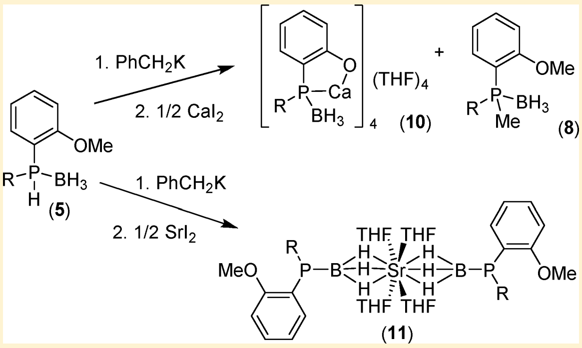
ORGANOMETALLICS
Article
pubs.acs.org/Organometallics

Alkali-Metal- and Alkaline-Earth-Metal-Mediated C−O Activation of an Anisole-Substituted Phosphido−Borane Ligand

Keith Izod,* James M. Watson, Salima M. El-Hamruni, Ross W. Harrington, and Paul G. Waddell

Main Group Chemistry Laboratories, School of Chemistry, Bedson Building, Newcastle University, Newcastle upon Tyne NE1 7RU, U.K.

Supporting Information



ABSTRACT: The reaction between $\{(Me_3Si)_2CH\}PH(C_6H_4\text{-}2\text{-}OMe)$ (**4**) and 1 equiv of $BH_3{\cdot}SMe_2$ yields the phosphine−borane $\{(Me_3Si)_2CH\}PH(BH_3)(C_6H_4\text{-}2\text{-}OMe)$ (**5**). Subsequent reaction between **5** and 1 equiv of n-BuLi in THF gives the phosphido−borane complex $[\{(Me_3Si)_2CH\}P(BH_3)(C_6H_4\text{-}2\text{-}OMe)]Li(THF)$ (**6a**), which was isolated as a colorless microcrystalline solid. Treatment of **5** with 1 equiv of $PhCH_2M$ yields the corresponding complexes $[\{(Me_3Si)_2CH\}P(BH_3)(C_6H_4\text{-}2\text{-}OMe)]ML$ (ML = Na(THF) (**6b**), K(pmdeta) (**6c**); pmdeta = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine), after crystallization in the presence of the corresponding coligand. While compounds **6b**,**c** are stable toward heat, compound **6a** decomposes on heating to 50 °C in toluene to give the cluster $[[\{(Me_3Si)_2CH\}PH(C_6H_4\text{-}2\text{-}O)]Li]_6$ (**7**) and the tertiary phosphine−borane $\{(Me_3Si)_2CH\}P(BH_3)(Me)(C_6H_4\text{-}2\text{-}OMe)$ (**8**). Related C−O cleavage reactions are observed when MgI_2 is treated with 2 equiv of **6a** and when CaI_2 is treated with 2 equiv of $[\{(Me_3Si)_2CH\}P(BH_3)(C_6H_4\text{-}2\text{-}OMe)]K$ in THF, giving $[\{(Me_3Si)_2CH\}P(BH_3)(C_6H_4\text{-}2\text{-}O)Mg(THF)_2]_2$ (**9**) and $[\{(Me_3Si)_2CH\}P(BH_3)(C_6H_4\text{-}2\text{-}O)Ca(THF)]_4$ (**10**), respectively, along with 1 equiv of **8** in each case. In contrast, the reaction between SrI_2 and 2 equiv of $[\{(Me_3Si)_2CH\}P(BH_3)(C_6H_4\text{-}2\text{-}OMe)]K$ in THF yields $[\{(Me_3Si)_2CH\}P(BH_3)(C_6H_4\text{-}2\text{-}OMe)Sr(THF)_4]$ (**11**).

INTRODUCTION

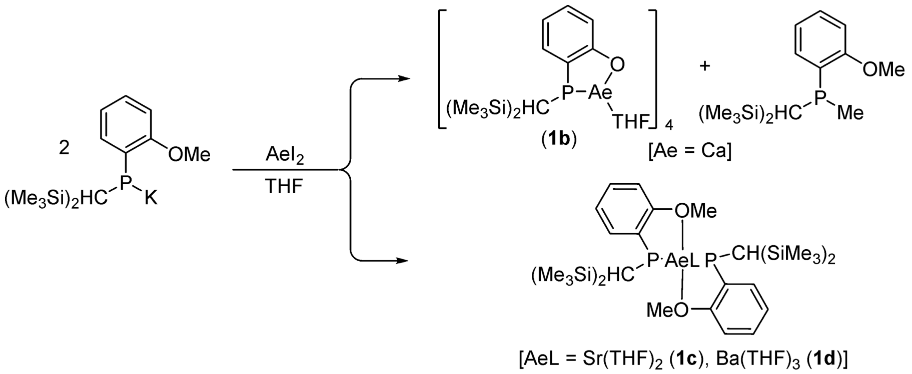
Phosphine−borane adducts R_3PBH_3 (R = H, alkyl, aryl, etc.) are of great current interest due to their potential applications in the synthesis of polyfunctional and/or polydentate (chiral) phosphines and as precursors to poly(phosphine−borane) materials, the latter of which are (valence) isoelectronic analogues of polyolefins.[1] In many of these applications complexes of the corresponding phosphido−borane anions $[R_2P(BH_3)]^-$ are either key intermediates or else have been implicated as the active species in catalytic cycles. Nonetheless, a surprisingly small number of such compounds have been isolated and characterized in the solid state: structurally characterized phosphido−borane complexes are limited to alkali-metal derivatives,[2] a small number of mid-to-late-transition-metal complexes,[3] and a very few p-block derivatives.[2e,4] There has been no previous report of an alkaline-earth-metal complex of this class of ligand. This is perhaps surprising, given the well-established chemistry of the analogous amido−boranes.[5] These latter compounds have been investigated as potential hydrogen storage materials and as catalysts for the dehydrocoupling of amine−boranes; complexes of amido−boranes with both alkali-metal and alkaline-earth-metal centers have been reported.[6]

While alkaline-earth-metal phosphido−borane complexes are as yet unknown, a rich structural chemistry has emerged for their phosphide analogues, with mononuclear, polynuclear, and polymeric species having been identified.[7−9] Our own work in this area has focused on the synthesis, structures, and dynamic behavior of alkaline-earth-metal complexes of sterically demanding, donor-functionalized phosphide ligands[9] and their relationship to the corresponding lanthanide(II) complexes.[10] During the course of this work, we found that certain alkaline-earth-metal complexes of anisole-functionalized phosphide ligands underwent an unexpected C−O cleavage reaction to generate the corresponding alkoxo−phosphides (Scheme 1).[9a] This reaction is highly dependent upon the identity of the alkaline-earth-metal cation: whereas the putative compound $[\{(Me_3Si)_2CH\}P(C_6H_4\text{-}2\text{-}OMe)]_2Ca(THF)_n$ (**1a**) undergoes C−O cleavage rapidly at room temperature to give $[[\{(Me_3Si)_2CH\}P(C_6H_4\text{-}2\text{-}O)]Ca(THF)]_4$ (**1b**) as the sole calcium-containing product, the corresponding strontium compound (**1c**) undergoes this decomposition only upon extended heating, while the barium analogue (**1d**) is stable toward C−O cleavage. We attributed this to the significant decrease in Lewis acidity of the metal centers with increasing atomic number. Müller and Knapp have also reported a related C−O cleavage reaction of an anisole-substituted phosphinomethanide ligand: the reaction between 2 equiv of $[(4\text{-}MeC_6H_4)_2PCH(C_6H_4\text{-}2\text{-}OMe)]Li(OEt_2)$ and CaI_2 in THF

Received: April 7, 2017

DOI: 10.1021/acs.organomet.7b00262

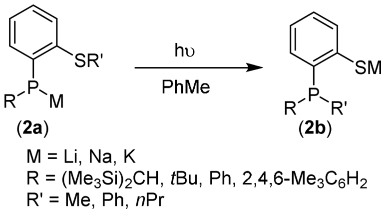
Scheme 1



yields the cluster $[[(4\text{-}MeC_6H_4)_2PCH(C_6H_4\text{-}2\text{-}O)]Ca(THF)]_4$; however, the side products from this reaction were not identified and so the fate of the cleaved methyl group is unknown.[11]

In related chemistry, we have also found that alkali-metal complexes of thioanisole-functionalized phosphide ligands $[RP(C_6H_4\text{-}2\text{-}SR')]M$ (**2a**; M = Li, Na, K; R = $(Me_3Si)_2CH$, *t*-Bu, Ph, 2,4,6-$Me_3C_6H_2$; R′ = Me, Ph, *n*-Pr) undergo a complementary, *photolytically induced* intramolecular alkyl/aryl migration to give the tertiary-phosphine-substituted thiolate complex $[RR'P(C_6H_4\text{-}2\text{-}S)]M$ (**2b**) (Scheme 2).[12] We have recently shown that this photolytic rearrangement is suppressed in the corresponding phosphido−borane complexes $[\{(Me_3Si)_2CH\}P(BH_3)(C_6H_4\text{-}2\text{-}SMe)]ML$ (ML = Li (THF) (**3a**), Na(tmeda) (**3b**), K(pmdeta) (**3c**)), such that these latter compounds are stable toward both heat and light (tmeda = *N,N,N′,N′*-tetramethylethylenediamine, pmdeta = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine).[13]

Scheme 2

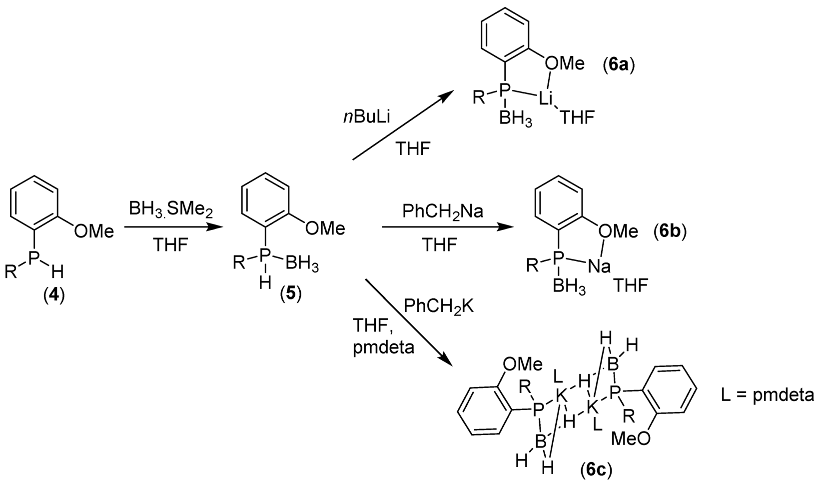


The foregoing prompted us to investigate whether anisole-substituted phosphido−borane complexes would undergo C−O cleavage similar to **1**, or whether this reactivity might be suppressed by the borane group, as observed in **3a**−**c**. We now describe the synthesis of a series of alkali-metal and alkaline-earth-metal complexes of the anisole-substituted phosphido−borane ligand $[\{(Me_3Si)_2CH\}P(BH_3)(C_6H_4\text{-}2\text{-}OMe)]^-$ and show the effect of the borane group and the metal center on the activation of the OMe functionality.

■ RESULTS AND DISCUSSION

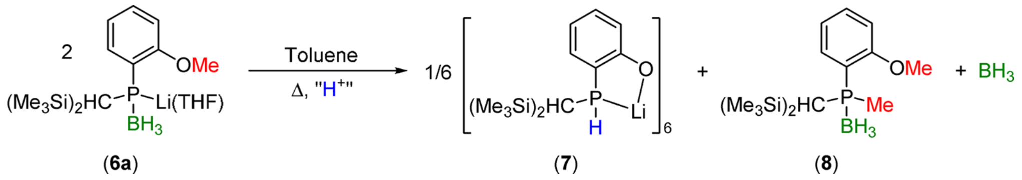
Synthesis and Stability. Treatment of the secondary phosphine $\{(Me_3Si)_2CH\}PH(C_6H_4\text{-}2\text{-}OMe)$ (**4**)[9a] with 1 equiv of $BH_3{\cdot}SMe_2$ in THF gives the air-stable phosphine−borane $\{(Me_3Si)_2CH\}PH(BH_3)(C_6H_4\text{-}2\text{-}OMe)$ (**5**) as a colorless solid in good yield (Scheme 3). The reaction between **5** and 1 equiv of *n*-BuLi in THF proceeds smoothly to give the phosphido−borane complex $[\{(Me_3Si)_2CH\}P(BH_3)(C_6H_4\text{-}2\text{-}OMe)]Li(THF)$ (**6a**), which was isolated as a colorless microcrystalline solid. Similarly, treatment of **5** with 1 equiv of either $PhCH_2Na$ or $PhCH_2K$ in THF yields the analogous complexes $[\{(Me_3Si)_2CH\}P(BH_3)(C_6H_4\text{-}2\text{-}OMe)]ML$ (ML = Na(THF) (**6b**), K(pmdeta) (**6c**)), after crystallization in the presence of the corresponding coligand.

Scheme 3[a]

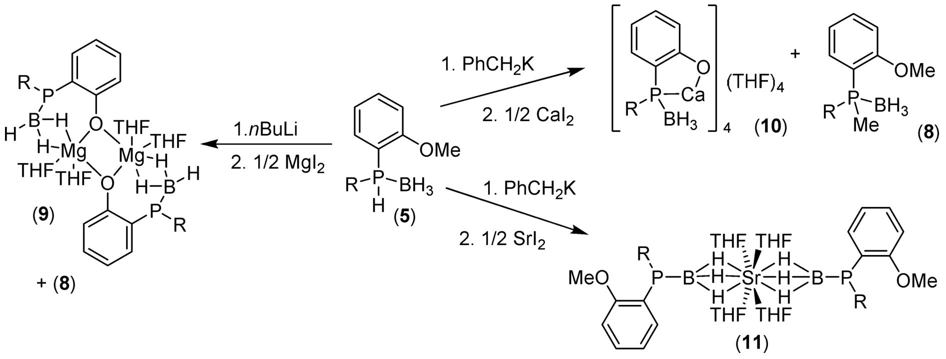


[a] R = $CH(SiMe_3)_2$.

Scheme 4



Scheme 5[a]



[a]R = CH(SiMe$_3$)$_2$.

The ^{1}H, ^{13}C{^{1}H}, ^{11}B{^{1}H}, and ^{31}P{^{1}H} NMR spectra of **5** and **6a–c** are as expected: in each case the diastereotopic SiMe$_3$ groups give rise to a pair of signals in both the ^{1}H and ^{13}C{^{1}H} NMR spectra, while for **5** the PH proton gives rise to a complex doublet of quartets of doublets in its ^{1}H{^{11}B} NMR spectrum, due to coupling to the adjacent phosphorus nucleus, the three BH$_3$ protons, and the methine proton of the CH(SiMe$_3$)$_2$ substituent. There is a significant upfield shift of the ^{31}P{^{1}H} NMR signal on metalation of **5**, although there is little difference in the chemical shifts of the metalated species (δ_P −22.3 (**5**), −62.5 (**6a**), −64.3 (**6b**) −63.0 ppm (**6c**)). We have noted previously that the ^{11}B–^{31}P coupling constant in related alkali-metal phosphido–borane complexes decreases with increasing ionic character of the P–M bond;[13,14] however, although there is a substantial difference between the ^{11}B–^{31}P coupling constants of the free phosphine–borane **5** and its metalated derivatives, there is only a small decrease in coupling constant among compounds **6a–c** (J_{PB} = 49.0 (**5**), 39.3 (**6a**), 37.3 (**6b**), 36.1 Hz (**6c**)), possibly as a consequence of these compounds adopting structures different from each other in solution.

Somewhat unexpectedly, we noted on several occasions that toluene solutions of **6a** appeared to decompose over a period of several days at room temperature; this decomposition appears to be accelerated at higher temperatures. In contrast, solutions of **6b** or **6c** in either THF or toluene are stable, even after prolonged periods at elevated temperatures. Monitoring the decomposition of **6a** by ^{31}P NMR spectroscopy revealed that the broad quartet at −62.5 ppm due to **5** was replaced by a broad quartet at 11.7 ppm (J_{PB} = 58.8 Hz) and a sharp doublet at −72.7 ppm (J_{PH} = 219.6 Hz) of approximately equal intensity. The appearance of a sharp doublet clearly suggests that the decomposition reaction involves cleavage of the P–B bond in at least part of the sample. Consistent with this, when the decomposition reaction was conducted in the presence of 1 equiv of tmeda, the known amine–borane adduct Me$_2$N(BH$_3$)CH$_2$CH$_2$N(BH$_3$)Me$_2$ was isolated,[15] suggesting that free BH$_3$ is liberated during the thermolysis reaction (the identity of the amine–borane adduct was confirmed by ^{1}H NMR spectroscopy and X-ray crystallography).

The nature of the decomposition reaction was finally revealed when single crystals of a toluene solvate of the unusual alkoxo–phosphine cluster [[{(Me$_3$Si)$_2$CH}PH(C$_6$H$_4$-2-O)]Li]$_6$ (**7**), from which the methyl group of the anisyl substituent has been cleaved, were isolated in moderate yield from the thermolysis reaction. The fate of the cleaved methyl group was revealed by analysis of the mother liquor from which **7** was isolated: NMR spectroscopy indicates that the tertiary phosphine–borane {(Me$_3$Si)$_2$CH}P(BH$_3$)(Me)(C$_6$H$_4$-2-OMe) (**8**) is the major side product in this reaction (the identity of **8** was confirmed by comparison with the NMR spectra of a deliberately prepared sample). Thus, the observed decomposition reaction involves P–B cleavage, along with protonation of the phosphorus center, and migration of a methyl group from the O atom of one ligand to the P atom of another (Scheme 4).

In order to identify the source of the PH proton in **7**, we have carried out a number of deuterium-labeling experiments. Thermolysis of toluene solutions of the labeled compounds [{(Me$_3$Si)$_2$CH}P(BD$_3$)(C$_6$H$_4$-2-OMe)]Li(THF), [{(Me$_3$Si)$_2$CH}P(BH$_3$)(C$_6$H$_4$-2-OCD$_3$)]Li(THF), and [{(Me$_3$Si)$_2$CH}P(BH$_3$)(C$_6$H$_4$-2-OMe)]Li(d_8-THF) led exclusively to mixtures of **7** and **8**; neither ^{2}H nor ^{31}P{^{1}H} NMR spectroscopy exhibited any evidence for the incorporation of deuterium at the phosphorus atom in **7**. Similarly, thermolysis of **6a** in d_8-toluene showed no evidence for incorporation of deuterium in **7**. We are, therefore, unable to identify unambiguously the source of this proton and can only conclude that it is derived from the presence of adventitious moisture.

The loss of the borane group during the degradation of **6a** is unexpected. However, it has previously been observed that (*S*)-(Ph)(Me)(C$_6$H$_4$-2-OMe)P(BH$_3$) racemizes slowly when it is heated under reflux in xylene.[16] This was attributed to abstraction of the borane group by the anisyl oxygen atom, followed by inversion at phosphorus and subsequent re-formation of the phosphine–borane adduct. A similar process

DOI: 10.1021/acs.organomet.7b00262

may account for the loss of BH_3 from the phosphorus center in **6a**, i.e. formation of an intermediate of the form $[\{(Me_3Si)_2CH\}P\{C_6H_4\text{-}2\text{-}O(BH_3)Me\}]Li(THF)_n$, from which the borane group could easily be abstracted by tmeda to give the isolated amine−borane.

Given the substantial effect of the borane group on the chemistry of thioanisole-substituted phosphide ligands, we were interested to see whether the presence of the borane group would suppress the alkaline-earth-metal-induced interligand methyl migration observed previously for the borane-free anisole-substituted analogue (see above).[9a] This was found not to be the case: the reaction between MgI_2 and 2 equiv of **6a** in THF gives the alkoxo−phosphido−borane complex $[[\{(Me_3Si)_2CH\}P(BH_3)(C_6H_4\text{-}2\text{-}O)]Mg(THF)_2]_2\cdot THF$ (**9**) as colorless crystals in reasonable yield, along with the tertiary phosphine−borane **8** as the sole phosphorus-containing products (Scheme 5). Once crystallized, compound **9** has surprisingly low solubility in aromatic and ethereal solvents, including THF, and so characterization by NMR spectroscopy is limited; however, the $^{31}P\{^1H\}$ and $^{11}B\{^1H\}$ NMR spectra of **9** in THF consist of broad signals at −74.3 and −30.0 ppm, respectively, consistent with a phosphido−borane complex.

Similarly, the reaction between CaI_2 and 2 equiv of in situ generated $[\{(Me_3Si)_2CH\}P(BH_3)(C_6H_4\text{-}2\text{-}OMe)]K$ in THF yields the alkoxo−phosphido−borane cluster complex $[[\{(Me_3Si)_2CH\}P(BH_3)(C_6H_4\text{-}2\text{-}O)]Ca(THF)]_4$ (**10**), along with **8** as the only phosphorus-containing species; these two compounds possess very similar solubilities, even in the extremely poor solvent hexamethyldisiloxane, and so are very difficult to separate, but a few single crystals of **10**, sufficient to obtain a crystal structure and elemental analysis, were isolated from cold methylcyclohexane. The $^{31}P\{^1H\}$, $^{11}B\{^1H\}$, and ^1H NMR spectra of samples of **10** contaminated with a small amount of **8** in d_8-toluene are highly complex and difficult to interpret. The low-temperature $^{31}P\{^1H\}$ NMR spectrum of this mixture consists of broad and overlapping signals in the range −64 to −77 ppm, which gradually broaden and coalesce as the temperature is increased until, at 90 °C, the spectrum consists of a very broad signal centered at −69.3 ppm, which we assign to the cluster **10**, and a broad multiplet at 11.7 ppm, due to **8**. This suggests the presence of numerous species in solution in rapid dynamic equilibrium and therefore indicates that the highly symmetrical tetrameric structure observed in the solid state (see below) fragments in toluene solution. In contrast, the $^{31}P\{^1H\}$, $^{11}B\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR spectra of **10** in d_8-THF exhibit a single set of signals for the ligands, suggesting either that a single species is present, possibly a solvated monomer, or else that any dynamic equilibria between oligomers are fast on the NMR time scale.

In contrast to the O−Me cleavage reactions observed for Mg and Ca, the reaction between SrI_2 and 2 equiv of $[\{(Me_3Si)_2CH\}P(BH_3)(C_6H_4\text{-}2\text{-}OMe)]K$ in THF cleanly yields the straightforward phosphido−borane complex $[\{(Me_3Si)_2CH\}P(BH_3)(C_6H_4\text{-}2\text{-}OMe)Sr(THF)_4]$ (**11**), which shows no evidence of decomposition, even after several weeks. The $^{31}P\{^1H\}$ and $^{11}B\{^1H\}$ NMR spectra of **11** in d_8-THF consist of a broad multiplet at −66.1 ppm and a broad doublet (J_{PB} = 41 Hz) at −29.3 ppm, respectively.

Solid-State Structures. In order that we might investigate the impact of metalation on the skeletal structure of the phosphine−borane, we have obtained the solid-state structure of the neutral precursor **5**. The molecular structure of **5** is shown in Figure 1, along with selected bond lengths and angles.

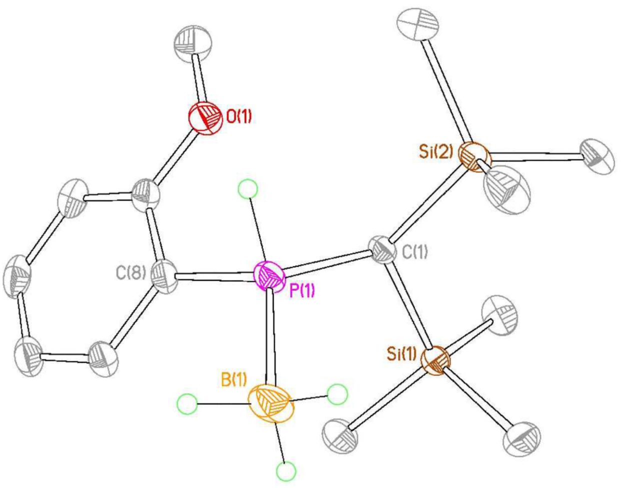


Figure 1. Molecular structure of **5** with 40% probability ellipsoids and with C-bound H atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1)−B(1) 1.925(2), P(1)−C(1) 1.8169(16), P(1)−C(8) 1.8107(18), P(1)−H(1) 1.32(2); C(1)−P(1)−B(1) 117.59(10), C(8)−P(1)−B(1) 112.72(9), C(1)−P(1)−C(8) 109.37(8).

We were unable to isolate single crystals of either **6a** or **6b** suitable for X-ray crystallography; however, single crystals of **6c** were obtained from cold toluene. Compound **6c** crystallizes as discrete centrosymmetric dimers in which the two potassium ions are bridged by B−H···K contacts, such that each borane group acts as a μ-η^2:η^1 bridge (Figure 2). Each potassium ion is thus coordinated by the phosphorus and η^1-borane groups of a phosphido−borane ligand, by the three nitrogen atoms of a molecule of pmdeta, and by an η^2-BH_3 contact. Somewhat surprisingly, there is no short contact between the potassium cation and the methoxy oxygen atom of the anisole substituent of the ligand.

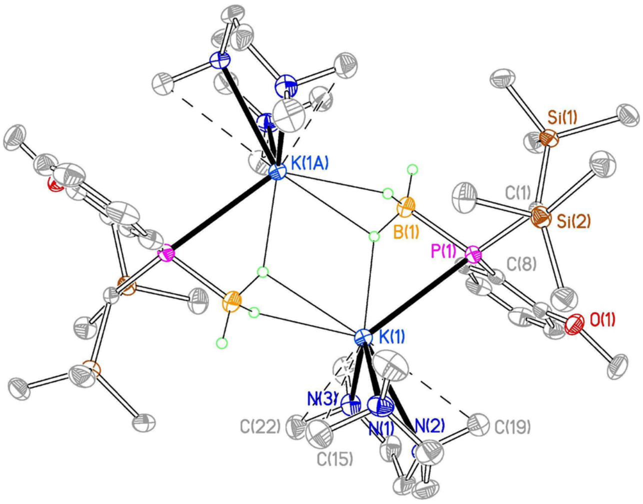


Figure 2. Molecular structure of **6c** with 40% probability ellipsoids and with C-bound H atoms omitted for clarity. Selected bond lengths (Å): K(1)−P(1) 3.2338(5), K(1)···B(1) 3.317(2), K(1)···H(1A) 2.77(2), K(1)···H(1B′) 2.76(2), K(1)···H(1C′) 3.35(2), K(1)−N(1) 2..8320(13), K(1)−N(2) 2.9373(12), K(1)−N(3) 2.8555(13), K(1)···C(15) 3.3512(17), K(1)···C(19) 3.3518(17), K(1)···C(22) 3.3373(18), P(1)−B(1) 1.9568(18), P(1)−C(1) 1.8772(15), P(1)−C(8) 1.8375(15).

DOI: 10.1021/acs.organomet.7b00262
Organometallics XXXX, XXX, XXX−XXX

The P−K distance of 3.2338(5) Å is similar to the corresponding distance in $[Ph_2P(BH_3)]K(18\text{-crown-6})$ (3.320(2) Å)[2f] and to the K−P distances in a range of potassium phosphide complexes[7] but is substantially shorter than the P−K distances in the related complexes $[[\{(Me_3Si)_2CH\}P(BH_3)(C_6H_4\text{-2-SMe})]K(pmdeta)]_2$[13] and $[[\{(Me_3Si)_2CH\}P(BH_3)(C_6H_4\text{-2-CH}_2OMe)]K(pmdeta)]_2$ (3.6617(6) and 3.7619(10) Å, respectively),[14] which exhibit either K−S(Me) or K−O(Me) contacts. The K···H (2.77(2), 2.76(2) and 3.35(2) Å) and the K···B distances (3.317(2) and 3.1365(18) Å) are typical of such contacts.

Compound **7** crystallizes with two independent molecules in the asymmetric unit and with solvent-accessible voids partially occupied by toluene, which is disordered over multiple positions; the molecular structure of **7** is shown in Figure 3, along with selected bond lengths and angles. Each of the two independent molecules of **7** contains a hexagonal-prismatic core structure which lacks any crystallographic symmetry, such that each ligand and each lithium ion in the cluster is unique. The hexanuclear Li_6O_6 core of **7** has been observed in several other species, including the phenoxide $[\{2,6\text{-(MeO)}_2C_6H_2O\}Li]_6$ (**12**),[17] and its formation is in line with the ring-stacking principles developed by Snaith et al.[18]

Each lithium ion is coordinated by three μ_3-O atoms and one phosphorus atom in a highly distorted tetrahedral geometry. In addition, Li(2), Li(3), and Li(6) have a close contact with the *ipso*-C(O) atom from an alkoxo−phosphide ligand in the opposite face of the hexagonal prism. The alkoxo−phosphide ligands chelate a single lithium ion in each face of the hexagonal prism (P−Li−O bite angles 84.3(3)−85.3(3)°), with the oxygen atom of the ligand bridging two lithium ions in one hexagonal face and forming a link to a third lithium ion in the second face. The Li−P distances in **7** range from 2.529(7) to 2.551(7) Å and are typical of such distances.[7] Similarly, the Li−O distances, which range from 1.854(9) to 2.067(9) Å, lie in the typical range of distances for these bonds; for example, the Li−O distances in **12** range from 1.908(4) to 2.058(4) Å.[17]

While phosphido−borane complexes of the alkali metals are reasonably well known,[2,13,14] and derivatives of the p-block[2e,4] and transition metals[3] have been reported, compounds **9**−**11** represent the first alkaline-earth-metal complexes of this ligand type. Compound **9** crystallizes as centrosymmetric dimers with a rhombus-shaped Mg_2O_2 core and with one molecule of THF of crystallization in the asymmetric unit; the structure of **9** is shown in Figure 4, along with selected bond lengths and angles. Each magnesium ion is coordinated by a μ_2-alkoxide oxygen atom, the oxygen atoms of two molecules of THF, and an η^2-BH_3 group in a pseudo-trigonal-bipyramidal geometry; there is no contact between the magnesium ions and the pyramidal phosphorus centers.

The binding mode of the alkoxo−phosphido−borane ligand in **9** (O and BH_3 chelation, but no P−Mg contacts) is in contrast with the binding mode of the precursor anisole-substituted phosphido−borane ligand in the potassium complex **6c** (P and BH_3 chelation, but no O−K contacts), and this is clearly related to the localization of charge on the oxygen atom in the former and the weak donor strength of the aryl ether in the latter. The Mg−O(alkoxo) distances of 1.961(3) and 2.017(3) Å are similar to previously reported Mg−O distances; for example, the Mg−O distances within the Mg_2O_2 core in $[(Ph_3SiO)Mg(\mu\text{-OSiPh}_3)(py)]_2$ are 1.965(2) and 1.988(2) Å.[19]

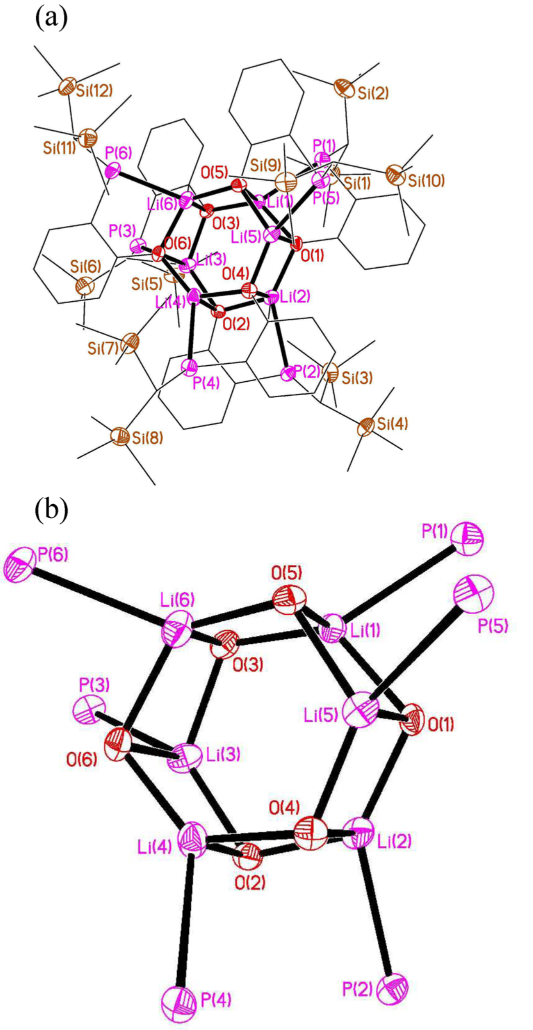


Figure 3. (a) Molecular structure of one of the two independent molecules of **7** with 40% probability ellipsoids and with H atoms omitted for clarity. (b) Core of the cluster with all C, Si, and H atoms omitted. Selected bond lengths for one of the two independent molecules (Å): Li(1)−P(1) 2.541(6), Li(1)−O(1) 1.912(8), Li(1)−O(3) 2.062(8), Li(1)−O(5) 2.062(8), Li(2)−P(2) 2.539(8), Li(2)−O(1) 1.913(8), Li(2)−O(2) 1.923(7), Li(2)−O(4) 2.065(8), Li(3)−P(3) 2.551(7), Li(3)−O(2) 1.887(9), Li(3)−O(3) 1.921(8), Li(3)−O(6) 2.067(9), Li(4)−P(4) 2.534(8), Li(4)−O(2) 2.059(9), Li(4)−O(4) 1.924(7), Li(4)−O(6) 1.854(9), Li(5)−P(5) 2.529(7), Li(5)−O(1) 2.062(8), Li(5)−O(4) 1.885(8), Li(5)−O(5) 1.920(9), Li(6)−P(6) 2.543(8), Li(6)−O(3) 2.040(9), Li(6)−O(5) 1.889(7), Li(6)−O(4) 1.931(8).

Compound **10** crystallizes with an unusual tetranuclear structure containing a crystallographic C_2 axis which lies perpendicular to the Ca_4 plane, midway along the Ca(1)···Ca(1A) vector; the molecular structure of **10** is shown in Figure 5, along with selected bond lengths. There are two distinct calcium environments: Ca(1) is coordinated by four oxygen atoms from four alkoxo−phosphido−borane ligands, which bridge to a second symmetry-equivalent calcium ion, two phosphorus atoms, and two η^1-BH_3 groups. In contrast, Ca(2) is coordinated by two alkoxo−phosphido−borane oxygen atoms, two η^2-BH_3 groups, and two molecules of THF, along with a short Ca···C_{ipso} contact with one of the aromatic rings. Thus, each alkoxo oxygen atom acts as a μ_3 bridge between two Ca(1) and one Ca(2) ion, while each BH_3 group acts as a μ_2-

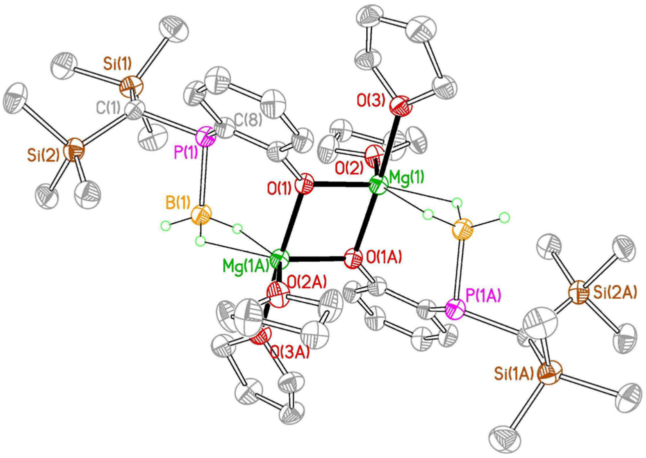


Figure 4. Molecular structure of **9** with 40% probability ellipsoids. Disorder components, solvent of crystallization, and C-bound H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mg(1)−O(1) 1.961(3), Mg(1)-O(1A) 2.017(3), Mg(1)−O(2) 2.049(3), Mg(1)−O(3) 2.068(3), Mg(1)···B(1A) 2.428(4), Mg(1)···H(1A) 1.98(4), Mg(1)···H(1B) 1.99(4), P(1)−C(1) 1.872(4), P(1)−C(8) 1.835(4), P(1)−B(1) 1.972(4); O(1)−Mg(1)−O(1A) 80.44(11), Mg(1)−O(1)−Mg(1A) 99.56(11).

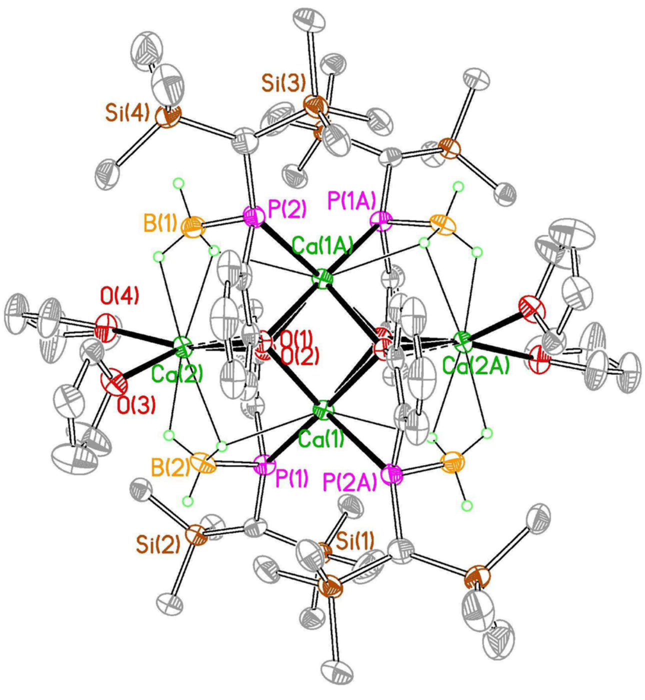


Figure 5. Molecular structure of **10** with 40% probability ellipsoids. Disorder components and C-bound H atoms are omitted for clarity. Selected bond lengths (Å): Ca(1)−O(1) 2.369(2), Ca(1)-O(2A) 2.387(2), Ca(1)−O(2) 2.517(2), Ca(1)-O(1A) 2.525(2), Ca(1)-P(2A) 2.8449(10), Ca(1)−P(1) 2.8783(9), Ca(1)···B(2) 3.223(4), Ca(1)···B(1A) 3.281(4), Ca(1)-H(1B) 2.64(1), Ca(2)−O(1) 2.295(2), Ca(2)−O(2) 2.298(2), Ca(2)−O(3) 2.350(2), Ca(2)−O(4) 2.370(2), Ca(2)···B(1) 2.872(4), Ca(2)···B(2) 2.901(4), Ca(2)···C(13) 3.1254(1), Ca(2)···C(26) 3.1333(1), Ca(2)···H(1A) 2.35(1), Ca(2)···H(1B) 2.39(1), Ca(2)···H(2F) 2.42(1), Ca(2)···H(2E) 2.52(1), P(1)−C(1) 1.865(3), P(1)−C(8) 1.823(3), P(1)−B(2) 1.966(4), P(2)−B(1) 1.984(4), P(2)−C(14) 1.867(5), P(2)−C(21) 1.825(4).

η^1:η^2 bridge between Ca(1) and Ca(2). The alkoxo−phosphido−borane ligands chelate Ca(1) through the P and O atoms (P−Ca(1)−O bite angles 67.53(6) and 67.04(6)°), while also formally chelating Ca(2) through the O and BH_3 hydrogen atoms (O−Ca(2)···B angles 72.92(11) and 74.55(12)°). The core structure of **10** may be considered as an O_4 square with one Ca ion lying over the center of each face and two calcium ions bridging two of its opposing edges. This structural motif is completely different from the heterocubane structure adopted by the borane-free cluster $[[\{(Me_3Si)_2CH\}P(C_6H_4\text{-}2\text{-}O)]Ca(THF)]_4$ (**1b**),[9a] clearly illustrating the structural influence of the borane groups.

The Ca−P distances (2.8778(11) and 2.8454(12) Å) are at the shorter end of the typical range for Ca−P distances (2.90−3.10 Å) but are similar to the corresponding distances in $[(Me_3Si)_2N\}Ca(THF)\{\mu_2\text{-}P(Si\mathit{t}Bu_3)_2\}_2]_2Ca$,[20] which range from 2.866(3) to 2.951(2) Å. The Ca(1)−O_{alkoxo} distances in **10** (2.369(2), 2.385(2), 2.518(2) and 2.524(2) Å) are significantly longer than the Ca(2)−O_{alkoxo} distances (2.297(2) and 2.299(2) Å) but lie in the typical range for such distances.

In contrast to the multinuclear structure adopted by **10**, compound **11** crystallizes as discrete molecules with a single pseudo-octahedral Sr ion. The structure of **11** is shown in Figure 6, along with selected bond lengths and angles. The strontium ion is coordinated in a trans configuration by two η^3-BH_3 groups and by the oxygen atoms of four molecules of THF. Somewhat surprisingly, given the potentially chelating nature of the phosphido−borane ligand (which may act as a P,O- or BH_3,O-donor; see above), there is no contact between the strontium ions and either the phosphorus or oxygen centers of the ligand. We have previously observed a related preference for BH_3 donation (over C donation) in the phosphine−borane-stabilized carbanion complex $[(Me_3Si)_2\{Me_2(H_3B)P\}C]_2Sr(THF)_5$.[21] In the present case, this preference for borane coordination may be attributed to the hard nature of the strontium cation and the better donor properties of THF in comparison to aryl ethers. The Sr···B distances in **11** (2.844(2) and 2.847(2) Å) are similar to previously reported Sr···B

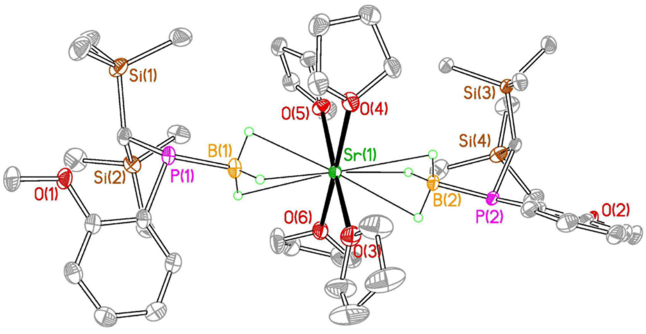


Figure 6. Molecular structure of **11** with 40% probability ellipsoids. Solvent of crystallization and C-bound H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sr(1)−O(3) 2.5069(14), Sr(1)−O(4) 2.5383(13), Sr(1)−O(5) 2.5556(13), Sr(1)−O(6) 2.5490(14), Sr(1)···H(1A) 2.59(2), Sr(1)···H(1B) 2.75(2), Sr(1)···H(1C) 2.63(2), Sr(1)···H(2A) 2.59(2), Sr(1)···H(2B) 2.74(2), Sr(1)···H(2C) 2.64(2), Sr(1)···B(1) 2.844(2), Sr(1)···B(2) 2.847(2), P(1)−C(1) 1.840(2), P(1)−C(8) 1.8898(19), P(1)−B(1) 1.952(2), P(2)−C(15) 1.8386(19), P(2)−C(22) 1.8882(19), P(2)−B(2) 1.952(2); B(1)···Sr···B(2) 174.68(7).

distances; for example, the Sr⋯B distance in Sr[HC{C(Me)-N(2,6-iPr$_2$C$_6$H$_3$)}$_2$](BH$_4$) (THF)$_2$ is 2.8206(18) Å.[22]

Comparison of the structure of **5** with those of **6c** and **9**−**11** reveals that metalation of the phosphine−borane precursor results in a significant lengthening of the P(1)−C(1), P(1)−C(8), and P(1)−B(1) distances by 0.02−0.07 Å.

■ CONCLUSIONS

While alkali-metal complexes of the anisole-substituted phosphide [{(Me$_3$Si)$_2$CH}P(C$_6$H$_4$-2-OMe)]M(THF)$_n$ (M = Li, K) are stable at room temperature, the presence of the borane group in the lithium complex **6a** appears to be sufficient to activate the C−O bond; C−O cleavage is not observed for the corresponding sodium and potassium complexes **6b**,**c**. Similarly, while an analogous C−O cleavage reaction is observed in the magnesium and calcium complexes **9** and **10**, this reaction is not seen for the strontium complex **11**. This suggests that the rate of the C−O cleavage reaction depends on the Lewis acidity of the alkali-metal or alkaline-earth-metal cation, paralleling the behavior of the borane-free derivatives.

The presence of the borane group additionally affects the solid-state structures of the resulting complexes, leading to a variety of ligand coordination modes, including (i) P,BH$_3$ chelation/bridging (**6c**), (ii) O,BH$_3$ chelation/bridging (**9**), (iii) P,BH$_3$,O chelation/bridging (**10**), and (iv) BH$_3$-donor-only (**11**) coordination modes.

■ EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. THF, light petroleum (bp 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; hexamethyldisiloxane was dried by distillation from CaH$_2$. THF and hexamethyldisiloxane were stored over activated 4A molecular sieves; all other solvents were stored over a potassium film. Deuterated THF, toluene, and benzene were distilled from potassium, and CDCl$_3$ was distilled from CaH$_2$ under nitrogen; all NMR solvents were deoxygenated by three freeze−pump−thaw cycles and were stored over activated 4A molecular sieves. Benzylsodium, benzylpotassium,[23] and {(Me$_3$Si)$_2$CH}PH(C$_6$H$_4$-2-OMe) (**4**)[9a] were prepared by previously published procedures; n-butyllithium was purchased from Aldrich as a 2.5 M solution in hexanes, and BH$_3$·SMe$_2$ was purchased from Aldrich as a 2.0 M solution in THF. tmeda and pmdeta were distilled from CaH$_2$ under nitrogen and were stored over activated 4A molecular sieves. All other compounds were used as supplied by the manufacturer.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a JEOL ECS500 spectrometer operating at 500.16 and 125.65 MHz, respectively, or a Bruker Avance300 spectrometer operating at 300.15 and 75.47 MHz, respectively; chemical shifts are quoted in ppm relative to tetramethylsilane. ^{31}P{^{1}H}, ^{11}B{^{1}H}, ^{7}Li, and ^{2}H NMR spectra were recorded on a JEOL ECS500 spectrometer operating at 202.35, 160.16, 194.38, and 76.78 MHz, respectively; chemical shifts are quoted in ppm relative to external 85% H$_3$PO$_4$, BF$_3$·Et$_2$O, and 0.1 M LiCl, respectively.

Where possible, compounds were subjected to combustion analysis to assess bulk purity; where this was not possible, the purity of compounds has been established by multielement NMR spectroscopy. Elemental analyses were obtained by the Elemental Analysis Service of London Metropolitan University.

{(Me$_3$Si)$_2$CH}PH(BH$_3$)(C$_6$H$_4$-2-OMe) (5). To a solution of {(Me$_3$Si)$_2$CH}PH(C$_6$H$_4$-2-OMe) (**4**; 6.55 g, 21.94 mmol) in THF (20 mL) was added BH$_3$·SMe$_2$ (11.0 mL, 22.00 mmol). This mixture was stirred at room temperature for 1 h, and then the solvent was removed in vacuo to yield a colorless solid. This was crystallized from a cold (−30 °C) mixture of n-hexane (20 mL) and THF (1 mL). Isolated yield: 5.00 g, 73%. ^{1}H{^{11}B} NMR (CDCl$_3$): δ −0.01 (s, 9H, SiMe$_3$), 0.29 (s, 9H, SiMe$_3$), 0.89 (dd, J_{PH} = 14.9, J_{HH} = 6.6 Hz, 3H, BH$_3$), 1.08 (d, J_{PH} = 20.2 Hz, 1H, CHP), 3.90 (s, 3H OMe), 5.86 (dqd, J_{PH} = 384.0, J_{HH} = 6.6, J_{HH} = 1.4 Hz, 1H, PH), 6.90 (m, 1H, ArH), 7.06 (m, 1H, ArH), 7.48 (m, 1H, ArH), 7.92 (m, 1H, ArH). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 1.25 (d, J_{PC} = 3.8 Hz, SiMe$_3$), 2.11 (d, J_{PC} = 2.8 Hz, SiMe$_3$), 6.51 (d, J_{PC} = 4.8 Hz, CHP), 55.54 (OMe), 110.28 (d, J_{PC} = 3.8 Hz, ArC), 116.87 (d, J_{PC} = 50.8 Hz, ArC), 121.05 (d, J_{PC} = 12.5 Hz, ArC), 133.49 (ArC), 136.19 (d, J_{PC} = 15.3 Hz, ArC), 160.78 (d, J_{PC} = 2.0 Hz, ArC). ^{11}B{^{1}H} NMR (CDCl$_3$): δ −40.6 (d, br, J_{PB} = 49.0 Hz). ^{31}P{^{1}H} NMR (CDCl$_3$): δ −22.3 (q, br, J_{PB} = 49.0 Hz).

[{(Me$_3$Si)$_2$CH}P(BH$_3$)(C$_6$H$_4$-2-OMe)]Li(THF) (6a). To a solution of **5** (0.20 g, 0.64 mmol) in diethyl ether (20 mL) was added n-BuLi (0.4 mL, 0.76 mmol). This mixture was stirred for 1 h, and the solvent was removed in vacuo. The yellow solid was dissolved in THF (2 mL), and light petroleum (20 mL) was added, precipitating the product as a colorless powder, which was isolated by filtration and washed with cold (−10 °C) light petroleum (5 mL). Yield: 0.13 g, 54%. ^{1}H{^{11}B} NMR (d_8-THF): δ −0.11 (s, 9H, SiMe$_3$), 0.15 (s, 9H, SiMe$_3$), 0.62 (d, J_{PH} = 3.2 Hz, 3H, BH$_3$), 0.73 (d, J_{PH} = 6.9 Hz, 1H, CHP), 1.76 (m, 4H, THF), 3.65 (m, 4H, THF), 3.75 (s, 3H, OMe), 6.61 (m, 1H, ArH), 6.65 (m, 1H, ArH), 6.90 (m, 1H, ArH), 7.69 (m, 1H, ArH). ^{13}C{^{1}H} NMR (d_8-THF): δ 2.45 (d, J_{PC} = 9.2 Hz, SiMe$_3$), 3.79 (SiMe$_3$), 7.15 (d, J_{PC} = 43.2 Hz, CHP), 26.43 (THF), 55.52 (OMe), 68.37 (THF), 110.22, 120.41, 125.62, 134.73 (ArC), 141.25 (d, J_{PC} = 36.2 Hz, ArC), 162.35 (d, J_{PC} = 11.1 Hz, ArC). ^{11}B{^{1}H} NMR (d_8-THF, 25 °C): δ −34.3 (d, J_{PB} = 39.3 Hz). ^{31}P{^{1}H} NMR (d_8-THF): δ −62.5 (d, J_{PB} = 39.3 Hz). ^{7}Li NMR (d_8-THF): δ −0.58.

[{(Me$_3$Si)$_2$CH}P(BH$_3$)(C$_6$H$_4$-2-OMe)Na](THF) (6b). To a solution of **5** (0.21 g, 0.67 mmol) in diethyl ether (10 mL) was added a solution of PhCH$_2$Na (0.08 g, 0.67 mmol) in diethyl ether (10 mL), and this mixture was stirred for 1 h. The solvent was removed in vacuo to yield a yellow solid. This solid was dissolved in the minimum amount of THF, and upon addition of light petroleum the product precipitated from solution as a colorless powder, which was isolated by filtration and washed with cold (−10 °C) light petroleum. Yield: 0.25 g, 96%. Anal. Calcd for [{(Me$_3$Si)$_2$CH}P(BH$_3$)(C$_6$H$_4$-2-OMe)]Na-(THF): C 53.19, H 9.18%. Found: C 53.06, H 9.31%. ^{1}H{^{11}B} NMR (d_8-THF): δ −0.07 (s, 9H, SiMe$_3$), 0.15 (s, 9H, SiMe$_3$), 0.66 (d, J_{PH} = 7.3 Hz, 1H, CHP), 0.72 (d, J_{PH} = 6.9 Hz, 3H, BH$_3$), 1.79 (m, 4H, THF), 3.63 (m, 4H, THF), 3.77 (s, 3H, OMe), 6.66 (m, 2H, ArH), 6.92 (m, 1H, ArH), 7.72 (m, 1H, ArH). ^{13}C{^{1}H} NMR (d_8-THF): δ 2.38 (d, J_{PC} = 8.6 Hz, SiMe$_3$), 3.76 (SiMe$_3$), 7.07 (d, J_{PC} = 40.2 Hz, CHP), 26.43 (THF), 55.55 (OMe), 68.31 (THF), 110.14, 120.58, 125.89, 134.92 (ArC), 140.41 (d, J_{PC} = 30.16 Hz ArC), 162.06 (d, J_{PC} = 11.1 Hz). ^{11}B{^{1}H} NMR (d_8-THF,): δ −34.5 (d, br, J_{BP} = 37.3 Hz). ^{31}P{^{1}H} NMR (d_8-THF): δ −64.3 (q, br, J_{PB} = 37.3 Hz).

[{(Me$_3$Si)$_2$CH}P(BH$_3$)(C$_6$H$_4$-2-OMe)]K(pmdeta) (6c). To a solution of **5** (0.88 g, 2.82 mmol) in THF (20 mL) was added a solution of PhCH$_2$K (0.37 g, 2.82 mmol) in THF (20 mL). This mixture was stirred for 1 h, and then the solvent was removed in vacuo to yield a yellow solid. The product was dissolved in the minimum amount of toluene, and pmdeta (0.6 mL, 2.87 mmol) was added. The solvent was then carefully reduced in vacuo until incipient crystallization. The solution was warmed to room temperature, dissolving the product, and upon cooling (5 °C) colorless crystals of **6c** suitable for X-ray crystallography were deposited. Isolated crystalline yield: 0.54 g, 37%. Anal. Calcd for [{(Me$_3$Si)$_2$CH}P(BH$_3$)(C$_6$H$_4$-2-OMe)]K(pmdeta): C, 52.75; H, 10.01; N, 8.02. Found: C, 52.69; H, 9.92; N, 7.87. ^{1}H{^{11}B} NMR (C$_6$D$_6$): δ −0.27 (s, 9H, SiMe$_3$), 0.45 (s, 9H, SiMe$_3$), 1.05 (d, J_{PH} = 5.5 Hz, 3H, BH$_3$), 1.07 (d, $^2J_{PH}$ = 7.8 Hz, 1H, CHP), 2.01 (s, 8H, NCH$_2$), 2.05 (s, 3H, NMe), 2.11 (s, 12H, NMe$_2$), 3.53 (s, 3H, OMe), 6.54 (m, 1H, ArH), 6.94 (m, 1H, ArH), 7.06 (m, 1H, ArH), 8.04 (m, 1H, ArH). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 2.42 (d, J_{PC} = 8.6 Hz, SiMe$_3$), 3.76 (SiMe$_3$), 7.04 (d, J_{PC} = 42.9 Hz, CHP), 43.23 (NMe), 46.22 (NMe$_2$), 55.35 (OMe), 57.34 (NCH$_2$), 58.79 (NCH$_2$), 109.93, 120.44, 125.75, 134.77 (ArC), 140.84 (d, J_{PC} = 31.4 Hz, ArC), 162.04 (d, J_{PC} = 10.1 Hz, ArC). ^{11}B{^{1}H} NMR (C_6D_6): δ −32.3 (d, br, J_{BP} = 36.1 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ −63.0 (q, br, J_{PB} = 36.1 Hz).

{$(Me_3Si)_2CH$}PMe(BH_3)(C_6H_4-2-OMe) (8). To a solution of **5** (0.31 g, 0.99 mmol) in THF (15 mL) was added *n*-BuLi (0.4 mL, 1.00 mmol). This mixture was stirred for 1/2 h, and then MeI (0.07 mL, 1.12 mmol) was added. The mixture was stirred for a further 1/2 h, and the solvent was removed in vacuo to give **8** as a colorless solid. Isolated yield: 0.32 g, 99%. ^{1}H{^{11}B} NMR ($CDCl_3$): δ −0.08 (s, 9H, $SiMe_3$), 0.31 (s, 9H, $SiMe_3$), 0.88 (d, J_{PH} = 14.7 Hz, 3H, BH_3), 1.46 (d, J_{PH} = 20.2 Hz, 1H, CHP), 1.66 (d, J_{PH} = 10.1 Hz, 3H, PMe), 3.91 (s, 3H, OMe), 6.88 (m, 1H, ArH), 7.06 (m, 1H, ArH), 7.48 (m, 1H, ArH), 7.92 (m, 1H, ArH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 2.43 (d, J_{PC} = 2.9 Hz, $SiMe_3$), 3.52 (d, J_{PC} = 1.9 Hz, $SiMe_3$), 10.39 (d, J_{PC} = 4.8 Hz, CHP), 16.71 (d, J_{PC} = 39.3 Hz, PMe), 55.22 (OMe), 110.68 (d, J_{PC} = 3.83 Hz, ArC), 120.82, 120.94, 132.90 (ArC), 135.71 (d, J_{PC} = 15.3 Hz, ArC), 161.35 (ArC). ^{11}B{^{1}H} NMR ($CDCl_3$): δ −37.5 (d, br, J_{PB} = 58.8 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 11.7 (q, br, J_{PB} = 58.8 Hz).

{$(Me_3Si)_2CH$}PH(BD_3)(C_6H_4-2-OMe). To a solution of **4** (0.37 g, 1.24 mmol) in THF (5 mL) was added BD_3·THF (1.2 mL of a 1.0 M solution in THF, 1.20 mmol). This mixture was stirred for 1 h, and the solvent was removed in vacuo to give a colorless solid. Yield: 0.33 g, 88%. ^{1}H NMR ($CDCl_3$): δ 0.00 (s, 9H, $SiMe_3$), 0.28 (s, 9H, $SiMe_3$), 1.08 (d, J_{PH} = 20.9 Hz, 1H, CHP), 3.90 (s, 3H, OMe), 5.83 (d, J_{PH} = 380.6 Hz, 1H, PH), 6.90 (m, 1H, ArH), 7.04 (m, 1H, ArH), 7.48 (m, 1H, ArH), 7.90 (m, 1H, ArH). ^{2}H NMR ($CHCl_3$): δ 0.95 (br s). ^{11}B{^{1}H} NMR ($CDCl_3$, 25 °C): δ −40.8 (br, s). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −22.3 (br m).

{$(Me_3Si)_2CH$}PH(BH_3)(C_6H_4-2-OCD_3). To a cold (0 °C) solution of KOH (0.63 g, 12.00 mmol) in acetonitrile (10 mL) was added 2-bromophenol (2.0 mL of a 5.0 M solution in acetonitrile, 10.00 mmol). This mixture was stirred for 1/2 h at 0 °C, and then CD_3I (0.75 mL, 12 mmol) was added. The reaction mixture was stirred for 40 h. The solvent was removed in vacuo, and the residue was extracted into light petroleum (3 × 20 mL) and filtered. The solvent was removed in vacuo from the filtrate to yield 2-bromo-d_3-anisole as a colorless oil. To a cold (0 °C) solution of 2-bromo-d_3-anisole (1.19 g, 6.23 mmol) in diethyl ether (10 mL) was added *n*-BuLi (2.5 mL, 6.25 mmol). The solution was stirred for 2 h at 0 °C and then added, dropwise, to a cold (−78 °C) solution of {$(Me_3Si)_2CH$}PCl_2 (1.70 g, 6.51 mmol) in diethyl ether (20 mL). The reaction mixture was stirred for 16 h and warmed to room temperature. Solid $LiAlH_4$ (0.28 g, 7.3 mmol) was carefully added to the solution, and this mixture was heated under reflux for 2 h. The solution was cooled, BH_3·SMe_2 (3.2 mL, 6.4 mmol) was added, and the solution was stirred for 1 h at room temperature. Water (40 mL) was carefully added, the organic phase was extracted into diethyl ether (3 × 20 mL), and the combined extracts were washed with brine (30 mL). The organic phase was dried over $MgSO_4$ and filtered, and the solvent was removed in vacuo. The crude product was dissolved in hot *n*-hexane, and crystals were deposited upon cooling to −30 °C. Isolated crystalline yield: 0.83 g, 42%. ^{1}H{^{11}B} NMR ($CDCl_3$): δ −0.01 (s, 9H, $SiMe_3$), 0.28 (s, 9H, $SiMe_3$), 0.89 (dd, J_{HH} = 6.6, J_{PH} = 14.9 Hz, 3H, BH_3), 1.07 (d, J_{PH} = 20.2 Hz, 1H, CHP), 5.84 (dq, J_{PH} = 384.0, J_{HH} = 12.9 Hz, 1H, PH), 6.89 (m, 1H, ArH), 7.04 (m, 1H, ArH), 7.47 (m, 1H, ArH), 7.91 (m, 1H, ArH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 1.28 (d, J_{PC} = 2.9 Hz, $SiMe_3$), 2.14 (d, J_{PC} = 2.9 Hz, $SiMe_3$), 6.52 (d, J_{PC} = 3.8 Hz, CHP), 110.23 (d, J_{PC} = 3.8 Hz, ArC), 116.91 (d, J = 50.8 Hz, ArC), 121.09 (d, J_{PC} = 12.5 Hz, ArC), 133.49 (ArC), 136.28 (d, J_{PC} = 15.3 Hz, ArC), 160.79 (ArC) [OCD_3 signal not observed]. ^{11}B{^{1}H} NMR ($CDCl_3$): δ −40.4 (d, br, J_{PB} = 49.0 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −22.3 (q, br, J_{PB} = 49.0 Hz).

[{$(Me_3Si)_2CH$}P(C_6H_4-2-O)(BH_3)Mg($THF)_2$]$_2$ (9). To a solution of **5** (0.73 g, 2.34 mmol) in THF (10 mL) was added *n*BuLi (0.93 mL, 2.33 mmol) in THF (10 mL), and this mixture was stirred for 1 h. This solution was added to a suspension of MgI_2 (0.33 g, 1.19 mmol) in THF (15 mL), and this mixture was stirred at room temperature for 48 h. The solution was filtered, and the filtrate was concentrated to ca. 10 mL. The colorless precipitate was redissolved by heating, and the solution was cooled to 5 °C for 5 days, after which time colorless crystals of **9** were isolated by filtration and washed with a small amount of diethyl ether. Yield: 0.35 g, 74% (based on MgI_2). Anal. Calcd for [{$(Me_3Si)_2CH$}P(BH_3)(C_6H_4-2-O)]Mg($THF)_2$]$_2$: C, 50.00; H, 8.41. Found: C, 49.84; H, 8.32. ^{31}P{^{1}H} NMR (THF): δ −74.3 (br), ^{11}B{^{1}H} NMR (THF): δ −30.0 (br)

[{$(Me_3Si)_2CH$}P(C_6H_4-2-O)(BH_3)Ca(THF)]$_4$ (10). To a solution of **5** (0.98 g, 3.14 mmol) in THF (15 mL) was added a solution of $PhCH_2K$ (0.47 g, 3.30 mmol) in THF (20 mL), and this mixture was stirred for 1 h. This solution was added to a slurry of CaI_2 (0.48 g, 1.63 mmol) in THF (20 mL), and this mixture was stirred for 16 h. The solvent was removed in vacuo, and the resulting sticky, colorless solid was extracted into hexamethyldisiloxane (30 mL) and filtered. The solvent was removed in vacuo from the filtrate to give a sticky solid, which was washed with hexamethyldisiloxane. A small number of single crystals of **10** suitable for X-ray crystallography were obtained from cold (5 °C) methylcyclohexane. Isolated yield: 0.48 g, 69% (based on CaI_2). Anal. Calcd for [[{$(Me_3Si)_2CH$}P(C_6H_4-2-O)-(BH_3)]Ca(THF)]$_4$: C, 51.67; H, 8.79. Found: C, 51.56; H, 8.64. ^{1}H NMR (d_8-THF): δ 0.15 (s, 9H, $SiMe_3$), 0.19 (s, 9H, $SiMe_3$), 1.06 (br s, 3H, BH_3), 1.78, (m, 4H, THF), 3.64 (m, 4H, THF), 6.48 (m, 1H, ArH), 6.75 (m, 1H, ArH), 7.03 (m, 2H, ArH). ^{13}C{^{1}H} NMR (d_8-THF): δ 2.25 ($SiMe_3$), 4.35 ($SiMe_3$), 5.74 (d, J_{PC} = 35.5 Hz, CHP), 26.44, 68.47 (THF), 116.16, 117.77, 124.89, 129.88 (Ar), 141.60 (d, J_{PC} = 18.1 Hz, Ar), 164.66 (d, J_{PC} = 16.6 Hz, Ar). ^{31}P{^{1}H} NMR (d_8-THF): δ −69.8 (br). ^{11}B{^{1}H} NMR (d_8-THF): −26.6 (br).

[{$(Me_3Si)_2CH$}P(C_6H_4-2-OMe)(BH_3)Sr($THF)_4$]·THF (11). To a solution of **5** (0.78 g, 2.50 mmol) in THF (15 mL) was added a solution of $PhCH_2K$ (0.31 g, 2.4 mmol), and this mixture was stirred for 1/2 h. This solution was added to a suspension of SrI_2 (0.43 g, 1.25 mmol) in THF, and this mixture was stirred for 24 h. The solution was filtered, and the filtrate was reduced in volume to ca. 5 mL and cooled to 6 °C for 16 h. The colorless crystals of **11** were isolated by filtration and washed with a small amount of cold diethyl ether. The THF of crystallization is held only weakly and is rapidly lost under vacuum. Yield: 0.79 g, 63%. Anal. Calcd for [[{$(Me_3Si)_2CH$}P(C_6H_4-2-OMe) (BH_3)]$_2$Sr($THF)_4$]: C, 52.92; H, 9.08. Found: C, 52.75; H, 8.95. ^{1}H NMR (d_8-THF) δ −0.06 (s, 18H, $SiMe_3$), 0.11 (s, 18H, $SiMe_3$), 0.70 (d, J_{PH} = 6.0 Hz, 2H, CHP), 0.90 (br q, J_{BH} = 83.8 Hz, 6H, BH_3), 1.79 (m, 16H, THF), 3.62 (m, 16H, THF), 3.76 (s, 6H, OMe), 6.65 (m, 4H, ArH), 6.95 (m, 2H, ArH), 7.65 (m, 2H, ArH). ^{13}C{^{1}H} NMR (d_8-THF): δ 2.31 (d, J_{PC} = 9.0 Hz, $SiMe_3$), 3.58 ($SiMe_3$), 7.23 (d, J_{PC} = 44.2 Hz, CHP), 26.52 (THF), 55.50 (OMe), 68.39 (THF), 110.39, 120.31, 134.43, 134.71 (Ar), 162.50 (d, J_{PC} = 11.5 Hz, Ar). ^{31}P{^{1}H} NMR (d_8-THF): δ −66.1 (m, br). ^{11}B{^{1}H} NMR (d_8-THF): δ −29.3 (d, J_{PB} = 41.4 Hz).

Crystal Structure Determinations of 5, 6c, 7, and 9–11. Measurements were made at 150 K on an Oxford Diffraction (Agilent Technologies) Gemini A Ultra diffractometer using Mo Kα radiation (λ = 0.71073 Å), except for the structure of **9**, which was collected using Cu Kα radiation (λ = 1.54178 Å). Cell parameters were refined from the observed positions of all strong reflections. Intensities were corrected semiempirically for absorption, on the basis of symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined on F^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 1.2 (1.5 for methyl groups) times U_{eq} for the parent C atom. The structure of **10** contains large solvent-accessible voids along the crystallographic [001] direction. These voids contain multiple, partially occupied diethyl ether sites, disordered about a center of symmetry. No sensible model for this disorder was forthcoming; therefore, the electron density in the void space was treated using PLATON/SQUEEZE. Programs were Oxford Diffraction CrysAlisPro for data collection and processing and SHELXTL for structure solution, refinement, and molecular graphics.[24]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00262.

> ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, and ^{11}B{^{1}H} NMR spectra for all compounds, ^{7}Li NMR spectrum for **6a**, and crystal data for **5**, **6c**, **7**, and **9**–**11** (PDF)

Accession Codes

CCDC 1548771–1548776 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for K.I.: keith.izod@ncl.ac.uk.

ORCID

Keith Izod: 0000-0003-3882-9343

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are grateful to Newcastle University and the Libyan government for support.

■ REFERENCES

(1) For reviews see: (a) Staubitz, A.; Robertson, A. P. M.; Sloan, M. E.; Manners, I. *Chem. Rev.* **2010**, *110*, 4023–4078. (b) Gaumont, A.-C.; Carboni, B. *Science of Synthesis* **2004**, *6*, 485–512. (c) Carboni, B.; Monnier, L. *Tetrahedron* **1999**, *55*, 1197–1248. (d) Paine, R. T.; Nöth, H. *Chem. Rev.* **1995**, *95*, 343–379. (e) Ohff, M.; Holz, J.; Quirmbach, M.; Borner, A. *Synthesis* **1998**, *1998*, 1391–1415.

(2) (a) Kückmann, T. I.; Dornhaus, F.; Bolte, M.; Lerner, H.-W.; Holthausen, M. C.; Wagner, M. *Eur. J. Inorg. Chem.* **2007**, *2007*, 1989–2003. (b) Fuller, A.-M.; Mountford, A. J.; Scott, M. L.; Coles, S. J.; Horton, P. N.; Hughes, D. L.; Hursthouse, M. B.; Lancaster, S. J. *Inorg. Chem.* **2009**, *48*, 11474–11482. (c) Dornhaus, F.; Bolte, M.; Lerner, H.-W.; Wagner, M. *Eur. J. Inorg. Chem.* **2006**, *2006*, 1777–1785. (d) Dornhaus, F.; Bolte, M. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2006**, *62*, m3573–m3575. (e) Müller, G.; Brand, J. *Organometallics* **2003**, *22*, 1463–1467. (f) Dornhaus, F.; Bolte, M.; Lerner, H.-W.; Wagner, M. *Eur. J. Inorg. Chem.* **2006**, *2006*, 5138–5147. (g) Izod, K.; Watson, J. M.; Clegg, W.; Harrington, R. W. *Inorg. Chem.* **2013**, *52*, 1466–1475.

(3) (a) Amor, I.; Garcia-Vivo, D.; Garcia, M. E.; Ruiz, M. A.; Sáez, D.; Hamidov, H.; Jeffery, J. C. *Organometallics* **2007**, *26*, 466–468. (b) McNamara, W. F.; Duesier, E. N.; Paine, R. T.; Ortiz, J. V.; Kölle, P.; Nöth, H. *Organometallics* **1986**, *5*, 380–383. (c) Hooper, T. N.; Weller, A. S.; Beattie, N. A.; MacGregor, S. A. *Chem. Sci.* **2016**, *7*, 2414–2426. (d) Abdellah, I.; Bernoud, E.; Lohier, J.-F.; Alayrac, C.; Toupet, L.; Lepetit, C.; Gaumont, A.-C. *Chem. Commun.* **2012**, *48*, 4088–4090. (e) Dorn, H.; Singh, R. A.; Massey, J. A.; Nelson, J. M.; Jaska, C. A.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 6669–6678. (f) Gaumont, A.-C.; Hursthouse, M. B.; Coles, S. J.; Brown, J. M. *Chem. Commun.* **1999**, 63–64. (g) Dornhaus, F.; Bolte, M.; Lerner, H.-W.; Wagner, M. *J. Organomet. Chem.* **2007**, *692*, 2949–2955. (h) Jaska, C. A.; Dorn, H.; Lough, A. J.; Manners, I. *Chem. - Eur. J.* **2003**, *9*, 271–281. (i) Lee, K.; Clark, T. J.; Lough, A. J.; Manners, I. *Dalton Trans.* **2008**, 2732–2740. (j) Jaska, C. A.; lough, A. J.; Manners, I. *Dalton Trans.* **2005**, 326–331. (k) Pican, S.; Gaumont, A.-C. *Chem. Commun.* **2005**, 2393–2395. (l) Schafer, A.; Jurca, T.; Turner, J.; Vance, J. R.; Lee, K.; Du, V. A.; Haddow, M. F.; Whittel, G. R.; Manners, I. *Angew. Chem., Int. Ed.* **2015**, *54*, 4836–4841.

(4) (a) Fernandez-Millan, M.; Allen, L. K.; Garcia-Rodriguez, R.; Bond, A. D.; Mosquera, M. E. G.; Wright, D. S. *Chem. Commun.* **2016**, *52*, 5993–5996. (b) Fuller, A.-M.; Mountford, A. J.; Scott, M. L.; Coles, S. J.; Horton, P. N.; Hughes, D. L.; Hursthouse, M. B.; Lancaster, S. J. *Inorg. Chem.* **2009**, *48*, 11474–11482.

(5) For recent reviews see: (a) Crimmin, M.; Hill, M. S. *Top. Organomet. Chem.* **2013**, *45*, 191–241. (b) Hill, M. S.; Liptrot, D. J.; Weetman, C. *Chem. Soc. Rev.* **2016**, *45*, 972–988. (c) Stennett, T. E.; Harder, S. *Chem. Soc. Rev.* **2016**, *45*, 1112–1128.

(6) For selected examples see: (a) Spielmann, J.; Piesik, D. F.-J.; Harder, S. *Chem. - Eur. J.* **2010**, *16*, 8307–8318. (b) Liptrot, D. J.; Hill, M. S.; Mahon, M. F.; MacDougall, D. J. *Chem. - Eur. J.* **2010**, *16*, 8508–8515. (c) Wolstenholme, D. J.; Fiogeras, J.; Che, F. N.; Decken, A.; Sean McGrady, G. *J. Am. Chem. Soc.* **2013**, *135*, 2439–2442. (d) Jones, C.; Bonyhandy, S. J.; Nembenna, S.; Stasch, A. *Eur. J. Inorg. Chem.* **2012**, *2012*, 2596–2601. (e) Spielmann, J.; Harder, S. *J. Am. Chem. Soc.* **2009**, *131*, 5064–5065. (f) Nöth, H.; Thomas, S.; Schmidt, M. *Chem. Ber.* **1996**, *129*, 451–458. (g) Harder, S.; Spielmann, J.; Tobey, B. *Chem. - Eur. J.* **2012**, *18*, 1984–1991. (h) Bellham, P.; Hill, M. S.; Kociok-Kohn, G. *Organometallics* **2014**, *33*, 5716–5721.

(7) Izod, K. *Adv. Inorg. Chem.* **2000**, *50*, 33–108.

(8) For selected examples see: (a) Reuter, K.; von Hanisch, C. *Chem. Commun.* **2014**, *50*, 7709–7711. (b) Kopecky, P.; von Hanisch, C.; Weigend, F.; Kracke, A. *Eur. J. Inorg. Chem.* **2010**, *2010*, 258–265. (c) Westerhausen, M.; Digiser, M. H.; Krofta, M.; Wiberg, N.; Noth, H.; Knizek, J.; Ponikwar, W.; Seifert, T. *Eur. J. Inorg. Chem.* **1999**, *1999*, 743–750. (d) Hey, E.; Engelhardt, L. M.; Raston, C. L.; White, A. H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 81–82. (e) Crimmin, M. R.; Barrett, A. G. M.; Hill, M. S.; Hitchcock, P. B.; Procopiou, P. A. *Inorg. Chem.* **2007**, *46*, 10410–10415. (f) Gartner, M.; Gorls, H.; Westerhausen, M. *Z. Anorg. Allg. Chem.* **2007**, *633*, 2025–2031. (g) Westerhausen, M.; Digiser, M. H.; Weineke, B.; Noth, H. *Eur. J. Inorg. Chem.* **1998**, *1998*, 517–521. (h) Westerhausen, M.; Lang, G.; Schwarz, W. *Chem. Ber.* **1996**, *129*, 1035–1040. (i) Gartner, M.; Gorls, H.; Westerhausen, M. *Inorg. Chem.* **2008**, *47*, 1397–1405. (j) Westerhausen, M.; Krofta, M.; Mayer, P. *Z. Anorg. Allg. Chem.* **2000**, *626*, 2307–2312.

(9) (a) Izod, K.; Clegg, W.; Liddle, S. T. *Organometallics* **2000**, *19*, 3640–3643. (b) Blair, S.; Izod, K.; Clegg, W. *Inorg. Chem.* **2002**, *41*, 3886–3893. (c) Blair, S.; Izod, K.; Clegg, W.; Harrington, R. W. *Eur. J. Inorg. Chem.* **2003**, *2003*, 3319–3324. (d) Blair, S.; Izod, K.; Clegg, W.; Harrington, R. W. *Inorg. Chem.* **2004**, *43*, 8526–8531.

(10) (a) Izod, K.; Liddle, S. T.; Clegg, W. *Chem. Commun.* **2004**, 1748–1749. (b) Izod, K.; Liddle, S. T.; McFarlane, W.; Clegg, W. *Organometallics* **2004**, *23*, 2734–2743. (c) Blair, S.; Izod, K.; Clegg, W. *J. Organomet. Chem.* **2003**, *688*, 92–99. (d) Clegg, W.; Izod, K.; Liddle, S. T. *J. Organomet. Chem.* **2000**, *613*, 128–131. (e) Izod, K.; O'Shaughnessy, P.; Sheffield, J. M.; Clegg, W.; Liddle, S. T. *Inorg. Chem.* **2000**, *39*, 4741–4748. (f) Clegg, W.; Izod, K.; Liddle, S. T.; O'Shaughnessy, P.; Sheffield, J. M. *Organometallics* **2000**, *19*, 2090–2096.

(11) Knapp, V.; Muller, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 183–186.

(12) Izod, K.; Clark, E. R.; Foster, P.; Percival, R. J.; Riddlestone, I. M.; Clegg, W.; Harrington, R. W. *Chem. - Eur. J.* **2013**, *19*, 6094–6107.

(13) Izod, K.; Watson, J.; Harrington, R. W.; Clegg, W. *Dalton Trans.* **2011**, *40*, 11712–11781.

(14) Izod, K.; Watson, J.; Harrington, R. W.; Clegg, W. *Eur. J. Inorg. Chem.* **2012**, *2012*, 1696–1701.

(15) Chitsaz, S.; Breyhan, T.; Pauls, J.; Neumüller, B. *Z. Anorg. Allg. Chem.* **2002**, *628*, 956–964.

(16) Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244–5252.

(17) Muñoz, M. T.; Urbajena, C.; Temprado, M.; Mosquera, M. E. G.; Cuenca, T. *Chem. Commun.* **2011**, *47*, 11757–11759.

(18) (a) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R.; Wade, K. *J. Chem. Soc., Chem. Commun.* **1986**, 295–297. (b) Mulvey, R. E. *Chem. Soc. Rev.* **1998**, *27*, 339–346.

(19) Zechmann, C. A.; Boyle, T. J.; Rodriguez, M. A.; Kemp, R. A. *Inorg. Chim. Acta* **2001**, *319*, 137−146.

(20) Westerhausen, M.; Krofta, M.; Mayer, P. *Z. Anorg. Allg. Chem.* **2000**, *626*, 2307−2312.

(21) Izod, K.; Wills, C.; Clegg, W.; Harrington, R. W. *Inorg. Chem.* **2007**, *46*, 4320−4325.

(22) Collins, R. A.; Unruangsri, J.; Mountford, P. *Dalton Trans.* **2013**, *42*, 759−769.

(23) (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.

(24) (a) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Adv.* **2015**, *71*, 3−8. (b) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112−122. (c) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339−341.