Coordination Chemistry

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NHC-Mediated Synthesis of an Asymmetric, Cationic Phosphoranide, a Phosphanide, and Coinage-Metal Phosphanido Complexes**

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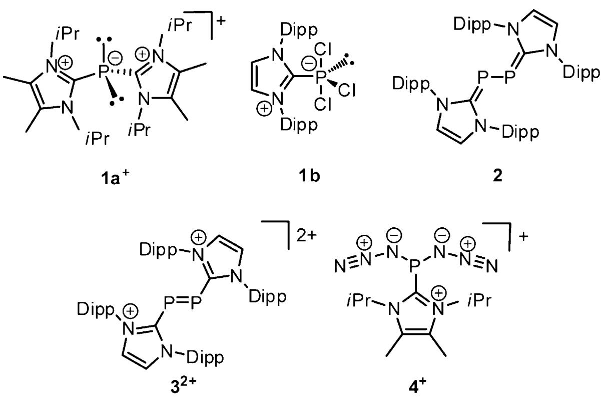
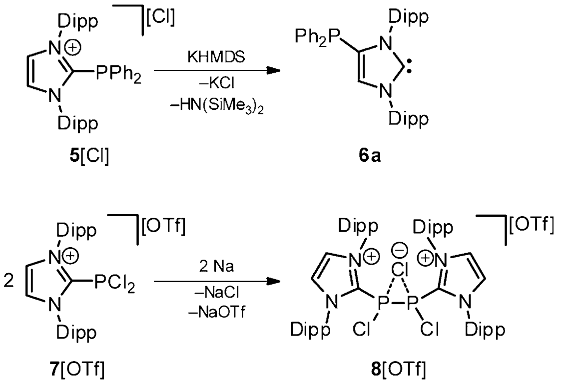
The use of imidazole-based N-heterocyclic carbenes (NHCs) as reagents in phosphorus chemistry resulted in an array of intriguing compounds (Figure 1). MacDonald and co-workers described cation **1a**$^+$ obtained by reacting PCl_3 with a carbene as a reducing reagent.[1a] Also starting from PCl_3, Robinson and co-workers reported the phosphoranide derivative **1b**, in which the P atom is hypercoordinated.[1b] Upon reduction of **1b**, 2,3-diphosphabutadiene **2** is obtained in which the P atoms are two-coordinate.[1c] This compound was oxidized to **3**$^{2+}$ by Bertrand[2] illustrating that imidazoliumyl substituents not only serve well for the stabilization of low- and hypercoordinated P atoms but also for the preparation of cations. We previously demonstrated that related organophosphorus cations show remarkable stability, for example, through the isolation of diazido P^{III} cation **4**$^+$.[3]



1a$^+$ **1b** **2** **3**$^{2+}$ **4**$^+$

Figure 1. Selected phosphorus compounds featuring imidazoliumyl substituents (only one representative Lewis structure is depicted). Dipp = 2,6-diisopropylphenyl, *i*Pr = isopropyl.

Additionally, the intriguing reactivity of certain phosphanyl-substituted imidazolium ions has been discussed. For example, treatment of **5**[Cl] with KHMDS results in the migration of the phosphanyl substituent to the 4 position of the imidazolium ring to give **6a** (Scheme 1).[4] Furthermore, we recently reported on the reduction of cation **7**$^+$ to compound **8**$^+$ in which a dicationic diphosphane acts as a chelating Lewis acid toward a chloride anion (Scheme 1).[5]



5[Cl] **6a** **7**[OTf] **8**[OTf]

Scheme 1. Preparation of **6a**[4] and **8**[OTf] (only one representative Lewis structure is depicted).[5] HMDS = bis(trimethylsilyl)amide, OTf = trifluoromethanesulfonate.

The above-mentioned examples are either described as donor–acceptor complexes of NHC ligands and the respective P-centered moiety or as imidazoliumyl-substituted P compounds that bear a positive charge on the imidazoliumyl substituent. Haaland[6] provides a general conceptual basis to describe such bonding environments, and thus, the latter model appears to be more realistic for us and is used throughout this paper. Independent of any such controversy, however, the imidazoliumyl substituents in the above compounds serve well for at least three purposes. First, they help to stabilize low- as well as hypercoordinated P atoms.[7] Second, they are advantageous for the stabilization of cations through delocalization of the positive charge.[7] Third, they serve to reduce the nucleophilicity of a directly bonded P^{III} atom, thus limiting decomposition pathways and rendering the molecules interesting electron-poor ligands for transition-metal catalysis.[7,8]

In this context, we were interested in the reactivity of cation **7**$^+$. Herein, we report on the reaction of salts of **7**$^+$ with an NHC, the formation of a remarkably stable, rare example of a cationic derivative of a phosphoranide, and investigations of its follow-up chemistry, including the preparation of a phosphanide cation and cationic phosphanido complexes of coinage metals.

The reaction of **7**[OTf] with **9** in *o*-$C_6H_4F_2$ gives **10**[OTf] in excellent yield (96 %, Scheme 2). Gallate salt **10**[$GaCl_4$] was prepared similarly.[9] The following discussion is focused on **10**[OTf], as the different anions exert very little influence on

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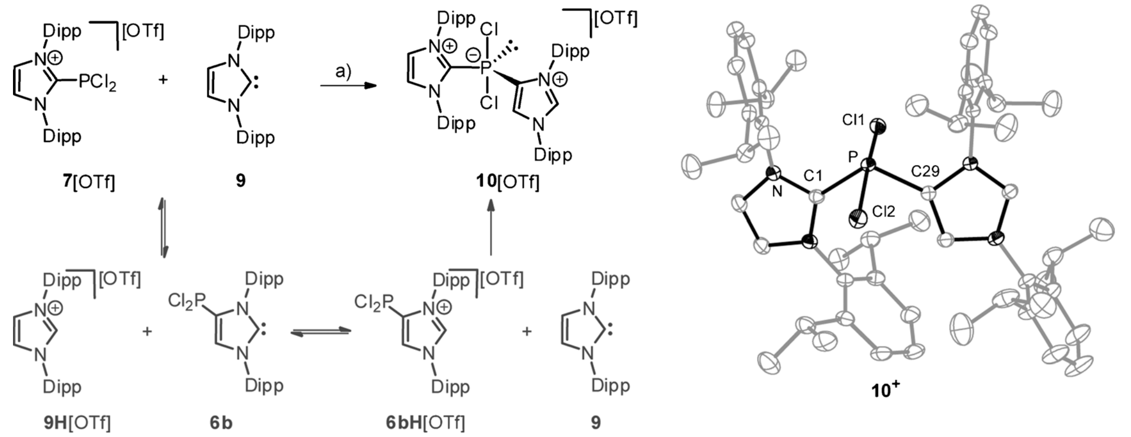


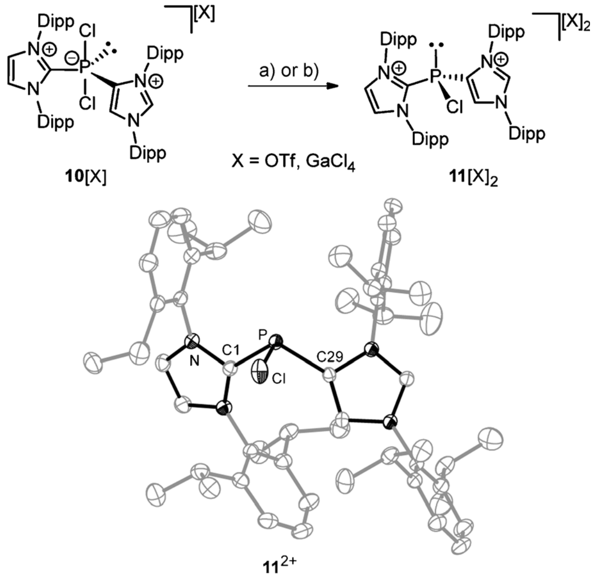
Scheme 2. Preparation of **10**[OTf] (left, a) o-$C_6H_4F_2$, −35 °C, 3 h, RT, 14 h, 96%), proposed reaction sequence for the formation of **10**$^+$ (left, grey) and molecular structure of cation **10**$^+$ (right, hydrogen atoms, solvate molecules, and anion are omitted for clarity, and thermal ellipsoids are displayed at 50% probability). Selected bond lengths [Å] and angles [°]: P1–C1 1.8679(2), P1–C29 1.8509(2), P1–Cl1 2.3135(6), P1–Cl2 2.3037(6); Cl1-P1-Cl2 166.9(2), C1-P1-C29 113.47(7), C1-P1-Cl1 84.02(5), C29-P1-Cl1 86.77(5), C1-P1-Cl2 87.27(5), C29-P1-Cl2 87.78(5).

the characteristics of the cation. The molecular structure of **10**$^+$ shows a distorted, ψ-trigonal bipyramidal coordination of the P atom, thus rendering **10**$^+$ a rare example of a cationic phosphoranide derivative.[10] Two chloro substituents occupy the axial positions, while a lone pair of electrons and the two imidazoliumyl substituents are located in the equatorial positions. Remarkably, one of the imidazoliumyl substituents is bonded at the 4 position.

The P−Cl bond lengths (P1–Cl1 2.3135(6) Å; P1–Cl2 2.3037(6) Å) are in the expected range for apical P−Cl bonds in phosphoranides[11] (e.g. in **1b**:[1b] P–Cl 2.492(1), 2.235(1) Å). The elongation of these bonds in comparison to P−Cl bonds involving three-coordinate P atoms (in **7**$^+$:[5] P–Cl 2.025(2), 2.040(2) Å)[5] reflects the low bond order in the [Cl-P-Cl] fragment as a result of its 3-center-4-electron bonding.[12]

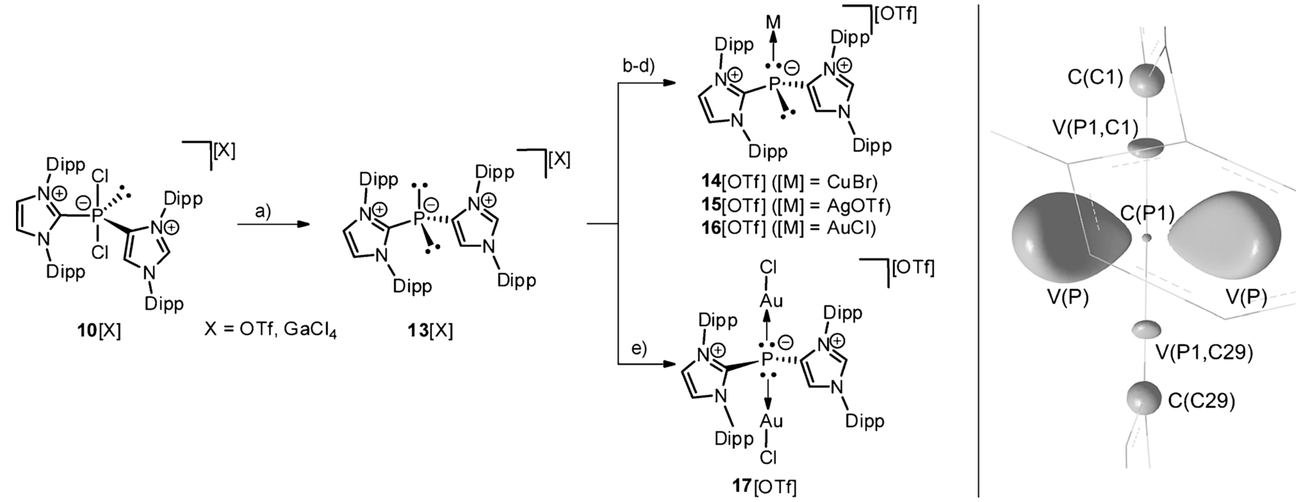
Mechanistically, we propose that **10**$^+$ forms via an abnormal carbene,[4b] giving **6b** and imidazolium **9H**$^+$ (Scheme 2), by analogy with Bertrand's mechanism for the formation of **6a**.[4a] In contrast to Bertrand's work, however, the presence of slightly acidic **9H**$^+$ and the Cl substituents on the P atom in **6b** may lead to the formation of **6bH**$^+$ and **9** in a deprotonation/reprotonation equilibrium and ultimately to the formation of **10**$^+$.

We proceeded to explore the follow up chemistry of **10**$^+$. Reacting **10**[X] (X = OTf, $GaCl_4$) with Me_3SiOTf or $GaCl_3$, respectively, resulted in the formation of the corresponding salt of racemic dication **11**$^{2+}$ (Scheme 3). The molecular structure of **11**$^{2+}$ shows a P−Cl bond (P1–Cl1 2.0458(1) Å), the length of which is in the expected range for three-coordinate P atoms (e.g., P−Cl in PCl_3: 2.039(1) Å).[12] Related dications were reported by Schmidpeter and Dillon.[13] The $^{31}P\{^1H\}$ NMR spectra of both salts show singlet resonances at identical chemical shifts ($\delta(P) = 8.3$ ppm), comparable to previously reported di(imidazoliumyl)-substituted dications (e.g., **12**$^{2+}$: L_2PCl^{2+}, L = 1,3-diisopropyl-4,5-dimethylimidazolium-2-yl, $\delta(P) = 19.9$ ppm).[3] In comparison, the resonance of **10**[OTf] ($\delta(P) = -98.9$ ppm) is substantially shifted to higher field. For related phosphoranides, the magnitude of this highfield shift is indicative of the extend of dissociation into the corresponding phosphane and a halide anion in solution. Less dissociation occurs when larger shifts are observed.[10b,14] We thus conclude that **10**$^+$ is not dissociated, even in polar solvents (e.g. CD_2Cl_2).



Scheme 3. Preparation of **11**[X]$_2$ (top, a) (X = OTf) + Me_3SiOTf, -Me_3SiCl, CH_2Cl_2, RT, 14 h, 95%; b) (X = $GaCl_4$) + $GaCl_3$, CH_2Cl_2, RT, 14 h, 98%) and molecular structure of cation **11**$^{2+}$ (bottom, hydrogen atoms, solvent molecules, and anions are omitted for clarity, and thermal ellipsoids are displayed at 50% probability). Selected bond lengths [Å] and angles [°]: P1–Cl1 2.0458(1), P1–C29 1.820(2), P1–Cl1 1.838(3); C1-P1-C29 106.62(1), C1-P1-Cl1 100.24(8), C29-P1-Cl1 97.59(8).

Reacting **10**[X] with two equivalents of potassium graphite results in P^I-centered species **13**[X] as yellow, moisture-sensitive solids in reasonable to good yields (**13**[OTf]: 68%, **13**[$GaCl_4$]: 85%; Scheme 4). Similar cations were reported by Schmidpeter et al.[15] and Macdonald et al.[1a] However, **13**$^+$ appears to be the first fully characterized P^I-centered cation



Scheme 4. Reduction of **10**[X] to **13**[X] (left, a) (X = OTf, $GaCl_4$) + 2 KC_8, −2 KCl, THF, −78 °C, 3 h, RT, 14 h; 68 % for **13**[OTf], 85 % for **13**[$GaCl_4$]), reaction of **13**[OTf] with CuBr(tht), Ag[OTf], or AuCl(tht), respectively (middle, b) + CuBr(tht), −0.5 tht, THF, RT, 6 h, 85 % **14**[OTf]; c) + Ag[OTf], THF, −78 °C, 3 h, 78 % **15**[OTf]; d) + AuCl(tht), −tht, THF, RT, 14 h, 92 % **16**[OTf];[24] e) + 2 AuCl(tht), −tht, THF, RT, 6 h, 88 % **17**[OTf]), and visualization of the ELF at the central [C-P-C] moiety in $\mathbf{13}^+$ (right, 0.948 isosurface). tht = tetrahydrothiophene.

featuring heteroleptic carbon-based substituents at the P atom.[16] The $^{31}P\{^1H\}$ NMR spectra of both compounds show a singlet at $\delta(P) = -66.1$ ppm. This is a remarkable low-field shift compared to **1a**[Cl] ($\delta(P) = -124.2$ ppm).[1a] We attribute this low-field shift to an increased deshielding of the P atom[17] as a result of a wider C-P-C angle in $\mathbf{13}^+$ (Figure 2, C1-P1-C29: 109.2(1)°) compared to $\mathbf{1a}^+$ (C-P-C: 97.35(9)°).[1a] Both P−C bond lengths in $\mathbf{13}^+$ are between those expected for typical single (1.87 Å) and double bonds (1.67 Å)[18] with the P−C1 bond (1.773(3) Å) being slightly shorter than the P−C29 bond (1.818(3) Å). This tendency was also observed in a DFT-optimized[19] (M06HF/cc-pvTZ) structure of cation $\mathbf{13}^+$ (P1-C1: 1.773(3) Å, P1-C29: 1.818(3) Å), indicating a slightly higher degree of π-bonding between P1 and C1 than between P1 and C29.

Accordingly, an atoms-in-molecules (AIM) topographical analysis[20] of the calculated electron density shows two rather polar covalent P−C bonds with a higher ellipticity (ε) for the P1−C1 bond ($\varepsilon = +0.48$, $\nabla^2\rho = +0.116$, $E = -0.129$, $G/\rho = 0.921$) than for the P1−C29 bond ($\varepsilon = +0.36$, $\nabla^2\rho = +0.010$, $E = -0.131$, $G/\rho = 1.069$).[9] Similarly, the electron localization function (ELF, Scheme 4, right)[21] gave a slightly higher population of the V(P1,C1) basin (2.52) compared to the V(P1,C29) basin (2.30). The observation of two monosynaptic basins at the P atom (V(P)), corresponding to the two lone pairs of electrons, renders $\mathbf{13}^+$ a versatile ligand.

In contrast to the coordination chemistry of phosphides[22] and recent reports on complexes of related neutral ligands featuring [X-P(I)-X] (X = C, P)[23] fragments, the coordination chemistry of cations similar to $\mathbf{13}^+$ has not yet been

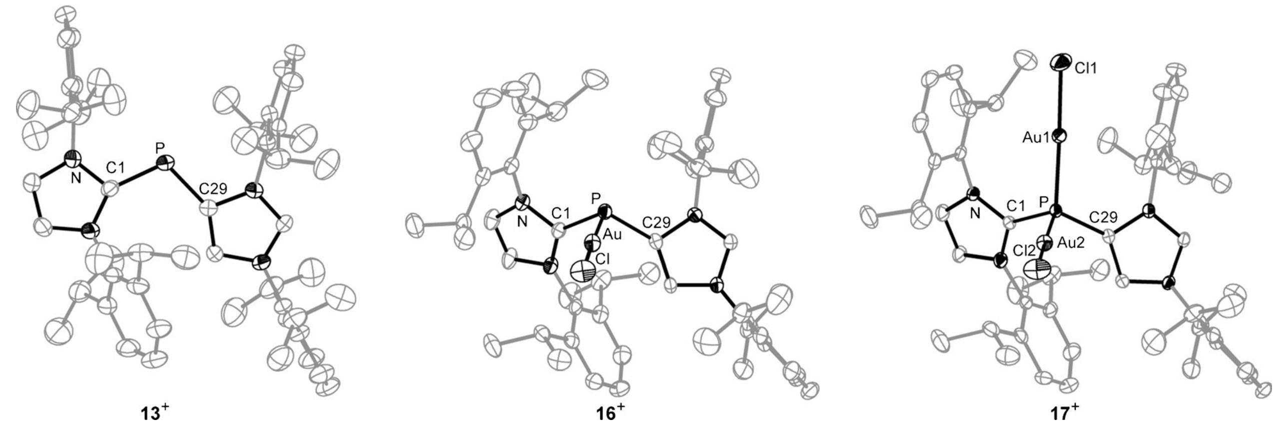


Figure 2. Molecular structures of $\mathbf{13}^+$, $\mathbf{16}^+$, and $\mathbf{17}^+$ (hydrogen atoms, solvate molecules, and anions are omitted for clarity, and thermal ellipsoids are displayed at 50 % probability); selected bond lengths [Å] and angles [°]; $\mathbf{13}^+$: P1–C1 1.773(3), P1–C29 1.818(3); C1-P1-C29 109.2(1); $\mathbf{16}^+$: P1–C1 1.831(3), P1–C29 1.839(3), P1–Au1 2.2556(8), Au1–Cl1 2.2932(9); C1-P1-C29 105.50(1), C1-P1-Au1 106.82(1), C29-P1-Au1 103.30(1), P1-Au1-Cl1 175.96(3); $\mathbf{17}^+$: P1–C1 1.843(3), P1–C29 1.829(3), P1–Au1 2.2359(8), P1–Au2 2.2259(8), Au1–Cl1 2.2783(9), Au2–Cl2 2.2883(9); C1-P1-C29 107.01(1), Au1-P1-Au2 103.41(3), C1-P1-Au1 113.51(1), C29-P1-Au1 106.31(1), C1-P1-Au2 110.80(1), C29-P1-Au2 115.89(1), P1-Au1-Cl1 173.76(3), P1-Au2-Cl2 170.89(4).

investigated. Employing 13^+ as a ligand, we successfully prepared a series of coinage-metal complexes. Complexes **14**[OTf]·(0.5 tht) (85% yield), **15**[OTf] (78% yield), and **16**[OTf] (92% yield) were obtained from the reactions of CuBr(tht), Ag[OTf], and AuCl(tht), respectively, with **13**[OTf] in a 1:1 stoichiometry (Scheme 4). The reaction of two equivalents of AuCl(tht) with **13**[OTf] gave the digold complex **17**[OTf]·(tht) (88% yield). The $^{31}P\{^1H\}$ NMR spectra of the compounds indicate the successful coordination of the respective metal fragment(s) to 13^+. For copper complex **14**[OTf]·(0.5 tht), a very broad singlet is observed ($\delta(P) = -67.2$ ppm, $\Delta\nu_{1/2} = 210$ Hz, compare with **13**[OTf]: $\delta(P) = -66.1$ ppm, $\Delta\nu_{1/2} = 6$ Hz). The broadening is attributed to the fast quadrupole relaxation of the ^{63}Cu nucleus ($I = 3/2$).[25] The silver complex **15**[OTf] shows two characteristic doublets as a result of the coupling to two silver isotopes ($\delta(P) = -96.6$ ppm, $^1J(^{31}P^{107}Ag) = 420$ Hz, $^1J(^{31}P^{109}Ag) = 484$ Hz).[26] The chemical shift of gold complex **16**[OTf] ($\delta(P) = -67.2$ ppm) is very close to the chemical shift of the free ligand ($\delta(P) = -66.1$ ppm). In contrast, the digold complex **17**[OTf]·(tht) shows a singlet that is shifted to lower field ($\delta(P) = -40.4$ ppm). Single crystals suitable for X-ray single-crystal structure determination were obtained of **16**[OTf] and **17**[OTf]·(tht). The P atom of 16^+ has a ψ-tetrahedral geometry, and that of 17^+ a slightly distorted tetrahedral coordination (Figure 2). Both complexes show the expected almost linear coordination of the gold chloride fragments (16^+: Cl1-Au1-P1 175.96(3)°; 17^+: P1-Au1-Cl1 173.76(3)°, P1-Au2-Cl2 170.89(4)°). The P1−Au bond lengths in 16^+ (2.2556(8) Å) and 17^+ (P1−Au1 2.2359(8) Å, P1−Au2 2.2259(8) Å) are very similar to one another and compare well with the corresponding bond lengths in phosphide–Au^{I}[27] or related zwitterionic triphosphenium–Au^{I} complexes.[22] Interestingly, complex **17**[OTf]·(tht) was found to be stable to air and even moisture.

In summary, the efficient preparation of the remarkable cations 10^+, 11^{2+}, and 13^+ illustrates that imidazoliumyl substituents serve well for the stabilization of high- and low-coordinated P atoms. Furthermore, the complexes 14^+, 15^+, and 16^+ were prepared in high yields. These constitute the first examples of transition-metal complexes that feature a cationic P^{I}-centered ligand. The preparation of air- and moisture-stable complex 17^+ may constitute the first step toward the preparation of a series of transition-metal complexes, including bimetallic species, that may find applications in catalysis.

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[1] a) C. A. Dyker, A. Decken, B. D. Ellis, C. L. B. Macdonald, *Chem. Commun.* **2005**, 1965; b) Y. Wang, Y. Xie, M. Y. Abraham, R. J. Gilliard, Jr., P. Wie, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson, *Organometallics* **2010**, *29*, 4778; c) Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2008**, *130*, 14970; for further examples for related low-coordinated species, see: A. J. Arduengo III, H. V. R. Dias, J. C. Calabrese, *Chem. Lett.* **1997**, *26*, 143; A. J. Arduengo III, J. C. Calabrese, A. H. Cowley, H. V. R. Dias, J. R. Goerlich, W. J. Marshall, B. Riegel, *Inorg. Chem.* **1997**, *36*, 2151.

[2] O. Back, B. Donnadieu, P. Parameswaran, G. Frenking, G. Bertrand, *Nat. Chem.* **2010**, *2*, 369.

[3] J. J. Weigand, K.-O. Feldmann, F. D. Henne, *J. Am. Chem. Soc.* **2010**, *132*, 16321.

[4] a) D. Mendoza-Espinosa, B. Donnadieu, G. Bertrand, *J. Am. Chem. Soc.* **2010**, *132*, 7264; b) E. Aldeco-Perez, A. J. Rosenthal, B. Donnadieu, P. Parameswaran, G. Frenking, G. Bertrand, *Science* **2009**, *326*, 556; compare also: J. I. Bates, P. Kennepohl, D. P. Gates, *Angew. Chem.* **2009**, *121*, 10028; *Angew. Chem. Int. Ed.* **2009**, *48*, 9844; for further derivatives of 5^+, see: N. Burford, T. S. Cameron, P. J. Ragogna, *J. Am. Chem. Soc.* **2001**, *123*, 7947; N. Kuhn, J. Fahl, *Z. Anorg. Allg. Chem.* **1999**, *625*, 729.

[5] F. D. Henne, E.-M. Schnökelborg, K.-O. Feldmann, J. Grunenberg, R. Wolf, J. J. Weigand, *Organometallics* **2013**, DOI: 10.1021/om4002268.

[6] A. Haaland, *Angew. Chem.* **1989**, *101*, 1017; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 992.

[7] a) D. J. D. Wilson, S. A. Couchman, J. L. Dutton, *Inorg. Chem.* **2012**, *51*, 7657; b) M. H. Holthausen, S. K. Surmiak, P. Jerabek, G. Frenking, J. J. Weigand, *Angew. Chem.* **2013**, *125*, 11284; *Angew. Chem. Int. Ed.* **2013**, *52*, 11078.

[8] a) O. Back, M. Henry-Ellinger, C. D. Martin, D. Martin, G. Bertrand, *Angew. Chem.* **2013**, *125*, 3011; *Angew. Chem. Int. Ed.* **2013**, *52*, 2939; b) Y. Canac, C. Maaliki, I. Abdellah, R. Chauvin, *New J. Chem.* **2012**, *36*, 17, and references therein.

[9] See the Supporting Information for details.

[10] a) G. Müller, J. Brand, S. B. Jetter, *Z. Naturforsch. B* **2001**, *56*, 1163; for neutral and anionic derivatives, see also: b) K. B. Dillon, *Chem. Rev.* **1994**, *94*, 1441, and Ref. [11].

[11] a) G.-V. Röschenthaler, T. Heine, L. Zhechkov, B. S. Basil, T. Böttcher, *Chem. Sci.* **2013**, *4*, 77; b) P. Kilian, A. M. Slawin, A. L. Fuller, P. Wawrzyniak, *Inorg. Chem.* **2009**, *48*, 2500; c) K. B. Dillon, A. W. G. Platt, A. Schmidpeter, F. Zwaschka, W. S. Sheldrick, *Z. Anorg. Allg. Chem.* **1982**, *488*, 7.

[12] W. S. Sheldrick, J. Kiefer, *Z. Naturforsch. B* **1989**, *44*, 609.

[13] a) A. Schmidpeter, S. Lochschmidt, K. Karaghiosoff, W. S. Sheldrick, *J. Chem. Soc. Chem. Commun.* **1985**, 1447; b) R. O. Day, A. Willhalm, J. M. Holmes, R. R. Holmes, A. Schmidpeter, *Angew. Chem.* **1985**, *97*, 775; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 764.

[14] J. G. Verkade, L. D. Quin, *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, VCH, Deerfield Beach, **1987**, chap. 20.

[15] A. Schmidpeter, S. Lochschmidt, A. Willhalm, *Angew. Chem.* **1983**, *95*, 561; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 545.

[16] a) B. D. Ellis, C. B. L. Macdonald, *Coord. Chem. Rev.* **2007**, *251*, 936; b) Unsymmetrically substituted phosphaallylic salts were described by A. Schmidpeter, M. Regitz, O. J. Scherer, *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, Thieme, Stuttgart, **1990**.

[17] a) M. Baudler, *Angew. Chem.* **1987**, *99*, 429; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 419; b) O. Kühl, *Phosphorus-31 NMR Spectroscopy*, Springer, Berlin, **2008**.

[18] A. F. Hollemann, N. Wiberg, *Lehrbuch der Anorganischen Chemie*, Walter de Gruyter, Berlin, **2007**.

[19] Gaussian 09, Revision A.02, **2009**; for a complete list of authors, see the Supporting Information.

[20] a) R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford, UK, **1995**, International Series of Monographs on Chemistry; b) R. F. W. Bader, *J. Phys. Chem. A* **1998**, *102*, 7314; c) T. A. Keith, AIMAll (Version 11.08.23); TK Gristmill Software, Overland Park KS, 2011 (aim.tkgristmill.com).

[21] a) A. D. Becke, K. E. J. Edgecombe, *J. Chem. Phys.* **1990**, *92*, 5397; b) B. Silvi, A. Savin, *Nature* **1994**, *371*, 683; c) B. Silvi, I. Fourré, M. E. Alikhani, *Monatsh. Chem.* **2005**, *136*, 855.

[22] a) E. J. Fernándes, A. Laguna, M. E. Olmos, *J. Chil. Chem. Soc.* **2007**, *52*, 1200; b) P. Mastrorilli, *Eur. J. Inorg. Chem.* **2008**, 4835; c) D. W. Stephan, *Coord. Chem. Rev.* **1989**, *95*, 41.

[23] a) J. Henn, K. Meindl, A. Oechsner, G. Schwab, T. Koritsanszky, D. Stalke, *Angew. Chem.* **2010**, *122*, 2472; *Angew. Chem. Int. Ed.* **2010**, *49*, 2422; b) J. W. Dube, C. L. B. Macdonald, P. J. Ragogna, *Angew. Chem.* **2012**, *124*, 13203; *Angew. Chem. Int. Ed.* **2012**, *51*, 13026.

[24] The gold complex was also synthesized as gallate salt from **13**[$GaCl_4$]; see the Supporting Information for further details.

[25] a) H. Friebolin, *Ein- und zweidimensionale NMR-Spektroskopie*, Wiley VCH, Weinheim, **2006**; b) H. Fujii, M. Tomura, T. Kurahashi, M. Kujime, *Inorg. Chem.* **2007**, *46*, 541.

[26] a) E. L. Muetterties, C. W. Alegranti, *J. Am. Chem. Soc.* **1970**, *92*, 4114; b) E. L. Muetterties, C. W. Alegranti, *J. Am. Chem. Soc.* **1972**, *94*, 6386; c) S. M. Socol, J. G. Verkade, *Inorg. Chem.* **1984**, *23*, 3487; d) H. Grützmacher, H. Rüegger, U. Fischbach, *Eur. J. Inorg. Chem.* **2007**, 2654.

[27] D. M. Stefanescu, H. F. Yuen, D. S. Glueck, J. A. Golen, L. N. Zakharov, C. D. Incarvito, A. L. Rheingold, *Inorg. Chem.* **2003**, *42*, 8891.