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A Dicationic Iminophosphane

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Supporting Information

ABSTRACT: A novel dicationic system containing a PN fragment has been synthesized and structurally characterized. According to the solid-state analysis and theoretical investigation, the dicationic iminophosphane resonance form is the most appropriate description for the dication. However, the contribution from the phosphorus mononitride resonance form is not negligible.

Neutral two-electron-donor carbenes have proven to be quite versatile ligands for the isolation of a wide variety of novel main-group species.[1−4] Examples include diatomic allotropes (L−E_2−L, where L = carbene and E = B, Si, Ge, P, As, etc.)[1a] of boron, silicon, germanium, phosphorus, arsenic, etc.[2−4] Nevertheless, these interesting molecules, among numerous other main-group species, sparked a debate about the most appropriate way to describe bonding in these compounds.[5,6] In particular, the arguments have been focused on whether the carbene moieties form typical covalent bonds or the use of dative-bond analogy is also valid. The latest evidence showed that the L−E bonds for L−B_2−L are quite strong, suggesting substantial covalent character.[6] However, Frenking argued that dative bonds could also be very strong by the combination of σ donation from L and π-back-bonding from the E_2 fragment in this case.[5b]

The same bonding arguments would also apply to the recently synthesized heteronuclear PN fragment stabilized by two carbene moieties (**A** in Figure 1).[7] The authors of this work describe it as a carbene-stabilized phosphorus mononitride or phosphinidene nitrene (**A′**) but did acknowledge that the phosphazabutadiene (**A″**) description was also appropriate. Furthermore, single-electron oxidation of **A** was demonstrated to form its radical cation **B**. On the other hand, double oxidation was not feasible with this system even though successful two-electron oxidations were achieved with the phosphorus and arsenic homonuclear analogues.[4c,e] This was presumably due to (i) the polarized nature of the P−N bond and (ii) the π-accepting properties of the carbenes, in particular the cyclic alkylaminocarbene.[8] It was then conceivable that the use of a good π donor would provide sufficient electronic stabilization for preparation of the doubly oxidized form of **A** that was predicted to have a P═N double bond.[9] Carbones[10,11] (**C** in Figure 1), which are neutral four-electron donors, certainly fit this description because they possess simultaneous σ- and π-donor properties, making them ideal ligands for the isolation of exceptionally electron-deficient species.[12] In this work, we report the use of a carbone−carbene synergy for stabilization of the doubly oxidized analogue of **A** whose structural parameters and frontier orbitals indicated formation of the first example of a dicationic iminophosphane. However, the dicationic phosphorus mononitride description for this molecule should not be completely dismissed.

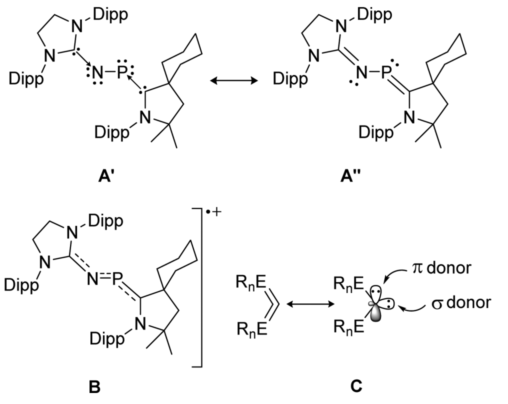
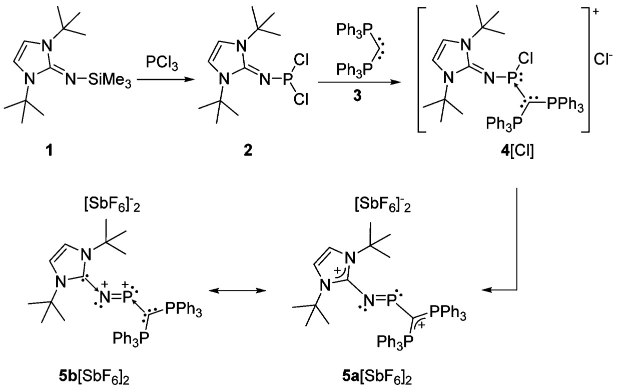


Figure 1. Recently isolated neutral (**A**) and radical cationic (**B**) phosphorus mononitrides and a general structure for carbones (**C**). Dipp = 2,6-diisopropylphenyl.

The overall synthesis of the target dication is summarized in Scheme 1. The initial P−N bond was formed by trimethylsilyl chloride elimination upon the treatment of imine **1** with PCl_3. The resulting phosphine **2** was then subjected to chloride displacement using carbodiphosphorane **3** to form **4**[Cl]. The ^{31}P NMR spectrum of **4**[Cl] contained two second-order signals observed at 21.8 and 262.5 ppm. The latter signal was assigned to

Scheme 1. General Synthetic Protocol



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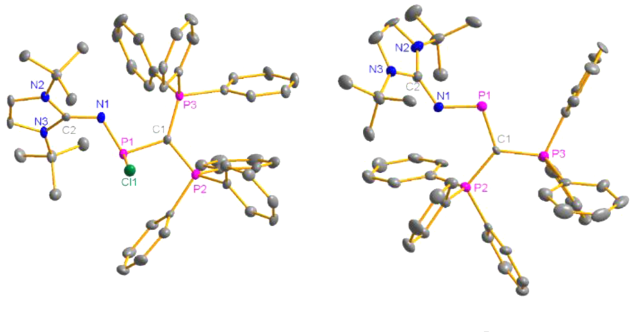
the central phosphorus, which was more than 130 ppm downfield-shifted with respect to $[^{i}Pr_2NP(Cl)(C(PPh_3)_2)][Cl]$ (δ_P = 133.4 ppm).[12c] After structural elucidation of **4**[Cl][13] (Figure 2), the unexpected downfield shift of this δ_P signal was attributed to the elongated nature of the P1−Cl1 bond of **4**$^+$ [2.3472(16) Å] with respect to $[^{i}Pr_2NP(Cl)(C(PPh_3)_2)]^+$ [2.173(2) Å].[14] This observation also hinted at incipient ionization toward the target dication.



4$^+$ **5**$^{2+}$

Figure 2. Molecular structures for **4**[Cl] and **5**[SbF$_6$]$_2$ with the ellipsoids drawn at 50% probability. All hydrogen atoms, solvent molecules, and counterions have been omitted for clarity.

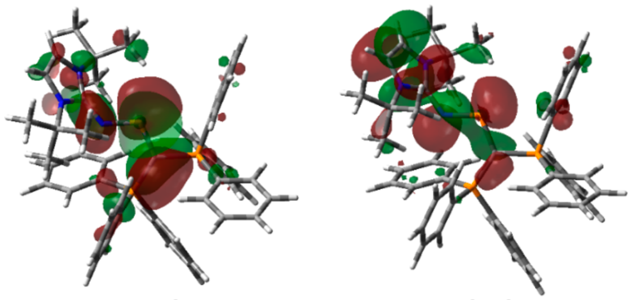
Indeed, the addition of 2 equiv of AgSbF$_6$ to a 1,2-difluorobenzene solution containing **4**[Cl] resulted in an immediate color change from yellow to orange, yielding **5**[SbF$_6$]$_2$. The δ_P signal assigned to the central phosphorus was observed at 410.2 ppm, which is more than 50 ppm downfield-shifted from $[^{i}Pr_2NP(C(PPh_3)_2)]^{2+}$ (δ_P = 355.7 ppm) but well within the range observed for similar two-coordinate phosphorus species.[15,16] The expected coordination geometry around the central phosphorus and the trans-bent C1−P1−N1−C2 fragment (torsion angle = 171.8°[17]) of the newly formed species was confirmed by single-crystal X-ray diffraction (Figure 2).

As predicted, the P1−N1 bond length of 1.594(6) Å for **5**[SbF$_6$]$_2$ was shorter than the same distances observed for neutral **A** [1.7085(16) Å] and its radical cation **B** [1.645(4) Å].[7] In fact, this bond distance for **5**[SbF$_6$]$_2$ is well within the range for the analogous bond distances observed for iminophosphanes that contain doubly bonded PN fragments.[16] The observed trend may be described as the stepwise removal of an electron pair from the highest occupied molecular orbital (HOMO) of **A**, which is a PN π^*-antibonding orbital, resulting in an increase in the bond order from 1 to 2.[7] This supports the depiction of **5**$^{2+}$ as a doubly oxidized analogue of **A**. Electron depletion at the PN fragment for **5**$^{2+}$ was also apparent by a longer N1−C2 bond distance [1.367(8) Å] and a larger P1−N1−C2−N2 torsion angle (55.5°) in comparison to the analogous values for both **A** [1.282(3) Å and 10.1°] and **B** [1.313(5) Å and 32.1°[17]]. This is presumably due to a decrease in π-back-donation from the increasingly electron-deficient PN fragment to the carbene, weakening the N1−C2 bond. In fact, this N−C bond distance for **5**$^{2+}$ is not only within the range for a single N−C(sp^2) bond[18] but also the longest N−C bond with respect to similar compounds (including **A** and **B**) containing a "guanidyl" moiety.[19]

Furthermore, the P1−C1 bond distance for **5**$^{2+}$ [1.748(7) Å], which was found to fall between the P−C bond distances for **A** [1.719(2) Å] and its radical cation **B** [1.788(5) Å], was essentially identical with the analogous bond distance for $[^{i}Pr_2NP(C(PPh_3)_2)]^{2+}$ [1.745(7) Å]. This observation, together with the coplanarity of the carbone with the PN moiety (N1−P1−C1−P2 torsion angle = 1.2°), was expected because creation of the electron-deficient PN fragment was compensated for by an increase in the C1 → P1 π donation. In fact, it was believed that the ability of the carbone **3** to π donate to the central phosphorus was crucial for the overall stability of the dication **5**$^{2+}$. Even though a close P···F interion contact was observed (3.04 Å; the sum of the van der Waals radii for phosphorus and fluorine is 3.36 Å[20]), it should not have any drastic consequences on the observed structural parameters for **5**$^{2+}$.[21] In fact, close interion contacts are virtually nonexistent in solution because the synthesis of **5**$^{2+}$ in the presence of $AlCl_4^-$ and $[BAr^f_4]^-$ [Ar^f = 3,5-(CF$_3$)-C$_6$H$_3$] had no effect on the value for the δ_P signal assigned to the central phosphorus.

Thus, the above-mentioned structural parameters (the P−N bond distance, the CPNC torsion angle, etc.) for **5**$^{2+}$ are very similar to analogous parameters observed for neutral iminophosphane containing electron-donating substituents,[16] implying that the resonance form **5a**$^{2+}$ is the most adequate for the description of this molecule.

Further insight into the bonding motif for the dicationic moiety of **5**[SbF$_6$]$_2$ was gained by performing density functional theory (DFT) calculations using the *Gaussian 09* package. The structure was optimized at the B3LYP/6-31G(d) level of theory, yielding a close match between the theoretical and experimental structural parameters. The HOMO and lowest unoccupied molecular orbital (LUMO) [B3LYP/6-311G(d)] for the dication **5**$^{2+}$ are depicted in Figure 3. As expected, the LUMO of **5**$^{2+}$ (antibonding for the PN fragment) is virtually equivalent to the HOMO of **A** and the singly occupied molecular orbital (SOMO) of **B**, while the HOMO of **5**$^{2+}$ is exactly the same as the HOMO−1 of **A** and **B**.[7] Furthermore, the frontier orbitals for **5**$^{2+}$ are very similar to the analogous orbitals observed for neutral iminophosphane containing electron-donating substituents,[16] supporting for the formation of dicationic iminophosphane **5a**$^{2+}$.



LUMO HOMO

Figure 3. LUMO and HOMO for **5**$^{2+}$.

Nevertheless, the σ-bond polarization of the P1−C1 and C2−N1 bonds, examined through natural bond order (NBO) analysis, suggested that their dative bond character is not negligible. This analysis revealed that the P1−C1 (68.0% contribution of C1) and C2−N1 (41.3% contribution of C2) bonds were more polarized toward the donor atoms (C1 and C2) than in the other similar cases (P2−C1 = 61.9% of C1; P3−C1 = 61.8% of C1; C2−N2 = 37.5% of C2; C2−N3 = 37.5% of C2).[22] Thus, these observations indicated that the resonance form **5b**$^{2+}$ (a base-stabilized diationic phosphorus mononitride) should not be completely disregarded from the overall description of the newly formed dication.

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In summary, the use of a novel carbone−carbene system allowed for the successful isolation of the doubly oxidized analogue of **A**. According to the structural parameters and nature of the frontier orbitals, the most appropriate resonance form for the newly synthesized molecule would be dicationic iminophosphane **5a**$^{2+}$. However, the dicationic phosphorus mononitride resonance form **5b**$^{2+}$ should also be included in the overall depiction of the dication.

ASSOCIATED CONTENT

Supporting Information

Synthetic procedures, details of theoretical calculations, and crystal data CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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DEDICATION

Dedicated to Professor Vlatko Vidović on the occasion of his 70th birthday.

REFERENCES

(1) (a) Dyker, C. A.; Bertrand, G. *Science* **2008**, *321*, 1050. (b) Wang, Y.; Robinson, G. H. *Dalton Trans.* **2012**, *41*, 337. (c) Martin, C. D.; Soleilhavoup, M.; Bertrand, G. *Chem. Sci.* **2013**, *4*, 3020. (d) Wang, Y.; Robinson, G. H. *Inorg. Chem.* **2014**, *53*, 11815.

(2) (a) Braunschweig, H.; Dewhurst, R. D.; Hammond, K.; Mies, J.; Radacki, K.; Vargas, A. *Science* **2012**, *336*, 1420. (b) Böhnke, J.; Braunschweig, H.; Ewing, W. C.; Hörl, C.; Kramer, T.; Krummenacher, I.; Mies, J.; Vargas, A. *Angew. Chem., Int. Ed.* **2014**, *53*, 9082.

(3) (a) Li, Y.; Mondal, K. C.; Samuel, P. P.; Zhu, H.; Orben, C. M.; Panneerselvam, S.; Dittrich, B.; Schwederski, B.; Kaim, W.; Mondal, T.; Koley, D.; Roesky, H. W. *Angew. Chem., Int. Ed.* **2014**, *53*, 4168. (b) Wu, D.; Li, Y.; Ganguly, R.; Kinjo, R. *Chem. Commun.* **2014**, *50*, 12378. (c) Wang, Y.; Xie, Y.; Wei, P.; King, R. B.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. *Science* **2008**, *321*, 1069. (d) Sidiropoulos, A.; Jones, C.; Stasch, A.; Klein, S.; Frenking, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 9701. (e) Jones, C.; Sidiropoulos, A.; Holzmann, N.; Frenking, G.; Stasch, A. *Chem. Commun.* **2012**, *48*, 9855.

(4) (a) 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. (b) Back, O.; Kuchenbeiser, G.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 5530. (c) Back, O.; Donnadieu, B.; Parameswaran, P.; Frenking, G.; Bertrand, G. *Nat. Chem.* **2010**, *2*, 369. (d) Abraham, M. Y.; Wang, Y.; Xie, Y.; Wei, P.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. *Chem.—Eur. J.* **2010**, *16*, 432. (e) Abraham, M. Y.; Wang, Y.; Xie, Y.; Gilliard, R. J., Jr.; Wei, P.; Vaccaro, B. J.; Johnson, M. K.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. *J. Am. Chem. Soc.* **2013**, *135*, 2486. (f) Kretschmer, R.; Ruiz, D. A.; Moore, C. E.; Rheingold, A. L.; Bertrand, G. *Angew. Chem., Int. Ed.* **2014**, *53*, 8176.

(5) (a) Himmel, D.; Krossing, I.; Schnepf, A. *Angew. Chem., Int. Ed.* **2014**, *53*, 370. (b) Frenking, G. *Angew. Chem., Int. Ed.* **2014**, *53*, 6040. (c) Himmel, D.; Krossing, I.; Schnepf, A. *Angew. Chem., Int. Ed.* **2014**, *53*, 6047.

(6) Köppe, R.; Schnöckel, H. *Chem. Sci.* **2015**, *6*, 1199.

(7) Kinjo, R.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 5930.

(8) Back, O.; Henry-Ellinger, M.; Martin, C. D.; Martin, D.; Bertrand, G. *Angew. Chem., Int. Ed.* **2013**, *52*, 2939.

(9) According to ref 7, the HOMO of **A** and the SOMO of **B** are antibonding with respect to the PN fragment, so their complete electron depopulation would result in a shortening of the P−N bond.

(10) The term "carbones" was coined by Frenking et al.: (a) Tonner, R.; Frenking, G. *Angew. Chem., Int. Ed.* **2007**, *46*, 8695. (b) Deshmukh, M. M.; Gadre, S. R.; Tonner, R.; Frenking, G. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2298. (c) Tonner, R.; Frenking, G. *Chem.—Eur. J.* **2008**, *14*, 3260. (d) Takagi, N.; Shimizu, T.; Frenking, G. *Chem.—Eur. J.* **2009**, *15*, 8593. (e) Frenking, G.; Tonner, R. *Pure Appl. Chem.* **2009**, *81*, 597. (f) Takagi, N.; Shimizu, T.; Frenking, G. *Chem.—Eur. J.* **2009**, *15*, 3448. (g) Tonner, R.; Frenking, G. *Chem.—Eur. J.* **2008**, *14*, 3273.

(11) The first time the concept of carbone was experimentally demonstrated was in the following: Dyker, C. A.; Lavallo, V.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 3206.

(12) (a) Inés, B.; Patil, M.; Carreras, J.; Goddard, R.; Thiel, W.; Alcarazo, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 8400. (b) Khan, S.; Gopakumar, G.; Thiel, W.; Alcarazo, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 5644. (c) Tay, M. Q. Y.; Lu, Y.; Ganguly, R.; Vidović, D. *Angew. Chem., Int. Ed.* **2013**, *52*, 3132. (d) Tay, M. Q. Y.; Lu, Y.; Ganguly, R.; Vidović, D. *Chem.—Eur. J.* **2014**, *20*, 6628. (e) Chen, W.-C.; Lee, C.-Y.; Lin, B.-C.; Hsu, Y.-C.; Shen, J.-S.; Hsu, C.-P.; Yap, G. P. A.; Ong, T.-G. *J. Am. Chem. Soc.* **2014**, *136*, 914.

(13) Apart from the chloride anion (40%), $[PO_2Cl_2]^-$ (60%) was also identified (confirmed by ^{31}P NMR spectroscopy) during the structural refinement of **4**[Cl], presumably due to hydrolysis.

(14) P−Cl bond elongation has already been observed for ylidyl chlorophosphanes: Jochem, G.; Breitsameter, F.; Schier, A.; Schmidpeter, A. *Heteroat. Chem.* **1996**, *7*, 239.

(15) (a) Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367. (b) Cowley, A. H.; Cushner, M. C.; Lattman, M.; McKee, M. L.; Szobota, J. S.; Wilburn, J. C. *Pure Appl. Chem.* **1980**, *52*, 789.

(16) (a) Niecke, E.; Gudat, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 217. (b) Miqueu, K.; Sotiropoulos, J.-M.; Pfister-Guillouzo, G.; Rudzevich, V. L.; Gonitzka, H.; Lavallo, V.; Romanenko, V. D. *Eur. J. Inorg. Chem.* **2004**, 2289.

(17) Only the absolute values are reported.

(18) March, J. *Advanced Organic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1992.

(19) (a) Dielmann, F.; Back, O.; Henry-Ellinger, M.; Jerabek, P.; Frenking, G.; Bertrand, G. *Science* **2012**, *337*, 1526. (b) Inoue, S.; Leszczyńska, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 8589. (c) Dielmann, F.; Moore, C. E.; Rheingold, A. L.; Bertrand, G. *J. Am. Chem. Soc.* **2013**, *135*, 14071. (d) Dielmann, F.; Andrada, D. M.; Frenking, G.; Bertrand, G. *J. Am. Chem. Soc.* **2014**, *136*, 3800. (e) Franz, D.; Inoue, S. *Chem.—Asian J.* **2014**, *9*, 2083. (f) Tamm, M.; Randoll, S.; Herdtweck, E.; Kleigrewe, N.; Kehr, G.; Erker, G.; Rieger, B. *Dalton Trans.* **2006**, 459. (g) Beer, S.; Hrib, C. G.; Jones, P. G.; Brandhorst, K.; Grunenberg, J.; Tamm, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 8890. (h) Tamm, M.; Petrovic, D.; Randoll, S.; Beer, S.; Bannenberg, T.; Jones, P. G.; Grunenberg, J. *Org. Biomol. Chem.* **2007**, *5*, 523. (i) Beer, S.; Brandhorst, K.; Hrib, C. G.; Wu, X.; Haberlag, B.; Grunenberg, J.; Jones, P. G.; Tamm, M. *Organometallics* **2009**, *28*, 1534. (j) Panda, T. K.; Trambitas, A. G.; Bannenberg, T.; Hrib, C. G.; Randoll, S.; Jones, P. G.; Tamm, M. *Inorg. Chem.* **2009**, *48*, 5462. (k) Zhang, S.; Tamm, M.; Nomura, K. *Organometallics* **2011**, *30*, 2712. (l) Glöckner, A.; Bannenberg, T.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. *Inorg. Chem.* **2012**, *51*, 4368.

(20) Alvarez, S. *Dalton Trans.* **2013**, *42*, 8617.

(21) (a) Burford, N.; Losier, P.; Macdonald, C.; Kyrimis, V.; Bakshi, P. K.; Cameron, T. S. *Inorg. Chem.* **1994**, *33*, 1434. (b) Muthaiah, S.; Do, D. C. H.; Ganguly, R.; Vidović, D. *Organometallics* **2013**, *32*, 6718.

(22) These observations could also be due to the highly polarized nature of the PN fragment (the NBO partial charges for P and N are +1.12 and −0.97e, respectively) and/or hybridization effects.