ORGANOMETALLICS

Observation of a Chloride-Bridged P–P Bond in the Phosphorus Cation $[L(CI)P(\mu-CI)P(CI)L]^+$ (L = NHC)

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Supporting Information

ABSTRACT: A bridging chloride anion between two electrophilic phosphorus centers was observed for the first time in the molecular structure of the novel P–P bonded cation $[L^{Dipp}_2P_2Cl_3]^+$ (2⁺; $L^{Dipp} = 1,3$ -bis(2,6-diisopropylphenyl)-imidazol-2-ylidene). Cation 2⁺ is prepared by the reduction of the monophosphorus species $[L^{Dipp}PCl_2]^+$ (1⁺) with sodium. DFT calculations, AIM and mechanochemical (compliance constants) analyses are used to examine the



bonding situation of this unusual species. The monochloro-substituted cation $[L^{Dipp}_2P_2Cl]^+$ (3⁺) was likewise observed as a reduction product of 1⁺.

INTRODUCTION

Phosphorus has the highest homoatomic single bond energy (205 kJ/mol) of any group 15 element and therefore shows a high propensity to form P–P-bonded frameworks.¹ The chemistry of neutral and anionic polyphosphorus compounds has therefore been flourishing for decades.² Recently, this area has received fresh impetus from the use of stable N-heterocyclic carbenes (NHCs) for the preparation of P–P-bonded species that display P₂, P₃, P₄, and P₁₂ frameworks.³

Several novel types of P–P-bonded phosphorus *cations* have emerged in recent years.⁴ One interesting challenge in this area is the synthesis of cationic polyphosphorus compounds that carry halide substituents.⁵ Mono-, di-, and trichlorophosphanylphosphonium ions have been recently described.⁶ Chloride substituents have also been incorporated into a few oligophosphonium cations through ion transfer.⁷ We recently reported a convenient protocol for the synthesis of cations $[L^{iPr}PCl_2]^+$ and $[L^{iPr}_2PCl]^{2+}$ $(L^{iPr} = 1,3$ -diisopropylimidazol-2ylidene), using an imidazolium-transfer reagent $[L^{iPr}SiMe_3]$ -[OTf].⁸ The chlorine atoms in these reactive cations can be substituted by cyano and azido groups.

Aiming at the synthesis of new polyphosphorus species, we initiated a study of the reaction behavior of our $[LPCl_2]^+$ cations toward low-valent transition metalates and strong reducing agents. Here, we describe the synthesis of the novel cationic diphosphane derivative $[L^{Dipp}_2P_2Cl_3]^+$ (2^+ ; $L^{Dipp} = 1,3$ -bis(2,6-diisopropylphenyl)imidazol-2-ylidene) and the related cation $[L^{Dipp}_2P_2Cl]^+$ (3^+), which are obtained via the reduction of the novel dichloro-substituted cation $[L^{Dipp}PCl_2]^+$ (1^+). The molecular structure of cation 2^+ shows an unprecedented arrangement where a chloride anion symmetrically bridges two

phosphorus centers. The bonding situation in this unusual compound is analyzed by DFT calculations and compliance constant analysis.⁹

RESULTS AND DISCUSSION

 $[L^{Dipp}_{2}P_{2}Cl_{3}][OTf]$ (2[OTf]) and $[L^{Dipp}_{2}P_{2}Cl][OTf]$ (3[OTf]) were initially obtained as a product mixture by reacting the triflate salt $[L^{Dipp}PCl_{2}][OTf]$ (1[OTf]) with the recently reported low-valent iron(0) naphthalene complex $[K(18\text{-crown-6}){Cp*Fe(\eta^{4}\text{-naphthalene})}]$ (K[Fe]) (Scheme 1).¹⁰ K[Fe] acts as a two-electron reducing agent in this reaction. The cationic complex $[Cp*Fe(\eta^{6}\text{-naphthalene})]Cl$ ([Fe]Cl) was identified as the oxidation product by X-ray crystallography and ¹H NMR spectroscopy.¹¹

It is interesting to note that the ratio of 2[OTf] and 3[OTf] formed in the reactions of 1[OTf] (2 equiv) with K[Fe] strongly depends on the temperature and the order of addition of the reagents (Table 1 and Figure S1.5 (Supporting Information)). When K[Fe] is added slowly to a refluxing solution of 1[OTf] in THF, the trichloro-substituted product 2[OTf] is formed as the major product (>90% of the total P content, Table 1, entry 1).

Significant quantities of the monochloro-substituted species 3[OTf] are formed when the reaction is performed at lower temperatures (Table 1, entries 2–4). Compound 3[OTf]

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Scheme 1. Formation of 2[OTf] and 3[OTf] by Reduction of $1[OTf]^a$



^aSee Table 1 for reducing agent, reaction conditions, and ${}^{31}P{}^{1}H$ NMR spectroscopically observed product distribution.

Table 1. Ratio of Cations 2⁺ and 3⁺ Obtained in Selected Reductions of 1[OTf] in THF According to ${}^{31}P{}^{1}H$ NMR Spectra of the Reaction Mixture

entry	reducing agent and reaction conditions	$2[OTf]:3[OTf]^a$
1	1.0 equiv of K[Fe], reflux, 8 h	9.9:0.1
2	1.0 equiv of K[Fe], +65 $^{\circ}$ C	4.5:1
3	1.0 equiv of K[Fe], +30 $^{\circ}$ C	1.5:1
4	1.0 equiv of K[Fe], -30 °C	1:2
5	1.0 equiv of K[Fe], -90 °C	1:8
6	1.2 equiv of KC $_{8\prime}$ –78 $^{\circ}\mathrm{C}$	1.5:1
7	1.1 equiv of K, THF, 50 $^\circ\text{C}$, ultrasonic bath	4:1
8	1.2 equiv of Na, THF, 50 $^\circ\text{C}$, ultrasonic bath	9.5:0.5 ^b

^{*a*}Ratio 2[OTf]:3[OTf] determined by integration of the ³¹P NMR spectra. ^{*b*}Side products are removed quantitatively by fractional crystallization of 2[OTf] (CH₂Cl₂/*n*-hexane); isolated yield of 2[OTf] 60%.

eventually becomes the major product when a THF solution of 1[OTf] (2 equiv) is added slowly to K[Fe] in THF at -90 °C (Table 1, entry 5). Subsequent heating of the reaction mixture did not affect the ratio 2+:3+.

The purification of compounds 2[OTf] and 3[OTf] proved to be difficult, due to their similar solubilities and the presence of significant amounts of the undesired byproduct [L^{Dipp}H]-[OTf], which is difficult to remove by fractional crystallization. Subsequently, we screened other reducing agents in order to develop a more efficient synthetic protocol. Reductions of 1[OTf] with potassium and KC8 resulted in similar product mixtures under various conditions (Table 1, entries 6 and 7).¹² Therefore, it was gratifying to finally discover that cation 2^+ was formed in a clean fashion when the reduction of 1[OTf] was carried out with sodium (1:2) in THF at +60 °C (Table 1, entry 8). Using this procedure, 2[OTf]·2.5CH₂Cl₂ was isolated as air-sensitive orange crystals in 60% yield after crystallization from CH₂Cl₂/pentane.¹¹ Crystals of the solvate 2[OTf]·1.5THF, which contains 1.5 THF molecules in the crystal lattice per formula unit of 2[OTf], were obtained from THF/*n*-hexane. Single-crystal analysis revealed an ion-separated arrangement of the triflate anion and the remarkable cation $[L^{Dipp}_{2}P_{2}Cl_{3}]^{+}$ (2⁺) (Figure 1).¹³ The structure of the cation shows a diphosphorus moiety (P1-P2 = 2.242(1) Å; cf. $d_{cov}(P-P) = 2.22$ A) that is bridged symmetrically by a chlorine atom. To the best of our knowledge, this structural motif is



Figure 1. ORTEP plot of the molecular structure of the cation 2^+ in $2[OTf] \cdot 1.5THF$. Thermal ellipsoids are given at 50% probability (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): P1-P2 = 2.242(1), P1…Cl1 = 2.602(1), P2…Cl1 = 2.594(1), P1-Cl2 = 2.138(1), P2-Cl3 = 2.142(1), P1-C1 = 1.862(3), P2-C28 = 1.852(3), C1-N1 = 1.345(4), C1-N2 = 1.346(5), C28-N3 = 1.361(4), C28-N4 = 1.351(4), C29-N4 = 1.351(4), C29-N4 = 1.376(4), C29-C30 = 1.343(5), C30-N3 = 1.361(4); C1-P1-Cl2 = 92.7(1), C1-P1-P2 = 99.9(1), P1-P2-C28 = 99.6(1), Cl2-P1-P2 = 103.57(5), N1-C1-N2 = 106.6(3), N3-C28-N4 = 105.4(3) P1…Cl1…P2 51.1°, C1-P1-P2-C28 = 161.7(5), dihedral Cl2-P1-P2-C13 = 8.0(3).

unprecedented in phosphorus chemistry, whereas halidebridged structures are frequently observed in transition-metal clusters.¹⁴ A related three-membered P₂B ring was recently reported by Robinson et al., who reacted the diphosphabutadiene $[L^{Dipp}_{2}P_{2}]$ (4)¹² with BH₃ to afford the boronium salt $[L^{Dipp}_{2}P_{2}(\mu-BH_{2})][B_{2}H_{7}]$. In this compound the P–P bond length (2.199(1) Å) is only slightly shorter than that observed in cation $2^{+,15}$ Each phosphorus atom additionally binds to an imidazoliumyl substituent and a terminal chlorine atom with normal P-Cl bond lengths of P1-Cl2 = 2.138(1) Å and P2- $Cl_3 = 2.142(1)$ Å.^{16,17} In contrast, the bridging chlorine atom Cl1 shows unusually long P-Cl distances of P1…Cl1 = 2.602(1) Å and P2...Cl1 = 2.594(1) Å (cf. $d_{cov}(P-Cl) = 2.09$ Å and $d_{vdW}(P-Cl) = 3.7$ Å) and an acute P1-Cl1-P2 angle of merely 51.1°. While the overwhelming majority of chlorosubstituted phosphorus compounds feature P-Cl bond lengths between 1.95 and 2.15 Å,17 we could only find a very few structures with a P-Cl bond length greater than 2.4 Å. The structure of the chloro-phosphoranide $[NEt_4][PPh(CN)_2Cl]$ features a P–Cl distance of 2.810(1) Å.¹⁸ The structure of a *P*chloro-1,3,2-diazaphospholene displays P–Cl distances of 2.6915(4) and 2.759(2) Å, respectively.¹⁹ According to quantum chemical analyses, the weakening of the P-Cl bond in this compound results from hyperconjugation between a π orbital of the C₂N₂ fragment and the $\sigma^*(P-Cl)$ orbital. Finally, an N-heterocyclic carbene adduct of a P-chloroiminophosphane

also shows an elongated P–Cl bond (2.471(2) Å).²⁰ Note that the structure of the monophosphorus cation 1⁺ in 1[OTf] features P–Cl bond lengths of 2.025(2) and 2.040(2) Å.¹³ The single-crystal X-ray diffraction analysis of crystals of 3[OTf] was complicated by severe disorder of the triflate anion. Nevertheless, the NMR spectroscopic results and the preliminary Xray data clearly indicate that the chlorine atom in the molecular structure of cation 3⁺ interacts with one P atom only.

Consistent with the crystallographically determined structure, the ³¹P{¹H} NMR spectrum of compound 2[OTf] in [D₈]THF-d₈ exclusively shows a singlet at δ –34.4 ppm (Figure S1.3 (Supporting Information)). This resonance is shifted significantly to lower field in comparison to Robinson's neutral diphosphorus species [L^{Dipp}₂P₂] (4), which shows a chemical shift of δ –52.0 ppm.^{3c} In the ¹H NMR spectrum, resonances corresponding to four chemically inequivalent *i*Pr substituents are observed. Monochloro-substituted 3[OTf] features two doublets at δ –22.4 and 132.1 ppm (¹J_{PP} = 388.4 Hz) in the ³¹P{¹H} NMR spectrum in THF-d₈.

The Raman spectrum of compound 2[OTf] is highly complex and displays a multitude of bands corresponding to vibrations delocalized over the whole cation (vide infra for relaxed force constants as a local bonding descriptor). On the basis of a comparison with the experimental spectra of $[L^{Dipp}SiMe_3][OTf]$ and $[L^{Dipp}PCl_2][OTf]$ (1[OTf]) and DFT calculations, we tentatively assign bands corresponding to the P–P stretching mode (ν [P–P] 479 cm⁻¹), the P–Cl stretching mode (ν [P-CI] 402 cm⁻¹), and a symmetric deformation of the chlorodiphosphacyclopropane moiety (δ [P...Cl...P] 239 cm⁻¹).¹¹ While the P-P stretching mode is comparable to those in related diphosphanes (e.g., $\nu [\rm P-P]~50\bar{6}~cm^{-1}$ in $Ph(Br)P-P(Br)Ph)_{r}^{21}$ the P-Cl stretching frequency is remarkably small. The symmetrical stretching modes of the P–Cl bonds in PhPCl₂ (ν [P–Cl] 496 cm⁻¹)²² and 1[OTf] (ν [P–Cl] 550 cm⁻¹)¹¹ are at significantly larger wavenumbers. Apparently, the P-Cl bond in 2[OTf] is relatively weak in comparison.

Cation 2^+ may be represented by a multitude of canonical structures. The most intriguing of these, in which the central chlorine atom is either depicted as a chloride (A) or a chloronium (B), are shown in Figure 2. In order to shed more



Figure 2. Selected, plausible canonical structures for the trichloro-substituted cation 2^+ .

light on the bonding situation in 2^+ , DFT calculations were carried out on the model compound $[L'_2P_2Cl_3]^+$ ($2'^+$), where the bulky Dipp substituents were replaced by methyl groups.^{23,24} The P₂Cl₃ core of the optimized molecular structure of $2'^+$ (C_2 symmetry, M06HF/cc-pVTZ²⁵) is in very good agreement with the experimental structure of 2^+ .

A second-order perturbation theory analysis reveals significant interactions between the lone pairs of Cl1 and the σ^* orbitals of the adjacent P1–Cl2 and P2–Cl3 bonds. The P1– Cl1 and P2–Cl1 interactions with the bridging chlorine atom Cl1 show a low Wiberg bond index (WBI) of 0.25. In contrast, the terminal chlorine atoms Cl2 and Cl3 carry three lone pairs and are engaged in a polar covalent P–Cl bond (polarization: 30% P, 70% Cl) with a WBI of 0.81. In comparison with the WBI of the P–Cl bond in the hypothetical dication $[L'_2P_2Cl_2]^{2+}$ (S^{2+}) (WBI = 0.98; Figure 4), which is derived from $2'^+$ by removal of the bridging chlorine atom, this indicates a slightly increased electrostatic contribution to the P1–Cl2 (P2–Cl3) bond.

The charges of the chlorine atoms calculated with the NBO and atoms in molecules (AIM) definitions are summarized in Table 2. $^{26-28}$ With both methods, the bridging chlorine atom

Table 2. Characteristic Topological Data of the Electron
Density in the Bond Critical Points and Charges of the
Chlorine Atoms

bond	compd	$ ho \ ({ m electron} \ { m density})$	$ abla^2 ho $ (Laplacian of $ ho$)	E (electronic energy)			
$P1-P2^{a}$	2'+	0.112	-0.126	-0.052			
	5 ²⁺	0.116	-0.138	-0.057			
	6	0.109	-0.120	-0.050			
$P1-Cl2^a (P2-Cl3)^a$	2'+	0.111	-0.123	-0.082			
	5 ²⁺	0.123	-0.087	-0.107			
	6	0.133	-0.125	-0.120			
	7+	0.135	-0.136	-0.124			
$P1-C1^{a} (P2-C28)^{a}$	2'+	0.146	-0.094	-0.136			
	5 ²⁺	0.159	-0.232	-0.156			
	6	0.149	-0.076	-0.139			
	7+	0.146	-0.113	-0.137			
$P1\cdots Cl1^a (P2\cdots Cl1)^a$	2'+	0.046	0.054	-0.010			
			charge				
atom	compd	AI	M	NBO			
Cl2 (Cl3)	2'+	-0.	555	-0.115			
	5 ²⁺	-0.	516	-0.190			
	6	-0.	590	-0.283			
	7*	-0.	545	-0.220			
P1	2'+	1.	079	0.555			
	5 ²⁺	1.	149	0.534			
	6	1.	055	0.580			
	7^+	1.	748	0.844			
C1	2 ′ ⁺	0.	635	0.042			
	5 ²⁺	0.	533	0.095			
	6	-0.	597	-0.378			
	7* 0.5		585	0.101			
Cl1	$2'^{+}$	-0.	633	-0.386			
^a Numbering of atoms was adapted to fit the numbering of the molecular structure of 2^+ .							

Cl1 shows a significantly higher negative charge than the terminal atoms Cl2 and Cl3, indicating higher bond polarity. The charges of the terminal Cl atoms compare well with those of the related cations $[L'_2P_2Cl_2]^{2+}$ (5^{2+}) and $[L'PCl_2]^+$ (7^+) and are expectedly less negative than in the neutral diphosphane $[Ph_2P_2Cl_2]$ (6).

Further insight was gained from a topological analysis of the electron density using the AIM formalism.²⁷ The quantitative data for the topological parameters $\nabla^2 \rho(r)$, $\rho(r)$, and *E* of the electron density in the bond critical points (BCP) of $[L'_2P_2Cl_3]^+$ ($\mathbf{2'}^+$), $[L'_2P_2Cl_2]^{2+}$ ($\mathbf{5^{2+}}$), $[Ph_2P_2Cl_2]$ (**6**), and $[L'PCl_2]^+$ ($\mathbf{7^+}$) are given in Table 2. Figure 3 shows the contour map of the Laplacian $\nabla^2 \rho(r)$ of the electron density $\rho(r)$ and the topological features of $\rho(r)$ in the P1…Cl1…P2 plane of $\mathbf{2'^+}$.²⁷ A positive curvature (positive Laplacian $\nabla^2 \rho(r)$, blue



Figure 3. Contour map of the Laplacian $\nabla^2 \rho(r)$ of the electron density $\rho(r)$ of $\mathbf{2}'^+$: (black lines) bond paths; (blue lines) positive $\nabla^2 \rho(r)$; (dashed red lines) negative $\nabla^2 \rho(r)$; (orange dots) P atoms; (green dots) Cl atoms; (small red dots) BCPs.

lines) of the electron density dominates along the bond path P1-Cl1 (black lines). This is a typical feature of closed-shell interactions.²⁹ In contrast, a negative curvature is observed along the bond path corresponding to the P1-Cl2 bond. This indicates an accumulation of electron density, which is also reflected in the comparably large electron density ρ in the BCP (0.111) and is typical for a shared interaction. The electronic energy *E* at the BCP is expected to be positive for a closed-shell interaction.²⁹ The values of E for the BCPs of the P1-Cl1 and P2-Cl1 bonds are only marginally negative but significantly higher than the corresponding values for the P1-Cl2 and P2-Cl3 bonds. Figure 4 illustrates the analogous topological features of $\rho(r)$ in the C1–P1–Cl2 plane of compounds 2^{'+}, 5^{2+} , 6, and 7⁺. All four compounds feature very similar characteristics of the electron density. The topological parameters $\nabla^2 \rho(r)$, $\rho(r)$, and E of the P-C, P-P, and exocyclic P-Cl bonds are only marginally affected by the interaction with the bridging chloride ion in compound $2'^+$.

We completed our theoretical investigations with an analysis of the elastic properties of cation $2'^+$ and compounds 5^{2+} , 6, and 7^+ . Several recent papers demonstrate the additional benefit of mechanochemical simulations by means of computed relaxed force constants (inverse compliance constants), especially for an understanding of bond activation, unusual electronic situations, or eminently weak interactions.³⁰⁻³² According to our calculations, the mechanical bond strength of the P1–P2 bond (1.95 N/cm) in $2'^+$ is comparable to that of other covalent two-electron P-P bonds (e.g., in P_4).³³ The mechanical bond strengths of the P1-Cl2 and P2-Cl3 bonds of only 1.1 N/cm indicate a moderate activation of these bonds in comparison to the P–Cl bond in PCl_3 (2.5 N/cm) in dication 5^{2+} (2.7 N/cm), monocation 7^+ (2.9 N/cm), or diphosphane 6 (2.6 N/cm), respectively.³⁴ The P1–Cl2 (P2– Cl3) relaxed force constant of 1.1 N/cm in our model system $2'^+$ is nevertheless still consistent with a covalent bond. In marked contrast, the P1…Cl1 and P2…Cl1 interactions show relaxed force constants of only 0.38 N/cm.

In summary, the quantum chemical analysis confirms the predominantly electrostatic character of the P1–Cl1 and P2–Cl1 interactions. In contrast, the terminal P1–Cl2 and P2–Cl3 bonds are typical covalent single bonds. The results support the conclusion that cation 2^+ is best regarded as a Lewis acid base complex between the dicationic diphosphanediium derivative $[L^{\text{Dipp}}_2\text{P}_2\text{Cl}_2]^{2+}$ and a chloride anion (structure **A**, Figure 2), while a chloronium structure (structure **B**, Figure 2) does not appear to be relevant.

CONCLUSION

In conclusion, we have described the unusual P–P-bonded cation $[L^{\text{Dipp}}_{2}P_{2}Cl_{3}]^{+}$ (2⁺), which shows an unprecedented chloride-bridged structure. According to our quantum chemical calculations, the bonding situation in 2⁺ can be interpreted in terms of an interaction between a dicationic phosphorus-based Lewis acid and a chloride anion. The agreement between the relaxed force constants (inverse compliance constants) on the one hand and the experimental Raman data as well as the AIM analysis on the other hand confirms the appropriateness of compliance constants for the description of weak interactions. Cation 2⁺ is accessible in moderate yield and high purity via the reduction of the imidazolium salt $[L^{\text{Dipp}}PCl_{2}][OTf]$ (1[OTf]) with sodium. The monochloro-substituted cation $[L^{\text{Dipp}}_{2}P_{2}Cl]^{+}$ (3⁺) was identified as a further product of reactions of 1⁺ with the low-valent naphthalene complex K[Fe], indicating that the



Figure 4. Contour maps of the Laplacian $\nabla^2 \rho(r)$ of the electron density $\rho(r)$ of $2^{\prime+}$, 5^{2+} , 6, and 7^+ as depicted below the maps; (black lines) bond paths; (blue lines) positive $\nabla^2 \rho(r)$; (dashed red lines) negative $\nabla^2 \rho(r)$; (orange dots) P atoms; (green dots) Cl atoms; (small green dots) BCPs.

course of such reductions strongly depends on the reducing agent and the reaction conditions. More extensive experimental and theoretical studies are currently underway in order to elucidate the mechanism of formation of cations 2^+ and 3^+ . Ongoing work in our laboratories furthermore concerns the potential ability of other electrophilic phosphorus-based cations to act as halide anion acceptors in a manner similar to that for **2**⁺.

EXPERIMENTAL SECTION

General Remarks. All manipulations were performed in an MBraun Unilab Glovebox or using Schlenk techniques under an atmosphere of purified argon. Dry, oxygen-free solvents (CH2Cl2 C₆H₅F, (distilled from CaH₂, respectively), THF, toluene (distilled from Na/benzophenone respectively), n-hexane (distilled from Na)) were employed. Deuterated benzene (C_6D_6) and THF- d_8 was purchased from Sigma-Aldrich and distilled from Na. Anhydrous deuterated acetonitrile (CD_3CN) and dichloromethane (CD_2Cl_2) were purchased from Sigma-Aldrich. All distilled and deuterated solvents were stored either over molecular sieves (4 Å; CH₂Cl₂, C_6H_5F , toluene, THF- d_8 , C_6D_6 , CD_2Cl_2 , CD_3CN , THF- d_8) or potassium mirror (n-hexane). PCl₃ and Me₃SiOTf were purchased from Sigma-Aldrich. Me₃SiOTf was degassed by three freeze-pumpthaw cycles and distilled prior to use. 1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene³⁵ and $[K(18-crown-6)\{Cp*Fe(\eta^4-C_{10}H_8)\}]$ (K- $\ensuremath{\left[\text{Fe} \right]}\ensuremath{\right)^{10}}$ were prepared according to the literature procedure. All glassware was oven-dried at 160 °C prior to use. NMR spectra were measured on a Bruker AVANCE (III) (¹H (400.03 MHz), ¹³C (100.59 MHz), ³¹P (161.94 MHz)), a Bruker AVANCE (I) (¹H (400.13 MHz), ¹³C (100.61 MHz), ³¹P (161.98 MHz)), or a Bruker AVANCE (II) instrument (¹H (200.13 MHz), ³¹P (81.01 MHz)) at 300 K unless indicated otherwise. Chemical shifts were referenced to δ_{TMS} 0.00 ppm (¹H, ¹³C) and $\delta_{H_3PO_4(85\%)}$ 0.00 ppm (³¹P, externally). Chemical shifts (δ) are reported in ppm. Coupling constants (J) are reported in Hz. Absolute values are reported. Assignments of individual resonances were done using 2D techniques (HMBC, HSQC) where necessary. Melting points were recorded on an electrothermal melting point apparatus (Barnstead Electrothermal IA9100) in sealed capillaries under an argon atmosphere and are uncorrected. Infrared (IR) and Raman spectra were recorded at ambient temperature using a Bruker Vertex 70 instrument equipped with a RAM II module (Nd:YAG laser, 1064 nm). The Raman intensities are reported in percent relative to the most intense peak and are given in parentheses. An ATR cell (diamond) was used for recording IR spectra. The intensities are reported relative to the most intense peak and are given in parentheses using the following abbreviations: vw = very weak, w = weak, m = medium, s = strong, vs = very strong. Elemental analyses were performed on a Vario EL III CHNS elemental analyzer at the IAAC, University of Münster, Germany. Preparation of [L^{Dipp}SiMe₃][OTf].



A slight excess of Me₃SiOTf (19.00 mL, 23.20 g, 105.00 mmol) was slowly added at 0 °C to a suspension of 1,3-bis(2,6-diisopropyl)phenylimidazol-2-ylidene (37.00 g, 95.00 mmol) in fluorobenzene (150 mL). During the course of the addition, the light red suspension turned into a colorless solution. After ~ 1 h, *n*-hexane (100 mL) was added and the colorless precipitate that was formed was separated by filtration. The precipitate was washed with *n*-hexane $(3 \times 30 \text{ mL})$ and

dried in vacuo to yield analytically pure but very moisture sensitive [L^{Dipp}SiMe₃][OTf]: yield 54.00 g (88.40 mmol, 93%). Mp: 188–190 °C, colorless melt. Raman (80 mW, cm⁻¹): ν 3168 (9), 3084 (16), 3035 (6), 2979 (76), 2943 (11), 2910 (95), 2874 (38), 2773 (6), 2729 (9), 1592 (45), 1555 (22), 1469 (24), 1447 (17), 1378 (71), 1340 (31), 1305 (49), 1235 (20), 1104 (23), 1031 (57), 984 (32), 957 (12), 887 (42), 753 (17), 732 (6), 645 (25), 614 (34), 574 (15), 522 (8), 466 (9), 348 (23), 311 (31), 236 (7), 187 (20), 143 (31), 115 (17). IR (ATR, cm⁻¹): v 2968 (w), 1554 (vw), 1461 (w), 1446 (vw), 1414 (vw), 1391 (vw), 1370 (vw), 1326 (vw), 1263 (vs), 1224 (w), 1208 (vw), 1146 (m), 1119 (vw), 1061 (vw), 1030 (m), 936 (vw), 848 (vs), 809 (m), 794 (vw), 781 (vw), 764 (m), 718 (vw), 636 (vs). ¹H NMR (CD₃CN, 300 K, ppm): δ -0.19 (9H, s, C8-H), 1.19 (12H, d, ³J_{HH} = 6.8 Hz, CH(CH₃)₂), 1.36 (12H, d, ${}^{3}J_{HH} = 6.8$ Hz CH(CH₃)₂), 2.41 (4H, quart quart, pseudo sept, ${}^{3}J_{HH} = 6.8$ Hz, ${}^{3}J_{HH} = 6.8$ Hz, C7–H), 7.51 (4H, d, ${}^{3}J_{\rm HH}$ = 7.8 Hz, C5–H), 7.69 (2H, t, ${}^{3}J_{\rm HH}$ = 7.8 Hz, C6– H), 7.95 (2H, s, C2–H). ${}^{13}C{}^{1}H$ NMR (CD₃CN, 300 K, ppm): δ -1.0 (s, C8), 22.4 (s, CH(CH₃)₂), 26.3 (s, CH(CH₃)₂), 30.1 (s, C7), 122.3 (quart, ${}^{1}J_{CF}$ = 320 Hz, CF₃), 125.9 (s, C5), 129.9 (s, C2), 133.0 (s, C3), 133.5 (s, C6), 146.6 (s, C4), 153.5 (s, C1). ¹⁹F{¹H} NMR (CD₃CN, 300 K, ppm): δ -79.2 (s, CF₃). ²⁹Si{¹H} NMR (CD₃CN, 300 K, ppm): δ –1.0 (s). Anal. Calcd for C₃₁H₄₅F₃N₂O₃SSi: C, 60.95; H, 7.43; N, 4.59. Found: C, 60.48; H, 7.13; N, 4.56.

Preparation of 1[OTf].



A suspension of [L^{Dipp}SiMe₃][OTf] (20.00 g, 32.70 mmol) in fluorobenzene (100 mL) was added dropwise to a slight excess of PCl₃ (5.80 g, 3.70 mL, 42.60 mmol). After the mixture was stirred overnight, n-hexane (150 mL) was added. A colorless precipitate was formed, separated by filtration and washed with *n*-hexane (3×30) mL). Analytically pure but very moisture sensitive 1[OTf] was obtained after drying in vacuo: yield 20.44 g (31.79 mmol, 98%). Dec pt: >240 °C, yellow-brown melt. Raman (80 mW, cm⁻¹): ν 3170 (10), 3073 (32), 3033 (5), 2984 (16), 2968 (17), 2939 (40), 2914 (14), 2869 (39), 2769 (7), 2724 (9), 1592 (55), 1540 (33), 1467 (34), 1444 (25), 1365 (91), 1325 (51), 1298 (46), 1237 (25), 1185 (6), 1105 (27), 1032 (59), 984 (32), 955 (14), 886 (50), 754 (24), 732 (14), 617 (32), 573 (11, ν_{asym} [P–Cl]), 550 (8, ν_{sym} [P–Cl]), 522 (98), 485 (10), 463 (18), 445 (12), 418 (5, ν [P–C]), 390 (8), 349 (18), 313 (14), 294 $(16, \delta[P-C-N-C(Me)])$, 237 (20), 165 (93), 117 (33). IR (ATR, cm⁻¹): ν 3169 (vw), 2967 (w), 1539 (vw), 1506 (vw), 1458 (w), 1389 (vw), 1364 (vw), 1325 (vw), 1280 (vw), 1257 (s), 1223 (w), 1204 (vw), 1150 (m), 1060 (vw), 1031 (s), 936 (vw), 811 (w), 782 (vw), 759 (m), 709 (vw), 636 (vs). ¹H NMR (CD₃CN, 300 K, ppm): δ 1.23 (12H, d, ${}^{3}J_{\text{HH}}$ = 6.7 Hz, CH(CH₃)₂), 1.33 (12H, d, ${}^{3}J_{\text{HH}}$ = 6.7 Hz, $CH(CH_3)_2$), 2.37 (4 H, quart quart, pseudo sept, ${}^{3}J_{HH}$ = 6.7 Hz, ${}^{3}J_{HH} = 6.7$ Hz, C7–H), 7.53 (4H, d, ${}^{3}J_{HH} = 7.8$ Hz, C5–H), 7.74 (2H, d, ${}^{3}J_{HH}$ = 7.8 Hz, C6–H), 8.25 (2H, s, C2–H). ${}^{13}C{}^{1}H$ NMR (CD₃CN, 300 K, ppm): δ 22.8 (s, CH(CH₃)₂), 25.8 (s, CH(CH₃)₂), 30.5 (s, C7), 122.3 (quart, ${}^{1}J_{CF}$ = 319.7 Hz, CF₃), 126.2 (s, C6), 130.0 (s, C3), 131.5 (s, C2), 134.2 (s, C5), 143.5 (d, ${}^{1}J_{CP} = 119.0$ Hz, C1), 146.5 (s, C4). ³¹P{¹H} NMR (CD₃CN, 300 K, ppm): δ 113.8 (s). ¹⁹F{¹H} NMR (CD₃CN, 300 K, ppm): δ –79.2 (s, CF₃). Anal. Calcd for C₂₈H₃₆Cl₂F₃N₂O₃PS: C, 52.58; H, 5.67; N, 4.38. Found: C, 52.09; H, 5.50; N, 4.29.



1[OTf] (1.30 g, 2.00 mmol) was combined with sodium (0.10 g, 4.00 mmol), suspended in THF (20 mL), and stirred overnight. The colorless suspension was subsequently heated in an ultrasonic bath at 60 °C for ~12 h. The suspension turned from colorless to orange. This suspension was then filtered, all volatile compounds from the filtrate were removed in vacuo, and the obtained orange solid was dried in vacuo. 2[OTf] was obtained as a yellow solid after recrystallization from dichloromethane/n-hexane; crystals of 2[OTf] suitable for X-ray crystallography were obtained from THF/n-hexane: yield 0.65 g (0.59 mmol, 60%). Recrystallization of 2[OTf] from CH₂Cl₂/pentane at -35 °C yields yellow blocks of 2[OTf]·2.5CH2Cl2, which readily loses one molecule of CH2Cl2 per formula unit when removed from the mother liquor. Dec pt: >216 $^{\circ}$ C, yellow-brown melt. Raman (95 mW, cm⁻¹): ν 3173 (9), 3073 (38), 3038 (5), 2968 (14), 2938 (95), 2915 (14), 2871 (48), 2765 (9), 2721 (13), 1591 (43), 1551 (19), 1466 (40), 1445 (20), 1392 (33), 1364 (47), 1328 (53), 1304 (43), 1255 (5), 1237 (24), 1182 (4), 1166 (10), 1140 (6), 1104 (24), 1045 (15), 1033 (53), 981 (22), 960 (33), 885 (43), 808 (5), 755 (19), 732 (14), 713 (4), 703 (10), 615 (29), 575 (14), 552 (6), 524 (11), 496 (15, ν [P–P]), 479 (16), 466 (5, ν [P– C]), 449 (10, δ[C-P-P-C]), 402 (20, ν[P-Cl]), 349 (20, δ[Cl-P-P-Cl]), 312 (29), 293 (4), 239 (34, δ [P-Cl-P]), 190 (10), 150 (50). IR (ATR, cm⁻¹): ν 3170 (vw), 3073 (vw), 2965 (w), 2932 (vw), 2870 (vw), 1681 (vw), 1590 (vw), 1552 (vw), 1463 (w), 1442 (w), 1419 (w), 1386 (w), 1364 (w), 1328 (w), 1265 (vs), 1223 (vw), 1206 (w), 1182 (vw), 1154 (m), 1121 (vw), 1059 (w), 1030 (m), 929 (vw), 803 (w), 781 (vw), 754 (w), 730 (w), 710 (vw), 635 (s), 572 (w), 517 (w), 497 (vw), 470 (vw), 439 (w). ¹H NMR (THF- d_{8} , 300 K, ppm): δ 0.47 (6H, d, ${}^{3}J_{HH}$ = 6.5 Hz, CH(CH₃)₂ Dipp_B), 0.84 (6H, d, ${}^{3}J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$ Dipp_B), 1.01 (6H, d, ${}^{3}J_{HH} = 6.7$ Hz, $CH(CH_3)_2$ Dipp_{A}), 1.03 (6H, d, ${}^{3}J_{\text{HH}}$ = 6.8 Hz, $\text{CH}(\text{CH}_{3})_{2}$ Dipp_{A}), 1.07 (6H, d, ${}^{3}J_{HH}$ = 6.8 Hz, CH(CH₃)₂ Dipp_B), 1.24 (6H, d, ${}^{3}J_{HH}$ = 6.7 Hz, CH(CH₃)₂ Dipp_A), 1.26 (6H, d, ${}^{3}J_{HH} = 6.8$ Hz, CH(CH₃)₂ Dipp_A), 1.32 (6H, d, ${}^{3}J_{HH} = 6.5$ Hz, CH(CH₃)₂ Dipp_B), 2.51 (2H, quart quart, pseudo sept, ${}^{3}J_{HH} = 6.7$ Hz, ${}^{3}J_{HH} = 6.7$ Hz, CH(CH₃)₂ Dipp_A), 2.56 (2H, quart quart, pseudo sept., ${}^{3}J_{HH} = 6.8$ Hz, ${}^{3}J_{H} = 6.8$ Hz, ${}^{3}J_$ $CH(CH_3)_2$ Dipp_A), 2.59 (2H, quart quart, pseudo sept, ${}^{3}J_{HH} = 6.8$ Hz, ³J_{HH} = 6.8 Hz, CH(CH₃)₂ Dipp_B), 2.69 (2H, quart quart, pseudo sept, ${}^{3}J_{\rm HH}$ = 6.5 Hz, ${}^{3}J_{\rm HH}$ = 6.5 Hz, $CH(CH_{3})_{2}$ Dipp_B), 7.04 (2H, d, ${}^{3}J_{\rm HH}$ = 7.9 Hz, *m*-CH Dipp_B), 7.27 (2H, d, ${}^{3}J_{HH}$ = 7.9 Hz, *m*-CH Dipp_B), 7.37 $(2H, d, {}^{3}J_{HH} = 7.6 \text{ Hz}, \text{ m-CH Dipp}_{A}), 7.42 (2H, d, {}^{3}J_{HH} = 7.6 \text{ Hz}, \text{ m-}$ CH Dipp_A), 7.46 (2H, t, ${}^{3}J_{HH}$ = 7.9 Hz, *p*-CH Dipp_B), 7.57 (2H, t, ${}^{3}J_{HH}$ = 7.6 Hz, p-CH $Dipp_A$), 8.00 (2H, s, C2-H), 8.06 (s, 2H, C3-H). ¹³C{¹H} NMR (THF- d_{8} , 300 K, ppm): δ 21.6 (s, CH(CH₃)₂ Dipp_B), 22.6 (s, CH(CH₃)₂ Dipp_A), 23.2 (s, CH(CH₃)₂ Dipp_{A,B}), 26.3 (s, $CH(CH_3)_2 \text{ Dipp}_A$), 26.4 (s, $CH(CH_3)_2 \text{ Dipp}_{AB}$), 26.6 (s, $CH(CH_3)_2$ Dipp_B), 29.4 (s, CH(CH₃)₂ Dipp_B), 29.9 (s, CH(CH₃)₂ Dipp_A), 30.3 $(s, CH(CH_3)_2 \text{ Dipp}_A), 30.4 (s, CH(CH_3)_2 \text{ Dipp}_B), 122.4 (quart, {}^1J_{CF} =$ 321.8 Hz, CF₃), 124.4 (s, m-C Dipp_B), 125.2 (s, m-C Dipp_A), 125.8 (s, *m*-C Dipp_B), 126.0 (s, *m*-C Dipp_A), 128.4 (s, C2), 130.5 (s, C3), 132.1 (s, *i*-C Dipp_B), 132.3 (s, *i*-C Dipp_A), 132.9 (s, *p*-C Dipp_A), 133.4 (s, *p*-C Dipp_B), 147.2 (s, o-C Dipp_A), 147.8 (s, o-C Dipp_A), 148.0 (s, o-C Dipp_B), 148.8 (s, o-C Dipp_B), 152.0 (dd, ${}^{1}J_{CP} = 53.5$ Hz, ${}^{2}J_{CP} = 46.2$ Hz, C1). ³¹P{¹H} NMR (THF- d_8 , 300 K, ppm): δ –34.4 (s). ¹⁹F{¹H} NMR (THF- d_{8} , 300 K, ppm): δ -79.1 (s, CF₃). Anal. Calcd for

2[OTf]·1.5CH₂Cl₂ ($C_{56.5}H_{75}Cl_6F_3N_4O_3P_2S$): C, 55.16; H, 5.99; N, 4.59. Found: C, 55.53; H, 6.19; N, 4.59 (consistent with the integration of the ¹H NMR spectrum of dissolved crystalline material in CD₂Cl₂ after recrystallization from CH₂Cl₂/pentane at -35 °C). Preparation of 3[OTf].



Dipp

A solution of 1[OTf] (0.48 g, 0.75 mmol) in 10 mL of THF was added dropwise to a solution of $[K(18\text{-crown-6})\{Cp^*Fe(\eta^4\text{-}C_{10}H_8)\}]$ (K[Fe], 0.23 g, 0.38 mmol) in 20 mL of THF at -90 °C. The reaction mixture turned green at first and then yellow within 2 days. An orange precipitate of [Fe]Cl was formed, which was isolated and characterized as described in the Supporting Information. The mother liquor of this crystalline precipitate was evaporated. The residue was washed with toluene $(3 \times 20 \text{ mL})$ and dissolved in THF (20 mL). The THF solution was filtered and layered with 20 mL of toluene. The first fraction, containing mostly [L^{Dipp}H]Cl and [L^{Dipp}H][OTf], crystallized first at -18 °C. A second crystalline fraction was obtained from the concentrated mother liquor that contained 90% 3[OTf] and 10% 2[OTf] according to ³¹P NMR spectroscopy. All attempts to separate these two compounds by crystallization were not successful: yield of 3[OTf] 0.065 g (0.06 mmol, 15%), ¹H NMR (THF-*d*₈, 300 K, ppm): δ 0.79 (d, 6H, CH(CH₃)₂), 0.86 (d, 6H, CH(CH₃)₂), 1.00 (d, 6H, CH(CH₃)₂), 1.02 (d, 6H, CH(CH₃)₂), 1.05 (d, 6H, CH(CH₃)₂), 1.09 (d, CH(CH₃)₂), 1.19 (d, 6H, CH(CH₃)₂), 1.22 (d, 6H, CH(CH₃)₂), 2.25 (quart quart, pseudo sept, 2H, CH(CH₃)₂), 2.39 (sept, 2H, CH(CH₃)₂), 2.50 (overlapping sept, 4H, CH(CH₃)₂), 7.17 (d, 4H, m-H Dipp), 7.25 (d, 2H, m-H Dipp), 7.32 (d, 2H, m-H Dipp), 7.44 (t, 2H, *p*-H Dipp), 7.49 (t, 2H, *p*-H Dipp), 7.49 (s, 2H, H_{2,3}), 8.05 (s, 2H, H_{29,30}). ¹³C{¹H} NMR (THF- d_8 , 300 K, ppm): δ 22.4 (CH(CH₃)₂), 23.2 $(CH(CH_3)_2)$, 23.5 $(CH(CH_3)_2)$, 23.6 $(CH(CH_3)_2)$, 24.9 $(CH(CH_3)_2)$, 25.6 $(CH(CH_3)_2)$, 25.8 $(CH(CH_3)_2)$, 26.0 $(CH-CH_3)_2)$, 26.0 $(CH-CH_3)_2$), 26.0 $(CH-CH_3)_2$)), 26.0 $(CH-CH_3)_2$)), 26.0 (CH-C $(CH_3)_2$, 29.8 $(CH(CH_3)_2)$, 29.9 $(CH(CH_3)_2)$, 122.4 (quart, ${}^1J_{CF} =$ 323 Hz, CF₃), 124.9 (*m*-C of Dipp), 125.6 (*m*-C of Dipp), 126.0 (*m*-C of Dipp), 126.7 (C_{2,3}), 129.5 (C_{29,30}), 132.1 (p-C Dipp), 132.8 (p-C Dipp), 132.8 (i-C Dipp), 133.7 (i-C Dipp), 146.0 (o-C Dipp), 146.3 (o-C Dipp), 147.1 (o-C Dipp), 147.8 (o-C Dipp), 151.8 (dd, ${}^{1}J_{CP}$ = (b) C Dipp), 147.1 (b) C Dipp), 147.3 (b) C Dipp), 131.3 (dd, $J_{CP} = 87.3 \text{ Hz}, {}^{2}J_{CP} = 27.4 \text{ Hz}, C28), 165.7 (dd, {}^{1}J_{CP} = 118.9 \text{ Hz}, {}^{2}J_{CP} = 34.6 \text{ Hz}, C1). {}^{31}P{}^{1}H{}$ NMR (THF- d_8 , 300 K, ppm): $\delta - 22.4$ (P1, d, {}^{1}J_{PP} = 382.2 \text{ Hz}, PPCl), 132.1 (P1, d, {}^{1}J_{PP} = 382.2 \text{ Hz}, PPCl). {}^{19}F{}^{1}H{} NMR (THF- d_{8} , 300 K, ppm): δ -79.1 (s, CF₃).

ASSOCIATED CONTENT

S Supporting Information

Text, tables, figures, and CIF files giving experimental, spectroscopic, and crystallographic data for compounds 1[OTf], 2[OTf], 3[OTf], 4, and [Fe]Cl. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC files 782415–782419 also contain crystallographic data for these compounds.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Wiberg, N. Holleman-Wiberg: Lehrbuch der Anorganischen Chemie, 102nd ed., de Gruyter: Berlin, 2007; p 310.

(2) (a) Cowley, A. H. Chem. Rev. 1965, 65, 617. (b) von Schnering,
H. G. Angew. Chem. 1981, 93, 44; Angew. Chem., Int. Ed. Engl. 1981,
20, 33. (c) Baudler, M. Angew. Chem. 1982, 94, 520; Angew. Chem., Int. Ed. 1982, 21, 492. (d) Baudler, M. Angew. Chem. 1987, 99, 429; Angew. Chem., Int. Ed. 1987, 26, 419. (e) Baudler, M.; Glinka, K. Chem. Rev.
1993, 93, 1623. (e) Dyker, C. A.; Bertrand, G. Science 2008, 321, 1050. (f) Wolf, R.; Uhl, W. Angew. Chem. 2009, 121, 6905; Angew. Chem., Int. Ed. 2009, 48, 6774. (g) Gomez-Ruiz, S.; Hey-Hawkins, E. Coord. Chem. Rev. 2011, 255, 1360.

(3) Selected recent references: (a) Masuda, J. D.; Schoeller, W. W.; Donnadieu, B.; Bertrand, G. J. Am. Chem. Soc. 2007, 129, 14180.
(b) Masuda, J. D.; Schoeller, W. W.; Donnadieu, B.; Bertrand, G. Angew. Chem. 2007, 119, 7182; Angew. Chem., Int. Ed. 2007, 46, 7052.
(c) Wang, Y.; Xie, Y.; Wei, P.; King, R. B.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. J. Am. Chem. Soc. 2008, 130, 14970.
(d) Back, O.; Kuchenbeiser, G.; Donnadieu, B.; Bertrand, G. Angew. Chem. 2009, 121, 5638; Angew. Chem., Int. Ed. 2009, 48, 5530.

(4) (a) Weigand, J. J.; Burford, N.; Decken, A.; Schulz, A. Eur. J. Inorg. Chem. 2007, 4868. (b) Dyker, C. A.; Burford, N. Chem. Asian J. 2008, 3, 28.

(5) (a) Tarasova, R. I.; Zykova, T. V.; Shagvaleev, F. Sh.; Sitdikova, T. Sh.; Moskva, V. V. Zh. Obshch. Khim. 1989, 60, 1775. (b) Tarasova, R. I.; Sitdikova, T. Sh.; Zykova, T. V.; Shagvaleev, F. Sh.; Moskva, V. V.; Kormachev, V. V.; Rusanov, V. M.; Baranov, Yu. I.; Danilov, S. D. U.S.S.R. Patent SU 1449565, July 1, 1989; Scifinder Scholar: 1989:497499. (c) Shagvaleev, F. Sh.; Zykova, T. V.; Tarasova, R. I.; Sitdikova, T. Sh.; Moskva, V. V. Zh. Obshch. Khim. 1990, 60, 1775. (d) Tarasova, R. I.; Zykova, T. V.; Shagvaleev, F. Sh.; Sitdikova, T. Sh.; Moskva, V. V. Zh. Obshch. Khim. 1990, 60, 1775. (d) Tarasova, R. I.; Zykova, T. V.; Shagvaleev, F. Sh.; Sitdikova, T. Sh.; Moskva, V. V. Zh. Obshch. Khim. 1991, 61, 2529. (e) Krossing, I.; Raabe, I. Angew. Chem. 2001, 113, 4544; Angew. Chem., Int. Ed. 2001, 40, 4406. (f) Gonsior, M.; Krossing, I.; Müller, L.; Raabe, I.; Jansen, M.; van Wüllen, L. Chem. Eur. J. 2002, 8, 4475. (g) Krossing, I. Dalton Trans. 2002, 500. (h) Holthausen, M. H.; Feldmann, K.-O.; Schulz, S.; Hepp, A.; Weigand, J. J. Inorg. Chem. 2012, 51, 3374.

(6) Carpenter, Y.-Y.; Burford, N.; Lumsden, M. D.; McDonald, R. Inorg. Chem. 2011, 50, 3342.

(7) Weigand, J. J.; Burford, N.; Davidson, R. J.; Cameron, T. S.; Seelheim, P. J. Am. Chem. Soc. 2009, 131, 17943.

(8) Weigand, J. J.; Feldmann, K.-O.; Henne, F. D. J. Am. Chem. Soc. 2010, 132, 16321.

(9) Brandhorst, K.; Grunenberg, J. Chem. Soc. Rev. 2008, 37, 1558.

(10) (a) Wolf, R.; Schnöckelborg, E.-M. Chem. Commun. 2010, 46, 2832. (b) Schnöckelborg, E.-M.; Weigand, J. J.; Wolf, R. Angew. Chem. 2011, 123, 6786; Angew. Chem., Int. Ed. 2011, 50, 6657.
(c) Schnöckelborg, E.-M.; Khusniyarov, M.; de Bruin, B.; Hartl, F.; Langer, T.; Eul, M.; Schulz, S.; Pöttgen, R.; Wolf, R. Inorg. Chem. 2012, 51, 6719.

(11) See the Supporting Information for details.

(12) We note that Robinson's landmark diphosphabutadiene $[L^{Dipp}_{2}P_{2}]$ (4)^{3c} can be isolated in high (>95%) yield by reducing 1[OTf] using a slight excess of KC₈ (1:3.5) in THF (cf. the Supporting Information).

(13) Details of the X-ray analyses of 1[OTf], 2[OTf]. 1.5THF, and [Fe]Cl are given in the Supporting Information.

(14) Shriver, D. F.; Kaesz, H. D.; Adams, R. D. The Chemistry of Metal Cluster Complexes; Wiley-VCH: Weinheim, Germany, 1990.

(15) Wang, Y.; Xie, Y.; Abraham, M. Y.; Wei, P.; Schaefer, H. F., III;
Schleyer, P. v. R.; Robinson, G. H. Chem. Commun. 2011, 47, 9224.
(16) Wiberg, N. Holleman-Wiberg: Lehrbuch der Anorganischen Chemie, 102nd ed.; de Gruyter: Berlin, 2007; p 777.

(17) A survey in the Cambridge Crystal Structure database (CSD version 5.33, Nov 2011) yielded 3355 entries with P–Cl distances in the range 1.851–2.810 Å (median 2.005 Å). Out of these entries, 3196 structures showed P–Cl distances between 1.938 and 2.155 Å (median 2.004 Å).

(18) Deng, R. M. K.; Dillon, K. B.; Sheldrick, W. S. J. Chem. Soc., Dalton Trans. 1990, 551.

(19) (a) Gudat, D.; Haghverdi, A.; Hupfer, H.; Nieger, M. Chem. Eur. J. 2000, 6, 3414. (b) Denk, M. K.; Gupta, S.; Lough, A. J. Eur. J. Inorg. Chem. 1999, 41.

(20) Burford, N.; Cameron, T. S.; LeBlanc, D. J.; Phillips, A. D.; Concolino, T. E.; Lam, K.-C.; Rheingold, A. L. J. Am. Chem. Soc. 2000, 122, 5413.

(21) Hassler, K.; Höfler, F. Z. Anorg. Allg. Chem. 1978, 448, 125.

(22) Schindlbauer, H.; Stenzenberger, H. Spectrochim. Acta, Part A 1970, 26, 1707.

(23) *Gaussian 09, Revision A.02,* 2009; for a complete list of authors see the Supporting Information.

(24) See the Supporting Information for further details regarding the choice of the functional and basis set and the effects of using methyl instead of diisopropylphenyl substituents.

(25) Zhao, Y.; Truhlar, D. G. J. Phys. Chem. A 2006, 110, 13126.

(26) (a) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. NBO Version 3.1. (b) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. Chem. Rev. **1988**, 88, 899.

(27) Bader, R. F. W. Atoms in Molecules: A Quantum Theory; Oxford University Press: Oxford, U.K., 1995; International Series of Monographs on Chemistry (cf. the Supporting Information).

(28) Keith, T. A. AIMAll (Version 11.08.23); TK Gristmill Software, Overland Park KS, 2011 (aim.tkgristmill.com).

(29) Bader, R. F. W. J. Phys. Chem. A 1998, 102, 7314.

(30) Shaik, S.; Danovich, D.; Wu, W.; Su, P.; Rzepa, H. S.; Hiberty, P. C. Nat. Chem. 2012, 4, 195.

(31) Espinosa, A.; Streubel, R. Chem. Eur. J. 2011, 17, 3166.
(b) Schreiner, P. R. Angew. Chem. 2009, 121, 8277; Angew. Chem., Int. Ed. 2009, 48, 8133.

(32) Grunenberg, J.; Barone, G. RSC Adv. 2013, 3, 4757.

(33) (a) Katsyuba, S.; Schmutzler, R.; Grunenberg, J. Dalton Trans. 2005, 1701. (b) Brandhorst, K.; Grunenberg, J. Chem. Soc. Rev. 2008, 37, 1558.

(34) In order to test the robustness of our numerical results, we calculated the mechanical bond properties for the experimental species 2^+ with 2,6-diisopropylphenyl (Dipp) substituents applying the M06HF method and a smaller basis set of double- ζ quality (6-31G(d)). The mechanical bond strength is more or less unaffected (0.40 N/m); cf. the Supporting Information.

(35) Arduengo, A. J., III; Krafczyk, R.; Schmutzler, R. Tetrahedron 1999, 50, 14523.