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Article

Cationic Phosphorus Compounds Based on a Bis(1-piperidinyl)-Substituted Carbodiphosphorane: Syntheses, Structures, and C_{sp^3}–H Activation

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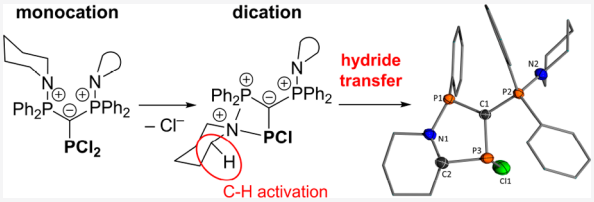
ABSTRACT: The use of the bis(1-piperidinyl)-substituted carbodiphosphorane $(Ph_2(Pip)P)_2C$ (**1**) as an NCN ligand for the stabilization of phosphorus cations was studied. A simple ligand for halide exchange allowed the synthesis and isolation of a series of phosphorus monocations of the type $[\mathbf{1}\text{-}PR_2]^+$ (with R = Cl, Br, I, CyCl, Ph). These cations exhibit characteristic NMR and structural properties which nicely correlate with the charge at the central phosphorus atom and the interaction between the ligand and the PR_2 moiety. Halide abstraction from the monocations does not result in isolable dicationic compounds but in an unexpected intramolecular C_{sp^3}–H activation in the piperidinyl group. DFT studies show that the selective activation of the CH_2 group next to the nitrogen atom instead of a CH group at the phenyl substituents proceeds via an iminium intermediate formed by hydride transfer from the carbon atom to the cationic phosphorus center. This observation clearly demonstrates the pronounced π acidity of the dicationic phosphorus species in comparison to compounds with a further π-donor substituent.



INTRODUCTION

The stabilization of low-valent main-group compounds has received intense research interest in the past years. The unique molecular and electronic structures of these compounds promise interesting reactivity, particularly in bond activation chemistry, a field which for a long time was thought to be exclusive to transition metals.[1] One strategy to stabilize reactive, low-valent main-group compounds is the use of strong donor ligands which moderate the electron deficiency and often also sterically protect the reactive center. With the discovery of the readily isolable N-heterocyclic carbenes[2] these ligands have become the donors of choice in this chemistry, thus leading to remarkable discoveries in main-group chemistry.[3,4]

In addition to carbenes, also bisylides such as carbodiphosphoranes (CDP) and carbodicarbenes (CDC) have been parts of intense research efforts in main-group chemistry in the past years.[5,6] Due to their ability to function as strong σ and moderate π donors,[7] these ligands are excellently suited to stabilize electron-deficient compounds. For example, CDP **A** allowed the isolation of cationic germanium and boron compounds,[8] while CDC **B** even gave way to a dicationic boron compound[9] (Figure 1).[10] Both ligands have also been applied in phosphorus chemistry. As such, Vidović and co-workers reported on the isolation of a series of phosphorus cations, among them the dicationic species $[\mathbf{A}\cdot PNiPr_2]^{2+}$ and the trication $[\mathbf{B2}\cdot P]^{3+}$.[11] In case of the dication, a further amino substituent at the phosphorus atom was required to balance its electron deficiency through additional π donation

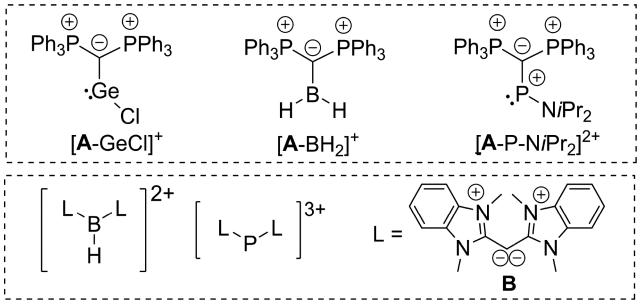


Figure 1. Main-group cations stabilized by carbodiphosphorane **A** and carbodicarbene **B**.

from N to P. Dications with other substituents were found to be highly reactive, and the trication could only be isolated in the form of a few crystals. In addition, diphenyl-substituted cations based on CDP **A** have been reported by Weigand and co-workers and used for the preparation of very Lewis acidic phosphonium dications.[12]

In the course of our research program on carbon ligands, we recently reported on the coordination chemistry of the

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diamino-substituted carbodiphosphorane **1** (Figure 2).[13,14] We became interested in its ability to stabilize main-group-element

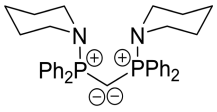

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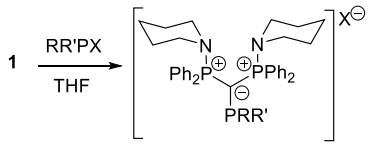
Figure 2. Structure of bis(1-piperidinyl)carbodiphosphorane **1**.

cations, particularly phosphorus cations, dications, or even trications. We envisioned that cationic species might be further stabilized by intramolecular coordination of the amino side arms and hence easier to isolate. This would be particularly interesting for accessing cations without further π-donor substituents. As in singlet carbenes, such π-donor substituents are commonly used in phosphorus cations (e.g., in N-heterocyclic phosphenium cations)[15,16] to temper their high π acidity. Since the strong π acidity distinguishes phosphorus cations from the typically used carbenes, we aimed at isolating cations without further π-donor substituents. Here, we report our findings.

■ RESULTS AND DISCUSSION

Isolation of Monocations. To access the desired cations, bis(amino)-CDP **1** was treated with an equivalent amount of phosphorus trihalide. In the case of the chloride and bromide, this simple CDP for halide exchange selectively gave way to the corresponding cations **2a**,**b** (Scheme 1). For comparison, also

Scheme 1. Synthesis of the Phosphorus Monocations 2



2a, R = R' = X = Cl; 81%
2b: R = Br, R' = X = Br; 77%
2c: R = R' = X = I; n.d.
2d: R = Cy, R' = X = Cl; 74%
2e: R = R' = Ph, X = Cl; 72%

the cyclohexyl and diphenyl compounds **2d**,**e** were synthesized. All monocations could be readily isolated as colorless solids in good yields between 72 and 81%. The cations are characterized by a doublet and a triplet in a 2:1 ratio in the $^{31}P\{^1H\}$ NMR spectrum. The signal of the CDP ligand appears in the same region for all cations (between 43.9 and 47.1 ppm), while the signal of the P(III) center expectedly varies strongly depending on the substituents at phosphorus (Table 1). Accordingly, the diphenyl-substituted compound **2c** exhibits the most high-field-shifted signal, while the dichloro and dibromo compounds **2a**,**b** feature the most deshielded signals.

Table 1. NMR Spectroscopic and Calculated Properties (PW6B95D3-def2svp/PW6B95D3-def2tzvp) of the Cations 2

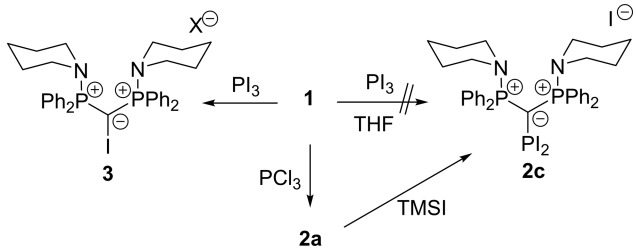
	2a	2b	2c	2d	2e
$\delta_P(P^V)$ (ppm)	43.9	44.4	43.1	45.3[a]	47.1
$\delta_P(P^{III})$ (ppm)	172.2	161.2	107.6	121.3[a]	−8.15
$^2J_{PP}$ (Hz)	106.7	112.0	117.8	nd[a]	64.6
q_{cal}(C)	−1.45	−1.44	−1.43	−1.43	−1.42
q_{cal}(P)	0.84	0.67	0.42	0.85	0.87
WBI(P−C)	0.99	1.01	1.04	0.96	0.67

[a]ABX splitting pattern.

In contrast to the other cations, compound **2d** gives rise to a rather complex $^{31}P\{^1H\}$ NMR spectrum. This can be explained by the asymmetry of the phosphorus center, the hindered rotation about the P−C bond, and the preferred perpendicular arrangement of the lone pair at the central carbon atom of the CDP ligand and the lone pair at the central phosphorus atom. Thus, the phosphorus nuclei in the CDP become inequivalent. This results in an ABX spin pattern in the $^{31}P\{^1H\}$ NMR spectrum, which is only poorly resolved in the temperature range between +50 and −40 °C (see Figure S16 in the Supporting Information).

Analogously to **2a**,**b**, we also addressed the synthesis of the diiodo compound **2c**. However, treatment of **1** with an equivalent amount of PI_3 did not result in the expected cation. Instead, the $^{31}P\{^1H\}$ NMR spectrum showed two singlets at δ_P 41.3 and 41.2 ppm in a 1:1 ratio, suggesting no successful introduction of the PI_2 moiety to the CDP. Crystallization yielded two types of crystals, both being the iodo-CDP **3** with iodide and triiodide as counteranions, respectively (Scheme 2,

Scheme 2. Synthesis of Cation 2c



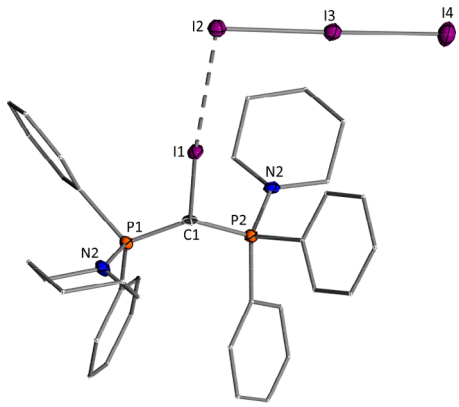


Figure 3. Molecular structure of **3**-I_3. Selected bond lengths (Å) and angles (deg): P1−C1 1.704(4), P1−N1 1.651(4), P1−C7 1.821(5), C1−I1 2.145(4); P1−C1−P2 135.5(3).

Figure 3, and Figure S21). Such halogenation reactions of carbon bases with main-group-element halides have frequently been observed: for example, also with N-heterocyclic carbenes.[17] Analogous halogenated compounds have also been reported for the parent hexaphenylcarbodiphosphorane **A**. These compounds exhibited unusually long C−X bond lengths as a consequence of the repulsion between the lone pairs at the halogen and the carbon atom.[18] Similarly, **3** features a C−I bond of 2.145(4) Å, which is slightly longer than that in **A-I** (2.134 Å)[19] and is in the range of C−I bonds at a carbanionic carbon center (carbenoids).[20] In the crystal structure of **3**, the iodo substituents exhibits a weak interaction

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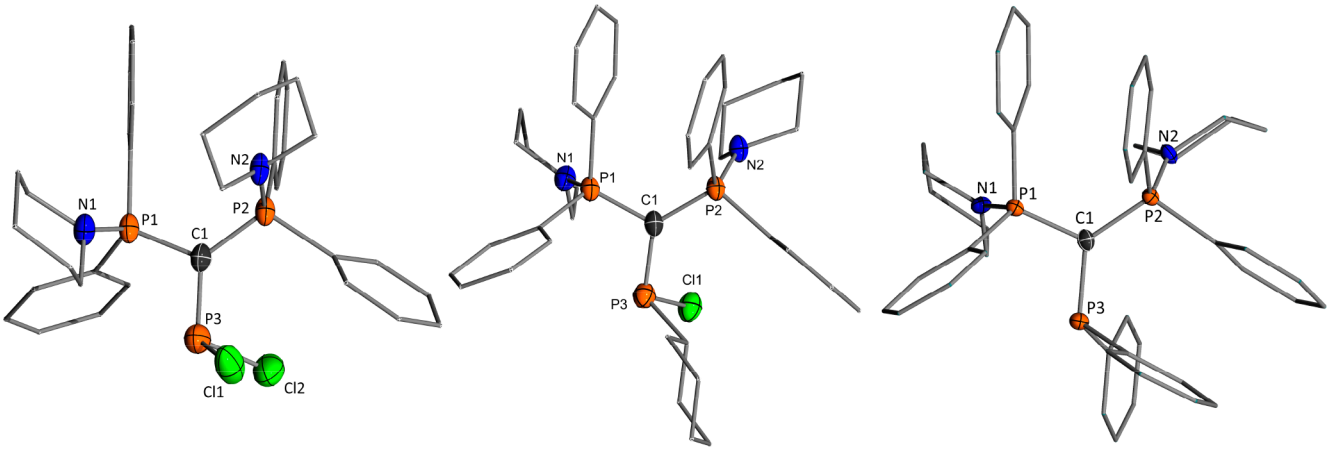

Figure 4. Molecular structures of (left to right) **2a,d,e.** Only the cationic compounds are shown; the halide anions, hydrogen atoms, and solvent molecules are omitted for clarity. Ellipsoids are shown at the 50% probability level. Important bond lengths and angles are given in Table 2. Further details are provided in the Supporting Information.

with the I_3^- and I^- counteranions, respectively. Thus, short I–I interactions of 3.4544(6) and 3.5634(4) Å are observed in both structures.

Since the direct synthesis of **2c** failed, its preparation was attempted via halide exchange from the dichloro compound **2a**. Indeed, treatment of **2a** with an equivalent amount of iodotrimethylsilane (TMSI) gave **2c** as a colorless solid in approximately 65% yield according to ^{31}P NMR spectroscopy. The ^{31}P{^{1}H} NMR spectrum shows the expected pattern with a triplet at δ_P 107.6 ppm and a doublet at δ_P 43.1 ppm ($^2J_{PP}$ = 117.8 Hz). **2c** was also found to be unstable in THF and thus could not be isolated in pure form. After 3 days in THF solution full conversion of **2c** to the diprotonated ligand **1-H$_2$** was observed.

It is interesting to note that the $^2J_{PP}$ coupling constants in **2** increase in the series **1**-PCl$_2$ < **1**-PBr$_2$ < **1**-PI$_2$. This suggests a shortening of the C-PX$_2$ bond in this series of compounds. This trend is nicely reflected by the calculated Wiberg bond indices of the P–C bond (Table 1, PW6B95D3-def2tzvp), which increases in the series **1**-PPh$_2$ < **1**-P(Cl)Cy < **1**-PCl$_2$ < **1**-PBr$_2$ < **1**-PI$_2$: i.e., with increasing coupling constant. In contrast, the calculated natural charges at the phosphorus atom decrease in this series as a consequence of the decreasing electronegativity of the halogens. On first glance, this observation is in contradiction with the shortening of the P–C bonds, since one would expect a stronger electrostatic interaction in the C$^-$–P$^+$ linkage with increasing positive charge at the phosphorus atom (note that the charge at C is similar in all cations). However, the bond shortening can be explained either by the π-donor ability of the substituents or by means of Bent's rule. The π-donor ability considerably decreases with increasing size of the atoms. Thus, the lone pair at phosphorus is the most destabilized in the chloro compound and thus results in the strongest repulsion with the lone pair at C (bond weakening). According to Bent's rule, electronegative substituents form bonds with higher p character, thus leaving higher s character for the remaining bonds, which thus should become shorter (higher s character–higher coupling constant).

X-ray Structures of the Phosphorus Monocations. Single crystals for XRD analyses could be obtained for all monocations **2** by slow diffusion of diethyl ether, hexane, or pentane into saturated solutions of the respective compounds in DCM (Figure 4). All cations feature similar structures in the solid state comparable to those reported with carbodiphosphorane **A**.[11] As such, the central phosphorus atom P3 always adopts a pyramidal geometry (e.g., sum of angles around P3 in **2a** 311.4(2)°) and lies in the plane of the P–C–P linkage of the CDP ligand. The lone pair at P3 is also in plane with the P–C–P unit to minimize the repulsion with the π-symmetric lone pair at C1. Such an arrangement has already been observed for other phosphorus cations[11] and phosphines with carbanionic substituents in an α position.[21] It is interesting to note that this arrangement is favored over a possible alignment of the lone pair at C1 with a P3–X/C bond, which would allow for a delocalization of electron density via negative hyperconjugation. Consequently, the P3–C1 bonds are in the range of single bonds and are longer than the P–C bond distances within the CDP ligand. It is also noteworthy that the P3–C1 distances increase in the order **2b** < **2a** < **2d** < **2e**. This corresponds to the decreasing $^2J_{PP}$ coupling constant and the decreasing positive charge at the phosphorus atom P3 in this series of compounds. Hence, the diphenyl-substituted cation **2e** exhibits the longest P–C bond (vide supra).

The P–C bond lengths in the CDP ligand are similar in all cations (Table 2) and are slightly longer than in the free ligand

Table 2. Crystallographic Properties of the Cations 2: Important Bond Lengths (Å) and Angles (deg)

	2a	2b	2d	2e
P1–C1	1.746(3)	1.757(3)	1.751(3)	1.753(5)
P2–C1	1.756(3)	1.760(4)	1.744(4)	1.736(5)
P3–C1	1.773(4)	1.763(4)	1.803(4)	1.824(5)
P1–N1	1.661(3)	1.663(3)	1.673(3)	1.655(5)
P2–N2	1.647(3)	1.657(3)	1.664(3)	1.665(5)
P3–X	2.0984(17) 2.0698(18)	2.2831(11) 2.2384(11)	2.1357(13)	
P1–C1–P2	122.8(2)	122.3(2)	121.9(2)	121.9(3)
P1–C1–P3	109.23(18)	108.17(19)	109.32(19)	108.8(2)
P2–C1–P3	128.0(2)	129.5(2)	128.6(2)	128.2(3)

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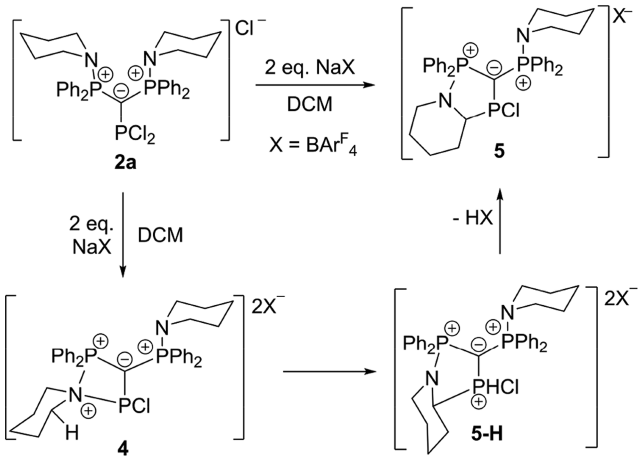
1 (1.632(2) Å) but comparable with those in the protonated ligand **1-H**$^+$ (1.7091(9) Å). The P−C1−P angles are likewise similar in all cations with two larger angles between 120 and 130° and a smaller angle of approximately 110°. The latter is always found for P1−C1−P3: i.e., between the cationic phosphorus center and the phosphorus atom in the CDP where the lone pair at P3 is directed to. This suggests weak electrostatic interactions in addition to steric effects. The P3−Cl bonds in **2a**,**d** are shorter compared to those found in the CDP complex **A**•P(N*i*Pr$_2$)Cl with an further amino substituent,[11] thus suggesting that halide abstraction might be more difficult in the compounds with CDP **1**.

Halide Abstraction. To access the phosphorus dications based on **2a**−**d**, halide abstraction from the monocations was attempted. We expected that coordination of the amino substituent would provide further stabilization of the dications. Thus, **2a**−**d** were treated with various halide abstraction reagents under different reaction conditions. Unfortunately, most of the reactions delivered complex product mixtures, which we found difficult to analyze. The best results were obtained with the dihalide compounds **2a**−**c**, in particular with the PCl_2 adduct and $NaBAr^F{}_4$ ($BAr^F{}_4$ = 3,5-bis-(trifluoromethyl)phenyl)borate) in DCM at room temperature. Two equivalents of $NaBAr^F{}_4$ is necessary to first exchange the chloride anion in **2a** and subsequently perform the actual chloride abstraction from the phosphorus atom. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed the formation of the protonated CDP ligand (δ_P 39.6 ppm) along with a new species characterized by three doublets of doublets at 129.9, 59.7, and 41.1 ppm. Although this splitting pattern perfectly fits with the expected features for a dication such as **4** coordinated by one of the amino side arms, the chemical shifts are somewhat too high-field shifted to argue for a true phosphorus dication, which usually gives rise to highly deshielded signals (Scheme 3).[11a,22] A single-crystal XRD analysis (Figure 5) finally revealed the product to be the monocationic C−H activation product **5**. Surprisingly, C−H activation did not occur at a phenyl substituent but at a CH_2 group next to the nitrogen in the piperidinyl moiety. While C−H activations are generally challenging transformations, they are frequently observed with low-valent main-group species: however, mostly at aryl substituents.[23] The activation of C_{sp^3}−H bonds is less common and is mostly observed for activated bonds, such as in benzylic positions.[24] The selective formation of **5** is thus very unusual, particularly since phenyl groups are also available in **2a**, which have already been shown to undergo C−H activations in CDP **A**.[25] Unfortunately, efforts to isolate any intermediate species to **5** were unsuccessful. Also, when the reaction was performed at low temperatures, exclusive formation of **5** was observed, thus suggesting a low barrier for the C−H activation process.

Scheme 3. C−H Activation via Phosphorus Dication 4 to Cation 5



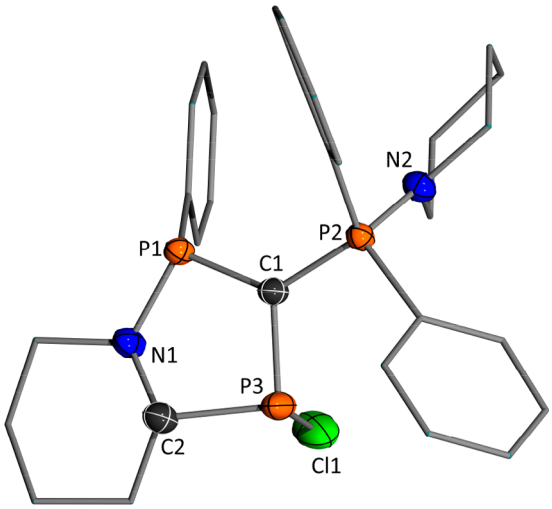


Figure 5. Molecular structure of the cation of **5**. Selected bond lengths (Å) and angles (deg): P1−C1 1.735(3), C1−P2 1.730(3), P1−N1 1.659(3), P2−N2 1.654(3), C1−P3 1.777(3), C2−P3 1.853(3); P2−C1−P1 129.64(18).

The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture (three doublets of doublets) is well in line with the formation of **5**. The most downfield shifted signal at 129.9 ppm corresponds to the P(III) nucleus, which is involved in the coupling with the P(V) nuclei in the CDP ligand, thus giving rise to a small coupling constant of $^2J_{PP}$ = 14.0 Hz to the phosphorus atoms in the ring system and a larger coupling constant ($^2J_{PP}$ = 76.5 Hz) to the other P atom. The observed formation of the protonated ligand **1-H**$^+$ can easily be explained by the proposed mechanism outlined in Scheme 3. After C−H activation in **4**, the protonated dicationic compound **5-H** is formed, which is subsequently deprotonated, probably by a $BAr^F{}_4$ anion or an ylide present in solution. The thus-formed $HBAr^F{}_4$ acts as an acid to protonate any species along the mechanism, which ultimately may result in a P−C cleavage and the formation of **1-H**$^+$.

In the molecular structure of **5** (Figure 5), the central phosphorus atom P3 is pyramidalized with a sum of angles of 296.46(13) °. The P−C and P−N bond distances in the CDP ligand are similar to those in the cations **2**, while the P1−C1−P2 angle is slightly larger (129.6(2)°), presumably due to the formation of the new five-membered ring. The P3−C1 bond amounts to 1.777(3) Å and is thus in the range of those in the cations **2** and slightly shorter than the C2−P3 bond to the piperidinyl group (1.853(3) Å). The P−Cl bond is still short, thus being in line with unsuccessful attempts to abstract the chloride from **5**.

DFT Calculations. To obtain further insights into the mechanism of the C−H activation and the formation of **5**, we performed computational studies. Since the C−H activation selectively takes place in a position α to the nitrogen atom, we

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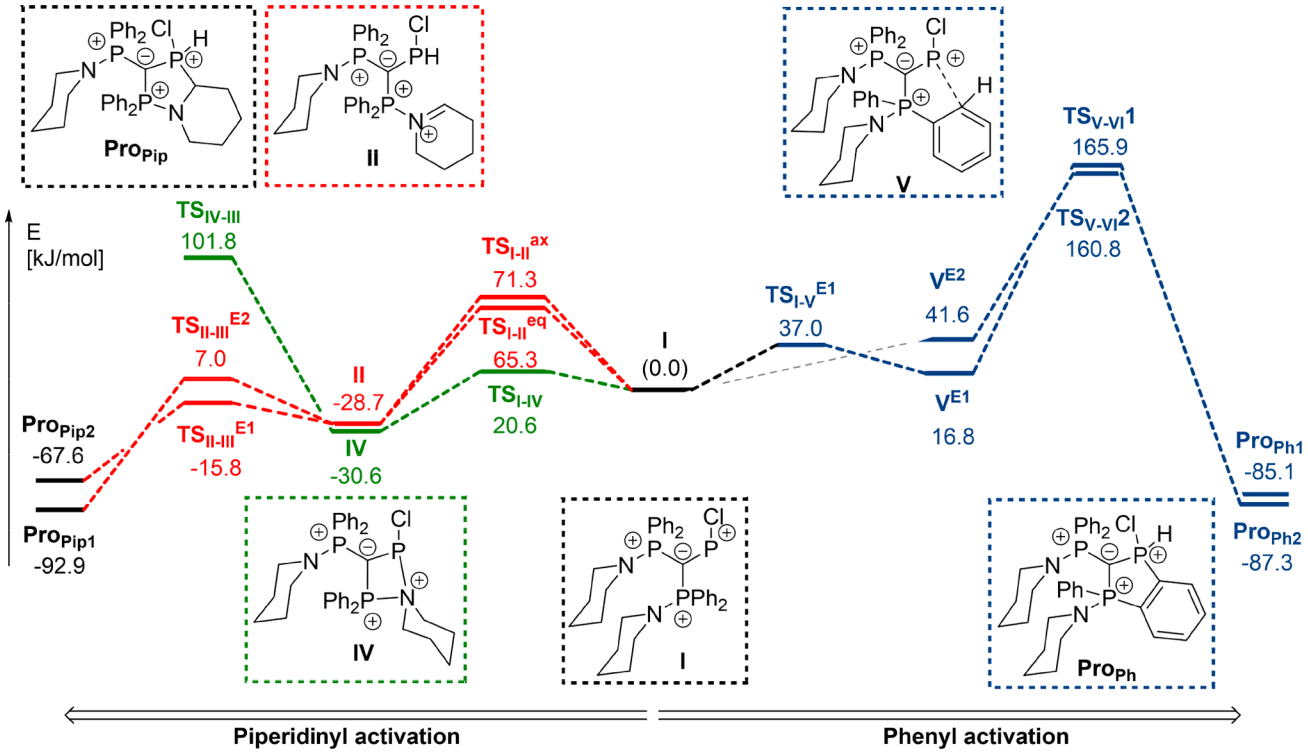

Figure 6. Calculated pathways for the C−H activation at the piperidinyl (left) and phenyl substituents in **I** (right). Energies are given relative to **I**, PW6B95D3-def2tzvp. $\mathbf{Pro_{Ph1}}$ and $\mathbf{Pro_{Ph2}}$ are the two diastereomeric C−H activation products.

hypothesized a precoordination-induced activation mechanism as shown in Scheme 3, where at first the N-coordinated dication **4** is formed after halide abstraction. Indeed, the DFT calculations (PW6B95D3-def2tzvp/PW6B95D3-def2svp) show that this N-coordinated species **IV** is thermodynamically favored by 30.6 kJ mol^{-1} over the noncoordinated dication **I** as well as complex **V** with a weak C−H interaction to one of the phenyl groups (Figure 6). The subsequent concerted C−H activation from the piperidinyl-coordinated intermediate **IV** to the final product $\mathbf{Pro_{Pip}1}$ requires 102 kJ mol^{-1} and is thus too high to be overcome at low temperatures (green pathway). Thus, further pathways were considered. Due to the high electrophilicity of the dication (as a consequence of a missing π-donor substituent), also a hydride shift in **I** might be possible. This is confirmed by a low activation barrier of only 65.3 kJ mol^{-1} to iminium cation **II**, which readily undergoes P−C bond formation in the next step to form the two isomeric products $\mathbf{Pro_{Pip}1}$ and $\mathbf{Pro_{Pip}2}$ (red pathway). $\mathbf{Pro_{Pip}1}$ and $\mathbf{Pro_{Pip}2}$ differ in the position of the newly formed P−C bond, which can be in either an equatorial or axial position of the piperidinyl moiety. The thermodynamically favored product $\mathbf{Pro_{Pip}1}$ matches with the isomer observed in experiment. According to the calculations the formation of the other diastereoisomer $\mathbf{Pro_{Pip}2}$ is also possible. However, this should be in equilibrium with **II**, so that under thermodynamic control only $\mathbf{Pro_{Pip}1}$ is formed.

Overall, the hydride transfer mechanism via **II** is the pathway with the overall lowest activation barrier. It is favored over the concerted C−H activation at the piperidine ring as well as over the C_{sp^2}−H activation at one of the phenyl substituents, which features a considerably higher barrier of more than 160 kJ mol^{-1} (blue pathway). The low activation barrier of the hydride transfer is also well in line with the facile product formation in experiment even at low temperatures and the impossible isolation of any intermediate.

■ CONCLUSION

In conclusion, we reported on the isolation of a series of phosphorus cations stabilized by the bis(1-piperidinyl)-substituted carbodiphosphorane **1**. The monocations of type $[\mathbf{1}\text{-}PR_2]^+$ (R = Cl, Br, I, Ph, Cy) are easily accessible by ligand for halide exchange and feature characteristic NMR and crystallographic properties well in line with the electronics of the cationic phosphorus center and its interaction with the CDP ligand. Halide abstraction to form dicationic species was revealed to be difficult and resulted in the formation of a monocation, which underwent formal C−H bond activation at the piperidinyl moiety. DFT studies showed that the activation process does not proceed via a concerted C−H activation step but via an iminium intermediate formed by initial hydride transfer and subsequent P−C bond formation. This observation clearly demonstrates the pronounced electrophilicity of the dications, particularly without further π-donor substituents at phosphorus. This pronounced π acidity might be interesting for applications of these species as ligands in transition-metal chemistry or directly in bond activations, particularly in reactions which make use of hydride rather than proton transfer reaction steps. Here, undesired intramolecular hydride transfer reactions from the substituents need to be considered for an advanced ligand design.

■ EXPERIMENTAL SECTION

Experimental details are provided in the Supporting Information.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00412.

Computational XYZ coordinates for all structures (XYZ)

Experimental procedures, spectroscopic details and NMR spectra for all new compounds as well as crystallographic and computational details (PDF)

Accession Codes

CCDC 2005265−2005271 and 2018899 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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