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# Synthesis and Ligand Properties of Silsesquioxane-Caged Phosphite $T_7Ph_7P$

Marc Hunsicker,<sup>[a]</sup> Johannes Krebs,<sup>[a]</sup> Michael Zimmer,<sup>[a]</sup> Bernd Morgenstern,<sup>[b]</sup> Volker Huch,<sup>[a]</sup> and David Scheschkewitz<sup>\*[a]</sup>

Dedicated to Professor Michael Veith on occasion of his 80<sup>th</sup> birthday

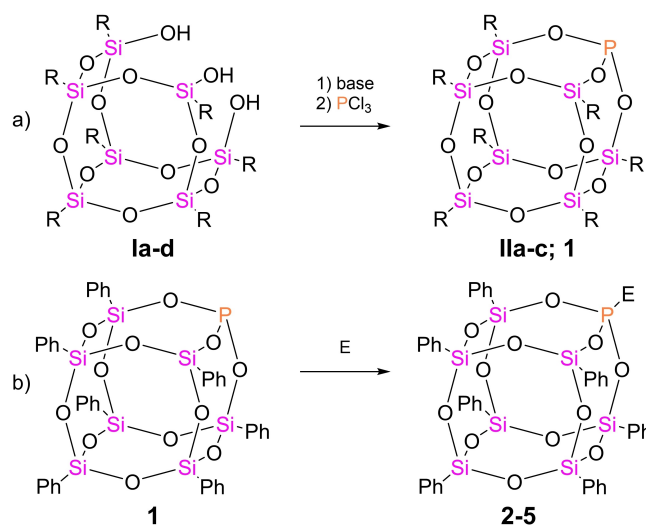
The synthesis of the phosphorus-capped heptaphenylsilsesquioxane  $T_7Ph_7P$  is reported. We show that, unlike previous examples, it readily forms Lewis acid-base adducts with boranes of different steric demand and the  $FeCO_4$  fragment. All complexes were characterized by multinuclear NMR and IR spectroscopy in solution and the solid state. The molecular

structures of the adducts with  $BPh_3$  and  $B(C_6F_5)_3$  were determined from XRD suitable single crystals. The relative conformation of the Ph and  $C_6F_5$  rings in  $T_7Ph_7P-B(C_6F_5)_3$  suggests favorable  $\pi$ -interactions, stabilizing the adducts to such a degree that attempts to activate  $H_2$  or  $CO_2$  were unsuccessful.

## Introduction

Trisubstituted phosphanes and phosphite esters are ubiquitous as reagents in organic chemistry,<sup>[1]</sup> and as ligands in transition metal complexes.<sup>[2]</sup> The inherent Lewis basicity associated to the lone pair of electrons leads to the facile formation of adducts with suitable electron deficient Lewis acids.<sup>[3]</sup> The strength of this donor-acceptor interaction can be tuned by the electronic nature of the substituents. Framework phosphanes with the donor-center in an oligocyclic bridgehead position can offer additional control of the ligand properties due to their structural rigidity.

In this context, the incompletely condensed  $T_7R_7(OH)_3$  silsesquioxanes of type I have proven to be valuable precursors for the incorporation of various heteroelements into the cubic framework.<sup>[4]</sup> Feher and coworkers reported the synthesis of the heterosilsesquioxane **IIa** in which a phosphorus atom closes the  $T_7Cy_7$  backbone (Scheme 1).<sup>[5]</sup> So far only limited information is available on its coordination chemistry and that of related



**Scheme 1.** a) Corner capping of partially condensed silsesquioxanes **Ia-c** (a:  $R=Cy$ , b:  $R=Oct$ , c:  $R=Bu$  d:  $R=Ph$ ) with  $PCl_3$  to heterosilsesquioxane cages with a phosphorus vertex **IIa,b,c**<sup>[5,8,11]</sup> and **1** (this work). b) Treatment of the phosphorus capped heptaphenylsilsesquioxane **1** with various Lewis acids generates Lewis acid-base adducts **2** to **5** (**2**:  $E=BPh_3$ ; **3**:  $E=B(C_6F_5)_3$ ; **4**:  $E=BCl_3$ ; **5**:  $E=Fe(CO)_4$ ).

[a] M. Hunsicker, J. Krebs, Dr. M. Zimmer, V. Huch, Prof. Dr. D. Scheschkewitz  
Krupp-Chair of General and Inorganic Chemistry  
Saarland University  
66123 Saarbrücken, Germany  
E-mail: scheschkewitz@mx.uni-saarland.de

[b] Dr. B. Morgenstern  
Service Center X-Ray Diffraction  
Saarland University  
66123 Saarbrücken, Germany

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compounds: **IIa** reportedly forms a 1:1 adduct with  $AlMe_3$  according to NMR spectroscopic evidence, although the lack of suitable single crystals prevented full characterization. The steric demand of the cyclohexyl groups<sup>[5,6]</sup> may prevent coordination of **IIa** to transition metal centers as it did not induce catalytic activity when added to  $[Rh(acac)(CO)_2]$  under hydroformylation conditions.<sup>[7]</sup> In contrast, the heptaisooctyl-substituted **IIb** reported by Marciniak and coworkers acted as inhibitor towards Karstedt's catalyst in hydrosilylation reactions and was proven to coordinate to the platinum center by  $^{31}P$  NMR.<sup>[8]</sup>

In the context of the functionalization of polyhedral silsesquioxanes,<sup>[9]</sup> we explored their interconnection by donor/acceptor interactions. In particular, we were interested in the phenyl-substituted version of **II** in view of its intermediate steric bulk and the somewhat reduced electron density<sup>[10]</sup> compared to the cyclohexyl derivative **IIa**. Herein, we report on the synthesis of the phenyl-substituted cage phosphite  $T_7Ph_7P$  and its conversion to Lewis pairs with several boron-centered Lewis acids as well as with the iron tetracarbonyl fragment.

## Results and Discussion

**Synthesis.** In adaption of the reported corner capping reaction of the partially condensed cyclohexyl-substituted **Ia**,  $T_7Ph_7(OH)_3$  **Id** was treated with triethylamine and a slight excess of  $PCl_3$  (1.1 eq) in toluene at 0 °C. Filtration after five minutes of stirring followed by removal of the volatiles and washing with minimal amounts of toluene yielded the colorless phosphite  $T_7Ph_7P$  **1** in 41% yield. Phosphite  $T_7Ph_7P$  **1** gives rise to a  $^{31}P$  NMR singlet at 86.3 ppm, in  $C_6D_6$  almost identical with those of **IIa** (86.1 ppm),<sup>[5]</sup> **IIb** (84.6 ppm)<sup>[8]</sup> and **IIc** (84.7 ppm).<sup>[11]</sup> The phenyl groups of **1** produce two uniform multiplets in the  $^1H$  NMR spectrum in  $C_6D_6$  between 7.85 to 7.79 ppm and 7.15 to 7.00 ppm.

The alternative use of  $T_7Ph_7(ONa)_3$  results in the formation of several unidentified byproducts with overlapping  $^1H$  NMR resonances in the aromatic region, unlike in case of  $T_7^{i}Oct_7(ONa)_3$  from which Marciniec et al. obtained near-quantitative yields of  $T_7^{i}Oct_7P$ .<sup>[8]</sup> These byproducts give rise to several  $^{31}P$  NMR signals between 180 and –21 ppm after stirring overnight (see Figure S36). Resonances at –19 and –26 ppm were reported by Copéret et al. for the grafting of  $T_7^iBu_7P$  to OH-terminated silica and rationalized by the formation of phosphonates through OH transfer from the surface to the P center.<sup>[11]</sup>

In an initial attempt to elucidate the geometric constraints between the phosphite and a boron-centred Lewis acid, we prepared Lewis acid-base complex **2** by treatment of  $T_7Ph_7P$  with a slight excess of triphenylborane in toluene. Stirring for 35 minutes at room temperature and isolation of the resulting precipitate by filtration yields the colorless product in 51% yield (reaction of  $Ph_3BPCl_3$  adduct with  $T_7Ph_7(OH)_3$  resulted in much lower yields of **2**).  $^1H$  NMR spectra confirm a new species, although the  $^{11}B$  and  $^{31}P$  NMR spectra in  $C_6D_6$  do not show any signals (*vide infra*).

Next, tris(pentafluorophenyl)borane was used as Lewis acid component to increase acidity and steric demand of the borane in the hope to induce frustration. Reaction of a 1:1 stoichiometric ratio of  $T_7Ph_7P$  **1** and  $B(C_6F_5)_3$  in toluene for 30 minutes, however, results in the formation of a new adduct as well, as evidenced by its uniform  $^1H$  NMR spectrum and  $^{11}B$  and  $^{31}P$  NMR signals at –14.9 ppm and 37.1 ppm, respectively, in  $C_6D_6$  solution. The adduct **3** was isolated by crystallization at room temperature from a hot-saturated toluene solution in 42% yield. In order to increase steric demand of the Lewis acid even more, a mixture of  $T_7Ph_7P$  and tris(4-bromo-2,3,5,6-tetramethylphenyl)borane in toluene was stirred at room temperature,

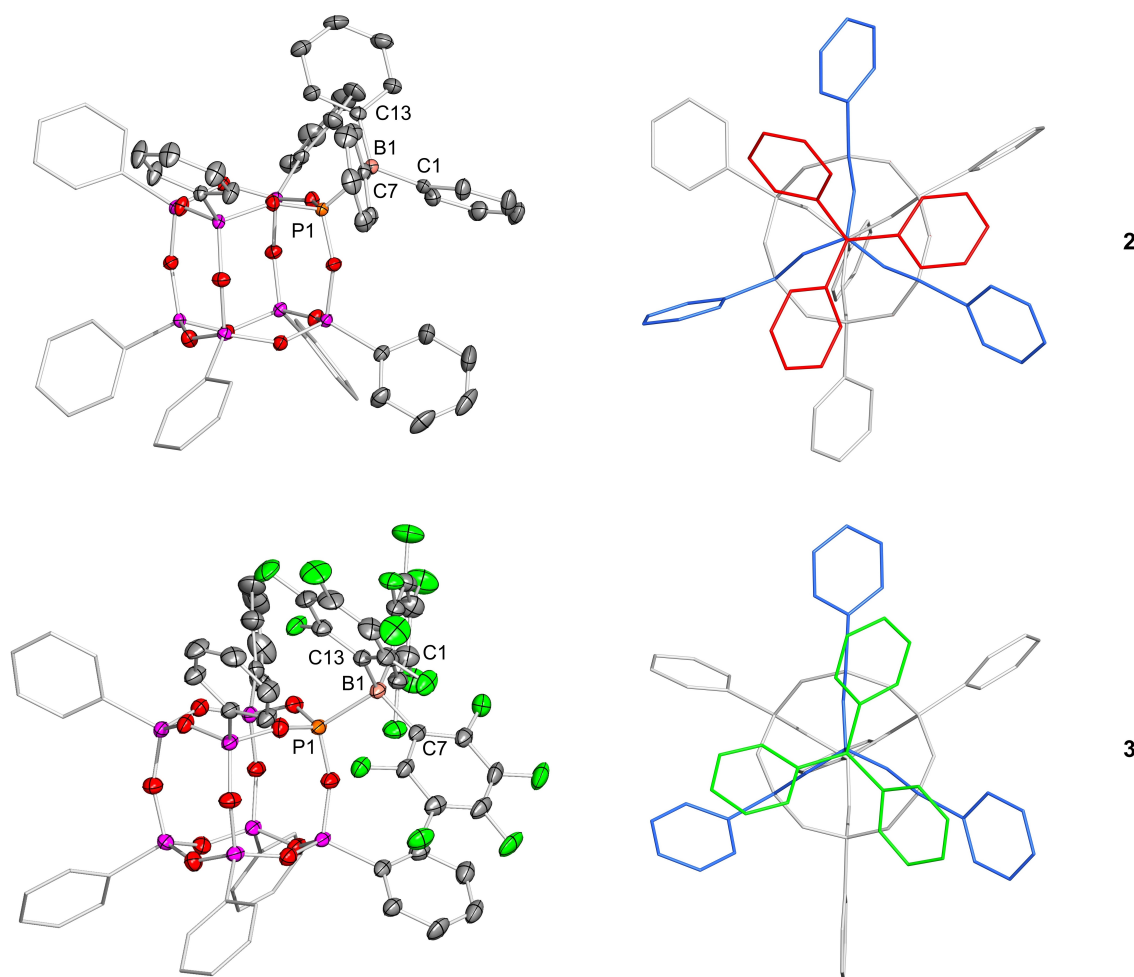
and indeed no adduct formation took place according to NMR monitoring.

Initial attempts to obtain the boron trichloride adduct  $T_7Ph_7P\cdot BCl_3$  **4** by combining toluene solutions of  $BCl_3$  and **1** led to inseparable mixtures with about 35% of a major product ( $^{11}B$  NMR at 1.4 ppm). In an improved procedure, careful layering a concentrated toluene solution of **1** with a stock solution of  $BCl_3$  in toluene affords **4** as a microcrystalline colorless product in 43% yield.

Stirring a twofold excess of  $Fe_2(CO)_9$  (in order to assure complete conversion) and the cage phosphite **1** in toluene results in the immediate formation of a new species at room temperature as well. The  $Fe(CO)_4$  adduct **5** shows a single resonance at 124.1 ppm in the  $^{31}P$  NMR spectrum and is thus downfield shifted by  $\Delta\delta = 37.8$  ppm. Various alkoxy- and amino-substituted phosphite iron carbonyl complexes (in  $CH_2Cl_2$  or  $CDCl_3$ ) showed  $^{31}P$  NMR signals, downfield shifted by  $\Delta\delta$  between 20.2 and 55.1 ppm compared with the free ligands.<sup>[12]</sup> The adduct **5** was isolated by extraction from the dried product mixture with toluene in 47% yield. Unlike in case of **2** and **3**, single crystals of **5** could not be obtained despite crystallization attempts from a saturated toluene solution at room temperature, or from storing slightly more diluted solutions at reduced temperatures between +4 °C and –27 °C.

**Crystal structure discussion.** Single crystals of the borane adducts **2** and **3** suitable for XRD were obtained from toluene at 4 °C and room temperature, respectively.<sup>[13]</sup> The free phosphite ligand **1** and its  $Fe(CO)_4$  adduct **5** precipitated in amorphous form, the microcrystals of the  $BCl_3$  adduct **4** proved unsuitable for XRD.

The molecular structures of adducts **2** and **3** in the solid state confirm the anticipated constitutions as borane adduct (Figure 1, left). Both structures show approximate  $C_3$  symmetry. Notably, while the B-bonded phenyl groups of **2** are staggered with respect to the adjacent phenyl groups of the cage phosphite without clear-cut stabilizing interactions, the perfluorinated phenyl groups of **3** adopt an almost eclipsed conformation (Figure 1, right). The centroids of the phenyl and pentafluorophenyl groups of adduct **3** are 4.1794(6) Å apart on average, which is significantly farther than the corresponding distance calculated for the  $\pi$ -stacked benzene-dimer (3.914 Å)<sup>[14]</sup> but intriguingly close to those in Lewis adducts of the type  $Ph_3E\cdot B(C_6F_5)_3$  with similar eclipsed conformations ( $E=P$ : 4.169 Å,  $As$ : 4.215 Å).<sup>[15a,b]</sup> The authors concluded a certain attractive interaction between the aromatic rings in the arsenic case, which was supported by DFT calculations.<sup>[15b]</sup> The average angle between the planes of the  $C_6H_5$  and  $C_6F_5$  rings of 7.8(4)° in **3** is much closer to coplanarity than in the abovementioned phosphorus and arsenic Lewis adducts with angles of 24.49° (P) and 22.64° (As). We tentatively attribute the near-coplanarity in **3** to the much smaller distortions from the idealized tetrahedral structure of the Lewis base required for effective  $\pi$  stacking. A theoretical study investigating non covalent interactions (NCI) in several Lewis adducts and FLP systems also found weakly stabilizing effects of  $\pi$  stacking between the aromatic rings in  $Ph_3P\cdot B(C_6F_5)_3$ .<sup>[15c]</sup> Stephan et al. reported parallel alignment of phenyl and  $C_6F_5$  groups in an ethylene bridged P–B adduct and interpreted it as  $\pi$  stacking effect.<sup>[15d]</sup>



**Figure 1.** Left: molecular structures of the  $\text{BPh}_3$  adduct **2** and  $\text{B}(\text{C}_6\text{F}_5)_3$  adduct **3** in the solid state. Co-crystallized solvent molecules, disordered phenyl groups and hydrogen atoms are omitted for clarity. Thermal ellipsoids at 50% probability. Right: top-views of  $\text{BPh}_3$  adduct **2** and  $\text{B}(\text{C}_6\text{F}_5)_3$  **3** down the boron-phosphorus bonds. **Blue:** phenyl groups on the first substituents attached to phosphorus in both complexes. **Red:** phenyl groups of  $\text{BPh}_3$ . **Green:** aromatic rings of the  $\text{C}_6\text{F}_5$  moieties on boron. Selected bond lengths and angles for **2**: P1-B1: 1.9604(2) Å, P1-O1: 1.5636(1) Å, P1-O4: 1.5652(1) Å, P1-O8: 1.5625(1) Å, B1-C1: 1.629(2) Å, B1-C7: 1.632(2) Å, B1-C13: 1.626(2) Å, O1-P1-O4: 106.34(6)°, O8-P1-O4: 105.05(6)°, O8-P1-O1: 105.39(6)°, C1-B1-C7: 114.62(1)°, C13-B1-C7: 112.54(1)°, C13-B1-C1: 113.47(1)°. Selected bond lengths and angles for **3**: P1-B1: 1.994(4) Å, P1-O6: 1.547(2) Å, P1-O10: 1.545(2) Å, P1-O11: 1.550(2) Å, B1-C1: 1.638(5) Å, B1-C7: 1.638(5) Å, B1-C13: 1.641(5) Å; O6-P1-O11: 106.32(1)°, O10-P1-O11: 106.81(1)°, O10-P1-O6: 107.25(1)°, C1-B1-C7: 114.0(3)°, C1-B1-C13: 112.3(3)°, C7-B1-C13: 115.0(3)°.

The staggered conformation of the triphenylborane adduct **2** with angles of 71.7(6)° on average between the planes of adjacent phenyl groups of the  $\text{PPh}_3$  and the cage phosphite moieties is best described as a threefold T-shaped interaction between electronically similar benzene rings. The average distance between the centroids of 4.9654(7) Å is substantially longer than in **3** and similar to the distance in the T-shaped benzene dimer (4.913 Å).<sup>[14]</sup> The boron-phosphorus bond lengths of **2** and **3** are at the short end of the range of typical Lewis-acid base adducts (for **2**: 1.9604(2) Å, for **3**: 1.994(4) Å). In comparison, the reported  $\text{Ph}_3\text{P}-\text{B}(\text{C}_6\text{F}_5)_3$ <sup>[15a]</sup> and  $(\text{MeNCH}_2\text{CH}_2)_3\text{N}-\text{P}-\text{B}(\text{C}_6\text{F}_5)_3$ <sup>[15b]</sup> adducts display P–B bond lengths of 2.180 Å, and 2.096 Å, respectively. Phosphite-borane adducts without aromatic substituents at phosphorus also feature significantly longer P–B distances, for instance 2.0209 Å in  $(\text{MeO})_3\text{P}-\text{B}(\text{C}_6\text{F}_5)_3$ .<sup>[15c]</sup>

Due to a lack of single crystals of the free ligand **1**, an unbiased comparison of the steric shielding provided by the substituents with that in  $\text{T}_7\text{Cy}_7\text{P}$  **IIa** is difficult. Nonetheless, some trends can be derived from the available solid state structures. Feher and coworkers determined a Tolman cone angle of  $\sim 167^\circ$ ,<sup>[5]</sup> by using solely the H–P–L angles as basis for the calculation. A more refined method was introduced shortly thereafter by Mingos et al.,<sup>[16]</sup> in which the van der Waals radius of the hydrogen atoms is accounted for when determining the P–L–H angles. According to the latter approach, Tolman cone angles of  $\theta = 181.1^\circ$  for **2** and  $\theta = 174.3^\circ$  for **3** are obtained from solid state structures truncated to the free  $\text{T}_7\text{Ph}_7\text{P}$  ligand. Both cone angles are smaller than that of **IIa** ( $\theta = 189^\circ$ ) recalculated by the same method. As discussed by Sigman and Doyle et al.,<sup>[17]</sup> the reactivity of a (phosphine or phosphite) ligand can only be vaguely rationalized on grounds of the Tolman

cone angle. The percent buried volume  $\%V_{\text{bur}}^{[18a]}$  parameter (determined with the Sambvca open-source application<sup>[18b]</sup> using a distance of 2.28 Å between the phosphorus atom and the center of the putative sphere) is larger for **IIa** (23.8%) than for the phosphite ligands of **2** (23.0%) and **3** (22.2%). This confirms the general trend of the Tolman cone angles and is keeping with other distance values in the  $\%V_{\text{bur}}$  calculation, such as the 2.0 Å chosen by Nolan and coworkers,<sup>[18a]</sup> albeit at inherently larger values of  $\%V_{\text{bur}}$ . Overall, the change from cyclohexyl to phenyl, and from phenyl to pentafluorophenyl is 3–4% irrespective of the steric parameter, reflecting the anticipated higher steric bulk of the cyclohexyl substituent and the different conformations of the aromatic groups in **2** and **3**.

**NMR spectroscopy.** In  $C_6D_6$  solution, the free cage-phosphite **1** gives rise to a diagnostic  $^{31}P$  NMR signal emerging as a singlet at 86.3 ppm along with a satellite doublet with a coupling constant of 37.2 Hz attributed to coupling to the silicon atoms of the silsesquioxane. This compares well with the reported cyclohexyl and isooctyl-substituted congeners (86.1 ( $^2J_{P, Si} = 35.8$  Hz) and 84.6 ppm, respectively).<sup>[5,8]</sup> The corresponding CP/MAS spectrum shows two signals of approximately equal intensity at 83.8 and 82.1 ppm, most likely because of at least two symmetry-independent environments in the solid state as previously discussed by Erker et al. for boron-phosphorus frustrated Lewis pairs.<sup>[20]</sup> The  $BPh_3$  (**2**) and  $BCl_3$  complexes (**4**) do not show  $^{31}P$  NMR signals in solution, presumably due to coalescence phenomena of temperature dependent processes. Unfortunately, the low solubility of both adducts was prohibitive of VT NMR studies that could have shed further light on this aspect. In the  $^{31}P$  CP/MAS NMR spectra, however, the  $BPh_3$  adduct **2** exhibits a broad signal at 48.1 ppm (full width at half maximum FWHM = 340 Hz, Figure S9), and the  $BCl_3$  adduct **4** a quartet centered at 8.3 ppm, in accordance with the  $I = 3/2$  spin of the  $^{11}B$  nucleus. Further signals of minor intensity are strongly concealed by overlap but may be attributable to the  $^{10}B$  isotopomer ( $I = 3$ ) and/or impurities (Figure S26 and S27). The estimated coupling constant of  $^1J_{P, B} = \sim 300$  Hz suggests an exceptionally strong donor-acceptor bond in **4** as a result of relatively small steric encumbrance.

The  $B(C_6F_5)_3$  and  $Fe(CO)_4$  adducts **3** and **5** in  $C_6D_6$  show  $^{31}P$  NMR resonances in  $C_6D_6$  solution at 37.3 (broad quartet,  $^1J_{P, B} = 150$  Hz) and 124.1 (singlet with a satellite doublet,  $^2J_{P, Si} = 27.4$  Hz) ppm, respectively. The solid-state  $^{31}P$  NMR isotropic shifts of the adducts **3** and **5** match the solution data reasonably well (**3**: 32.8 ppm,  $^1J_{P, B} = 150$  Hz; **5**: 120.2 ppm). The  $^1J_{P, B}$  coupling constant of about 150 Hz (**3**) is comparable to the  $B(C_6F_5)_3$  adduct of Verkade's base ( $^1J_{P, B} = 130$  Hz).<sup>[15]</sup> The  $^{11}B$  NMR spectrum in  $C_6D_6$  of **3** shows a broad singlet at  $-14.9$  ppm, while **4** displays a doublet at 1.4 ppm with a  $^1J_{B, P} = 300$  Hz, the same as observed in the  $^{31}P$  CP/MAS spectrum. In solution, no signal for the  $BPh_3$  adduct **2** could be observed, whereas in the solid state two singlets at  $-4.0$  and  $-7.3$  ppm are found with no discernible splitting due to coupling with the  $^{11}B$  nucleus. As in case of **1**, the occurrence of two signals is most likely due to differing solid state environments, as the FWHM of the  $^{31}P$  signal in the solid state is clearly insufficient to conceal a  $^1J_{P, B}$  coupling constant of 420 Hz (corresponding to  $\Delta\delta = 3.3$  ppm of the two CP-MAS  $^{11}B$  NMR signals of **2**). The  $^{13}C$  NMR spectrum of the iron carbonyl adduct **5** shows two singlets at 213.2 and 213.0 ppm,

in agreement with the corresponding  $^{13}C$  CP/MAS isotropic shift at 211.4 ppm (broad singlet).

Only the  $B(C_6F_5)_3$  and  $FeCO_4$  adducts **3** and **5** are sufficiently soluble in  $C_6D_6$  for the acquisition of  $^{29}Si$  NMR spectra in solution. For **1**, **2**, and **4**,  $^{29}Si$  CP/MAS solid state NMR spectra were obtained instead. The silicon atoms of all compounds give rise to broad, overlapping resonances between  $-77.1$  and  $-83.2$  ppm in the expected region of phenylsubstituted  $T_7$  silsesquioxane backbones without discernible indications for  $^2J$  coupling to the  $^{31}P$  nucleus. Phosphite **1**,  $B(C_6F_5)_3$  adduct **3** and  $FeCO_4$  adduct **5** give rise to two isotropic shifts in a ratio of 2:1 each,  $BPh_3$  adduct **2** displays three signals (in a ratio of 1:1:2) and  $BCl_3$  adduct **4** shows two barely resolved signals in approximate 1:1 ratio. In contrast, the  $B(C_6F_5)_3$  adduct **3** displays three signals at  $-76.7$ ,  $-77.6$  and  $-80.1$  ppm (3:1:3) in  $C_6D_6$  solution, the latter as a doublet with a coupling constant of 27.9 Hz, which is again attributed to  $^2J$  coupling to phosphorus. The presence of a doublet was furthermore confirmed by a second  $^{29}Si$  NMR experiment at a frequency of 59.62 MHz (before: 79.49 MHz), which produces a  $^2J_{P, Si}$  coupling constant of 28.2 Hz (see Figures S15 to S17). The iron carbonyl adduct **5** shows two singlets at  $-76.3$ ,  $-77.4$  and a doublet at  $-81.3$  ppm (3:1:3,  $^2J_{Si, P} = 27.9$  Hz) in  $C_6D_6$ .

The IR spectrum of **5** (ATR) shows a distinct broad signal at  $1938\text{ cm}^{-1}$ , and two smaller bands at  $1985$  and  $2064\text{ cm}^{-1}$  for the carbonyl groups, which are at slightly higher wavenumbers compared to  $(PhO)_3P-Fe(CO)_4$  ( $\nu = 1961, 1996, 2070\text{ cm}^{-1}$ , pentane solution;  $1945, 1985, 2051\text{ cm}^{-1}$  (chloroform solution))<sup>[12,19a]</sup> and in reasonable agreement with IR bands reported for  $Ph_3P-Fe(CO)_4$  ( $1945, 1979, 2044\text{ cm}^{-1}$ , heptane solution).<sup>[19b]</sup>

**Reactivity.** In more recent years it was discovered that even classical Lewis adducts may exhibit FLP reactivity.<sup>[15]</sup> Based on computations, it has been proposed that certain adducts should even be more reactive than FLPs.<sup>[21]</sup> We therefore investigated the  $B(C_6F_5)_3$  adduct **3** and the non-coordinated mixture of  $T_7Ph_7P$  and tris(4-bromo-2,3,5,6-tetramethylphenyl)borane with regards to small molecule activation. As adduct **3** contains the most Lewis acidic borane and features the smallest  $^1J_{P, B}$  coupling constant, we treated it with dihydrogen, carbon dioxide and phenylacetylene to gain insight into potential FLP type reactivity. Unfortunately, the adduct proved to be too unreactive; even at elevated temperatures of up to  $120^\circ\text{C}$  no reaction took place in either case. From a thermodynamic point of view, even small structural deviations from reactive FLPs can inhibit reactivity completely.<sup>[22]</sup> The apparent  $\pi$  interactions between the aromatic systems may stabilize the adduct to a degree that completely prevents any FLP reactivity. Even Lewis pairs with a relatively small tendency towards dissociation were shown to activate phenylacetylene, such as  $Ph_3P-B(C_6F_5)_3$ .<sup>[23]</sup> Nonetheless, a mixture of **1** and tris(4-bromo-2,3,5,6-tetramethylphenyl)borane resulted in the consumption of the phosphite, when treated with dihydrogen. However, the  $^1H$  NMR spectrum in  $C_6D_6$  shows an intractable mixture of signals in the aromatic region, whereas the methyl substituents of the duryl groups and the  $^{11}B$  NMR resonance of the starting material remain unchanged. Signals between  $-14$  and  $-20$  ppm in the  $^{31}P$  NMR spectrum suggest the presence of similar (by-) products to the synthesis of phosphite **1**. The obtained spectroscopic information does not allow for any conclusions on the nature of the product(s). In this case, either the phosphites



donor ability is too low due to the aforementioned electron-withdrawing effect of the T<sub>7</sub> backbone, or the boron center is too sterically encumbered to engage in FLP reactivity. Consequently, phosphite **1** does also not react with small molecules on its own in a straightforward manner, as had been observed with more electron-rich phosphines.<sup>[24]</sup>

## Conclusions

We presented first insights into the donor abilities of phosphite T<sub>7</sub>Ph<sub>7</sub>P **1** and the properties of adducts with boron-centered Lewis acids. Despite large ligand cone angles, the phenyl-substituted **1** coordinates to Lewis acidic boranes of different steric demand, unlike the previously reported cyclohexyl derivative. The short bond length of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> adduct **3** (1.994(4) Å) indicates that even larger Lewis acids may be accommodated, suggesting the propensity of **1** for a rich coordination chemistry, unlike the cyclohexyl substituted **1**a. The inability of adduct **3** to engage in FLP type chemistry is tentatively explained by the attractive π stacking between the aromatic substituents of the ligand and the Lewis acid. Cage phosphite **1** does not form a Lewis adduct with tris(4-bromo-2,3,5,6-tetramethylphenyl)borane, indicating a latent FLP in solution yet no according reactivity was observed.

## Experimental Section

**General.** All manipulations were conducted under a protective argon atmosphere using standard Schlenk techniques or a glovebox. Non-chlorinated solvents were dried over Na/benzophenone (in the presence of tetraglyme in case of aromatic and aliphatic solvents) and distilled under argon atmosphere. Deuterated solvents were dried by reflux over potassium and distilled under argon atmosphere prior to use. Chlorinated deuterated solvents were refluxed and distilled over P<sub>4</sub>O<sub>10</sub> and stored under Argon atmosphere. NMR spectra were recorded on either a Bruker Avance III 300 NMR spectrometer (<sup>1</sup>H: 300.13 MHz, <sup>13</sup>C: 75.46 MHz, <sup>29</sup>Si: 59.63 MHz, <sup>19</sup>F: 282 MHz) or a Bruker Avance III 400 spectrometer (<sup>1</sup>H: 400.13 MHz, <sup>11</sup>B: 128.38 MHz <sup>13</sup>C: 100.61 MHz, <sup>29</sup>Si: 79.49 MHz, <sup>31</sup>P: 161.98 MHz) at 300 K. Melting points were measured in sealed NMR tubes under Ar atmosphere. Elemental analysis was carried out with an elemental analyzer Leco CHN-900. T<sub>7</sub>Ph<sub>7</sub>(OH)<sub>3</sub> was obtained from Hybrid Plastics, Inc. and dried under vacuum prior to use. Phosphorus trichloride was obtained from commercial sources and distilled prior to use. Tris(pentafluorophenyl)borane was obtained from BLD Pharm. Boron trichloride was obtained from Praxair Deutschland and condensed into toluene before use. Triphenylborane was obtained from abcr and used as received. Diiron nonacarbonyl was obtained from Sigma Aldrich and used as received. Triethylamine was obtained from Sigma Aldrich and distilled over CaH<sub>2</sub> prior to use.

**Preparation of T<sub>7</sub>Ph<sub>7</sub>P **1**.** A suspension of 10.35 g of T<sub>7</sub>Ph<sub>7</sub>(OH)<sub>3</sub> in 100 mL toluene is treated with 4.65 mL of NEt<sub>3</sub> and stirred for 10 minutes at room temperature. Then it is cooled down with an ice-water bath for 20 minutes and 1.1 mL of PCl<sub>3</sub> are added. The mixture is stirred for five minutes in the ice bath, then filtered into an equally cooled flask. Another 20 mL of toluene are used to wash the residue. The resulting filtrate is again washed with 20 mL toluene. The mixture is evaporated to dryness to obtain 4.40 g (41%) of a colorless powder (m.p. 200 °C, decomposition). <sup>1</sup>H NMR (400.13 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K) 7.85–7.79 (m, 14H, *m*-Ar-H), 7.15–7.00 (m, 21H, *o*,*p*-Ar-H, overlapping with toluene H). <sup>31</sup>P NMR (161.98 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K) 86.3 (s, <sup>2</sup>J<sub>P, Si</sub> = 37.2 Hz for <sup>29</sup>Si satellites, (SiO)<sub>3</sub>P) ppm. CP/MAS <sup>29</sup>Si NMR (79.49 MHz, 13 kHz, 300 K)

–77.7, –83.2 (each br, (RO)<sub>3</sub>Si-Ar) ppm. CP/MAS <sup>31</sup>P NMR (161.98 MHz, 13 kHz, 300 K) 83.8, 82.1 (each br, (SiO)<sub>3</sub>P) ppm. **Elemental Analysis:** Calc. for C<sub>42</sub>H<sub>35</sub>O<sub>12</sub>PSi<sub>7</sub>: C: 52.59, H: 3.68, Found: C: 54.90, H: 4.12.

**Preparation of T<sub>7</sub>Ph<sub>7</sub>P-BPh<sub>3</sub> **2**:** A mixture of 406 mg of T<sub>7</sub>P and 117 mg of BPh<sub>3</sub> in 5 mL toluene is stirred for 35 minutes at room temperature. The resulting colorless precipitation is separated from the volatiles by filtration and purified by washing with 2 mL of toluene. Drying the product under reduced pressure yields 259 mg (51%) of a colorless solid (m.p. 231–233 °C, decomposition). <sup>1</sup>H NMR (400.13 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K) 7.81–7.75 (m, 14H, *m*-Ar-H), 7.47–7.45 (m, 6H, *m*-Ar-H), 7.21–7.18 (m, 9H, *o*,*p*-Ar-H, overlapping with C<sub>6</sub>D<sub>6</sub>), 7.13–6.96 (m, 21H, *o*,*p*-Ar-H, overlapping with toluene-H) ppm. <sup>11</sup>B NMR (128.38 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K) no signal observed. <sup>31</sup>P NMR (161.98 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K) no signal observed. CP/MAS <sup>11</sup>B NMR (128.38 MHz, 13 kHz, 300 K) –4.0, –7.3 (each s, P-BPh<sub>3</sub>) ppm. CP/MAS <sup>13</sup>C NMR (100.61 MHz, 13 kHz, 300 K) 149.0, 138.3, 135.6, 133.3, 131.2, 128.0, 125.5, 122.6 (each s, Ar-C), 47.4, 9.5 ppm. CP/MAS <sup>29</sup>Si NMR (79.49 MHz, 13 kHz, 300 K) –77.1, –78.2, –80.4 (each br, (RO)<sub>3</sub>Si-Ar) ppm. CP/MAS <sup>31</sup>P NMR (161.98 MHz, 13 kHz, 300 K) 48.1 (br, (SiO)<sub>3</sub>P-B) ppm. **Elemental Analysis:** Calc. for C<sub>60</sub>H<sub>50</sub>BO<sub>12</sub>PSi<sub>7</sub>: C: 59.98, H: 4.20, Found: C: 60.40, H: 4.60.

**Preparation of T<sub>7</sub>Ph<sub>7</sub>P-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> **3**.** A suspension of 458 mg of T<sub>7</sub>Ph<sub>7</sub>P and 273 mg tris(pentafluorophenyl)borane in 5 mL of toluene is stirred for 30 minutes at room temperature, then it is gently heated until fully dissolved. Standing at room temperature overnight affords colorless crystals, whose yield is increased by keeping the flask at 4 °C for three days. Separation of the crystals from the mother liquor yields 292 mg (42%) of a colorless solid (m.p.: above 300 °C, partial decomposition). <sup>1</sup>H NMR (400.13 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K) 7.84–7.79 (m, 6H, *m*-Ar-H), 7.77–7.74 (m, 2H, *m*-Ar-H), 7.66–7.62 (m, 6H, *m*-Ar-H), 7.14–7.003 (m, 17H, *o*,*p*-Ar-H, overlapping with toluene-H), 6.996–6.94 (m, 6H, *o*,*p*-Ar-H). <sup>11</sup>B NMR (128.38 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K) –14.9 (s, P-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>) ppm. <sup>13</sup>C NMR (100.61 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K) 134.3, 134.2, 133.8, 132.6, 132.0, 131.8, 128.7, 128.5 (overlap with toluene), 128.13, 125.49, 125.46 (each s, Ar-C) ppm. <sup>19</sup>F NMR (282 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K) –131.3 (s, *o*-Ar-F), –155.6 (dtr, J = 21 Hz, 6 Hz, *p*-Ar-F), –163.8 (dtr, J = 23 Hz, J = 6 Hz, *m*-Ar-F) ppm. <sup>29</sup>Si NMR (79.49 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K) –76.7, –77.6 (each s, (SiO)<sub>3</sub>Si-Ar), –80.1 (d, <sup>2</sup>J<sub>Si, P</sub>: 27.9 Hz, (PO)(SiO)<sub>2</sub>Si-Ar) ppm. <sup>31</sup>P NMR (161.98 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K) 37.1 (br) ppm. CP/MAS <sup>29</sup>Si NMR (79.49 MHz, 13 kHz, 300 K) –78.3, –82.1 (each br, (RO)<sub>3</sub>Si-Ar) ppm. CP/MAS <sup>31</sup>P NMR (161.98 MHz, 13 kHz, 300 K) 32.7 (overlapping q, <sup>1</sup>J<sub>P, B</sub>: 150 Hz, (SiO)<sub>3</sub>P-B) ppm. **Elemental Analysis:** Calc. for C<sub>60</sub>H<sub>35</sub>BF<sub>15</sub>O<sub>12</sub>PSi<sub>7</sub>: C: 48.98, H: 2.40, Found: C: 50.50, H: 2.62.

**Preparation of T<sub>7</sub>Ph<sub>7</sub>P-BCl<sub>3</sub> **4**.** A stock solution of 3 molar boron trichloride in toluene was added slowly to a solution of 348 mg T<sub>7</sub>Ph<sub>7</sub>P in 18 mL of toluene with a layer of 2 mL toluene in between without stirring. Standing overnight afforded small crystals along with precipitation, which were separated from the volatiles via filtration and purified by washing with another 5 mL of toluene. 169 mg (43%) of a colorless solid were obtained (m.p.: 160 °C, decomposition). <sup>1</sup>H NMR (400.13 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K) 8.01–7.98 (m, 6H, *m*-Ar-H), 7.80, 7.77 (m, 2H, *m*-Ar-H), 7.61–7.58 (m, 6H, *m*-Ar-H), 7.14–6.94 (m, 21H, *o*,*p*-Ar-H, overlap with toluene). <sup>11</sup>B NMR (128.38 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K) 1.4 (d, <sup>1</sup>J<sub>P, B</sub> = 301 Hz P-BCl<sub>3</sub>) ppm. CP/MAS <sup>13</sup>C NMR (100.61 MHz, 13 kHz, 300 K) 133.5, 131.6, 127.7, 125.0 (each s, Ar-C) ppm. CP/MAS <sup>29</sup>Si NMR (79.49 MHz, 13 kHz, 300 K) –78.3, –79.5 (each br, (RO)<sub>3</sub>Si-Ar) ppm. CP/MAS <sup>31</sup>P NMR (161.98 MHz, 13 kHz, 300 K) 8.3 (overlapping q, <sup>1</sup>J<sub>P, B</sub>: 310 Hz, (SiO)<sub>3</sub>P-B) ppm. **Elemental Analysis:** Calc. for C<sub>42</sub>H<sub>35</sub>BCl<sub>3</sub>O<sub>12</sub>PSi<sub>7</sub>: C: 46.86, H: 3.28, Found: C: 49.72, H: 3.82.

**Preparation of T<sub>7</sub>Ph<sub>7</sub>P-FeCO<sub>4</sub> **5**.** A mixture of 301 mg of T<sub>7</sub>Ph<sub>7</sub>P and 248 mg Fe<sub>2</sub>(CO)<sub>9</sub> is stirred in 8 mL of toluene for two hours at room temperature. The volatiles are evaporated under reduced pressure using a warm water bath. The mixture is filtered with 6 mL toluene and the residue washed with another 4 mL. The resulting dark brown filtrate is reduced to dryness to obtain 168 mg (47%) of an equally dark brown solid (m.p.: 180 °C, decomposition). <sup>1</sup>H NMR (400.13 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K)

8.02–7.99 (m, 6H, *m*-Ar-H), 7.80–7.76 (m, 2H, *m*-Ar-H), 7.76–7.73 (m, 6H, *m*-Ar-H), 7.14–6.98 (m, 21H, *o,p*-Ar-H, overlap with toluene). <sup>13</sup>C NMR (100.61 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K) 213.2, 213.0 (each s, Fe-CO), 134.52, 134.47, 132.3, 131.7, 131.6, 129.5, 128.9, 128.7, 128.6, 128.54, 128.48, 127.51, 127.49 (each s, Ar-C) ppm. <sup>29</sup>Si NMR (79.49 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K) –76.3, –77.4 (each s, (SiO)<sub>3</sub>Si-Ar), –81.3 (d, <sup>2</sup>J<sub>P, Si</sub> = 27.9 Hz, (PO)(SiO)<sub>2</sub>Si-Ar) ppm. <sup>31</sup>P NMR (161.98 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K) 124.1 (s, <sup>2</sup>J<sub>P, Si</sub> = 27.4 for <sup>29</sup>Si satellites, (SiO)<sub>3</sub>P-Fe) ppm. CP/MAS <sup>13</sup>C NMR (100.61 MHz, 13 kHz, 300 K) 211.4 (br, Fe-CO), 133.3, 127.6 (each br, Ar-C) ppm. CP/MAS <sup>29</sup>Si NMR (79.49 MHz, 13 kHz, 300 K) –77.5, –83.1 (each br, (RO)<sub>3</sub>Si-Ar) ppm. CP/MAS <sup>31</sup>P NMR (161.98 MHz, 13 kHz, 300 K) 120.2 (s, (SiO)<sub>3</sub>P-Fe) ppm. Elemental Analysis: Calc. for C<sub>46</sub>H<sub>35</sub>FeO<sub>16</sub>Si<sub>7</sub>P: C: 49.02, H: 3.13, Found: C: 50.47, H: 3.63.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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