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Synthesis of Phosphorus(V)-Stabilized Geminal Dianions. The Cases of Mixed P=X/P→BH₃ (X = S, O) and P=S/SiMe₃ Derivatives

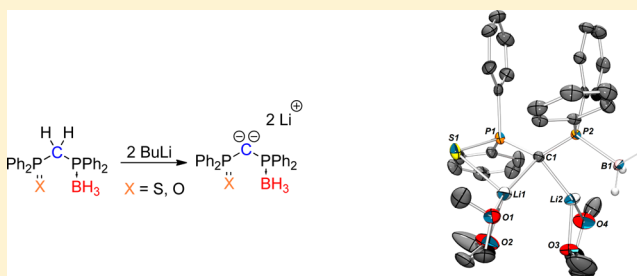
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S Supporting Information

ABSTRACT: The monodeprotonation of [CH₂(PPh₂→BH₃)(PPh₂=E)] (E = S (6), O (7)) afforded [CH(PPh₂→BH₃)(PPh₂=E)][−] (E = S (6[−]), O (7[−])), whose structures were confirmed by X-ray crystallography. The kinetics of the second deprotonation appeared to be crucial in efficient synthesis of the corresponding dianions. Thus, the double deprotonation of 6 only led to 6^{2−}; the analogous reaction with 7 was slower and resulted only in the partial formation of 7^{2−}. Double deprotonation of the compound [CH₂(SiMe₃)(PPh₂=S)] (8) also resulted in the partial formation of [C(SiMe₃)(PPh₂=S)]^{2−} (8^{2−}), whose structure was confirmed by X-ray crystallography. The rare monomeric Mg carbene compound [MgC(PPh₂→BH₃)(PPh₂=S)] (9) was obtained by the reaction of 6 with Mg(*n*Bu)₂. The X-ray structure of 9 is presented.



INTRODUCTION

The groundbreaking syntheses of electrophilic carbene complexes by Fischer in 1964¹ and of nucleophilic carbene complexes by Schrock roughly 10 years after² have opened the way for a considerable number of studies.³ The use of carbene complexes in organic synthesis, in stoichiometric as well as in catalytic processes, was then developed extensively. In particular, among the many processes involving carbene complexes as catalysts, the alkene metathesis reaction has seen a tremendous development over the past decades, leading to applications in various fields ranging from polymer science to total synthesis.⁴ The almost infinite variations of both the substitution scheme of the carbene fragment "CR²" and the metal fragment allow for a very fine tuning of the properties of the carbene complex, ranging from nucleophilic to electrophilic. In the past decade, a novel strategy relying on the use of geminal dianions to bring formally the four electrons of the M=C bond has been devised (Scheme 1).

This chemistry has been mainly developed with three geminal dilithiated compounds for which the carbon atom is substituted symmetrically by an iminophosphorane (PPh₂NSiMe₃), a thiophosphinoyl (PPh₂S), or a phosphonate moiety (P(O*i*Pr)₂O) (1^{a,2−}, 2^{2−}, and 3^{2−}; Scheme 2).^{5,6} These species have allowed the synthesis of a large variety of carbene complexes of transition metals, rare earths, and uranium.⁷ In 2006, Le Floch et al. developed a general method allowing the introduction of other substituents at the nitrogen atom of the iminophosphorane moiety (1_{b,c}^{2−})^{8,9} and subsequently proved the influence of the nitrogen substituent in a catalytic process

involving Nd carbene complexes.¹⁰ In 2006 and 2008, the Henderson group published the synthesis of geminal dianions incorporating other alkali metals,^{11,12} and in 2009, Harder and co-workers reported the synthesis of a bis(cesium) derivative of 1d.¹³ This strategy is currently limited because of (i) the very small number of known geminal dianions (A–E; Scheme 2) and (ii) a lack of an efficient access to them (1^{2−} to 4^{2−}) as, needless to say, these dianionic species are extremely water sensitive and cannot be readily purified. In this respect, it is noteworthy that double deprotonation of the ligand in the coordination sphere of the metal has been used in some instances as an alternative strategy to yield the same carbene complexes.¹⁴

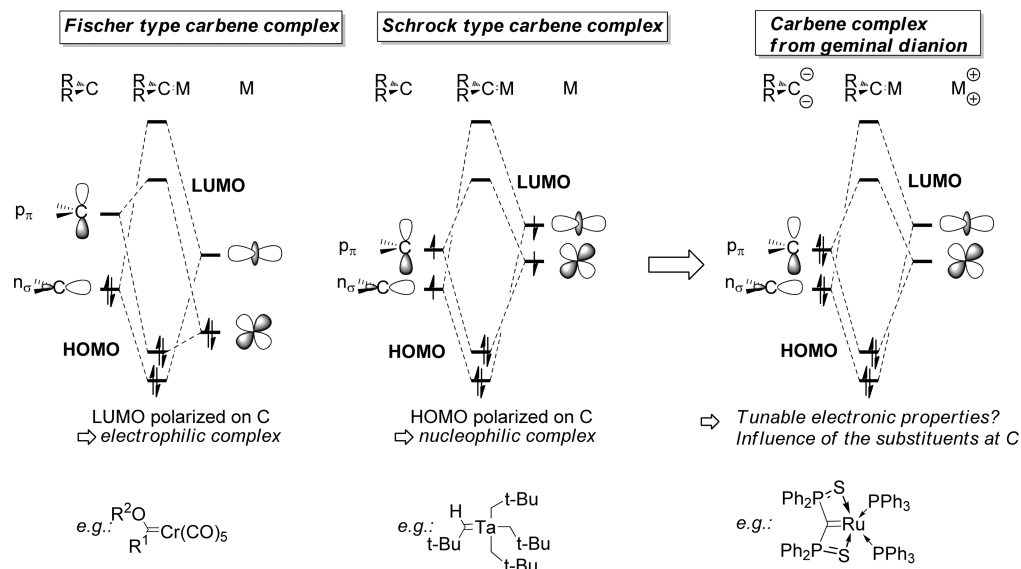
The underlying reason for the paucity of geminal dianions lies in the required efficient stabilization of two charges on the same carbon atom. We have shown using DFT calculations in the thiophosphinoyl case, 2^{2−}, that these two lone pairs interact in donor–acceptor type interactions with empty antibonding orbitals of appropriate energy and symmetry. Upon coordination of the dianions with metal fragments, an electron transfer from the carbon center to the metal center occurs to lead to a formal M=C interaction. The extent of this electron transfer depends on two factors: (i) the energy match between the orbitals of the dianion and those of the metal fragment and (ii) the orbital overlap. The electron transfer to the metal center is obviously in competition with the electron transfer from the

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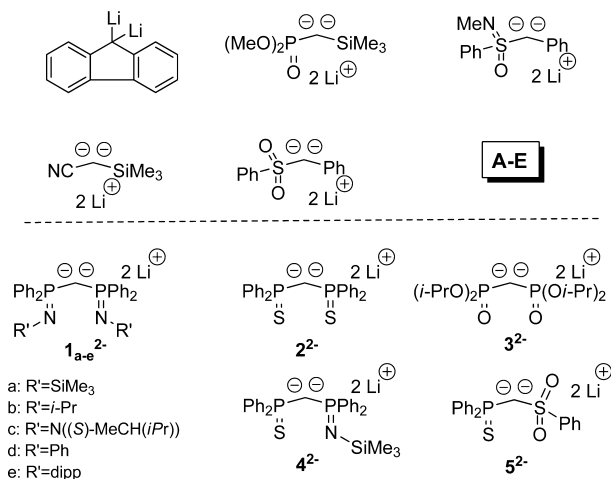
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Scheme 1. Strategies for the Synthesis of Carbene Complexes

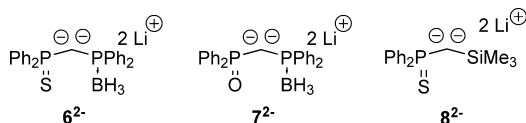


Scheme 2. Geminal Dianions Reported in the Literature



central C to the P substituents which is necessary for the stability of the dianion. A fine tuning of the $\text{M}=\text{C}$ interaction, and therefore of the reactivity of the complexes, is to be expected from a modification of the substituents at the carbon center. Our goals here are manifold. First, we investigate syntheses for novel types of dianions bearing two different substituents at C (Scheme 3). Several examples of such

Scheme 3. Targets of This Study



“unsymmetrical geminal dianions” are known (Scheme 2; A–E, 4^{2-} , and 5^{2-}) but only 4^{2-} , reported in 2009 by So and co-workers, and 5^{2-} , reported by Gessner and Schröter very recently have been obtained efficiently.^{15,16} On the way to the desired dianions, the monoanionic species were synthesized and characterized. The results of the present study clearly demonstrate that the efficient synthesis of geminal dianions is a

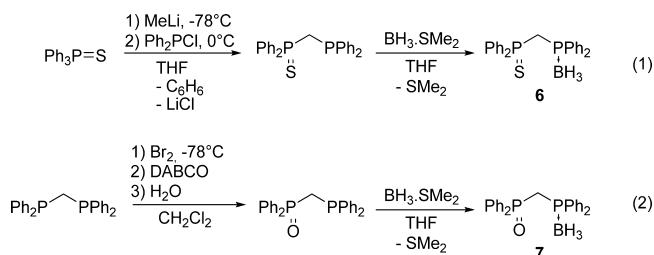
very complex matter based not only on thermodynamic stabilization but also on kinetic factors.

RESULTS AND DISCUSSION

We have shown previously that two Ph_2PS substituents at C allow a very efficient stabilization of the dianion 2^{2-} . In a first approach, it was thus interesting to keep at least one of them in conjunction with an a priori less stabilizing moiety such as PPh_2BH_3 (target 6^{2-}). The monoanion derived from the bis-borane adduct of dppm (bis(diphenylphosphino)methane) has been successfully synthesized and used in coordination.¹⁷ The corresponding dianion with group 1 metals has not been reported yet, although Harder and co-workers have obtained the dianionic calcium species.¹⁸ In parallel, the related phosphine oxide was targeted (compound 7^{2-}), allowing a direct comparison of the stabilizing power of $\text{P}=\text{S}$ and $\text{P}=\text{O}$. Moreover, the only $\text{P}=\text{O}$ moieties reported to stabilize dianions are phosphonate derivatives (Scheme 2).

Compound 6 was synthesized in a one-pot fashion by simple borylation of ((diphenylphosphino)methyl)diphenylphosphine sulfide. The latter was prepared according to a procedure reported by Mitchell and Grim (Scheme 4, eq 1).¹⁹ Formation

Scheme 4. Synthesis of Compounds 6 and 7



of the intermediate compound was verified by ^{31}P NMR (AB system at δ_{P} 40.1 ppm and δ_{P} −28 ppm with $^2J_{\text{P-P}} = 75$ Hz) before reaction with the borane–dimethyl sulfide. Compound 6 was obtained in decent yield (51%) as a white crystalline solid after purification. Another strategy was used for compound 7. Monobromination of dppm by 1 equiv of bromine in

dichloromethane²⁰ followed by hydrolysis of the reaction yielded the mono-oxidized species, which was reacted with $\text{BH}_3\text{-SMe}_2$ to yield compound **6** after workup in 50% yield (Scheme 4, eq 2).

In the ^{31}P NMR spectrum both compounds are characterized by an AX system at δ_{P} 34.4 ppm (d, $^2J_{\text{P-P}} = 9$ Hz) and δ_{P} 14.6 ppm (bd) for compound **6** and at δ_{P} 23.2 ppm (d, $^2J_{\text{P-P}} = 15$ Hz) and δ_{P} 13.9 ppm (br) for compound **7**, the broadening of the last doublet being characteristic of phosphine–borane compounds. In the ^1H NMR spectrum in CD_2Cl_2 , the central CH_2 protons are both seen as a doublet of doublets at δ_{H} 3.86 ppm ($^2J_{\text{P-H}} = 13$ Hz, $^2J_{\text{P-H}} = 10$ Hz) for **6** and at δ_{H} 3.37 ppm ($^2J_{\text{P-H}} = 10.5$ Hz, $^2J_{\text{P-H}} = 12$ Hz) for **7**, the corresponding carbon atoms being found at δ_{C} 29.6 ppm (dd, $^1J_{\text{P-C}} = 26$ Hz, $^1J_{\text{P-C}} = 47$ Hz) for **6** and at δ_{C} 30.4 ppm (dd, $^1J_{\text{P-C}} = 62$ Hz, $^1J_{\text{P-C}} = 26$ Hz) for **7**. Table 1 summarizes the main NMR data

Table 1. Significant NMR Data for All Compounds

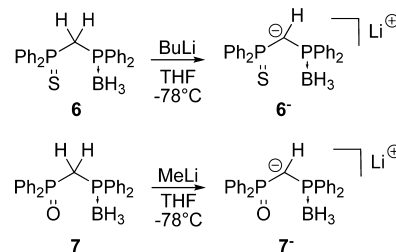
	$\delta_{\text{P}}(\text{P(X)})$	$\delta_{\text{P}}(\text{P(B)})$	$\delta_{\text{H}}(\text{PC(H)P})$	$\delta_{\text{C}}(\text{PCP})$	solvent
6 (X = S)	34.4	14.6	3.86	29.6	CD_2Cl_2
6⁻	40.7	8.7	1.15	13.6	$\text{THF-}d_8$
6²⁻	25.5	4.8			ether- d_{10}
7 (X = O)	23.2	13.9	3.37	30.4	CD_2Cl_2
7⁻	34.6	5.9	1.44	14.0	$\text{THF-}d_8$
7²⁻	42	5			$\text{Tol/Et}_2\text{O}$
8 (X = S)	37.7		2.00	21.1	CDCl_3
8⁻	44.5		0.50	11.7	C_6D_6
8²⁻					

for **6** and **7**. X-ray crystal structures were obtained for both compounds. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of concentrated solutions of **6** and **7** in dichloromethane. Views of **6** and **7** are given in Figure 1. Bond lengths and angles are completely standard in the two compounds (note that the structure of **6** features a statistical repartition of boron and sulfur atoms on the two positions).

Single deprotonation of **6** and **7** was easily achieved by reaction with respectively 2 equiv of butyllithium or methyllithium at -78°C in THF (Scheme 5).

Evidence of the complete conversion of the neutral compounds into the corresponding anions **6⁻** and **7⁻** was seen by ^{31}P NMR, both anions exhibiting two sets of doublets

Scheme 5. Synthesis of the Anions **6⁻ and **7⁻****



at δ_{P} 40.7 ppm (d, $^2J_{\text{P-P}} = 41$ Hz) and δ_{P} 8.7 ppm (br) for **6⁻** and at δ_{P} 34.6 ppm (br) and δ_{P} 5.9 ppm (br) for **7⁻**. Both anions could be isolated as pale yellow solids after evaporation of the solvent. They were further characterized by multinuclear NMR spectroscopy. In both compounds the central CH proton is shifted upfield at δ_{H} 1.15 and 1.44 ppm (for **6⁻** and **7⁻**, respectively, in deuterated THF) in comparison to the neutral compound (δ_{H} 3.86 and 3.37 ppm for **6** and **7**). Similarly, the bridging carbons were found at δ_{C} 13.6 and 14.0 ppm (in comparison to δ_{C} 29.6 ppm in **6** and δ_{C} 30.4 ppm in **7**). X-ray diffraction analysis gave definitive proof of the successful deprotonation of the neutral compounds. Single crystals of **6⁻** and **7⁻** were grown by slow diffusion of pentane into a concentrated solution in THF and diethyl ether, respectively, and views of the structures of **6⁻** and **7⁻** are given in Figures 2 and 3, respectively.

Both compounds crystallize as dimers. The lithium atoms are not directly coordinated to the central carbons but are stabilized by coordination with two sulfur or oxygen atoms, respectively, one BH₃ moiety, and one solvent molecule (THF or diethyl ether). Compound **6⁻** features an elongation of the P–S bond (2.0323(8) Å vs 1.963(2) Å in **6**) and a shortening of the two P–C bonds (1.699(3) and 1.722(3) Å vs 1.839(2) and 1.830(2) Å in **6**). Surprisingly, the P–B bond is not significantly affected by the deprotonation. The same pattern is seen in **7⁻**, with an elongation of the P–O bond length (1.523(1) Å vs 1.489(3) Å in **7**) and a subsequent shortening of the two P–C bonds (1.703(2) and 1.725(2) Å vs 1.819(3) and 1.829(3) Å in **7**).

The synthesis and characterization of monoanion **8⁻** have already been reported by Gessner,²¹ and we have reported its

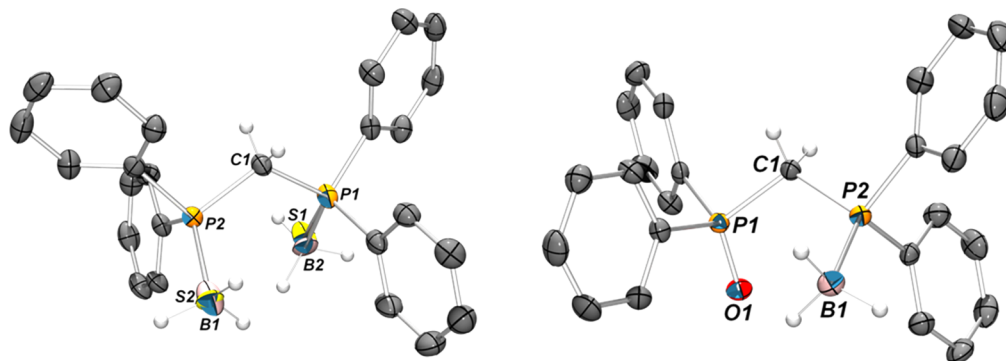


Figure 1. ORTEP plots (50% thermal ellipsoids) of the X-ray crystal structures of compounds **6** (left) and **7** (right). Selected bond lengths (Å) and angles (deg) for **6**: C(1)–P(1) = 1.839(2), C(1)–P(2) = 1.830(2), P(1)–S(1) = 1.963(2), P(1)–B(2) = 1.93(2), P(2)–S(2) = 1.963(2), P(2)–B(1) = 1.95(2), P(1)–C(2) = 1.821(2), P(1)–C(8) = 1.815(2), P(2)–C(14) = 1.817(2), P(2)–C(20) = 1.804(2); P(1)–C(1)–P(2) = 117.8(1). Selected bond lengths (Å) and angles (deg) for **7**: C(1)–P(1) = 1.819(3), C(1)–P(2) = 1.829(3), P(1)–O(1) = 1.489(2), P(2)–B(1) = 1.920(4), P(1)–C(2) = 1.810(3), P(1)–C(8) = 1.805(3), P(2)–C(14) = 1.822(3), P(2)–C(20) = 1.812(3); P(1)–C(1)–P(2) = 114.6(2).

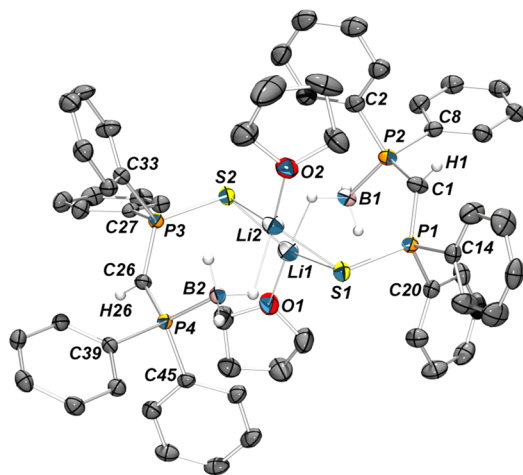


Figure 2. ORTEP plot (50% thermal ellipsoids) of the X-ray crystal structure of compound 6^- . Hydrogen atoms on the phenyl rings and on the solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)–P(1) = 1.699(3), C(1)–P(2) = 1.722(3), P(1)–S(1) = 2.0323(8), P(2)–B(1) = 1.933(3), S(1)–Li(1) = 2.478(5), S(1)–Li(2) = 2.466(5), P(1)–C(14) = 1.827(3), P(1)–C(20) = 1.831(3), P(2)–C(2) = 1.830(3), P(2)–C(8) = 1.835(3), P(3)–C(27) = 1.833(3), P(3)–C(33) = 1.824(2), P(4)–C(39) = 1.835(2), P(4)–C(45) = 1.832(2); P(1)–C(1)–P(2) = 126.4(2).

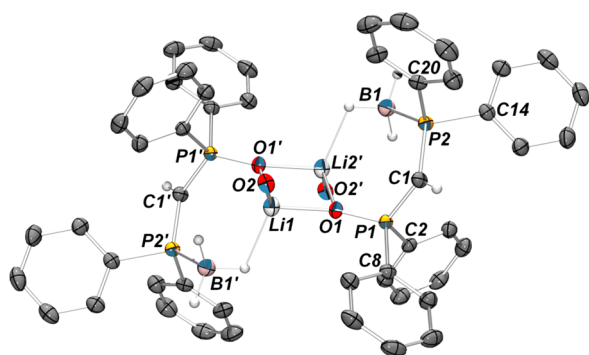
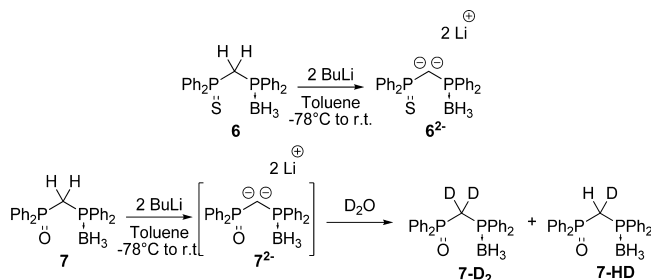


Figure 3. ORTEP plot (50% thermal ellipsoids) of the X-ray crystal structure of compound 7^- . Hydrogen atoms on the phenyl rings and carbon atoms of the solvent molecules (diethyl ether, O2, and O2') are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)–P(1) = 1.703(2), C(1)–P(2) = 1.725(2), P(1)–O(1) = 1.523(1), P(2)–B(1) = 1.937(2), O(1)–Li(1) = 1.900(3), O(1)–Li(1') = 1.940(3), B(1')–Li(1) = 2.651(3), P(1)–C(2) = 1.821(2), P(1)–C(8) = 1.811(2), P(2)–C(14) = 1.831(2), P(2)–C(20) = 1.831(2); P(1)–C(1)–P(2) = 126.5(1).

crystal structure.²² Its NMR shifts are included in Table 1 for comparison.

Encouraged by these results, and on the basis of the excellent stability of the three monoanionic species (over several days in solution under strict air- and water-free conditions), we then attempted to synthesize the corresponding dianions. It was proven that dianionic species of the type 1–4 (Scheme 2) are unstable in many solvents (including THF) and therefore double deprotonation of **6** was attempted in toluene. Addition of 2 equiv of butyllithium to a suspension of **6** in toluene resulted in a yellow reaction mixture and the solubilization of the starting material (Scheme 6). ^{31}P NMR spectroscopy confirmed the rapid formation of 6^{2-} . After 2 h, a yellow solid precipitated concomitant with the loss of all signals in ^{31}P NMR. After 3 h, this solid was extracted by filtration and

Scheme 6. Synthesis of Dianions 6^{2-} and 7^{2-}



purified. This solid was soluble in 1,2-dimethoxyethane and diethyl ether and could be characterized by multinuclear NMR spectroscopy. The ^{31}P NMR confirmed the total conversion of **6** into a single new product characterized by a doublet at δ_{p} 25.5 ppm ($^2J_{\text{P-P}} = 8$ Hz) and a broad doublet at 4.8 ppm. In the ^1H NMR spectrum, only aromatic protons are observed and no central proton could be located. The ^{13}C NMR spectrum suffered poor resolution, and no significant resonance could be located for the central carbon. This new compound was therefore identified as the dianion 6^{2-} .

No resonance corresponding to a cosolvent was seen in the NMR spectrum of 6^{2-} , which was confirmed by elemental analysis. We can therefore presume that 6^{2-} forms polymeric structures in toluene and its precipitation drives the equilibrium toward its complete formation. To confirm that double deprotonation of **6** did occur, a trapping experiment with D_2O was carried out. After addition of an excess of D_2O to a suspension of 6^{2-} , stirring for 1 h, and purification the bis-deuterated derivative of **6** was isolated (6-D_2). Indeed, the ^1H NMR spectrum lacks the signal of the central CH_2 protons and the bridging carbon signal is found as a highly coupled multiplet at δ_{C} 29.6 ppm in the ^{13}C NMR spectrum. Single crystals of 6^{2-} grown by diffusion of pentane into a concentrated solution in DME allowed the determination of a structure for 6^{2-} . A view of 6^{2-} is given in Figure 4.

Interestingly, compound 6^{2-} crystallizes as a monomer in DME. The two lithium atoms are coordinated to the central carbon, their coordination spheres being completed by one solvent molecule. The hydrogen atoms on the BH_3 group have been geometrically fixed; thus, no discussion is possible on the exact nature of the Li– BH_3 interaction. In 6^{2-} the P(B)–C bonds are even shorter than in **6** or 6^- (1.701(3) Å in 6^{2-} vs 1.722(3) Å in 6^-). In contrast, the P–B bond once again remains unchanged. A summary of the evolution of some bond lengths in **6**, 6^- , and 6^{2-} is given in Table 2.

With these encouraging results, similar reactions were attempted with both **7** and **8**. When 2 equiv of methylolithium or butyllithium was added to a solution of **7** in toluene at -78°C , followed by warming to room temperature, a yellow solution containing exclusively the monoanionic species 7^- was obtained within 5 min, as proved by ^{31}P and ^1H NMR spectroscopy (Scheme 6). After 12 h of stirring, a mixture of only two products was observed by ^{31}P NMR, the monoanion 7^- (doublet at δ_{p} 44.1 ppm and broad signal centered at δ_{p} 4.5 ppm in toluene) and another species with very close chemical shifts: δ_{p} 42.0 ppm and a broad signal at ca. δ_{p} 5 ppm overlapping with the signal of the anion 7^- . More interesting information was gathered from the ^1H NMR spectrum, which presented only one signal for a P–CH–P moiety. Moreover, it showed two kinds of aromatic signals: a set of sharp, well-resolved multiplets corresponding to the aromatic protons of

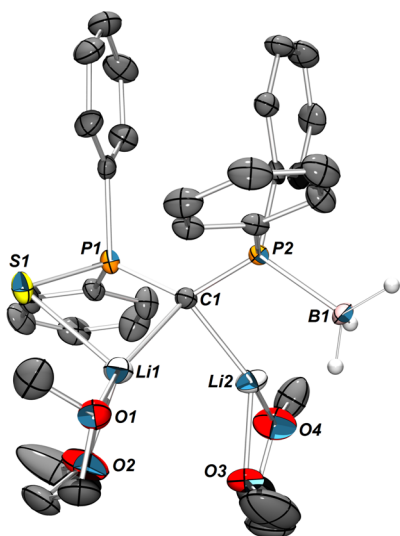


Figure 4. ORTEP plot (50% thermal ellipsoids) of the X-ray crystal structure of compound 6^{2-} . Hydrogen atoms on the phenyl rings and carbon atoms of the solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)–P(1) = 1.699(3), C(1)–P(2) = 1.701(3), P(1)–S(1) = 2.033(1), P(2)–B(1) = 1.943(3), C(1)–Li(1) = 2.225(6), C(1)–Li(2) = 2.162(6), P(1)–C(14) = 1.833(3), P(1)–C(20) = 1.834(3), P(2)–C(2) = 1.840(3), P(2)–C(8) = 1.835(3); P(1)–C(1)–P(2) = 126.4 (2).

7^- in toluene and a set of broad multiplets that belonged to the new species detected in ^{31}P NMR. Because of the lack of a CH proton for this second species, we proposed it to be the expected dianion 7^{2-} . The same trapping experiment with D_2O was carried out, proving our hypothesis right. Indeed, the neutral species 7_{HD} and 7_{D_2} were formed, as shown by the integration of the signal corresponding to the P–CH(D)–P moiety in comparison to the integration of the aromatic protons in the ^1H NMR spectrum (see the Supporting Information). Thus, after 12 h, ca. 70% of the desired dianion 7^{2-} had formed ($7_{\text{HD}}/7_{\text{D}_2}$ = ca. 3/7) from the monoanion 7^- . Unfortunately, the double-deprotonation reaction did not result in the expected full transformation of the anion into the dianion. Rather, several species started to appear after 1 day and after 1 week crystals had deposited from the crude mixture. X-ray analysis of these crystals revealed the formation of the SiMe_3OLi byproduct that crystallized with the monoanion (see the Supporting Information).²³ This result, although disappointing, proved that the kinetics of the deprotonation is crucial for the formation of the desired dianions. If the second deprotonation at the “central” carbon center is too slow, then side reactions such as deprotonation at the ortho position of a Ph group followed by nucleophilic attack on the opposite phosphorus substituent occur, preventing the clean formation of the desired dianion. These competitive reactions depend on many factors (nature of the cation, solvent, and substituents at

P).^{13,24} The same procedure was then carried out on compound **8**. Addition of 2 equiv of methyllithium in a mixture of diethyl ether and hexane at -78°C resulted in the instant formation of 8^- upon slow warming to room temperature, as shown by ^{31}P NMR spectroscopy.^{21,22} After several days of stirring at room temperature, several products were seen in ^{31}P NMR spectroscopy, together with 8^- . Few yellow crystals deposited spontaneously from the reaction media. X-ray diffraction analysis confirmed the existence of dianion 8^{2-} , as shown in Figures 5 and 6. Here also, one

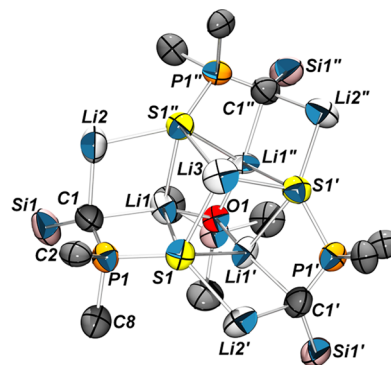


Figure 5. ORTEP plot (50% thermal ellipsoids) of the X-ray crystal structure of compound 8^{2-} . Phenyl rings (except ipso carbon atoms), methyl groups of the TMS moieties, hydrogen atoms, and solvent molecules are omitted for clarity. Selected bond lengths (Å): C(1)–P(1) = 1.633(8), S(1)–P(1) = 2.093(2), Si(1)–C(1) = 1.778(8), P(1)–C(8) = 1.827(8), P(1)–C(2) = 1.831(6), C(1)–Li(2') = 2.09(2), C(1)–Li(1') = 2.18(1), S(1)–Li(3) = 2.454(8), S(1)–Li(1) = 2.57(1), S(1)–Li(2) = 2.45(1), S(1)–Li(1') = 2.55(1), O(1) = Li(1'') 1.90(1), O(1)–Li(1) = 1.90(1), O(1)–Li(1') = 1.90(1), Si(2)–O(1) = 1.601(6).

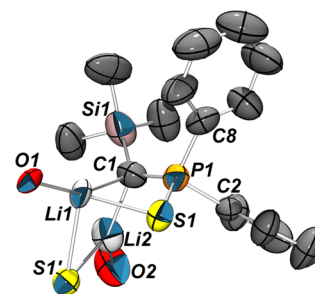


Figure 6. View of one molecular fragment of 8^{2-} .

anionic μ_3 -OSiMe₃ fragment which lies on the C_3 axis is present in the X-ray structure. We propose that this fragment originates from the slow reaction of the strong base with the silicon grease.²³ Each carbon atom of the parent ligand is bound to two lithium atoms, and each sulfur atom coordinates four lithium atoms. These lithium atoms are of two types. The inner ones are coordinated by two sulfur atoms, one carbon atom, and the

Table 2. Summary of Significant Bond Lengths (Å) in Compounds **6**–**8** and Related Anions

bond	6	6^-	6^{2-}	7	7^-	8	8^-	8^{2-}
P _X –C	1.839(2)	1.699(3)	1.699(3)	1.819(3)	1.703(2)	1.803(2)	1.701(1)	1.633(8)
P _B –C	1.830(2)	1.722(3)	1.701(3)	1.829(3)	1.725(2)			
P–X	1.963(2)	2.0323(8)	2.033(1)	1.489(2)	1.523(1)	1.9628(14)	2.0263(4)	2.093(2)
P–B	1.94(2)*	1.933(3)	1.943(3)	1.920(4)	1.937(2)			
Si–C						1.896(2)	1.827(1)	1.778(8)

μ_3 -oxygen atom from the OSiMe₃ fragment. The others are tricoordinated and bound to one sulfur atom, one carbon atom, and one solvent molecule (not shown in Figure 5). Compound **8**²⁻ features a highly elongated P–S bond (2.093(2) Å in **8**²⁻ vs 1.9628(14) Å in **8**). This elongation is of much greater amplitude than for compound **6**. As seen for compounds **6** and **7**, the P–C bond length shortens with the deprotonation of compound **8**, from 1.803(2) to 1.633(8) Å. This trend is also observed for the Si–C bond. Further characterization of **8**²⁻ was hampered by the amount of crystals gathered from this reaction. Nevertheless, these two experiments clearly show that, although the dianions **7**²⁻ and **8**²⁻ are thermodynamically stable, their efficient synthesis is highly challenging and appropriate conditions have not been found so far.

In order to gain insights into the electronic structure of these new species, a theoretical study has been carried out. We focused our attention on the description of dianion **6**²⁻, for which three states have been considered: neutral, monoanionic, and dianionic (**VI**, **VI**·Li, and **VI**·Li₂, respectively). Optimizations have been carried out on model compounds in which the solvent molecules (THF or DME) have been replaced by dimethyl ether (see the Supporting Information).

As seen in Table 3, the evolution of the different bond lengths and angles upon deprotonation is very well reproduced.

Table 3. Evolution of Characteristic Bond Lengths and Angles in VI and Its Derivatives

bond	VI	VI·Li	VI·Li ₂	$\Delta_{VI-VI\cdot Li_2}(DFT)$	$\Delta_{VI-VI\cdot Li_2}(RX)$
P _S –C	1.86	1.72	1.71	0.15	0.14
P _B –C	1.85	1.74	1.73	0.12	0.11
P–S	1.96	2.03	2.06	0.10	0.06
P–B	1.93	1.94	1.95	0.02	

In particular, the unexpected fact that the P–B bond length is hardly affected is also observed in the calculations. A NBO analysis was then performed on the three model compounds (see Tables 4 and 5). In the dianionic species, the C–Li interaction is mostly ionic ($q(Li) = 0.87$ and 0.86 and $n(C-Li) < 0.1$) and the central carbon bears a greater negative charge than in both the anionic and the neutral derivatives with a total difference of -0.6 e between the neutral and dianionic forms (-1.76 in **VI**·Li₂ compared to -1.41 in **VI**·Li and -1.16 in **VI**;

Table 5. NBO Analysis of the Hyperconjugation in VI·Li and VI·Li₂

	donor	acceptor	$E(2)$	ΔE_{ij}	F_{ij}
VI·Li	LP1	$\sigma^*(P-B)$			
		$\sigma^*(P-S)$	10.7	0.29	0.053
		$\sigma^*(P_S-C_{Ph})$	17.7	0.35	0.073
		$\sigma^*(P_B-C_{Ph})$	11.8	0.37	0.062
		$\sigma^*(P_B-C_{Ph})$	9.9	0.37	0.058
	total		50.1		
VI·Li ₂	LP1	$\sigma^*(P-B)$	1.9	0.48	0.029
		$\sigma^*(P-S)$			
		$\sigma^*(P_S-C_{Ph})$	15.8	0.43	0.075
		$\sigma^*(P_B-C_{Ph})$	10.1	0.44	0.061
		$\sigma^*(P_B-C_{Ph})$	4.9	0.44	0.043
		$\sigma^*(P_B-C_{Ph})$			
		$\sigma^*(P_S-C_{Ph})$	4.2	0.43	0.039
		total	36.9		
	LP2	$\sigma^*(P-B)$			
		$\sigma^*(P-S)$	19.9	0.28	0.071
		$\sigma^*(P_B-C_{Ph})$	18.5	0.36	0.077
		$\sigma^*(P_B-C_{Ph})$	13.6	0.35	0.066
		$\sigma^*(P_B-C_{Ph})$			
		$\sigma^*(P_S-C_{Ph})$	7.7	0.34	0.048
		$\sigma^*(P_S-C_{Ph})$	5.1	0.34	0.039
		total	64.8		
	total LP1 + LP2		101.7		

Table 4). Similarly, the charge at the sulfur atom increases in absolute value upon deprotonation steps as it ranges from -0.55 in **VI** to -0.80 in **VI**·Li₂, but the magnitude is much smaller than for C. This indicates, however, an electronic transfer from the central carbon to the sulfur atom. Both phosphorus atoms bear a positive charge in all species, and the charges only vary to a small extent. One notes that the charges of both P atoms increase from **VI** to **VI**·Li but decrease between **VI**·Li and **VI**·Li₂. Surprisingly, the charge at the boron atom does not vary much (-0.70 in average), which is coherent with a weak electron transfer from the central carbon to this heteroatom. As seen from the different X-ray diffraction analyses of the structures of the different derivatives of compound **6**, the deprotonation process causes geometrical

Table 4. Summary of NBO Data for VI, VI·Li, and VI·Li₂

	Wiberg bond index						
	$n(C-P_S)$	$n(C-P_B)$	$n(P-S)$	$n(P-B)$	$n(P_S-C_{Ph})$	$n(P_B-C_{Ph})$	$n(C-Li)$
VI	0.81	0.84	1.44	0.99	0.83, 0.84	0.90, 0.88	
VI·Li	1.08	1.08	1.18	0.97	0.84, 0.80	0.86, 0.85	
VI·Li ₂	1.21	1.22	1.12	0.96	0.80, 0.77	0.80, 0.80	0.052, 0.033
	NBO charge						
	q_C	q_{Li}	$q_{P(S)}$	$q_{P(B)}$	q_S	q_B	
VI	-1.16		1.37	1.40	-0.55	-0.70	
VI·Li	-1.41	0.86	1.45	1.42	-0.76	-0.76	
VI·Li ₂	-1.76	0.87, 0.86	1.41	1.35	-0.80	-0.70	
	lone pair						
	LP1			LP2			
	hybridization		occupation	hybridization		occupation	
	VI·Li		1.72	VI·Li ₂		1.63	
	$sp^{23.06}$			$p^{1.00}$			
	$sp^{2.75}$		1.73				

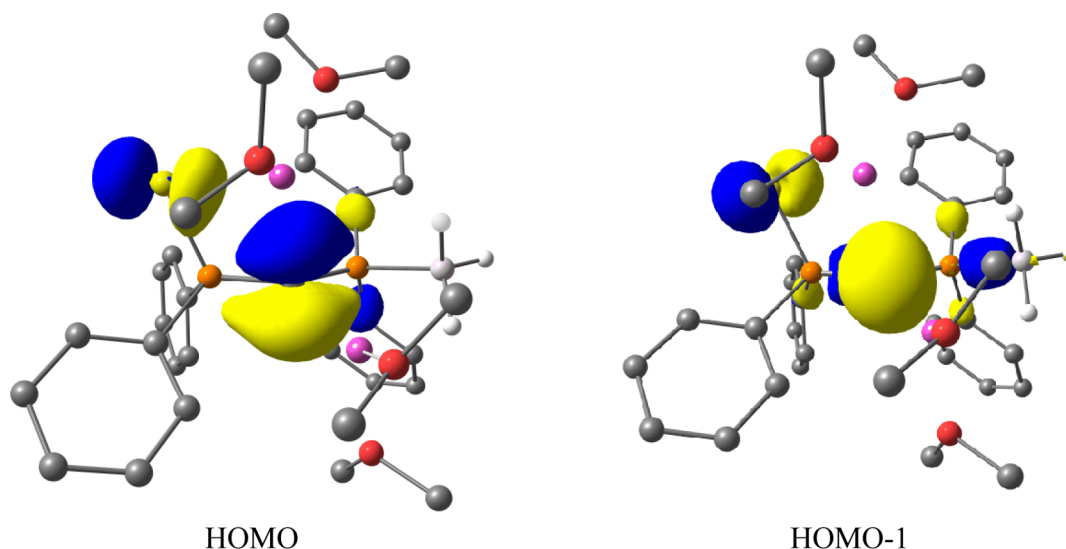


Figure 7. Map of the electronic density for a value of $0.052 \text{ e } \text{\AA}^{-3}$ for the two highest occupied molecular orbitals of $\text{VI}\cdot\text{Li}_2$.

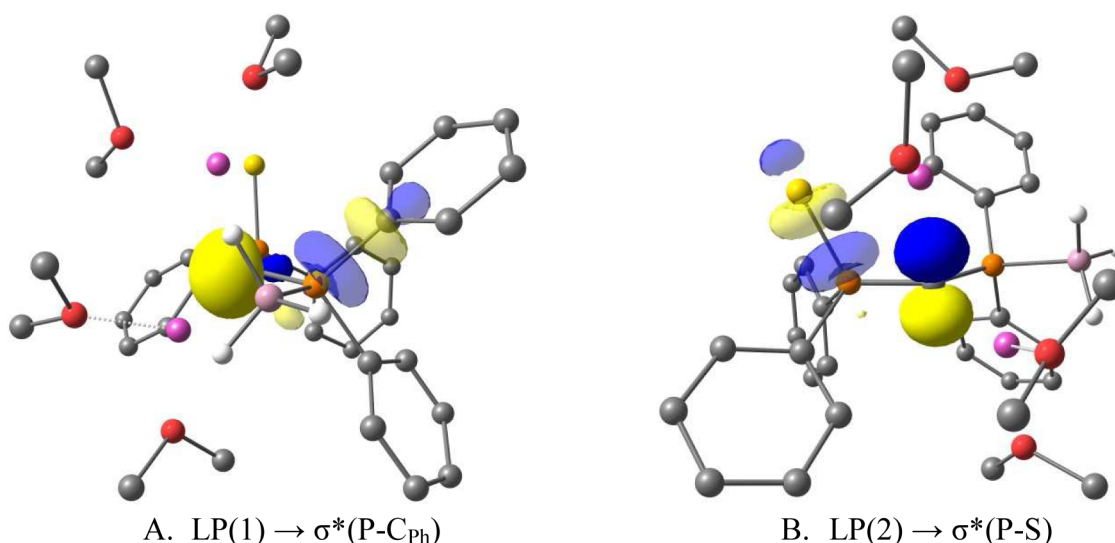


Figure 8. Electron density map for the donor (plain) and acceptor (shaded) NBO orbitals describing the hyperconjugation interaction resulting in the stabilization of lone pairs in $\text{VI}\cdot\text{Li}_2$.

changes in the ligand. The P–C bonds between the central carbon and the phosphorus atoms are shortened, and the P–S bond length is increased, but the P–B bond length remains surprisingly unchanged. The Wiberg bond indexes calculated for the different models are in agreement with these observations. Upon deprotonation, the bond index for the two P–C bonds increases (0.81 to 1.08 and then to 1.21, and 0.84 to 1.08 and then to 1.22 on going from **VI** to $\text{VI}\cdot\text{Li}_2$), which indicates a strengthening of these bonds. In contrast, the Wiberg bond index calculated for the P–S bond decreases (1.44 to 1.12), which is in accordance with the elongation of this bond upon successive deprotonations. On the other hand, the bond order for the P–B bond remains almost constant (0.99 to 0.96).

In order to explain these evolutions or lack thereof, we focused our attention on the stabilization of the negative charges at the central carbon atom. An NBO analysis was carried out on both $\text{VI}\cdot\text{Li}$ and $\text{VI}\cdot\text{Li}_2$. It shows that the carbon bears a lone pair in the anion, as expected from deprotonation, and that it is an almost pure p orbital ($\text{sp}^{23.1}$). It also confirms

that two orthogonal lone pairs are found in $\text{VI}\cdot\text{Li}_2$ (denoted LP1 and LP2), one of $\text{sp}^{2.75}$ character (LP1) and the other being a pure p orbital (LP2). These two orbitals have an important participation in the two highest orbitals of dianion $\text{VI}\cdot\text{Li}_2$ (LP2 is seen in the HOMO and LP1 in the HOMO-1; see Figure 7).

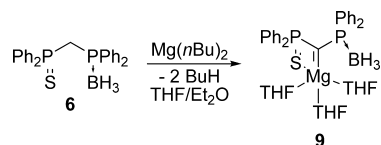
The two occupied lone pairs are stabilized by electronic donation into the neighboring empty antibonding orbitals of appropriate symmetry and energies, namely the $\sigma^*(\text{P-S})$, $\sigma^*(\text{P-B})$, and $\sigma^*(\text{P-C}_{\text{Ph}})$ orbitals. Table 5 summarizes these results. LP1 in $\text{VI}\cdot\text{Li}$ is stabilized by negative hyperconjugation into the neighboring $\sigma^*(\text{P-C}_{\text{Ph}})$ orbitals and $\sigma^*(\text{P-S})$ orbitals. The difference in energy (ΔE_{ij}) is rather small, because LP1 is almost p pure, and the overall stabilization is thus quite good, with a total of ca. 50 kcal/mol.

In $\text{VI}\cdot\text{Li}_2$, LP1 is stabilized mainly by negative hyperconjugation into the neighboring $\sigma^*(\text{P-C}_{\text{Ph}})$ orbitals (Figure 8A). Interestingly, the $\sigma^*(\text{P-B})$ orbital does not participate much in the stabilization of LP1 ($E(2) = 1.9 \text{ kcal/mol}$), though it has the right symmetry to do so (note that because of

symmetry considerations, $\sigma^*(\text{P}-\text{S})$ cannot participate in the stabilization of LP1). Because of an increased *s* character in this LP1 in comparison to the analogous lone pair in **VI**·Li, the energy difference is higher between donor and acceptor orbitals, and the total energy associated with these transfers is ca. 37 kcal/mol, smaller than in **VI**·Li. On the other hand, the stabilization of LP2 is much stronger (total stabilization energy of ca. 65 kcal/mol). LP2 is highly stabilized by donation into the $\sigma^*(\text{P}-\text{S})$ bond ($E(2) = 19.9$ kcal/mol, Figure 8B) and by donation into the $\sigma^*(\text{P}-\text{C})$ orbitals. Here also, the $\sigma^*(\text{P}-\text{B})$ bond is not involved in a major interaction (for symmetry reasons). When all the contributions are added, the total stabilization energy of LP2 is 101.7 kcal/mol. LP2 is a better electron donor than LP1, mainly because of its higher energy that narrows the gap between LP2 and the accepting orbitals $\sigma^*(\text{P}-\text{C})$ ($\Delta E \approx 0.35$ for LP2 and $\Delta E \approx 0.44$ for LP1). These results help us understand the geometrical changes in **6** upon double deprotonation. The stabilization of the lone pairs involves populating the antibonding $\sigma^*(\text{P}-\text{S})$ bond, which weakens the bond and results in its lengthening. The same applies for the different $\text{P}-\text{C}_{\text{phenyl}}$ bonds. As a result of these donor–acceptor interactions the two $\text{P}-\text{C}$ bonds of the $\text{P}-\text{C}-\text{P}$ bridge are shortened. As these interactions are much weaker, almost negligible, with the $\sigma^*(\text{P}-\text{B})$, the $\text{P}-\text{B}$ bond length remains nearly unchanged.

Finally, the synthesis of a group 2 derivative with the most rewarding reagent, **6**, was attempted. In 2010, Leung et al. had reported the synthesis of the magnesium carbene $[(\text{PPh}_2\text{S})_2\text{CMg}]_2$ by the reaction of the neutral derivative of compound **2**²⁻ with dibutylmagnesium.²⁵ The X-ray crystal structure shows that the magnesium carbene is dimerized in a head to head manner. We also reported the synthesis of the magnesium carbenes $[(\text{PPh}_2\text{NSiMe}_3)_2\text{CMg}]_2$ and $[(\text{PPh}_2\text{NSiMe}_3)(\text{PPh}_2\text{S})\text{CMg}]_2$ derived from **1a**²⁻ and **4**²⁻, respectively.²⁶ Unlike $[(\text{PPh}_2\text{S})_2\text{CMg}]_2$, they are dimerized in a head to tail manner in the solid state. The fact that the structures of the Mg carbenes are affected by the compositions of the geminal dianions prompted our interest in investigating the reaction of compound **6** with dibutylmagnesium. The reaction was performed in a $\text{Et}_2\text{O}/\text{THF}$ (1/1) mixture under reflux for 12 h, and compound **9** was isolated (Scheme 7).

Scheme 7. Synthesis of Complex **9**



Compound **9** was isolated as a highly air and moisture sensitive yellow crystalline solid which is soluble in hydrocarbon solvents. It has been characterized by NMR spectroscopy and X-ray crystallography. The ¹H NMR spectrum of **9** displays resonances for the BH₃, THF, and phenyl protons. It is noteworthy that the ¹³C{¹H} NMR signal for the carbenic carbon in **9** is not observed. Similarly, there is no ¹³C{¹H} NMR resonance for the carbenic carbon in $[(\text{PPh}_2\text{NSiMe}_3)(\text{PPh}_2\text{S})\text{CMg}]_2$ and $[(\text{PPh}_2\text{NSiMe}_3)_2\text{CMg}]_2$.²⁵ The ³¹P{¹H} NMR spectrum of **9** displays a doublet at δ_{P} 37.9 ppm (²*J*_{P-P} 56.3 Hz) for the PS moiety and a broad signal at δ_{P} 3.41 ppm for the PB moiety. The ¹¹B NMR spectrum shows one broad signal at δ_{B} −30.2 ppm.

The X-ray crystal structure of **9** shows that it is monomeric (Figure 9). The magnesium atom coordinates to the C(1) and

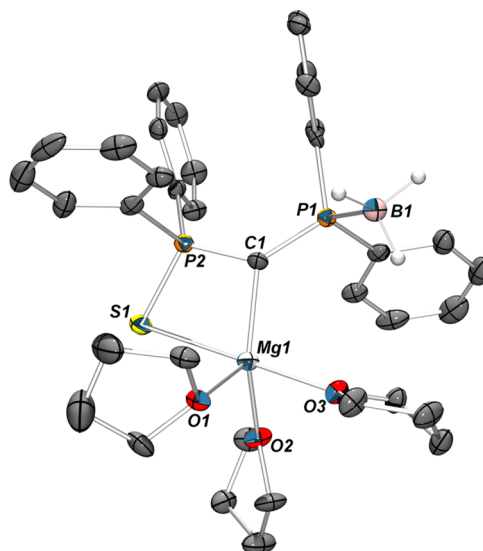


Figure 9. ORTEP plot (50% thermal ellipsoids) of the X-ray crystal structure of compound **9**. $\text{Mg}(1)-\text{C}(1) = 2.113(4)$, $\text{Mg}(1)-\text{O}(1) = 2.053(3)$, $\text{Mg}(1)-\text{O}(2) = 2.038(3)$, $\text{Mg}(1)-\text{O}(3) = 2.103(3)$, $\text{C}(1)-\text{P}(1) = 1.703(4)$, $\text{C}(1)-\text{P}(2) = 1.666(4)$, $\text{P}(1)-\text{B}(1) = 1.938(4)$, $\text{P}(2)-\text{S}(1) = 2.0308(13)$, $\text{Mg}(1)-\text{S}(1) = 2.6907(16)$; $\text{P}(1)-\text{C}(1)-\text{P}(2) = 132.6(2)$, $\text{P}(2)-\text{C}(1)-\text{Mg}(1) = 99.44(17)$, $\text{C}(1)-\text{Mg}(1)-\text{S}(1) = 76.17(11)$, $\text{Mg}(1)-\text{S}(1)-\text{P}(2) = 74.24(5)$, $\text{S}(1)-\text{P}(2)-\text{C}(1) = 107.98(13)$.

$\text{S}(1)$ atoms of the ligand. The coordination sphere of the magnesium atom is further supplemented by coordination with three THF molecules. The PPh_2BH_3 substituent is uncoordinated. The result is in contrast to that for $[(\text{PPh}_2\text{BH}_3)_2\text{CCa}]_2$, in which the BH_3 substituents coordinate to the Ca^{2+} atom in a bidentate fashion.¹⁷ The $\text{C}(1)-\text{Mg}(1)$ bond (2.113(4) Å) is comparable with that in $[(\text{PPh}_2\text{S})_2\text{CMg}]_2$ (2.156(5) Å).²⁵

CONCLUSION

In conclusion, we have presented here three novel examples of rare geminal dianions. Although the three species are thermodynamically stable, the kinetics of the double deprotonation appears to be crucial for their efficient formation. Eventually, only the mixed dianion **6**²⁻, where the two lone pairs are stabilized by a PPh_2S and a PPh_2BH_3 moieties, has been obtained selectively, opening ways for its use as a carbene precursor. Interestingly, the stabilization by the PPh_2BH_3 moiety appears to be weaker, which in turn should lead to increased donation of the lone pairs to a metal center. The synthesis of the rare Mg derivative **9** was also achieved with the same precursor, **6**. DFT calculations are currently being performed in order to quantify and compare the stabilizing properties of the different C substituents of the geminal dianions. In parallel, work in our laboratories using the novel compounds **6**²⁻ and **9** for the synthesis of carbene complexes is being pursued.

EXPERIMENTAL SECTION

General Procedures. All reactions were routinely performed under an inert atmosphere of argon or nitrogen by using Schlenk and glovebox techniques and dry deoxygenated solvents. Dry tetrahy-

drofuran, pentane, and 1,2-dimethoxyethane were obtained by distillation from Na/benzophenone. Dry dichloromethane was distilled on P_2O_5 and dry toluene on Na. Nuclear magnetic resonance spectra were recorded on a Bruker AC-300 SY spectrometer operating at 300.0 MHz for 1H , 75.5 MHz for ^{13}C , and 121.5 MHz for ^{31}P . Solvent peaks are used as internal reference relative to Me_4Si for 1H and ^{13}C chemical shifts (ppm); ^{31}P chemical shifts are relative to a 85% H_3PO_4 external reference. Coupling constants are given in hertz. The following abbreviations are used: s, singlet; bs, broad singlet; br, broad signal; d, doublet; bd, broad doublet; dd, doublet of doublets; t, triplet; m, multiplet. Triphenylthiophosphine was obtained by reaction of elemental sulfur with triphenylphosphine in THF. All other reagents and chemicals were obtained commercially and used as received. CCDC 893679–893685 contain crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of Compound 6. To a solution of triphenylthiophosphine (3.76 g, 12.77 mmol) in THF (40 mL) was added methyllithium (1.6 M in Et_2O , 8 mL, 12.8 mmol) at $-78^\circ C$. The solution was warmed to room temperature and stirred overnight. Upon reaction its changed from colorless to dark red. This solution was then added dropwise to a solution of chlorodiphenylphosphine (2.30 mL, 12.8 mmol) in THF (15 mL) at $0^\circ C$. The reaction mixture was warmed to room temperature and stirred for 12 h, and $BH_3 \cdot SMe_2$ (1.2 mL, 12.8 mmol) was added. The reaction mixture was stirred for 2 h. Volatiles were evaporated under vacuum, and dichloromethane (30 mL) was added. Insoluble impurities were discarded by filtration, and the remaining solution was concentrated. Pentane (40 mL) was added, which allowed the precipitation of a white solid that was isolated by filtration and washed twice with pentane (10 mL). The title compound was obtained as a white solid after drying under vacuum (2.8 g, 51%). ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ_P 34.1 (d, $J_{P-P} = 8.9$ Hz, PS), 14.8 (bd, PBH_3). 1H NMR (300 MHz, CD_2Cl_2): δ_H 8.04–7.93 (m, 8H, H_{arom}), 7.76–7.56 (m, 12H, H_{arom}), 3.86 (dd, $J_{P-H} = 10.2$ Hz, $J_{P-H} = 13.1$ Hz, 2H, PCH_2P), BH_3 . ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ_C 133.08 (d, $J_{P-C} = 10$ Hz, CH_{ortho}), 132.9 (dd, $J_{P-C} = 2$ Hz, $J_{P-C} = 83$ Hz, C_{ipso}), 131.6 (d, $J_{P-C} = 3$ Hz, CH_{para}), 131.4 (d, $J_{P-C} = 3$ Hz, CH_{para}), 131.0 (d, $J_{P-C} = 11$ Hz, CH_{ortho}), 128.6 (d, $J_{P-C} = 10$ Hz, CH_{meta}), 128.4 (d, $J_{P-C} = 10$ Hz, CH_{meta}), 128.1 (dd, $J_{P-C} = 3$ Hz, $J_{P-C} = 57$ Hz, C_{ipso}), 29.6 (dd, $J_{P-C} = 26$ Hz, $J_{P-C} = 48$ Hz, PCH_2P). ^{11}B NMR (89.0 MHz, CD_2Cl_2): δ_B –38.0 (bs). MS (HRMS EI): m/z 430.1244 (calcd for $C_{25}H_{25}BP_2S$ 430.1245). Anal. Calcd for $C_{25}H_{25}P_2SB$: C, 69.75; H, 5.86. Found: C, 69.84; H, 5.95.

Synthesis of Compound 7. To a solution of dppm (960.9 mg, 2.5 mmol) in 60 mL of dichloromethane was added bromine (129 μL , 2.5 mmol) dropwise at $-78^\circ C$, under a nitrogen atmosphere. The solution turned yellow and changed to colorless upon warming to room temperature. DABCO (281.8 mg, 2.5 mmol) was then added under a nitrogen flux followed by degassed water (45 μL , 2.5 mmol). After 1 h of stirring, the precipitate was removed by filtration. The solution was dried under high vacuum, and 60 mL of THF was added under an inert atmosphere. $BH_3 \cdot SMe_2$ (480 μL , 5 mmol) was added at $-78^\circ C$, and the solution was warmed to room temperature. Volatiles were removed under vacuum, and the title compound was obtained as a white solid after column chromatography in 50% yield. ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ_P 23.2 (d, $J_{P-P} = 15.5$ Hz, PO), 13.9 (b, PB). 1H NMR (300 MHz, CD_2Cl_2): δ_H 7.87 (m, 6H, H_{arom}), 7.61 (m, 6H, H_{arom}), 7.39 (m, 8H, H_{arom}), 3.37 (dd, $J_{P-H} = 10.5$ Hz, $J_{P-H} = 12.0$ Hz, 2H, PCH_2P), 1.56–0.34 (br, 3H, BH_3). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ_C 135.5 (dd, $J_{P-C} = 103.5$ Hz, $J_{P-C} = 1.5$ Hz, C_{ipso}), 135.3 (d, $J_{P-C} = 10.2$ Hz, CH_{ortho}), 134.0 (d, $J_{P-C} = 2.5$ Hz, CH_{para}), 133.6 (d, $J_{P-C} = 2.5$ Hz, CH_{para}), 132.7 (d, $J_{P-C} = 9.5$ Hz, CH_{ortho}), 130.8 (d, $J_{P-C} = 7.7$ Hz, CH_{meta}), 130.7 (d, $J_{P-C} = 6.3$ Hz, CH_{meta}), 130.3 (dd, $J_{P-C} = 56.8$ Hz, $J_{P-C} = 2.7$ Hz, CH_{ipso}), 30.4 (dd, $J_{P-C} = 26$ Hz, $J_{P-C} = 62$ Hz, PCH_2P). Anal. Calcd for $C_{25}H_{25}P_2OB$: C, 72.49; H, 6.08. Found: C, 72.28; H, 6.14.

Synthesis of Compound 6[–]. To a solution of 6 (206.5 mg, 0.48 mmol) in THF (5 mL) was added methyllithium (1.6 M in Et_2O , 0.3 mL, 0.48 mmol) at $-78^\circ C$. The yellow solution was warmed to room

temperature and stirred for 1 h. Solvents were evaporated under vacuum, and the remaining pale yellow solid was washed with 2×5 mL of pentane and dried (200 mg, 95%). ^{31}P NMR (121.5 MHz, $thf-d_8$): δ_P 40.4 (d, $J_{P-P} = 41$ Hz, PS), 8.7 (bd, PBH_3). 1H NMR (300 MHz, $thf-d_8$): δ_H 7.96–7.89 (m, 4H, H_{arom}), 7.81–7.74 (m, 4H, H_{arom}), 7.21–7.13 (m, 12H, H_{arom}), 1.15 (dd, $J_{P-H} = 4$ Hz, $J_{P-H} = 6$ Hz, 1H, $PC(H)P$), 1.3–0.23 (bs, BH_3). ^{13}C NMR (75.5 MHz, $thf-d_8$): δ_C 143.9 (dd, $J_{P-C} = 4$ Hz, $J_{P-C} = 85$ Hz, C_{ipso}), 141.5 (dd, $J_{P-C} = 4$ Hz, $J_{P-C} = 59$ Hz, C_{ipso}), 132.6 (d, $J_{P-C} = 10$ Hz, CH_{arom}), 132.1 (d, $J_{P-C} = 10$ Hz, CH_{arom}), 128.9 (d, $J_{P-C} = 3$ Hz, CH_{para}), 128.5 (d, $J_{P-C} = 3$ Hz, CH_{meta}), 127.6 (d, $J_{P-C} = 10$ Hz, CH_{arom}), 127.3 (d, $J_{P-C} = 11$ Hz, CH_{arom}), 13.6 (dd, $J_{P-C} = 78$ Hz, $J_{P-C} = 112$ Hz, $PC(H)P$). ^{11}B NMR (89.0 MHz, CD_2Cl_2): δ_B –37.3 (bs). Anal. Calcd for $C_{29}H_{32}P_2BLiOS$: C, 68.52; H, 6.35. Found: C, 68.35; H, 6.65.

Synthesis of Compound 7[–]. To a solution of 7 (66.2 mg, 0.16 mmol) in THF (8 mL) was added methyllithium (1.6 M in Et_2O , 0.1 mL, 0.16 mmol) at $-78^\circ C$ dropwise. The resulting pale yellow solution was warmed to room temperature and stirred for 1 h. Drying under vacuum allowed the isolation of 6[–] as a yellow solid (69 mg, 88%). ^{31}P NMR (121.5 MHz, $thf-d_8$): δ_P 34.6 (br, PO), 5.9 (br, PB). 1H NMR (300 MHz, $thf-d_8$): δ_H 7.80–7.72 (m, 8H, H_{arom}), 7.26–7.17 (m, 12H, H_{arom}), 3.62 (br, CH_2 of thf), 1.76 (br, CH_2 of thf), 1.44 (dd, $J_{P-H} = 7.0$ Hz, $J_{P-H} = 11.6$ Hz, $PCHP$), BH_3 . ^{13}C NMR (75.5 MHz, $thf-d_8$): δ_C 142.5 (dd, $J_{P-C} = 6$ Hz, $J_{P-C} = 108.3$ Hz, C_{ipso}), 141.6 (dd, $J_{P-C} = 5.3$ Hz, $J_{P-C} = 58.0$ Hz, C_{ipso}), 131.3 (d, $J_{P-C} = 9.4$ Hz, CH_{meta}), 131.2 (d, $J_{P-C} = 9.4$ Hz, CH_{meta}), 128.5 (d, $J_{P-C} = 2.6$ Hz, CH_{para}), 127.7 (d, $J_{P-C} = 2.3$ Hz, CH_{para}), 127.0 (d, $J_{P-C} = 10.9$ Hz, CH_{ortho}), 126.9 (d, $J_{P-C} = 12.8$ Hz, CH_{ortho}), 67.2 (s, C2 of thf), 25.4 (s, C1 of thf), 14.0 (dd, $J_{P-C} = 76.6$ Hz, $J_{P-C} = 142.7$ Hz, $PCHP$). Anal. Calcd for $C_{29}H_{34}P_2O_2BLi$: C, 70.47; H, 6.93. Found: C, 70.18; H, 7.14.

Synthesis of Compound 6^{2–}. To a suspension of 6 (688.8 mg, 1.6 mmol) in toluene (10 mL) was added butyllithium (1.6 M in hexanes, 2 mL, 3.2 mmol) at $-78^\circ C$. The solution was warmed to room temperature and stirred for 3 h. The reaction mixture progressively turned yellow, and a yellow solid precipitated. The solid was isolated by centrifugation and washed once with toluene (6 mL) then with 2×6 mL of pentane and dried under vacuum. The desired compound was obtained as a pale yellow solid (700 mg, 99%). ^{31}P NMR (300 MHz, $ether-d_{10}$): δ_P 25.5 (d, $J_{P-P} = 8$ Hz, PS), 4.8 (bd, PB). 1H NMR (300.0 MHz, $ether-d_{10}$): δ_H 7.94–7.85 (m, 1H, H_{arom}), 7.76–7.62 (m, 4H, H_{arom}), 7.49–7.44 (m, 4H, H_{arom}), 7.27–6.95 (m, 11H, H_{arom}), 1.40–0.34 (m, BH_3). ^{11}B NMR (89.0 MHz, $ether-d_{10}$): δ_B –29.6 (bs). Anal. Calcd for $C_{25}H_{23}P_2SBLi_2$: C, 67.85; H, 5.24. Found: C, 67.84; H, 5.35.

Synthesis of Compound 6-D₂. To a suspension of 6 (68.8 mg, 0.16 mmol) in toluene (4 mL) was added butyllithium (1.6 M in hexanes, 0.2 mL, 0.32 mmol) at $-78^\circ C$. The solution was warmed to room temperature and stirred for 3 h. Excess D_2O was added, and the reaction mixture was then stirred for 2 h. Solvents were evaporated under vacuum. Dichloromethane (5 mL) was added, and insoluble impurities were discarded by filtration. The remaining solution was dried over $MgSO_4$ and filtered. Evaporation of the solvent afforded the title compound as a white solid (65 mg, 94%). ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ_P 34.1 (d, $J_{P-P} = 8.9$ Hz, PS), 14.8 (bd, PBH_3). 1H NMR (300 MHz, CD_2Cl_2): δ_H 7.81–7.69 (m, 8H, H_{arom}), 7.62–7.31 (m, 12H, H_{arom}), 1.49–0.25 (PBH₃). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ_C 133.4 (d, $J_{P-C} = 10$ Hz, CH_{arom}), 133.2 (dd, $J_{P-C} = 2$ Hz, $J_{P-C} = 84$ Hz, C_{ipso}), 131.9 (d, $J_{P-C} = 3$ Hz, CH_{para}), 131.7 (d, $J_{P-C} = 3$ Hz, CH_{para}), 131.3 (d, $J_{P-C} = 10$ Hz, CH_{arom}), 128.8 (d, $J_{P-C} = 10$ Hz, CH_{arom}), 128.7 (d, $J_{P-C} = 12$ Hz, CH_{arom}), 128.5 (dd, $J_{P-C} = 3$ Hz, $J_{P-C} = 53$ Hz, C_{ipso}), 29.6 (m, PCD_2P).

Deuterolysis of Compound 7^{2–}. Two equivalents of methyllithium in diethyl ether (1.6 M, 0.2 mL, 0.32 mmol) was added dropwise to a solution of compound 7 (66 mg, 0.16 mmol) in toluene (4 mL) at $-78^\circ C$ with vigorous stirring. The solution was brought slowly to room temperature and the pressure frequently equilibrated. After 24 h, excess deuterated water was added. The solution was stirred for 6 h before the solvents were removed under vacuum. Organic products were extracted in dichloromethane and dried over

MgSO₄. Compound 7, as a mixture of the H and D isotopes, was isolated as a white powder (64 mg, 95%).

Many variations in the experimental conditions were attempted without success to obtain quantitative formation of 7²⁻, among which were using other solvents (DME or Et₂O) and bases (*n*-BuLi) and grease-free glassware. Using TMEDA to increase the kinetics of the deprotonation was also unsuccessful.

Synthesis of Compound 9. Mg(*n*Bu)₂ (1 M in heptane, 2.2 mL, 2.20 mmol) was added dropwise to 6 (0.86 g, 2.00 mmol) in THF/Et₂O (1/1, 20 mL) at room temperature. The reaction mixture was then refluxed for 12 h, while the solution changed from colorless to pale yellow. The reaction mixture was filtered, and the filtrate was concentrated to afford 9 as yellow crystals (0.60 g, 44.6%). Mp: 233 °C dec. ³¹P NMR (160.3 MHz, C₆D₆): δ_P 37.9 (d, ²J_{P-P} = 56.27 Hz, PS), 3.41 (bs, PBH₃). ¹H NMR (395.9 MHz, C₆D₆): δ_H 7.82 (m, 4H, Ph), 7.65 (m, 4H, Ph), 6.89 (m, 12H, Ph), 3.63 (m, 12H, THF), 1.85 (bs, 3H, BH₃), 1.38 (m, 12H, THF). ¹³C NMR (99.5 MHz, C₆D₆): δ_C 145.9 (d, J_{P-C} = 66.2 Hz, C_{ipso}), 144.3 (dd, J_{P-C} = 42.6 Hz, ³J_{P-C} = 6.64 Hz, C_{ipso}), 133.4 (d, J_{P-C} = 8.67 Hz, CH_{arom}), 132.5 (d, J_{P-C} = 10.9 Hz, CH_{arom}), 128.0 (d, ⁴J_{P-C} = 2.70 Hz, CH_{para}), 127.5 (d, ⁴J_{P-C} = 1.97 Hz, CH_{para}), 127.1 (d, J_{P-C} = 8.67 Hz, CH_{arom}), 126.9 (d, J_{P-C} = 10.9 Hz, CH_{arom}), 68.2 (s, THF), 26.4 (s, THF). ¹¹B NMR (127.0 MHz, C₆D₆): δ_B -30.2 (bs). Anal. Calcd for C₃₇H₄₇BMgO₃P₂S: C, 66.44; H, 7.08. Found: C, 66.12; H, 6.87.

■ ASSOCIATED CONTENT

■ Supporting Information

Figures, tables, and CIF files giving crystallographic data, NMR spectra, and details of the theoretical study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

We dedicate this article to the memory of the late Prof. P. Le Floch, an inspiring chemist and a missed friend.

■ REFERENCES

- (1) (a) Fischer, E. O.; Maasböl, O. *Angew. Chem., Int. Ed.* **1964**, *3*, 580. (b) Fischer, E. O.; Maasböl, O. *Chem. Ber.* **1967**, *100*, 2445.
- (2) Schrock, R. R. *J. Am. Chem. Soc.* **1974**, *96*, 6796.
- (3) (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (b) Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911. (c) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, *107*, 5606. (d) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122. (e) de Frémont, P.; Marion, N.; Nolan, S. P. *Coord. Chem. Rev.* **2009**, *253*, 862. (f) Dötz, K. H.

Stendel, J., Jr. *Chem. Rev.* **2009**, *109*, 3227. (g) Herndon, J. W. *Coord. Chem. Rev.* **2012**, *256*, 1281.

(4) (a) Fürstner, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3012. (b) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18. (c) Nicolau, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 4490. (d) Vougioukalakis, G. C.; Grubbs, R. H. *Chem. Rev.* **2010**, *110*, 1746.

(5) (a) Ong, C. M.; Stephan, D. W. *J. Am. Chem. Soc.* **1999**, *121*, 2939. (b) Kasani, A.; Babu, R. P. K.; McDonald, R.; Cavell, R. G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1483.

(6) (a) Cantat, T.; Mézailles, N.; Ricard, L.; Jean, Y.; Le Floch, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 6382. (b) Cantat, T.; Ricard, L.; Le Floch, P.; Mézailles, N. *Organometallics* **2006**, *25*, 4965.

(7) (a) Cavell, R. G.; Babu, R. P. K.; Kasani, A.; McDonald, R. J. *Am. Chem. Soc.* **1999**, *121*, 5805. (b) Kasani, A.; McDonald, R.; Cavell, R. G. *Chem. Commun.* **1999**, 1993. (c) Cantat, T.; Jaroschik, F.; Nief, F.; Ricard, L.; Mézailles, N.; Le Floch, P. *Chem. Commun.* **2005**, 5178. (d) Cantat, T.; Demange, M.; Mézailles, N.; Ricard, L.; Jean, Y.; Le Floch, P. *Organometallics* **2005**, *24*, 4838. (e) Cantat, T.; Jaroschik, F.; Ricard, L.; Le Floch, P.; Nief, F.; Mézailles, N. *Organometallics* **2006**, *25*, 1329. (f) Cantat, T.; Ricard, L.; Mézailles, N.; Le Floch, P. *Organometallics* **2006**, *25*, 6030. (g) Orzechowski, L.; Jansen, G.; Harder, S. *J. Am. Chem. Soc.* **2006**, *128*, 14676. (h) Cantat, T.; Arliguie, T.; Noël, A.; Thuéry, P.; Ephritikhine, M.; Le Floch, P.; Mézailles, N. *J. Am. Chem. Soc.* **2009**, *131*, 963. (i) Foo, C.; Lau, K.-C.; Yang, Y.-F.; So, C.-W. *Chem. Commun.* **2009**, 6816. (j) Cooper, O. J.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Dalton Trans.* **2010**, *39*, 5074. (k) Heuclin, H.; Grünstein, D.; Le Goff, X.-F.; Le Floch, P.; Mézailles, N. *Dalton Trans.* **2010**, *39*, 492. (l) Ma, G.; Ferguson, M. J.; Cavell, R. G. *Chem. Commun.* **2010**, *46*, 5370. (m) Tourneux, J.-C.; Berthet, J.-C.; Thuéry, P.; Mézailles, N.; Le Floch, P.; Ephritikhine, M. *Dalton Trans.* **2010**, *39*, 2494. (n) Fustier, M.; Le Goff, X. F.; Le Floch, P.; Mézailles, N. *J. Am. Chem. Soc.* **2010**, *132*, 13108. (o) Ma, G.; Ferguson, M. J.; McDonald, R.; Cavell, R. G. *Inorg. Chem.* **2011**, *50*, 6500. (p) Cooper, O. J.; Mills, D. P.; McMaster, J.; Moro, F.; Davies, E. S.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Angew. Chem., Int. Ed.* **2011**, *50*, 2383. (q) Mills, D. P.; Moro, F.; McMaster, J.; van Slageren, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Nat. Chem.* **2011**, *3*, 454. (r) Heuclin, H.; Cantat, T.; Le Goff, X. F.; Le Floch, P.; Mézailles, N. *Eur. J. Inorg. Chem.* **2011**, 2540. (s) Tourneux, J.-C.; Berthet, J.-C.; Cantat, T.; Thuéry, P.; Mézailles, N.; Le Floch, P.; Ephritikhine, M. *Organometallics* **2011**, *30*, 2957. (t) Tourneux, J.-C.; Berthet, J.-C.; Cantat, T.; Thuéry, P.; Mézailles, N.; Ephritikhine, M. *J. Am. Chem. Soc.* **2011**, *133*, 6162. (u) Fustier-Boutignon, M.; Heuclin, H.; Le Goff, X. F.; Mézailles, N. *Chem. Commun.* **2012**, *48*, 3306. (v) Mills, D. P.; Cooper, O. J.; Tuna, F.; McInnes, E. J. L.; Davies, E. S.; McMaster, J.; Moro, F.; Lewis, W.; Blake, A. J.; Liddle, S. T. *J. Am. Chem. Soc.* **2012**, *134*, 10047. For reviews see: (w) Heuclin, H.; Fustier, M.; Auffrant, A.; Mézailles, N. *Lett. Org. Chem.* **2010**, *7*, 596. (x) Mills, D. P.; Woolees, A. J. *Chem. Soc. Rev.* **2011**, *40*, 2164.

(8) Demange, M.; Boubekur, L.; Auffrant, A.; Mézailles, N.; Ricard, L.; Le Goff, X.; Le Floch, P. *New J. Chem.* **2006**, *30*, 1745.

(9) Cooper, O. J.; Woolees, A. J.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Angew. Chem., Int. Ed.* **2010**, *49*, 5570.

(10) Buchard, A.; Platel, R. H.; Auffrant, A.; Le Goff, X. F.; Le Floch, P.; Williams, C. K. *Organometallics* **2010**, *29*, 2892.

(11) Hull, K. L.; Noll, B. C.; Henderson, K. W. *Organometallics* **2006**, *25*, 4072.

(12) Hull, K. L.; Carmichael, I.; Noll, B. C.; Henderson, K. W. *Chem. Eur. J.* **2008**, *14*, 3939.

(13) Orzechowski, L.; Jansen, G.; Harder, S. *Angew. Chem., Int. Ed.* **2009**, *48*, 3825.

(14) (a) Babu, R. P. K.; McDonald, R.; Decker, S. A.; Klobukowski, M.; Cavell, R. G. *Organometallics* **1999**, *18*, 4226. (b) Kasani, A.; Ferguson, M.; Cavell, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 726. (c) Babu, R. P. K.; McDonald, R.; Cavell, R. G. *Chem. Commun.* **2000**, 481.

(d) Aparna, K.; Babu, R. P. K.; McDonald, R.; Cavell, R. G. *Angew. Chem., Int. Ed.* **2001**, *40*, 4400. (e) Leung, W.-P.; Wang, Z.-X.; Li, H.-W.; Mak, T. C. W. *Angew. Chem., Int. Ed.* **2001**, *40*, 2501. (f) Orzechowski, L.; Harder, S. *Organometallics* **2007**, *26*, 5501.

- (g) Orzechowski, S.; Harder, S. *Organometallics* **2007**, *26*, 2114.
- (h) Liddle, S. T.; McMaster, J.; Green, J. C.; Arnold, P. L. *Chem. Commun.* **2008**, 1747.
- (i) Mills, D. P.; Cooper, O. J.; McMaster, J.; Lewis, W.; Liddle, S. T. *Dalton Trans.* **2009**, 4547.
- (j) Mills, D. P.; Wooles, A. J.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Organometallics* **2009**, *28*, 6771.
- (k) Leung, W.-P.; Wan, C.-L.; Kan, K.-W.; Mak, T. C. W. *Organometallics* **2010**, *29*, 814.
- (l) Wooles, A. J.; Cooper, O. J.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Organometallics* **2010**, *29*, 2315.
- (m) Wooles, A. J.; Mills, D. P.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Dalton Trans.* **2010**, 39, 500.
- (n) Leung, W.-P.; Mak, Y.-C.; Mak, T. C. W. *Inorg. Chem.* **2011**, *50*, 10517.
- (15) Schröter, P.; Gessner, V. H. *Chem. Eur. J.* **2012**, *18*, 11223.
- (16) Chen, J.-H.; Guo, J.; Li, Y.; So, C.-W. *Organometallics* **2008**, *28*, 4617.
- (17) (a) Blug, M.; Grünstein, D.; Alcaraz, G.; Sabo-Etienne, S.; Le Goff, X.-F.; Le Floch, P.; Mézailles, N. *Chem. Commun.* **2009**, 4432.
- (b) Westerhausen, M.; Görls, H.; Wimmer, K.; Langer, J. *Dalton Trans.* **2009**, 2951.
- (18) Orzechowski, L.; Jansen, G.; Lutz, M.; Harder, S. *Dalton Trans.* **2009**, 2958.
- (19) Grim, S. O.; Mitchell, J. D. *Synth. React. Inorg. Met.-Org. Chem.* **1977**, *4*, 221.
- (20) Boubekeur, L.; Ricard, L.; Mézailles, N.; Le Floch, P. *Organometallics* **2005**, *24*, 1065.
- (21) Gessner, V. H. *Organometallics* **2011**, *30*, 4228.
- (22) Heuclin, H.; Carenco, S.; Le Goff, X.-F.; Mézailles, N. *Eur. J. Inorg. Chem.* **2012**, 1453.
- (23) Haiduc, I. *Organometallics* **2004**, *23*, 3.
- (24) Yang, Y.-F.; Foo, C.; Ganguly, R.; Li, Y.; So, C.-W. *Organometallics* **2012**, *31*, 6538.
- (25) Leung, W.-P.; Wan, C.-L.; Mak, T. C. W. *Organometallics* **2010**, *29*, 1622.
- (26) Guo, J.-Y.; Lee, J.-S.; Foo, M.-C.; Lau, K.-C.; Xi, H.-W.; Lim, K. H.; So, C.-W. *Organometallics* **2010**, *29*, 939.