mmol) in THF (15 mL) was added *n*BuLi (1.96 mL, 5.48 mmol). The reaction mixture was stirred for 30 mins and the yellow solution of Li[C₅H₄SiMe₃] was then added, dropwise, to a solution of (Me₃Si)₂CH(SiMe₂Br) (1.63 g, 5.48 mmol) in THF (30 mL). The reaction mixture was heated under reflux for 16 h. The cooled reaction mixture was added to water (50 mL) and the product was extracted into diethyl ether (3 x 30 mL). The combined organic extracts were dried over MgSO₄ and filtered. The solvent was removed *in vacuo* from the filtrate to give **1c** as a yellow oil, as a mixture of regioisomers. Yield 1.26 g, 65%. ¹H NMR of the mixture of regioisomers (CDCl₃, 24 °C): δ -0.54, -0.51 (s, Si₃CH), -0.06, 0.07, 0.08, 0.13, 0.19, 0.28, 0.29 (s, SiMe₃/SiMe₂), 3.00, 6.51, 6.60, 6.61, 6.65, 6.67, 6.78 (m, C₅H₄).

Preparation of (Me₃Si)CH{PMe₂(BH₃)}{SiMe₂Cl} (5): To a cold (0 °C) solution of (Me₃Si)CH₂{PMe₂(BH₃)} (10.0 g, 62.8 mmol) in THF (15 mL) was added *n*BuLi (24.8 mL, 61.8 mmol). The reaction mixture was allowed to warm to room temperature and was stirred for 1 h. This solution was added, dropwise, to a solution of Me₂SiCl₂ (14.9 mL, 123.6 mmol) in THF (30 mL). The reaction was stirred for 2 h and then volatiles were removed *in vacuo*. The product was extracted into dichloromethane (40 mL), filtered and the solvent was removed *in vacuo* from the filtrate, giving **5** as a white solid. Yield 14.9 g, 93%. Crystals suitable for X-ray crystallography were grown from cold (4 °C) diethyl ether. ¹H NMR (CDCl₃, 24 °C): δ 0.43 (s, 9H, SiMe₃), 0.78 (s, 3H, SiMeMeCl), 0.80 (s, 3H, SiMeMeCl), 0.84 (d, *J*_{PH} = 16.58 Hz, 1H, Si₂PCH), 1.58 (d, 3H, *J*_{PH} = 9.7 Hz, BH₃PMeMe), 1.61 (d, 3H, *J*_{PH} = 9.7 Hz, BH₃PMeMe). ¹³C{¹H} NMR (CDCl₃, 25 °C): δ 2.94 (d, ³*J*_{PC} = 2.3 Hz, SiMe₃), 6.43 (m, SiMeMeCl), 16.20 (d, *J*_{PC} = 5.05 Hz, Si₂PCH), 16.74 (d, *J*_{PC} = 5.22 Hz, BH₃PMeMe), 17.24 (d, *J*_{PC} = 5.60 Hz, BH₃PMeMe). ¹¹B{¹H} NMR (CDCl₃, 24 °C): δ -34.8 (d, *J*_{PB} = 62 Hz). ³¹P{¹H} NMR (CDCl₃, 24 °C): δ 6.0 (q, *J*_{PB} = 62 Hz).

Preparation of (Me₃Si)CH{PMe₂(BH₃)}{SiMe₂(C₅Me₄H)} (6): To a cold (-10 °C) solution of C₅Me₄H₂ (2.58 g, 21.1 mmol) in THF (25 mL) was added *n*BuLi (7.20 mL, 17.9 mmol). The reaction mixture was stirred for 30 min and the resulting suspension was added, dropwise, to a cold (-10 °C) solution of **5** (4.15 g, 16.3 mmol) in THF (20

mL). The reaction mixture was allowed to stir for 30 min and then heated under reflux for 16 h. After cooling, the reaction mixture was added to water (50 mL) and the product was extracted into dichloromethane (3 x 50 mL). The solvent was removed from the combined extracts *in vacuo* to give a white solid, which was washed with a little light petroleum. The solid was dissolved in diethyl ether and dried over activated 4 Å molecular sieves. Large crystals of a single regioisomer (**6'**) suitable for X-ray crystallography were grown from cold (-24 °C) diethyl ether. Yield 2.61 g, 47%. Data for **6'**: ¹H NMR (CDCl₃, 24 °C): δ 0.18 (s, 3H, SiMeMe), 0.24 (s, 3H, SiMeMe), 0.29 (s, 9H, SiMe₃), 0.58 (d, *J*_{PH} = 18.27 Hz, 1H, Si₂PCH), 0.76 (m, 1H, C₅Me₄H), 1.07 (d, *J*_{PH} = 6.76 Hz, 3H, PMeMe), 1.08 (d, *J*_{PH} = 6.76 Hz, 3H, PMeMe), 1.53 (m, 12H, C₅Me₄H). ¹³C{¹H} NMR (CDCl₃, 25 °C): δ -1.54 (SiMeMe), -1.50 (SiMeMe), 3.54 (d, ³*J*_{PC} = 2.73 Hz, SiMe₃), 6.05 (d, *J*_{PC} = 8.33 Hz, Si₂PCH), 11.95 (C₅Me₄), 12.48 (C₅Me₄), 23.46 (d, *J*_{PC} = 5.09 Hz, PMeMe) 39.51 (d, ³*J*_{PC} = 2.90 Hz, C₅Me₄), 46.04, 134.44 (C₅Me₄). ¹¹B{¹H} NMR (CDCl₃, 25 °C): δ -15.4 (br). ³¹P{¹H} NMR (CDCl₃, 25 °C): δ -0.5 (br).

Preparation of [(Me₃Si)₂C{SiMe₂(C₅H₄)}]K₂(OEt)_{0.5} (2a): To a cold (-78 °C) suspension of MeK (ca. 2.1 g, > 4 equiv) in diethyl ether (20 mL) was added a cold (-78 °C) solution of **1a** (2.70 g, 9.55 mmol) in diethyl ether (15 mL). The reaction mixture was stirred overnight and allowed to warm slowly to room temperature. The resulting reaction mixture was filtered and solvent was removed *in vacuo* from the filtrate to give **2a** as a yellow-orange foam. The solvated product **2a** was characterized by NMR spectroscopy. The product was desolvated by heating under reflux in benzene for 2 days, during which time the unsolvated dipotassium salt [(Me₃Si)₂C{SiMe₂(C₅H₅)}]K₂ (**2a'**) precipitated as an off-white powder, which was isolated by filtration. Yield of **2a'** 1.34 g, 39%. Solvated compound **2a**: ¹H NMR (*d*₈-THF, 21 °C): δ -0.10 (s, 18H, SiMe₃), 0.22 (s, 6H, SiMe₂), 1.11 (t, 3H, Et₂O), 3.38 (q, 2H, Et₂O), 5.87 (m, 4H, C₅H₄). ¹³C{¹H} NMR (*d*₈-THF, 21 °C): δ 4.07 (Si₃CK), 8.25 (SiMe₂), 9.16 (SiMe₃), 15.87 (Et₂O), 66.39 (Et₂O), 107.34, 111.84 (C₅H₄), 126.85 (C₄H₄C(SiMe₂)). Desolvated compound **2a'**: ¹H NMR (C₆D₆/*d*₈-THF, 21 °C): δ 0.48 (s, 18H, SiMe₃), 0.75 (s, 6H, SiMe₂), 6.27 (m, 4H, C₅H₄). ¹³C{¹H} NMR (C₆D₆/*d*₈-THF, 21 °C): δ 4.15 (Si₃CK), 8.31 (SiMe₂), 9.26 (SiMe₃), 107.25, 111.73 (C₅H₄), 127.54 (C₄H₄C(SiMe₂)).

Preparation of [(Me₃Si)₂C{SiMe₂(C₅Me₄)}]K₂(OEt)_{0.5} (2b): To a cold (-78 °C) suspension of MeK (ca. 1.3 g, > 4 equiv) in diethyl ether (30 mL) was added a cold (-78 °C) solution of **1b** (1.16 g, 3.42 mmol) in diethyl ether (20 mL). The reaction mixture was stirred overnight and allowed to warm slowly to room temperature. The resulting reaction mixture was filtered and solvent was removed *in vacuo* from the filtrate to give **2b** as an amber colored powder. Crystals of the alternative solvate [(Me₃Si)₂C{SiMe₂(C₅Me₄)}]K₂(OEt)₂ (**2b.OEt₂**) suitable for X-ray crystallography were grown from a cold (3 °C) solution in diethyl ether, over a period of three days. Yield of crystalline material 0.64 g, 42%. ¹H NMR (C₆D₆/*d*₈-THF, 21 °C): δ 0.50 (s, 18H, SiMe₃), 0.72 (s, 6H, SiMe₂), 1.11 (t, 3H, Et₂O), 2.27 (s, 6H, C₅Me₄), 2.53 (s, 6H, C₅Me₄) 3.26 (q, 2H, Et₂O). ¹³C{¹H} NMR (C₆D₆/*d*₈-THF, 21 °C): δ 3.69 (Si₃CK), 9.34 (SiMe₃), 11.23 (SiMe₂), 11.81, 15.28 (C₅Me₄), 15.58, 65.91 (Et₂O), 111.96, 115.41, 116.01 (C₅Me₄).

Preparation of [(Me₃Si)₂C{SiMe₂(C₅H₃-3-SiMe₃)}]K₂(C₆H₆)_{0.5} (2c): To a suspension of MeK (1.80 g, 33.25 mmol) in cold (-10 °C) diethyl ether (40 mL) was added **1c** (2.94 g, 8.31 mmol). This mixture was stirred for 16 h and allowed to warm slowly to room temperature. The reaction mixture was filtered and the solvent was removed *in vacuo* from the filtrate to give **2c** as a straw-colored sticky solid. Yield 2.56 g, 66%. Single crystals suitable for X-ray crystallography of the alternative solvate [(Me₃Si)₂C{SiMe₂(C₅H₃-3-SiMe₃)}]K₂(C₆H₆)₂.2C₆H₆ (**2c.C₆H₆**) were obtained from cold (5 °C) benzene. Exposure of these crystals to vacuum results in desolvation to the sticky solid **2c**. ¹H NMR (C₆D₆, 21 °C): δ 0.18 (s, 18H, C(SiMe₃)₂), 0.34 (s, 9H, SiMe₃), 0.51 (s, 6H, SiMe₂), 6.23 (m, 3H, C₅H₃), 7.16 (s, 3H, C₆H₆). ¹³C{¹H} NMR (C₆D₆, 21 °C): δ 1.74 (SiMe₃), 8.85 (CH(SiMe₃)₂), 8.90 (SiMe₂), 115.77, 115.94, 116.11, 119.99 (C₅H₃Si₂), 128.59 (C₆H₆), 129.51 (C₅H₃Si₂).

Preparation of [(Me₃Si)C{PMe₂(BH₃)}{SiMe₂(C₅Me₄)}]K₂(THF)_{0.5} (7): To a cold (-78 °C) solution of **6a** (0.48 g, 1.41 mmol) in THF (15 mL) was added a solution of BnK (0.37 g, 2.85 mmol) in

THF (15 mL). The reaction was stirred for 16 hours and allowed to warm slowly to room temperature. The solution was filtered and solvent was removed *in vacuo* from the filtrate to give **7** as a pale red foam. Yield 0.48 g, 71%. Crystals of the alternative solvate [(Me₃Si)C-(PMe₂(BH₃))₂{SiMe₂(C₅Me₄)}]K₂(THF) (**7.THF**) suitable for X-ray crystallography were grown at room-temperature from a 10:1 mixture of benzene and THF. ¹H NMR (C₆D₆/d₈-THF, 25 °C): δ 0.52 (s, 9H, SiMe₃), 0.66 (s, 6H, SiMe₂), 1.43 (m, 2H, THF), 1.63 (d, 6H, ²J_{PH} = 9.3 Hz, PMe₂), 2.18 (s, 6H, C₅Me₄), 2.62 (s, 6H, C₅Me₄), 3.51 (m, 2H, THF). ¹³C{¹H} NMR (C₆D₆/d₈-THF, 25 °C): δ 8.98 (d, ³J_{PC} = 2.4 Hz, SiMe₃), 10.10 (d, ³J_{PC} = 7.2 Hz, SiMe₂), 11.49, 14.96 (C₅Me₄), 22.04 (PMe₂), 25.87, 67.83 (THF), 110.71, 117.26 (C₅Me₄) [Signals for the remaining two quaternary carbon centers were not observed]. ¹¹B{¹H} NMR (C₆D₆/d₈-THF, 25 °C): δ -29.7 (d, J_{PB} = 93.8 Hz). ³¹P{¹H} NMR (C₆D₆/d₈-THF, 25 °C): δ -7.5 (br. q, J_{PB} = 93.8 Hz).

Preparation of [(Me₃Si)₂C{SiMe₂(C₅Me₄)}]La(I)(THF) (8**):** To a slurry of LaI₃(THF)₄ (1.58 g, 1.95 mmol) in THF (10 ml) was added, dropwise, a solution of **2b** (0.81 g, 1.95 mmol) in THF (15 ml) and this mixture was stirred for 5 h. The reaction mixture was filtered and the solvent was removed *in vacuo* from the filtrate to give a pale yellow foam, which was dissolved in toluene (ca. 10 ml) containing a few drops of THF. Colourless crystals of [(Me₃Si)₂C{SiMe₂(C₅Me₄)}]La(I)(THF)₂ (**8.THF**) suitable for X-ray crystallography were grown from this solution at -24 °C. Yield 0.70 g, 47%. One molecule of coordinated THF was lost very readily when the crystals were placed under vacuum to give [(Me₃Si)₂C{SiMe₂(C₅Me₄)}]La(I)(THF) (**8**) as a colorless powder. ¹H NMR (d₈-THF, 21 °C): δ 0.14 (s, 18H, SiMe₃), 0.56 (s, 6H, SiMe₂), 1.78 (m, 4H, THF), 2.10 (s, 6H, C₅Me₄), 2.14 (s, 6H, C₅Me₄), 3.62 (m, 4H, THF). ¹³C{¹H} NMR (d₈-THF, 20 °C): δ 3.97 (Si₃CLa), 8.75 (SiMe₃), 10.28 (SiMe₂), 13.33, 15.96 (C₅Me₄), 26.54, 68.39 (THF), 107.30, 129.96, 130.54 (C₅Me₄).

Crystal Structure Determinations of **1b, **2b**, **2c**, **5**, **6'**, **7.THF** and **8.THF**:** Data were collected at 150 K on an Oxford Diffraction (Agilent Technologies) Gemini A Ultra diffractometer using CuKα radiation (λ = 1.54178 Å), except for the structure of **2c** which was collected using MoKα radiation (λ = 0.71073 Å). Cell parameters were refined from the observed positions of all strong reflections. Intensities were corrected semi-empirically for absorption, based on symmetry-equivalent and repeated reflections, except for **2b** and **8.THF** where intensities were corrected analytically based on a multifaceted model created by indexing the faces of the crystal for which data were collected.²⁰ The structures were solved by direct methods and refined on *R*² values for all unique data; Table S1 in the Supporting Information gives further details. All non-hydrogen atoms were refined anisotropically, and C-bound H atoms were positioned with idealized geometry, while B-bound H atoms were located using peaks in the Fourier difference map. The displacement parameters for all hydrogen atoms were constrained with a riding model; *U*(H) was set at an appropriate multiple of the *U*_{eq} value of the parent C atom. Oxford Diffraction CrysAlisPro was employed during data collection and processing, and structure solution (XT), refinement (XL), and molecular graphics (XP) were performed through the Olex2 interface.²¹

ASSOCIATED CONTENT

Supporting Information

¹H, ¹³C{¹H}, ³¹P{¹H}, and ¹¹B{¹H} NMR spectra for all compounds, as appropriate. Crystal structure of **5** and crystallographic details for all compounds in tabular format. For **1b**, **2b**, **2c**, **5**, **6'**, **7.THF** and **8.THF** details of structure determination, atomic coordinates, bond lengths and angles, and displacement parameters in CIF format. The Supporting Information is available free of charge on the ACS Publications website.

AUTHOR INFORMATION

Corresponding Author

* keith.izod@ncl.ac.uk.

ORCID ID Keith Izod: 0000-0003-3882-9343

ACKNOWLEDGMENT

The authors are grateful to Newcastle University for financial support and to Ms. C. Fitzsimmons for assisting in the preparation of **1c** and **2c**.

REFERENCES

- For a review see: Braunschweig, H.; Breitling, F. M. *Coord. Chem. Rev.* **2006**, *250*, 2691-2720.
- For reviews see: (a) McKnight, A. L.; Waymouth, R. A. *Chem. Rev.* **1998**, *98*, 2587-2598. (b) Klosin, J.; Fontaine, P. P.; Figueroa, R. *Acc. Chem. Res.* **2015**, *48*, 2004-2016. (c) Rodriguez, A.-S.; Carpentier, J.-F. *Coord. Chem. Rev.* **2008**, *252*, 2137-2154. (d) Collins, R. A.; Russell, A. F.; Mountford, P. *Appl. Petrochem. Res.* **2015**, *5*, 153-171. (e) Baier, M. C.; Zuideveld, M. A.; Mecking, S. *Angew. Chem. Int. Ed.* **2014**, *53*, 9722-9744.
- (a) For a recent review see: Raith, A.; Altmann, P.; Cokoja, M.; Hermann, W. A.; Kuhn, F. E. *Coord. Chem. Rev.* **2010**, *254*, 608-634. (b) Horacek, M.; Stepnicka, P.; Kubista, J.; Fejfarova, K.; Gyepes, R.; Mach, K. *Organometallics* **2003**, *22*, 861-869. (c) Barnskoetter, W. H.; Pool, J. A.; Lobkovsky, E. L.; Chirik, P. J. *Organometallics* **2006**, *25*, 1092-1100. (d) Bazinet, P.; Tilley, T. D. *Organometallics* **2009**, *28*, 2285-2293. (e) Kumar, M.; Cervantes-Lee, F.; Sharma, H. K.; Pannell, K. H. *Organometallics* **2007**, *26*, 3005-3009. (f) Pinkas, J.; Cisarova, I.; Conde, A.; Fandos, R.; Horacek, M.; Kubista, J.; Mach, K. *J. Organomet. Chem.* **2009**, *694*, 1971-1980. (g) Honzicek, J.; Romao, J. J.; Calhorda, M. J.; Mukhopadhyay, A.; Vinklerek, J.; Padelkova, Z. *Organometallics* **2011**, *30*, 717-725. (h) Amor, F.; Royo, P.; Spaniol, T. P.; Okuda, J. *J. Organomet. Chem.* **2000**, *604*, 126-131. (i) McGovern, G. P.; Hung-Low, F.; Tye, J. W.; Bradley, C. A. *Organometallics* **2012**, *31*, 3865-3879.
- For selected examples see: (a) Jaroschik, F.; Momin, A.; Nief, F.; Le Goff, X.-F.; Deacon, G. B.; Junk, P. *Angew. Chem. Int. Ed.* **2009**, *48*, 1117-1121. (b) Summerscales, O. T.; Batista, E. R.; Scot, B. L.; Wilkerson, M. P.; Sutton, A. D. *Eur. J. Inorg. Chem.* **2016**, 4551-4556. (c) Takenaka, Y.; Hou, Z. *Organometallics* **2009**, *28*, 5196-5203. (d) Ihara, E.; Tanaka, M.; Yasuda, H.; Kanehisa, N.; Maruo, T.; Kai, Y. *J. Organomet. Chem.* **2000**, *613*, 26-32.
- (a) For a recent review see: Xie, Z. *Coord. Chem. Rev.* **2006**, *250*, 259-272. (b) Chui, K.; Yang, Q.; Mak, T. C. W.; Xie, Z. *Organometallics* **2000**, *19*, 1391-1401. (c) Shen, H.; Chan, H.-S.; Xie, Z. *Organometallics* **2008**, *27*, 5309-5316. (d) Xie, Z.; Chui, K.; Yang, Q.; Mak, T. C. W. *Organometallics* **1999**, *18*, 3947-3949. (e) Wang, S.; Yang, Q.; Mak, T. C. W.; Xie, Z. *Organometallics* **2000**, *19*, 334-343.
- Hitchcock, P. B.; Hu, J.; Lappert, M. F. *Chem. Commun.* **1998**, 143-144.
- Gupta, S. K.; Yumnam, S.; Hitchcock, P. B. *J. Mol. Struct.* **2012**, *1018*, 137-144.
- Eaborn, C.; Hitchcock, P. B.; Izod, K.; Jaggar, A. J.; Smith, J. D. *Organometallics* **1994**, *13*, 753-754.
- Izod, K.; Clegg, W.; Harrington, R. W.; Smith, J. D.; Eaborn, C. *Dalton Trans.* **2006**, 502-508.
- Harvey, M. J.; Hanusa, T. P.; Pink, M. *J. Chem. Soc., Dalton Trans.* **2001**, 1128-1130.
- For selected examples of s-block complexes see: (a) Izod, K.; Bowman, L. J.; Wills, C.; Clegg, W.; Harrington, R. W. *Dalton Trans.* **2009**, 3340-3347. (b) Izod, K.; Wills, C.; Clegg, W.; Harrington, R. W. *Organometallics* **2010**, *29*, 4774-4777. (c) Heuclin, H.; Fustier-Boutignon, M.; Ho, S. Y.-F.; Le Goff, X.-F.; Carencu, S.; So, C.-W.; Mézailles, N. *Organometallics* **2013**, *32*, 498-508. (d) Izod, K.; Wills, C.; Clegg, W.; Harrington, R. W. *Inorg. Chem.* **2007**, *46*, 4320-4325. (e) Orzechowski, L.; Jansen, G.; Lutz, M.; Harder, S. *Dalton Trans.* **2009**, 2958-2964. (f) Langer, J.; Wimmer, K.; Görls, H.; Westerhausen, M. *Dalton Trans.* **2009**, 2951-2957. (g) Langer, J.; Palfi, V. K.; Görls, H.; Reiher, M.; Westerhausen, M. *Chem. Commun.* **2013**, *49*, 1121-1123. (h) Schmidbaur, H.; Weiss, E.; Zimmer-Gasse, B. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 782-784. (i) Izod, K.; McFarlane, W.; Tyson, B. V.; Clegg, W.; Harrington, R. W. *Chem. Commun.* **2004**, 570-571.

(j) Sun, X.-M.; Manabe, K.; Lam, W. W.-L.; Shiraishi, N.; Kobayashi, J.; Shiro, M.; Utsumi, H.; Kobayashi, S. *Chem. Eur. J.* **2005**, *11*, 361-368.

12. For examples of p-block complexes see: (a) Izod, K.; McFarlane, W.; Tyson, B. V.; Carr, I.; Clegg, W.; Harrington, R. W. *Organometallics* **2006**, *25*, 1135-1143. (b) Izod, K.; McFarlane, W.; Wills, C.; Clegg, W.; Harrington, R. W. *Organometallics* **2008**, *27*, 4386-4394. (c) Izod, K.; Wills, C.; Clegg, W.; Harrington, R. W. *Organometallics* **2009**, *28*, 2211-2217. (d) Izod, K.; Wills, C.; Clegg, W.; Harrington, R. W. *Organometallics* **2009**, *28*, 5661-5568. (e) Wills, C.; Izod, K.; Clegg, W.; Harrington, R. W. *Dalton Trans.* **2010**, *39*, 2379-2384. (f) Izod, K.; Wills, C.; Harrington, R. W.; Clegg, W. *J. Organomet. Chem.* **2013**, *725*, 11-14. (g) Izod, K.; Dixon, C. M.; Harrington, R. W.; Probert, M. R. *Chem. Commun.* **2015**, *51*, 679-681.

13. For examples of f-block complexes see: Izod, K.; Clegg, W.; Harrington, R. W. *Dalton Trans.* **2010**, *39*, 6705-6709.

14. Hitchcock, P. B.; Lappert, M. F.; Smith, R. G.; Bartlett, R. A.; Power, P. P. *J. Chem. Soc. Chem. Commun.* **1988**, 1007-1008.

15. Harder, S. *Organometallics* **2005**, *24*, 373-379.

16. Evans, W. J.; Schmiede, B. M.; Lorenz, S. E.; Miller, K. A.; Champagne, T. M.; Ziller, J. W.; DiPasquale, A. G.; Rheingold, A. R. *J. Am. Chem. Soc.* **2008**, *130*, 8555-8563.

17. (a) Izod, K.; Rayner, D. G.; El-Hamruni, S. M.; Harrington, R. W.; Baisch, U. *Angew. Chem. Int. Ed.* **2014**, *53*, 3636-3640. (b) Lochmann, L.; Trekoval, J. *J. Organomet. Chem.* **1987**, *326*, 1-7.

18. (a) Weiss, E.; Sauermann, G. *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 133-134. (b) Lochmann, L. *Eur. J. Inorg. Chem.* **2000**, 1115-1126.

19. Kraihanzel, C. S.; Losee, M. L. *J. Am. Chem. Soc.* **1968**, *90*, 4701-4705.

20. Clark R. C.; Reid, J. S. *Acta Cryst.* **1995**, *A51*, 887-897.

21. (a) Sheldrick, G. M. *Acta Cryst.* **2015**, *A71*, 3-8. (b) Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112-122. (c) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard J. A. K.; Puschmann, H. *J. Appl. Cryst.*, **2009**, *42*, 339-341.

ToC graphic: