Hydrogen Splitting at a Single P^{III}-Center and Its Use for Hydrogenation

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Abstract: Main-group compounds that can mimic the behavior of the transition-metal (TM) complexes are of great interest due to their potential in TM-free catalysis. Here, we report the synthesis, isolation and full characterization of the geometrically constrained phosphenium cation with the 2,6-bis(o-carborano)pyridine pincer-type ligand. A preliminary reactivity study showed that this cation is capable of activating H−H bond by a formal oxidative addition to P^{III} cationic center, which is unprecedented reactivity for P^{III}-centers, producing new dihydrophosphonium cation. Remarkably, this new phosphenium cation is capable of catalyzing the hydrogenation reactions of C=C double bonds and fused aromatic systems.

Main-group compounds capable of mimicking transition-metal reactivity in the activation of small molecules, such as dihydrogen, attract much interest of the scientific community due to their potential to serve as alternatives to noble transition-metal catalysts (*1-3*). The basic principle for the design of main-group compounds capable of activating small molecules is that they have to possess a high-lying highest occupied molecular orbital (HOMO) and a low-lying lowest unoccupied molecular orbital (LUMO). This can be achieved at a single main-group center in certain low-valent compounds such as carbenes (*3-5*), borylenes (*6-9*) and their heavier analogs (*2,10-14*). Alternatively, two main-group centers in which one center is a strong Lewis base (high HOMO) and the other is a strong Lewis acid (low LUMO) known as frustrated Lewis pairs (FLPs) were also shown to activate small molecules between these two centers (*15-16*). Recently, the activation of small molecules by phosphorus-based species gained a lot of attention due to their ability to cycle between two stable oxidation states P^{III} and P^{V} (*17-18*). The strategy to obtain an ambiphilic (both nucleophilic and electrophilic) P^{III}-center, which can activate small molecules, is to geometrically constrain it by a rigid pincer-type ligand (*17-18*). This constraint causes the rehybridization of the molecular orbitals (MO) at P-center and as a result a decrease in the HOMO-LUMO gap (*17-18*). Ambiphilic, geometrically constrained P^{III}-centers were shown to activate O−H (*19-20*), N−H (*21-23*), Ar−F (*24-25*) and Si−H (*26*) bonds by their formal oxidative addition, producing new P^{V} species. In some cases, these activation processes were reversible and the initial P^{III} compounds could be obtained back as a result of the reductive elimination type reaction (*21-23*). Despite recent progress in the activation of small molecules at the ambiphilic P^{III}-centers, a highly desirable activation of H−H bond by a formal oxidative addition to P^{III}-center was never reported to the best of our knowledge. Noteworthy, only recently the first example of the oxidative addition of H_2 to transient stibinidene, generated from distibene, was reported (*27*), which up to date is the only Group 15 based molecular center capable of such reactivity. Although, dehydrogenation of ammonia-borane (H_3NBH_3) by an ambiphilic P^{III}-center producing dihydridophosphorane (P^{V}) and catalytic transfer hydrogenation to azobenzene was reported (*28*).

Furthermore, while the activation of H−H bond by the ambiphilic single main-group centers is known (*2-14*), catalytic hydrogenation using these species was never reported.

Here, we report the synthesis, isolation and full characterization of the ambiphilic, geometrically constrained phosphenium cation (**1**$^+$) with the 2,6-bis(o-carborano)pyridine pincer-type ligand (**2**) (Fig. 1). The reaction of **1**$^+$ with dihydrogen produces the dihydrophosphonium cation (**1**$^+$**-H**$_2$) via a formal oxidative addition of H−H bond to P^{III}-center in **1**$^+$ (Fig. 3). Density functional theory (DFT) calculations of the possible mechanism of this activation (Fig. 3) as well as the use of **1**$^+$ in the catalytic hydrogenation reactions of C=C double bonds and fused aromatic systems are also described (Fig. 4).

To design a molecule with highly reactive, ambiphilic P^{III} cationic center, a pincer-type ligand bearing two ortho-carborane (*o*Cb) "arms" and a neutral central pyridine donor (**2**) was chosen (Fig. 1A) (*29*). We envisioned that **2** would provide the necessary rigidity and robustness to structurally constrain the P^{III} cationic center, the pyridine donor would stabilize this cationic center, while the strongly electron-withdrawing *o*Cb "arms" (*30-32*) would make this P^{III}-center highly electrophilic (low-lying LUMO). Thus, **2** was doubly deprotonated by ^{n}BuLi and reacted with excess of PCl_3 producing chlorophosphine **1-Cl** (Fig. 1A). Colorless crystals of **1-Cl** were obtained from a mixture of CH_2Cl_2/n-hexane (10:1) and its molecular structure was determined by X-ray crystallography (Fig. 1B). In an attempt to obtain the desired **1**$^+$, **1-Cl** was reacted with AgOTf (1 equiv.), however instead of a separated [**1**$^+$][OTf] ion pair, **1-OTf** was obtained (Fig. 1A). **1-OTf** was crystallized from CH_2Cl_2 at room temperature and its molecular structure was determined using X-ray crystallography (Fig. 1B). The ^{31}P NMR chemical shift of **1-OTf** at $\delta = 36.0$ ppm resembles the chemical shift of **1-Cl** ($\delta = 33.8$ ppm), indicating that despite the trans effect from the pyridine donor, no dissociation to **1**$^+$ and TfO$^-$ occurs in solution at room temperature on the NMR timescale. This points to the highly electrophilic P^{III}-center in **1-OTf**. To obtain a non-coordinated, "free" **1**$^+$ cation, the chloride in **1-Cl** was abstracted by $[Et_3Si][B(C_6F_5)_4]$, giving the desired [**1**$^+$]$[B(C_6F_5)_4]$ (Fig. 1A). [**1**$^+$]$[B(C_6F_5)_4]$ was crystallized from $CHCl_3$ as light yellow crystals and its molecular structure was determined by X-ray crystallography (Fig. 1B). [**1**$^+$]$[B(C_6F_5)_4]$ is a separated ion pair both in solid and solution with a low-field signal in ^{31}P NMR at $\delta = 132.2$ ppm. The P-center in **1**$^+$ is pyramidalized and strongly deviated from a local C_{3v} symmetry, which is typical to trigonal pyramidal σ^3P centers, with bond angles around phosphorus atom being $\angle$C1−P1−C2 = 124.1°, $\angle$C1−P1−N1 and $\angle$N1−P1−C2 = 87.2°. Thus, ligand **2** enforces a distorted trigonal pyramidal geometry of P1 center in **1**$^+$ with a C_s local symmetry, which could also be described as a cis-divacant pseudo trigonal bipyramid in which C1 and C2 atoms of the *o*Cb units are at the equatorial positions and the central N1 is at the axial one.

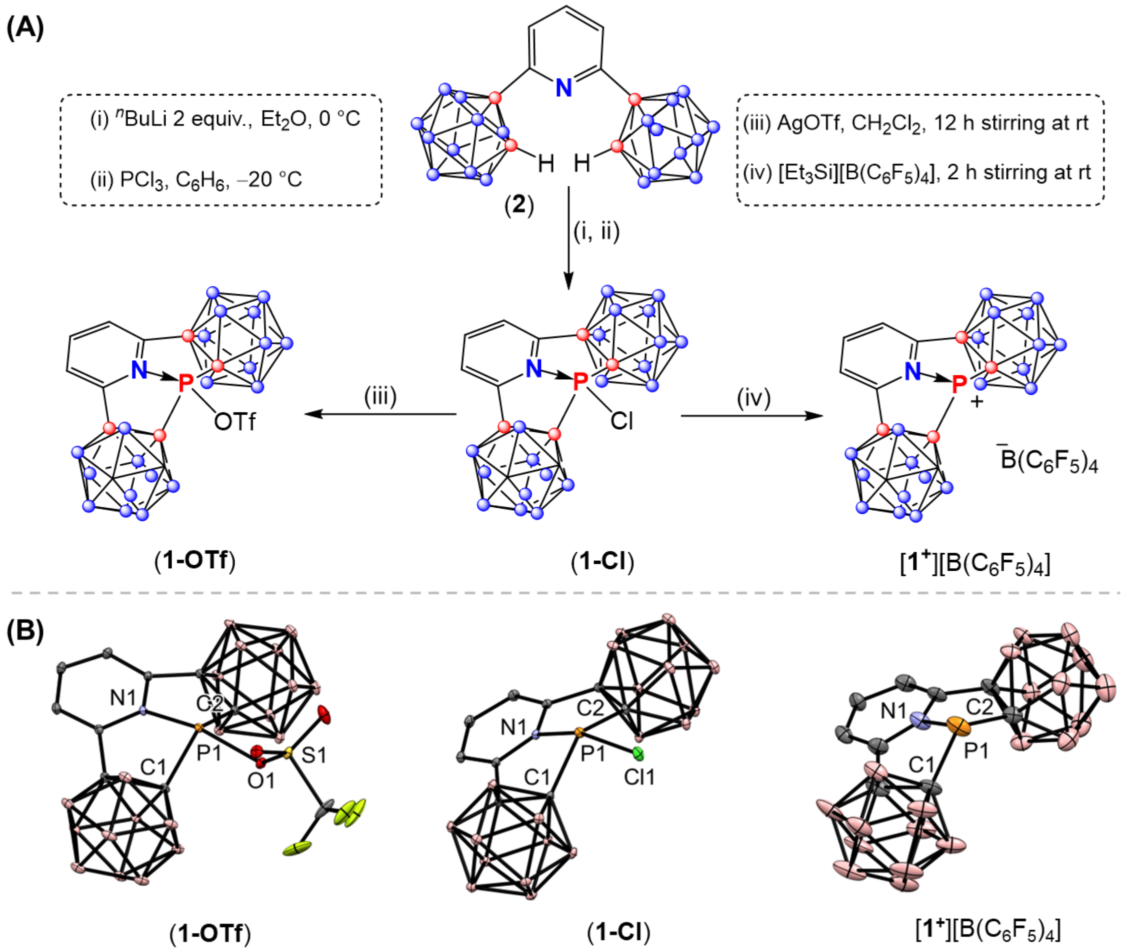

Fig. 1. (**A**) Synthesis of **1-Cl**, **1-OTf** and $[\mathbf{1}^+][B(C_6F_5)_4]$. (**B**) POV-ray depictions of **1-OTf** (left), **1-Cl** (middle) and $\mathbf{1}^+$ (right), thermal ellipsoids at the 30% probability level, hydrogens and $[B(C_6F_5)_4]^-$ were omitted for clarity.

The electronic structure of $\mathbf{1}^+$ was further studied by DFT calculations performed at BP86(D3)/def2-TZVP level of theory (*33*-*37*). The optimized geometry of $\mathbf{1}^+$ is in good agreement with the experimentally obtained structure (Fig. 1B). The MOs analysis of the calculated $\mathbf{1}^+$ reveals that the HOMO is primarily located on the P-center, while the LUMO is located on the P-center with the expected delocalization into the pyridine π-system. The HOMO-LUMO energy gap of 2.8 eV suggests a highly reactive nature of the P-center in $\mathbf{1}^+$ (Fig. 2A). The natural bond orbital (NBO) analysis shows that the lone pair (LP) at P-center (occupancy of 1.85 e) resides on an $sp^{0.87}$ hybrid with a dominant s character. The natural population analysis (NPA) exhibits charges of −0.47 and +1.26 on N- and P-centers, respectively. An electron occupancy of N1–P1 bond of 1.53 e was calculated, with the bonding coefficients significantly polarized towards the N1 center (92.76% and 7.24% on N1 and P1 respectively). The calculated Wiberg bond index (WBI) value for N1–P1 bond is 0.6419. The nature of N−P bond in $\mathbf{1}^+$ was also analyzed by Baders quantum theory of atoms in molecules (QTAIM) (*38*). A positive Laplacian ($\nabla^2\rho(r_{BCP}) = 0.075159$) and low magnitude of electron density ($\rho = 0.136520$) at the bond critical point (BCP) of the N−P bond in $\mathbf{1}^+$ indicate the donor acceptor interactions between these two atoms (Fig. 2B). Considering all these factors, the nature of **1**$^+$ can be most accurately described as a pyridine-supported phosphenium cation.

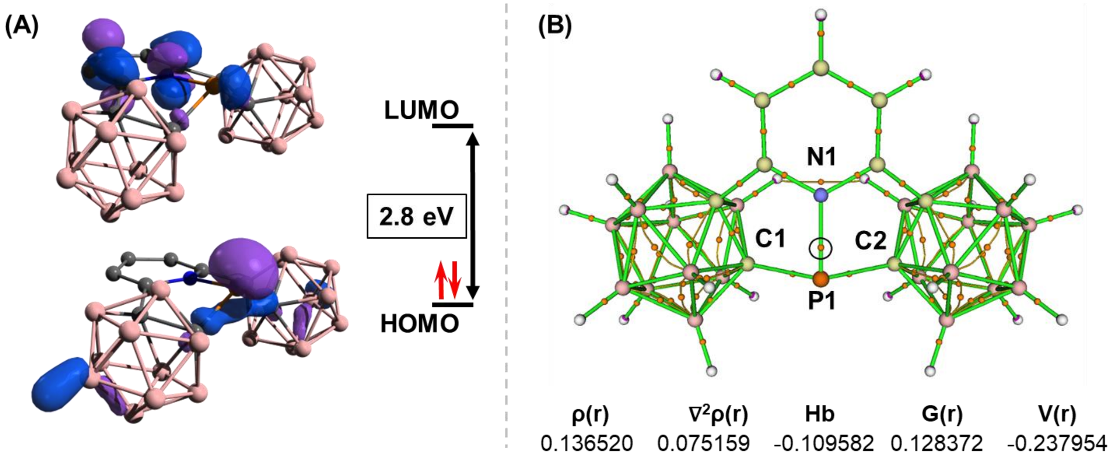

Fig. 2. (**A**) DFT calculated FMOs (isovalue = 0.05) and the HOMO-LUMO gap in **1**$^+$. (**B**) AIM analysis of **1**$^+$.

The low HOMO-LUMO gap in **1**$^+$ suggests a high reactivity of this P^{III}-center, which encouraged us to check its reactivity with H_2. Thus, a J-Young NMR tube containing CH_2Cl_2 solution of **1**$^+$ was pressurized with H_2 (4 atm) and the reaction was left at r.t. while the reaction progress was monitored by multinuclear NMR spectroscopy. After ~7 days, the formation of **1$^+$-H$_2$**, the formal oxidative addition product of the H−H bond to the P^{III} cationic center in **1**$^+$ (Fig. 3A), could be observed by the ^{31}P NMR as a triplet at $\delta = -42.66$ ppm with ^1J(PH) of 504 Hz (Fig. 3B). The corresponding doublet with same coupling constant was measured by ^{1}H NMR at $\delta = 7.35$ ppm (^1J(PH) = 504 Hz). To the best of our knowledge, **1**$^+$ is the first compound with a single P^{III}-center that is capable of splitting H−H bond in a formal oxidative addition reaction. The reaction time could be significantly reduced (~48 h) by heating the reaction to 60 °C, however, the outcome was not as clean. **1$^+$-H$_2$** was precipitated from CH_2Cl_2/n-hexane solution (1:3) as an off-white powder, however, multiple attempts to obtain crystals suitable for a single crystal X-ray diffraction failed.

To get a deeper insight into the mechanism of H_2 activation by **1**$^+$, DFT computations were carried out at BP86(D3)/def2-TZVP level of theory (*33-37*) in CH_2Cl_2 using the conductor-like polarizable continuum (CPCM) model (*39-40*). These calculations show that the oxidative addition type reaction of H–H bond to P^{III}-center in **1**$^+$ producing **1$^+$-H$_2$** is both exothermic and exergonic ($\Delta H = -16.3$ and $\Delta G = -7.8$ kcal·mol^{-1}) (Fig. 3C). Gibbs free energy barrier of $\Delta G^\ddagger = 32.6$ kcal·mol^{-1} (**TS**) of this H_2 activation reaction is reasonable and can explain long reaction times and/or heating requirement. The geometry of the transition state (**TS**) suggests that this activation is most probably an electrophilically driven process, as the H–H σ bond approaches the P-center from the direction in which the LUMO points (Fig. 3C).

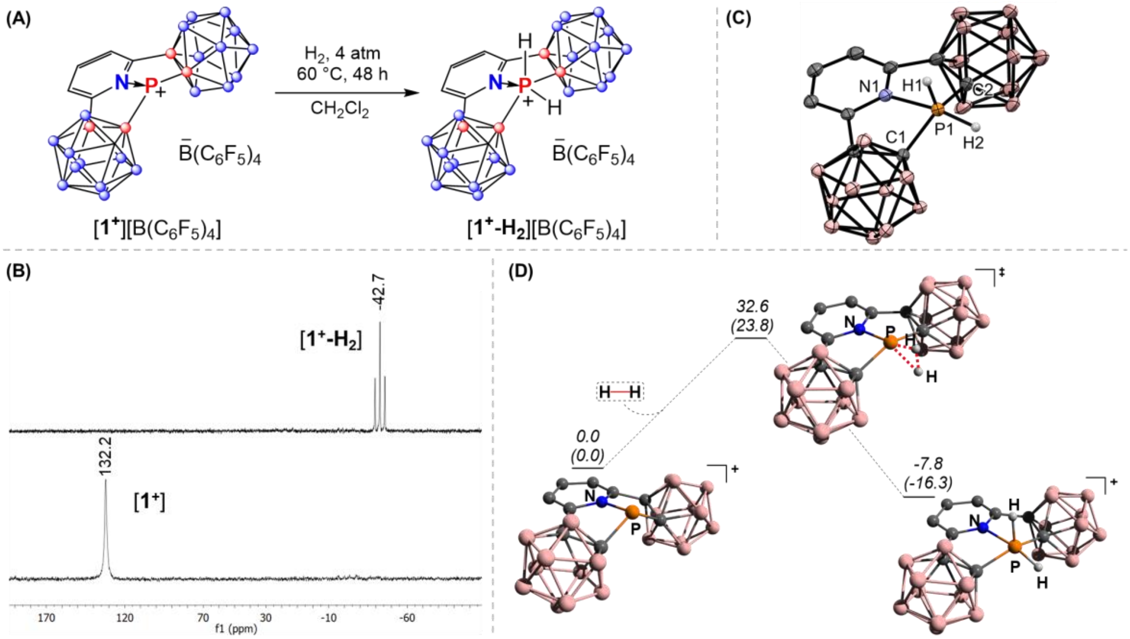

Fig. 3. (**A**) Formal oxidative addition of H−H bond to P^{III} cationic center in **1**$^+$. (**B**) Stacked ^{31}P NMR spectra showing the formation of [**1$^+$-H$_2$**] from [**1**$^+$] and H$_2$. (**C**) POV-ray depictions of [**1$^+$-H$_2$**], thermal ellipsoids at the 30% probability level, non-relevant hydrogens and [B(C$_6$F$_5$)$_4$]$^-$ were omitted for clarity. (**D**) DFT calculated mechanism for the activation of H$_2$ by **1**$^+$, free Gibbs energies (enthalpies) are given relative to the starting materials.

The ability of **1**$^+$ to transfer hydrogen catalytically was tested with various unsaturated C−C bond containing systems. First the reaction of highly active terminal alkene, 1,1-diphenylethylene (**3**) with H$_2$ (4 atm) and 10 mol% of [**1**$^+$][B(C$_6$F$_5$)$_4$] was probed. This reaction, however, led to the 1,1-diphenylethylene dimerization product (**4**) in minutes (~5 min) at room temperature (*41*), while the desired 1,1-diphenylethane, a hydrogenation product, was not obtained. Similar reaction was conducted with 1-hexene (**5**), H$_2$ (4 atm) and [**1**$^+$][B(C$_6$F$_5$)$_4$] (10 mol%) at 40 ºC affording mostly isomerization product (**6**) (*41*) after 6 h, and again no hydrogenation of the C=C double bond occurred even after prolonged heating. Importantly, both reactions of **3** and **5** in presence of 10 mol% of [**1**$^+$][B(C$_6$F$_5$)$_4$] without the addition of H$_2$ gave the same results i.e., formation of **4** and **6**, respectively (Fig. 4A). Meaning that the dimerization of **3** as well as isomerization of **5** are catalyzed by **1**$^+$, indicating once again the high Lewis acidity of this cation (*41*).

To overcome this obstacle, the unsaturated C−C bond containing systems that are not capable of isomerization, dimerization or polymerization, which precludes the desired hydrogenation, were tested next. Thus, a reaction of 1-methylcyclopentene (**7**) with H$_2$ (4 atm) in the presence of 10 mol% of [**1**$^+$][B(C$_6$F$_5$)$_4$] gave after 20 h at 50 ºC quantitative formation of the hydrogenated product, methylcyclopentane (**7-H$_2$**) (Fig. 4B). Similar reaction with 1-methylcyclohexene (**8**) at 50 ºC, after 24 h afforded the corresponding hydrogenated product, methylcyclohexane (**8-H$_2$**) in high yields (Fig. 4B). The hydrogenation (H$_2$, 4 atm) of indene (**9**) and acenaphthylene (**10**) catalyzed by [**1**$^+$][B(C$_6$F$_5$)$_4$] (10 mol%) was also successful leading to indane (**9-H$_2$**) and acenaphthene (**10-H$_2$**), respectively after 48 h at 50 ºC (Fig. 4B). The hydrogenation of fused aromatic systems anthracene (**11**) and 9,10-dimethylanthracene (**12**) was also attempted. Thus, the reaction of **11** with H$_2$ (4 atm) and [**1**$^+$][B(C$_6$F$_5$)$_4$] (10 mol%) at 50 ºC afforded after 48 h 9,10-

dihydroanthracene (**11-H$_2$**). Similar result was obtained for the [**1**$^+$][B(C_6F_5)$_4$] (10 mol%) catalyzed hydrogenation (H_2, 4 atm) of **12**, producing **12-H$_2$** after 40 h at 50 ºC (Fig. 4B). To the best of our knowledge, **1**$^+$ is the first main-group compound capable of splitting H_2 at a single main-group center and transfer it catalytically to unsaturated C−C bonds.

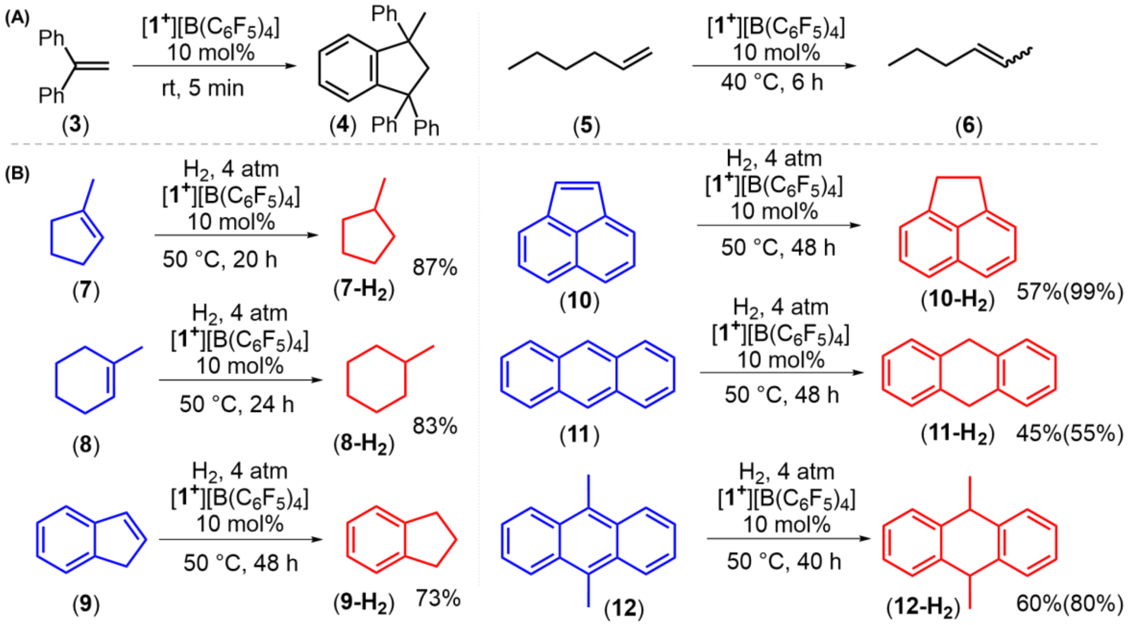

Fig. 4. (**A**) [**1**$^+$][B(C_6F_5)$_4$] catalyzed dimerization and isomerization reactions. (**B**) [**1**$^+$][B(C_6F_5)$_4$] catalyzed hydrogenation reactions of unsaturated C−C systems (GC or isolated yields (NMR yields)).

We have developed an ambiphilic, geometrically constrained phosphenium cation with a pincer-type ligand that is capable of activating H_2 in a metallomimetic fashion by a formal oxidative addition of H−H bond to P^{III} cationic center. Preliminary mechanistic studies suggest that this H_2 splitting, similarly to TM-based H_2 activation, is an electrophilically driven process. Notably, the ability of this new phosphenium cation to activate H_2 was used for catalytic hydrogenation reactions of C=C doubly bonded and fused aromatic systems. This finding shows the potential of phosphorus and possibly other main-group elements in the metallomimetic catalytic hydrogenation reactions.

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Data and materials availability: All data are available in the main text or the supplementary materials.