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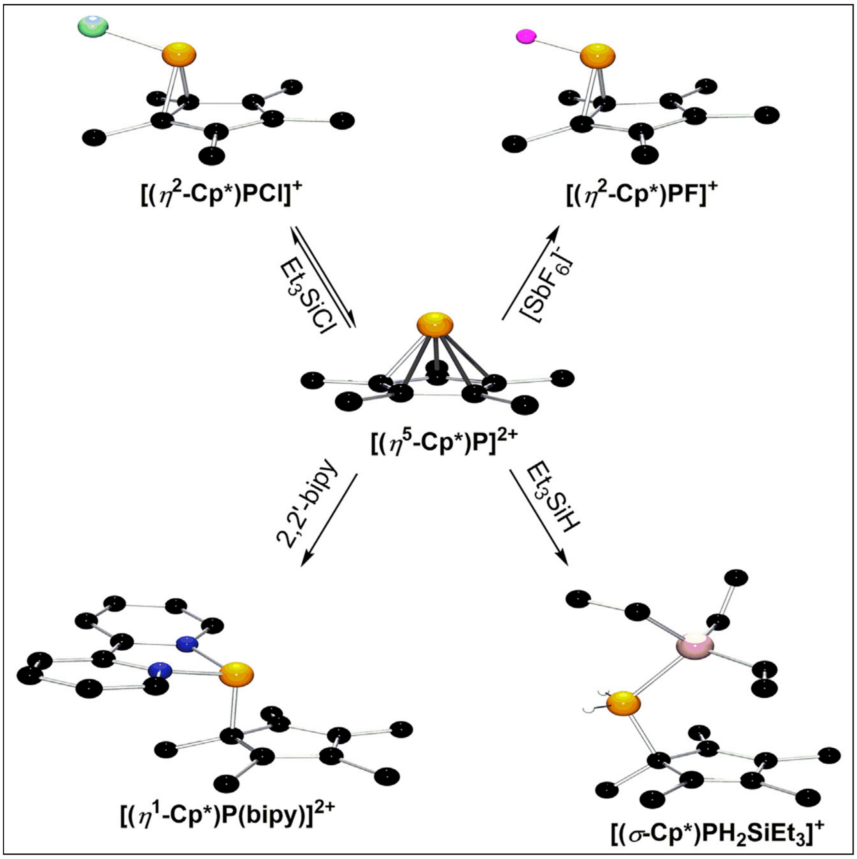
A Phosphorus Lewis Super Acid: η^5-Pentamethylcyclopentadienyl Phosphorus Dication



An η^5-pentamethylcyclopentadienyl phosphorus dication $[(\eta^5\text{-Cp*})P]^{2+}$ has been synthesized and characterized, representing an η^5-cyclopentadienyl-bound phosphorus species. The reactivity of the dication reveals its phosphorus-centered Lewis super acidity and interesting hapticity shifts of the cyclopentadienyl ring.

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HIGHLIGHTS

η^5-Pentamethylcyclopentadienyl phosphorus dication

Unique phosphorus-centered Lewis super acid reactivity

Intriguing hapticity shifts of the cyclopentadienyl ring

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A Phosphorus Lewis Super Acid: η^5-Pentamethylcyclopentadienyl Phosphorus Dication

Jiliang Zhou,[1] Liu Leo Liu,[1] Levy L. Cao,[1] and Douglas W. Stephan[1,2,*]

SUMMARY

Abstraction of chloride from (Cp*PCl$_2$) with the silylium salt [Et$_3$Si][B(C$_6$F$_5$)$_4$] afforded [(η^2-Cp*)PCl][B(C$_6$F$_5$)$_4$] (**1**), whereas further chloride abstraction using another equivalent [Et$_3$Si][B(C$_6$F$_5$)$_4$] was unsuccessful. The corresponding species [(η^2-Cp*)PF][B(C$_6$F$_5$)$_4$] (**2**) was derived by fluoride abstraction from (Cp*PF$_2$). Treatment of (Cp*PF$_2$) with 2 equiv of [Et$_3$Si][B(C$_6$F$_5$)$_4$] gave [(η^5-Cp*)P][B(C$_6$F$_5$)$_4$]$_2$ (**3**), representing an η^5-Cp that is bound to phosphorus. **3** behaves as a phosphorus-based Lewis super acid, abstracting fluoride from [SbF$_6$]$^-$ anion with concurrent η^5-η^2-Cp* rearrangement to give **2**. Similarly, the extremely high Lewis acidity and chlorophilicity of **3** is indicated by the equilibration of **3** with Et$_3$SiCl to generate **1** and [Et$_3$Si][B(C$_6$F$_5$)$_4$]. The coordination of 2,2′-bipyridine (bipy) to the phosphorus of **3** induces the η^5-η^1-Cp* rearrangement, leading to a "slipped sandwich" compound [(η^1-Cp*)P(bipy)][B(C$_6$F$_5$)$_4$]$_2$ (**4**). **3** also reacts with Et$_3$SiH via η^5-σ-Cp* rearrangement, affording [(σ-Cp*)PH$_2$SiEt$_3$][B(C$_6$F$_5$)$_4$] (**5**) and [Et$_3$Si][B(C$_6$F$_5$)$_4$].

The Bigger Picture

The last two decades have witnessed the renaissance of main-group chemistry. Of particular interest are instances in which main-group elements behave analogously to transition metals. The landmark work that described metallocene complexes over 60 years ago has continuously evolved and influenced modern organometallic chemistry and catalysis. The present work describes an η^5-pentamethylcyclopentadienyl phosphorus dicationic species, mimicking the common coordination mode of cyclopentadienyl ligands with transition metals. This η^5-pentamethylcyclopentadienyl phosphorus dication is shown to exhibit unique phosphorus-centered Lewis super acidity by undergoing interesting hapticity shifts of the cyclopentadienyl ring upon reactions. Although main-group-centered Lewis acids have been extensively exploited in organic transformations, catalysis, and material chemistry, the present work provides a unique perspective on phosphorus-based Lewis acids.

INTRODUCTION

Since the landmark discovery of ferrocene by Kealy and Pauson,[1] and subsequent seminal work on metallocene complexes by Fischer and Wilkinson in the 1950s,[2–4] systems containing π-bound ligands have permeated organometallic and inorganic chemistry. Among the most prevalent organometallic ligands have been 6-electron aromatic anionic cyclopentadienyl (Cp) groups, which typically adopt an η^5-binding mode. Indeed, a wide variety of transition-metal derivatives containing η^5-Cp ligands have been used in countless organic transformations and catalyses.[5] Although efforts to mimic transition-metal chemistry with main-group compounds have garnered much attention in recent years,[6–9] the use of η^5-Cp ligands in *p*-block element compounds remains relatively underexplored.[10–12] Among the known examples, group 13 decamethylmetallocenium cations [(Cp*)$_2$E]$^+$ (E = B,[13,14] Al,[15] Ga[16]) have been reported, in which only [(η^5-Cp*)$_2$Al]$^+$ adopts an η^5/η^5 binding mode analogous to ferrocene.[17] In contrast to the discrete cations, the low valent neutral compounds [(η^5-Cp*)E]$_n$ (E = Al[18], Ga[19], In[20], Tl[21]) (Figure 1A) form cluster structures in the solid state. In addition, a terminal borylene complex containing an η^5-Cp* ligand, namely [(η^5-Cp*)BFe(CO)$_4$],[22] was described by Cowley. In addition, examples of dicationic [(η^5-Cp*)B(L)]$^{2+}$ species have been reported.[23,24] For group 14 derivatives, the heavier elements form metallocenes(II) [(η^5-Cp*)$_2$E] (E = Si,[25] Ge,[26] Sn,[26] Pb[27]) and half-naked E(II) cations of the form [(η^5-Cp*)E]$^+$ (E = Si,[28] Ge,[26] Sn,[29] Pb[30]) (Figure 1B). Interestingly, a carbon dication [C$_6$(CH$_3$)$_6$]$^{2+}$, recently reported by Malischewski and Seppelt,[31] could be described as an η^5-Cp*-bonded carbon dication [(η^5-Cp*)CCH$_3$]$^{2+}$.[32] Group 15 analogs of formulae [(Cp*)$_2$Pn]$^+$ (Pn = P,[33] As,[34]

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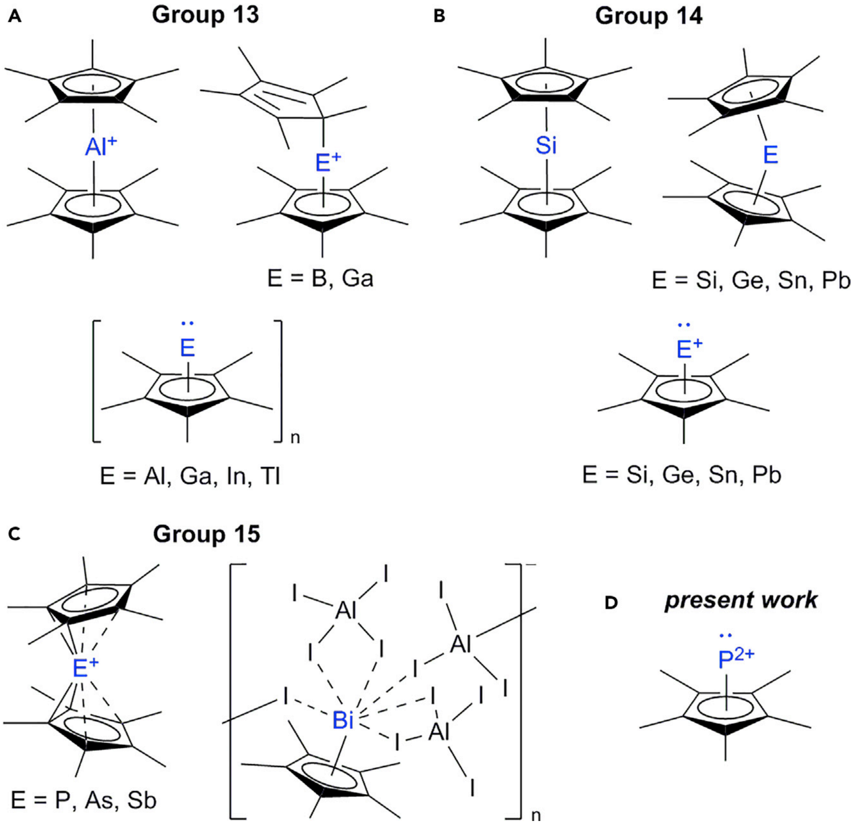

Figure 1. Cp*-Bonded Main-Group Species

(A–C) Representative examples of (A) group 13, (B) group 14, and (C) group 15 Cp*-bonded main-group species.

(D) Present work.

Sb[35,36]) have been isolated (Figure 1C), and NMR data show fluxionality of the Cp* ligands in solution[37] consistent with rapid haptotropic shifts, and X-ray structure analysis revealed that the Cp* ligands are not ideally η^5-bonded to the central Pn atoms. For example, crystallographically nonequivalent C–P distances were described for $[(\eta^2\text{-Cp*})_2\text{P}]^+$. Although a number of related group 15 cations $[(\eta^2\text{-Cp*})\text{PnX}]^+$ (Pn = P, X = NMe_2,[38] *t*Bu,[39] NH*t*Bu,[40] Cl[33]; Pn = As, X = Cl[33]) have been studied, the only dication of the form $[(\eta^5\text{-Cp*})\text{Pn}]^{2+}$ was reported in the bismuth salt $(\eta^5\text{-Cp}_2\text{Al})\,(\eta^5\text{-Cp*Bi})\,(\mu\text{-AlI}_4)\,(\text{AlI}_4)_2\cdot 2\text{C}_7\text{H}_8$.[41]

Strong Lewis acids based on main-group elements have gained increasing attention.[42–45] Our group has a longstanding interest in phosphorus-based Lewis acids, as well as their application in frustrated Lewis pair chemistry and Lewis acid catalysis.[46,47] This prompted us to envision the synthetic target $[(\eta^5\text{-Cp*})\text{P}]^{2+}$. In this article, we describe the synthesis of this target. In addition, we examine its reactivity, demonstrating that this species features a half-naked dicationic phosphorus center that exhibits unique phosphorus-based Lewis super acid reactivity proceeding with changes in the hapticity of the Cp* ring.

RESULTS AND DISCUSSION

We hypothesized that $[\text{Cp*P}]^{2+}$ would feature an η^5-structure and obtained preliminary confirmation of this proposal using density functional theory (DFT) calculations at the M06-2X/Def2-SVP level of theory. No local minima featuring η^n (n = 1–4)

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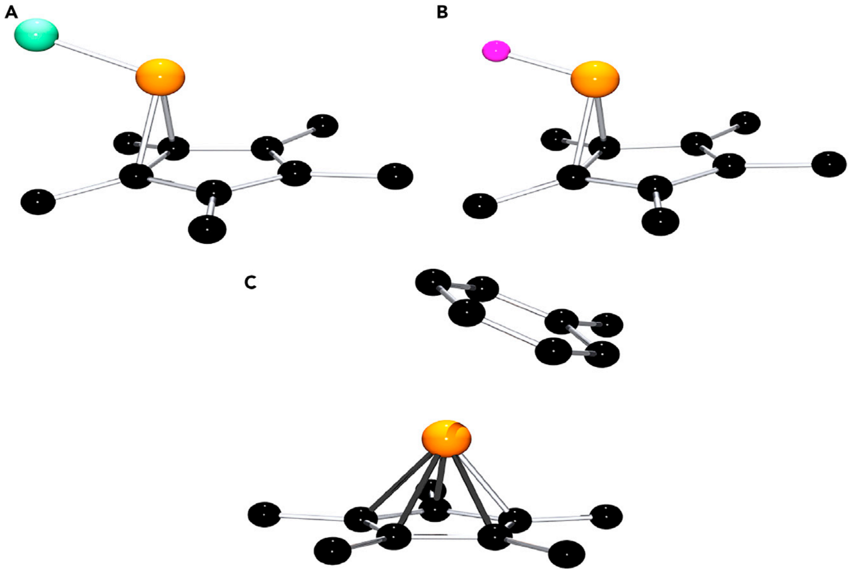

Figure 2. X-Ray Structures of 1–3

POV-ray depictions of the cations of (A) **1**, (B) **2**, and (C) **3**. Coloring is as follows: C, black; P, orange; Cl, green; F, pink. All H atoms, solvent residue, and the $[B(C_6F_5)_4]^-$ anions are omitted for clarity.

binding modes were identified in unrestricted geometry optimizations. Targeting the synthesis of $[Cp^*P]^{2+}$, we initially attempted dechlorination of the Cp*-substituted dichlorophosphine (Cp^*PCl_2) with an equimolar portion of silylium salt $[Et_3Si][B(C_6F_5)_4]$. This reaction afforded the salt $[(\eta^2\text{-}Cp^*)PCl][B(C_6F_5)_4]$ (**1**) (Figures S1–S5),[33] the formulation of which was confirmed crystallographically (Table S1; Figures 2A and S38A). Further chloride abstraction using an additional equivalent $[Et_3Si][B(C_6F_5)_4]$ was unsuccessful.

Noting the high fluorophilicity of silylium cations, the corresponding difluorophosphine Cp^*PF_2 was prepared. Defluorination of Cp^*PF_2 with an equimolar portion of $[Et_3Si][B(C_6F_5)_4]$ afforded $[(\eta^2\text{-}Cp^*)PF][B(C_6F_5)_4]$ (**2**) (Figures S6–S10), with distinctive doublet resonances at −73.9 ppm ($^1J_{PF}$ = 1,211 Hz) and 17.2 ppm ($^1J_{PF}$ = 1,211 Hz) in the $^{31}P\{^1H\}$ NMR and $^{19}F\{^1H\}$ NMR spectra, respectively. The formulation of **2** was further unambiguously confirmed by an X-ray diffraction study (Table S1; Figures 2B and S38B).

Gratifyingly, double defluorination of Cp^*PF_2 with 2 equiv of $[Et_3Si][B(C_6F_5)_4]$ in toluene immediately produced a yellow precipitate **3**. The formation of Et_3SiF was confirmed by ^{19}F NMR spectroscopy of the crude mixture. After workup, **3** was isolated as a pale yellow solid in 97% yield (Scheme 1; Figures S11–S15). Compound **3** was sparingly soluble in common organic solvents. Nevertheless, it dissolved in 1,2-difluorobenzene (DFB), allowing for spectroscopic characterization. The ^{31}P NMR spectrum of **3** revealed a very upfield sharp singlet at −401.6 ppm, and the ^{19}F NMR spectrum showed a set of signals attributable to the $[B(C_6F_5)_4]^-$ anion. Moreover, the single resonances in the ^1H (C_5Me_5, 2.17 ppm) and ^{13}C (C_5Me_5, 137.3 ppm; C_5Me_5, 8.8 ppm) NMR spectra imply the presence of a symmetrically bound Cp* ligand in the solution state (Figures S11 and S12). Single crystals of **3** were obtained by layering pentane on a toluene/DFB solution of **3** at room temperature, and the formulation of **3** was confirmed as $[(\eta^5\text{-}Cp^*)P][B(C_6F_5)_4]_2$ by X-ray diffraction (Table S1; Figures 2C and S38C). Notably, the Cp* ligand is η^5-bonded to the central P atom, with C–P bond lengths ranging from 2.063(6) to

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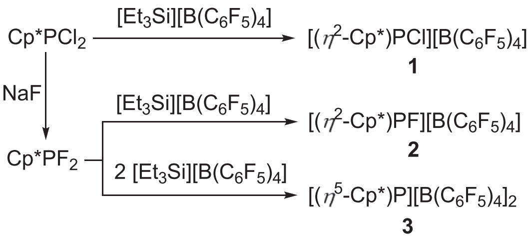

Scheme 1. Synthesis of 1–3

2.122(6) Å, which are slightly longer than those reported for the cationic phosphapyramidane species [(Me$_3$SiC)$_4$P][B(C$_6$F$_5$)$_4$] (1.934(2)–1.946(2) Å).[48] The mean P–C–C angle in [(η^5-Cp*)P]$^{2+}$ is 70.0°. The Lewis acidity of the [(η^5-Cp*)P]$^{2+}$ dication is demonstrated by the weak coordination of the phosphorous with the aromatic ring of a toluene molecular. The P–C distances range from 2.79 to 3.04 Å, which are shorter than those in η^6-arene complexes of the (2,4,6-tri-*tert*-butylphe-nyl)iminophosphenium cation (2.87–3.38 Å),[49–55] indicating the interaction of all the ring carbons of the toluene molecular with the phosphorous. Thus, the cation of **3** can be considered as a "bent sandwich" structure.

The lowest unoccupied molecular orbital + 1 (LUMO+1) (−9.89 eV) and LUMO (−9.89 eV) of [(η^5-Cp*)P]$^{2+}$ are degenerate and primarily comprise the vacant *p* orbitals of the P atom (Figures 3A and 3B). This result parallels that obtained from calculations on [(Cp*)E]$^+$ (E = Si, Ge, Sn) and Cp*E (E = Al, Ga, In)[56], but with significantly lower energies due to the additional cationic charge (Table S2). The highest occupied molecular orbital (HOMO) (−18.90 eV) and HOMO−1 (−18.90 eV) are also degenerate and involve the bonding *p* orbitals of the P and ring C atoms (Figures 3D and 3E). This is in contrast to the observations for the HOMOs of Cp*E (E = B, Al, Ga, In), which primarily involve the lone pair of electrons at main-group center.[56] The lone pair of electrons on the P center is in HOMO−2 (−19.82 eV) (Figure 3F), indicating a low predicted nucleophilicity for [(η^5-Cp*)P]$^{2+}$. Natural bond orbital (NBO) analysis (M06-2X/Def2-TZVP//M06-2X/Def2-SVP) demonstrates a highly positively charged phosphorus center (1.08 a.u.), whereas the remaining positive charge is delocalized across the H atoms of the methyl groups. This is also reflected by an electrostatic potential analysis (Figure 3C). The Wiberg bond indices (WBIs) of C–P bonds are small (0.49), consistent with η^5-coordination of the Cp* ligand to P. Collectively, these data suggest that P should exhibit significant Lewis acidity, although being very weakly basic.

The strong Lewis acidity of **3** is reflected by its reaction with [NBu$_4$][SbF$_6$], giving **2** within seconds as indicated by ^{31}P NMR (−73.5 ppm, $^1J_{PF}$ = 1,211 Hz) and ^{19}F NMR (16.1 ppm, $^1J_{PF}$ = 1,211 Hz) analyses (Figures S16–S19) (Scheme 2). The formation of **2** is concurrent with the formation of [NBu$_4$][B(C$_6$F$_5$)$_4$] and SbF$_5$. Remarkably, treatment of **3** with an equimolar portion of Et$_3$SiCl in toluene-d$_8$/DFB (1:1) (Figures S20–S25) immediately led to an equilibrium mixture of **3**, Et$_3$SiCl, **1**, and [Et$_3$Si][B(C$_6$F$_5$)$_4$], with a molar ratio for **3**:**1** of 100:76 (Figure S22). At −45°C, the equilibrium favors **3**, with the molar ratio for **3**:**1** increasing to 100:55 (Figure S23). The generation of [Et$_3$Si][B(C$_6$F$_5$)$_4$] demonstrates that **3** has a stronger chlorophilicity but lower fluorophilicity relative to [Et$_3$Si]$^+$. Whereas related η^5- to η^3- or η^2-ring slippages have been observed for base-[Cp*E]$^+$ (E = Ge, Sn) adducts,[57,58] the conversion of **3** to **1** or **2** represents has not yet been reported for phosphorus.

A DFB solution of **3** was treated with 2,2′-bipyridine (bipy) in a molar ratio of 1:1, immediately resulting in the full consumption of the starting material and formation

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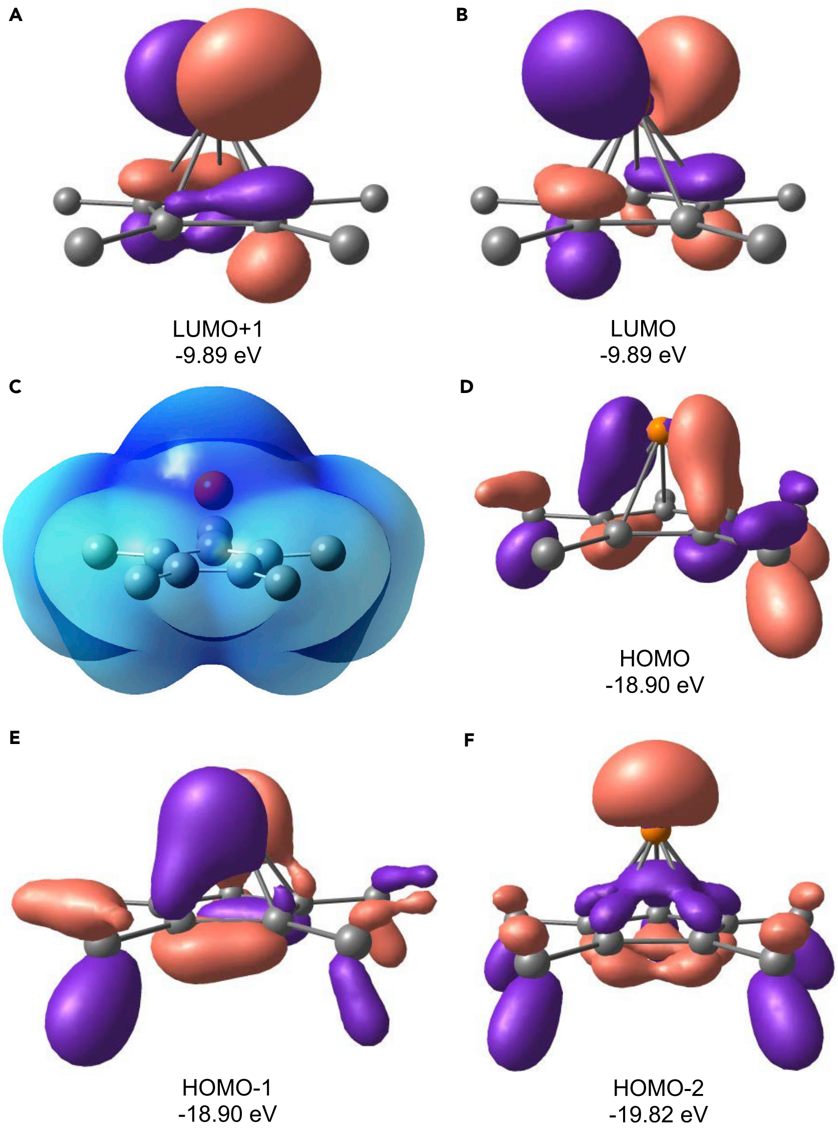


LUMO+1
-9.89 eV

LUMO
-9.89 eV

HOMO
-18.90 eV

HOMO-1
-18.90 eV

HOMO-2
-19.82 eV

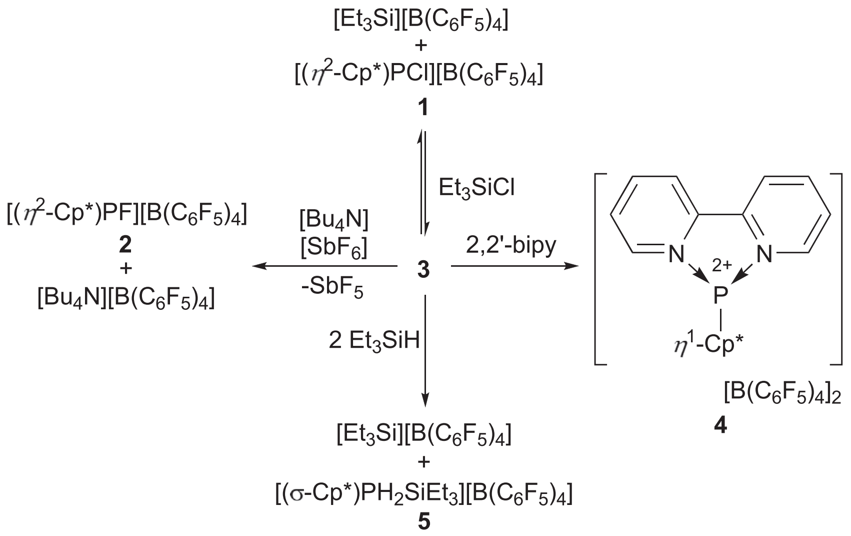
Figure 3. Frontier Molecular Orbitals

(A and B) LUMO+1 (A) and LUMO (B) for the cation of **3**.

(C) Molecular electrostatic potential (MEP) map for the cation of **3**. The blue areas indicate attractive MEPs toward a negative point charge.

(D–F) HOMO (D), HOMO-1 (E), and HOMO-2 (F) for the cation of **3**.

of a clear pink solution. A new phosphorus species **4** (Figures S26–S30) exhibits a broad singlet at 33.6 ppm in the ^{31}P NMR spectrum (Figure S28). Both ^1H (C_5Me_5, 1.50 ppm) and ^{13}C (C_5Me_5, 143.6 ppm; C_5Me_5, 10.9 ppm) NMR data (Figures S26 and S27) of the isolated **4** suggest that the Cp* ligand is in rapid dynamic circumambulation. Single-crystal X-ray diffraction study revealed the formulation of **4** as $[(\eta^1\text{-Cp*})P(\text{bipy})][B(C_6F_5)_4]_2$ (Table S1; Figures 4A and S38D). In the solid state, the cation of **4** exhibits a "slipped half sandwich" structure with an η^1-Cp* ligand. The P–C bond length is 1.870(11) Å, whereas the P–N bond lengths are 1.847(12) and 1.850(11) Å. The Cp* ring is capped by the PN_2 plane. Despite the η^1-binding mode, the C–C bond lengths of the ring are close to each other (average 1.445 Å). The P is almost vertical to the ring plane with angles of P-C1-C2 and



Scheme 2. Reactions of 3

P-C1-C5 of 92.0(7)° and 93.3(8)°, respectively. On the basis of an NBO analysis, the P atom of the cation of **4** carries a large portion of the positive charge (1.23 a.u), whereas both N atoms are negatively charged (−0.52 a.u. each). The WBIs of the P–C and two P–N bonds are 0.78, 0.53, and 0.53, respectively. Thus, the electronic structure of the cation of **4** is most suitably described as bipy-stabilized $[(\eta^1\text{-Cp*})P]^{2+}$. Such bipy-stabilized phosphorus dications have very recently found applications in catalytic C–F bond reduction.[59] **4** is reminiscent of a few examples of bipy-stabilized phosphorus cations reported by the Burford group.[60,61]

The mechanism of the formation of **4** was investigated via DFT calculations (SMD-M06-2X/Def2-TZVP//M06-2X/Def2-SVP). The reaction begins with the approach of the lone pair of electrons at N(1) of a bipy molecule toward the P atom of the cation of **3** (Figure 5). This prompts an η^5-η^2 haptotropic rearrangement to form an intermediate **IN1** (−16.7 kcal/mol) in a barrier-less process (Figure S37; Table S2). Subsequent rotation of the C–C single bond in the bipy ligand and the ensuing coordination of N(2) to the P atom is concurrent with the η^2-η^1 rearrangement and proceeds via **TS1**, with a low energy barrier of 2.8 kcal/mol, to produce the stable product cation of **4** (−39.4 kcal/mol).

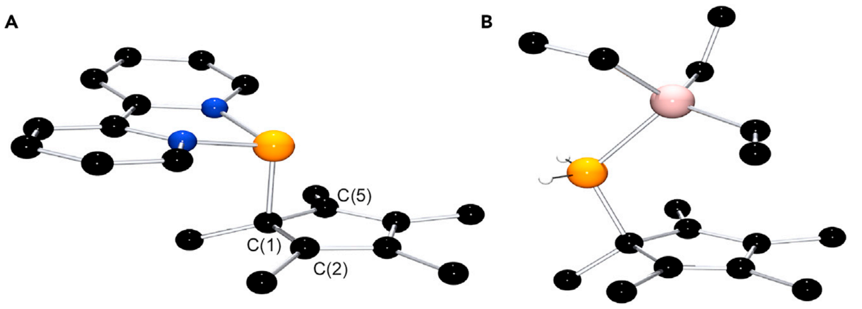


Figure 4. X-Ray Structures of 4 and 5

POV-ray depictions of the cations of (A) **4** and (B) **5**. Coloring is as follows: C, black; P, orange; N, blue; Si, pale-pink; H, white. All H atoms (except P–H), solvent residue, and $[B(C_6F_5)_4]^-$ anions, as well as disordered parts and the cocrystallized cation $[\text{toluene}\cdot Et_3Si]^+$ in **5**, are omitted for clarity.

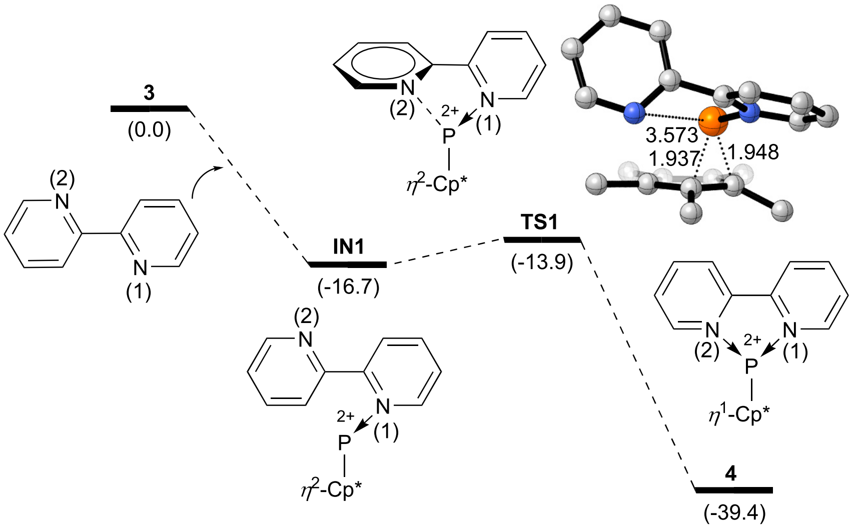


Figure 5. Free Energy (kcal/mol) Profile for the Formation of the Cation of 4

In the 3D structure of **TS1**, selected bond lengths are given in angstroms.

Compound **3** was also shown to react with excess Et_3SiH in a toluene/DFB (1:1) solution. The resulting ^{31}P NMR spectrum revealed a triplet resonance at −72.3 ppm ($^1J_{PH}$ = 383 Hz), which collapses into a singlet upon proton decoupling, indicating the presence of a PH_2 fragment (Figures S33 and S34). Interestingly, co-crystals of $[(\sigma\text{-Cp*})PH_2SiEt_3][B(C_6F_5)_4]$ **5** (Figures 4B and S38E) and $[toluene\cdot SiEt_3][B(C_6F_5)_4]$ in a ratio of 1:1 were obtained by layering of pentane on the reaction mixture at −35°C (Figures S31–S36; Table S1). The bond lengths of P–Si and P–C were 2.354(5) and 1.879(8) Å, respectively. In the Cp* group, three C–C single bonds (1.463(12), 1.466(13), and 1.516(11) Å), and two C=C double bonds (1.335(9) and 1.348(9) Å), were observed. These data, in addition to the three ^1H NMR signals for the methyl groups (1.46, 1.39, and 0.82 ppm) and the corresponding ^{13}C resonances (18.8, 10.8, and 9.5 ppm), are consistent with a description of the binding as a σ-Cp* ligand (Figures S31 and S32).

A computational study of the mechanism of the formation of **5** reveals that the $[SiEt_3]^+$ was generated via barrier-less hydride abstraction from Et_3SiH by the Lewis acidic cation of **3**, affording $[(\eta^2\text{-Cp*})PH]^+$ **IN2** (−28.3 kcal/mol) with a concurrent η^5-η^2-Cp* rearrangement (Figure 6). In the presence of excess Et_3SiH, **IN2** activates a second Et_3SiH molecule to form **IN3** (−19.7 kcal/mol), prompting η^2-σ-Cp* rearrangement. The ensuing cleavage of the Si–H bond is facile via **TS2** (−18.3 kcal/mol) with an activation energy of 10.0 kcal/mol (**IN2**→**TS2**), producing the stable cation of **5** (−47.0 kcal/mol) (Table S2). Coordination of Et_3Si-H to Lewis acidic centers, such as a boraindene[62] and $Al(C_6F_5)_3$,[63] has been previous reported; however, the present result is a rare example in which such an interaction of Si–H with a main-group Lewis acid prompts its addition to a P atom to give P–H and P–Si bonds.

In summary, more than six decades after the discovery of the η^5-cyclopentadienyl derivatives of iron, this work uncovers an η^5-Cp ligand on phosphorus with the isolation of $[(\eta^5\text{-Cp*})P][B(C_6F_5)_4]_2$ **3** via a defluorination strategy. The two degenerate LUMOs at the P center prompt **3** to react as a P-based Lewis super acid, binding toluene and reacting with Et_3SiCl, $[SbF_6]^-$, bipy, and Et_3SiH to give **1**, **2**, **4**, and **5**, respectively. In the case of **1** and **2**, the reactions prompt η^2-Cp* binding, whereas for **4** an η^1 binding is seen. Notably, the reaction of **3** with silane effects hydride

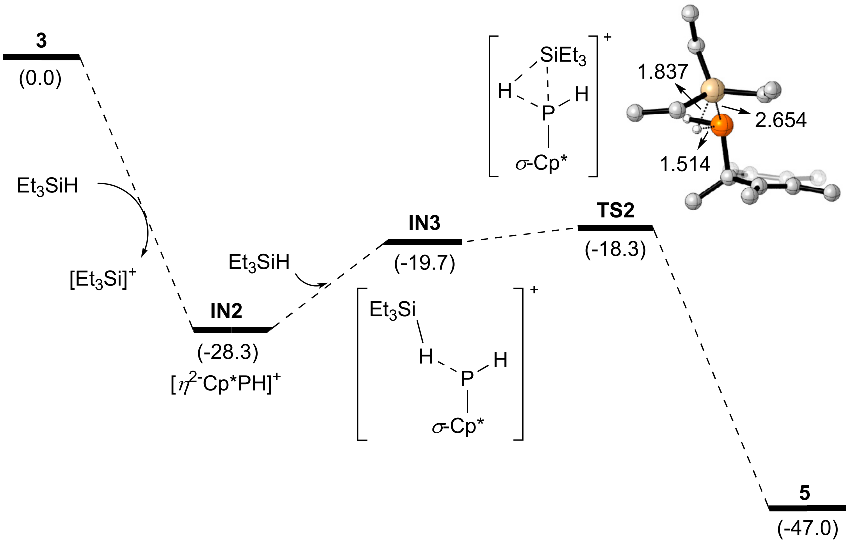


Figure 6. Free Energy (kcal/mol) Profile for the Formation of the Cation of 5
In the 3D structure of **TS2**, selected bond lengths are given in angstroms.

abstraction and addition of $[R_3Si]^+$ to P to give **5**, concurrent with an η^5-σ rearrangement of the binding of the Cp* ligand. The isolation of **3** illuminates a unique aspect of P-based Lewis acids and super acid chemistry. The potential application of such species in further reactivity and catalysis is the subject of current efforts in our laboratory.

EXPERIMENTAL PROCEDURES

Full experimental procedures are provided in the Supplemental Information.

DATA AND SOFTWARE AVAILABILITY

Crystallographic data have been deposited in the Cambridge Crystallographic Data Center under accession numbers CCDC: 1849893–1849897. These data can be obtained free of charge from the Cambridge Crystallographic Data Center at http://www.ccdc.cam.ac.uk/data_request/cif.

SUPPLEMENTAL INFORMATION

Supplemental Information includes Supplemental Experimental Procedures, 38 figures, 3 tables, and 5 data files and can be found with this article online at https://doi.org/10.1016/j.chempr.2018.08.038.

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AUTHOR CONTRIBUTIONS

J.Z. performed the synthetic studies. L.L.L. performed the computational experiments. J.Z. and L.L.C. carried out single-crystal X-ray diffraction studies. D.W.S. directed the project. D.W.S., L.L.L., and J.Z. wrote the manuscript with input from all authors. All authors analyzed the results and commented on the manuscript.

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DECLARATION OF INTERESTS

The authors declare no competing interests.

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