Bis-Phosphaketenes $\text{LM(PCO)}_2$ (M = Ga, In): A New Class of Reactive Group 13 Metal-Phosphorus Compounds

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Abstract: Phosphaketenes are versatile reagents in organophosphorus chemistry. We herein report on the synthesis of novel bis-phosphaketenes, $\text{LM(PCO)}_2$ (M = Ga 2a, In 2b; L = H(C(Me)N(Ar))$_2$; Ar = 2,6-i-Pr$_2$C$_6$H$_3$) by salt metathesis reactions and their reactions with LGa to metallaphosphenes LGa(OCP)PML (M = Ga 3a, In 3b). $3b$ represents the first compound with significant In–P π-bonding contribution as was confirmed by DFT calculations. Compounds 3a and 3b selectively activate the N–H and O–H bonds of aniline and phenol at the Ga–P bond and both reactions proceed with a rearrangement of the phosphaethynolate group from Ga–OCP to M–PCO bonding. Compounds 2–5 are fully characterized by heteronuclear (1H, 13C(1H), 31P(1H)) NMR and IR spectroscopy, elemental analysis, and single crystal X-ray diffraction (sc-XRD).

Introduction

The 2-phosphaethynolate (OCP) anion is widely applied as ligand in s-, p- and d-block element chemistry, in decarboxylation reactions, and as building block for the synthesis of phosphorus-containing compounds, i.e. heterocycles.$^{[1]}$ 2-Phosphaethynolate-substituted metal complexes are easily accessible by salt metathesis reactions using Na(OCP)(dioxane)$_2$.$^{[2]}$ Depending on the electronic nature of the metal center, the OCP anion either binds via the “hard” oxygen or the “soft” phosphorus atom.$^{[2]}$ In 2012, the first structurally characterized metallaphosphakete $\text{Re(PCO)(CO)}$(triphos) was reported by Grützmacher et al.$^{[3a]}$ followed by the synthesis of a variety of p- and d-block metal phosphaketenes (Figure 1).$^{[3–6]}$ P-bonded main group element and transition metal phosphaketenes are versatile reagents, which can liberate carbon monoxide due to the relatively weak P–CO bond and/or undergo cycloaddition reactions at the P–C double bond.$^{[3–6]}$ In remarkable contrast to the well-developed chemistry of mono-phosphaketenes, phosphaketenes are unknown, to date, most likely resulting from the high tendency of the PCO groups to undergo cycloaddition reactions, whereas OCP-bonded bis-phosphaethynolate compounds are known.$^{[7]}$

We recently synthesized gallaphosphakete, LGa(Cl)PCO (L = H(C(Me)N(Ar))$_2$; Ar = 2,6-i-Pr$_2$C$_6$H$_3$) and reported on its reaction with LGa to an unprecedented gallaphosphene LGa(Cl)PGa$_2$.$^{[8a]}$ which was found to reversibly react with heteroallenes such as CO$_2$ and carbohdiimides.$^{[8b]}$ This remarkable finding and the scarcity of bis-phosphaketenes prompted our interest to bis-phosphaketenes of group 13 metals, and we herein report on the syntheses of two bis-phosphaketenes $\text{LM(PCO)}_2$ (M = Ga 2a, In 2b). These were found to react with...
LGa to gallaphosphene LGa(OCP)PGaL (3a) and indaphosphene LGa(OCP)PGaL (3b), which represents the first structurally characterized compound with significant In–P π-bonding contribution. The promising potential of 3a and 3b in N–H and O–H bond activation reactions is also reported.

Results and Discussion

Salt elimination reactions of LGaCl₂ (1a) and LinCl₂ (1b) with two equivalents of Na(OCP)(dioxane)₂ yielded the corresponding bis-phosphaketenes LGa(PCO)₂ (2a) and Lin(PCO)₂ (2b) as pale yellow crystalline solids in high yields (>86%, Scheme 1).

Compounds 2a and 2b are soluble in common organic solvents and stable under an inert gas atmosphere at ambient temperature in both solution and solid state, but it decomposes rapidly when exposed to air. The ¹H NMR spectra of 2a and 2b each exhibit one set of resonances for the aryl (Ar) groups of the β-diketiminate ligand, indicating a symmetric nature of the molecules in solution (Table S1). ¹³C(¹H) NMR spectra of 2a (183.6 ppm, ¹JC= 98.2 Hz) and 2b (181.0 ppm, ¹JC= 105.8 Hz) show the expected doublets for the phosphaketeny carbon atoms, whereas the ³¹P(¹H) NMR spectra display sharp singlets at −356.0 ppm (2a) and −375.8 ppm (2b), respectively, which are in a typical region of monophosphaketenes (−354.9 to −394.6 ppm). The IR spectra of 2a (1934, 1907 cm⁻¹) and 2b (1918, 1894 cm⁻¹) each show two strong absorption bands for the PCO stretching vibrations most likely due to the symmetrical and unsymmetrical stretches, which are in a comparable range to that observed for monophosphaketenes LGa(Cl)PCO (1910 cm⁻¹). To the best of our knowledge, compounds 2a and 2b are the first metal bis-phosphaketenes reported, to date.

The solid-state molecular structures of compounds 2a and 2b were determined by sc-XRD (Figure 2). The compounds crystallize in the orthorhombic space groups P2₁2₁2₁ (2a) and Pna₂₂ (2b), respectively. The Ga and In atoms are four-coordinate and adopt distorted tetrahedral geometries and the PCO units are almost linear (174.2(8), 176.7(13)°), which represents the first structurally characterized compound with significant In⁻P π-bonding contribution. Interestingly, the In1–PSi₃ bond in LIn(PCO)₂ (1918, 1894 cm⁻¹) is slightly shorter than the In1–PSi₃ bond, which agrees with the sum of the calculated single-bond radii (In 1.42 Å; P 1.11 Å). The In1–P (1.26 Å) and In–P single bonds in [(2,4,6-tBu₅C₆H₃)₂In-PSi₃]₂ each exhibit one set of resonances for the aryl (Ar) groups of the β-diketiminate ligand, indicating a comparable structural motif was previously observed for 3a. The IR spectra of 3a (2022, 2001 cm⁻¹) and 3b (1918, 1894 cm⁻¹) each show two strong absorption bands for the PCO stretching vibrations, which are in a comparable range to that observed for monophosphaketenes LGa(Cl)PCO (1910 cm⁻¹). Reactions of compounds 2a and 2b with equimolar amounts of LGa yielded metallaphosphenes L(OCP)GaPGaL (3a) and L(OCP)GaPlnL (3b) as orange crystalline solids (Scheme 1). Compound 3a was previously prepared by a different synthetic route reacting gallaphosphene LGa(Cl)PGaL with Na(OCP)(dioxane)₂, while compound 3b represents the first compound with In–P π-bonding contribution. Interestingly, upon reaction of 2b with LGa, the In–PCO bond rearranges to a Ga–OCP bond in 3b, while the phosphorus datively coordinates to the indium atom. A comparable structural motif was previously observed for 3a. Compound 3b is sparingly soluble in organic solvents and stable under an inert gas atmosphere at ambient temperature in both solution and solid state, but it decomposes rapidly when exposed to air. The ¹H and ¹³C(¹H) NMR spectra of 3b show two distinct sets of signals for the inequivalent β-diketiminate ligands at ambient temperature, and the ³¹P(¹H) NMR spectrum of 3a (−290.5, −320.8 ppm) and 3b (−313.1, −333.1 ppm) show two singlets, which are shifted to higher field compared to the phosphaketenes (2a −356.0; 2b −375.8 ppm), respectively. The ¹JC= 98.2 Hz and 105.8 Hz, respectively.
coupling constant in 3a (40.1 Hz) and 3b (48.1 Hz) are far smaller than those observed in 2 (98.2 Hz 2a; 105.8 Hz 2b) and other p-block element phosphaketenes (85.4–101.0 Hz).\textsuperscript{[12,14]} These small \( \nu_{CP} \) coupling constants indicate a phosphaethynolate (–OCP) bonding in 3a and 3b rather than the phosphaketene (–PCO) bonding due to a greater contribution of the P 3s orbital to the C–P bond in the latter.\textsuperscript{[16]} The IR spectra of 3a and 3b confirmed the phosphaketynolate bonding with strong –OCP asymmetric stretches at 1739 and 1729 cm\(^{-1} \), respectively, which are comparable to that of Na(OCP)(dioxane),\textsubscript{2}5 (\( \nu(C\equiv P) = 1755 \) cm\(^{-1} \)).\textsuperscript{[14]} Unfortunately, we were unable to assign the O–C stretches because of the overlapping region of C–N/C stretches of the ligand L. Variable temperature (VT) \(^1\)H NMR spectra (Figures S37, S38) revealed that 3a and 3b are stable in solution up to 100 °C. Moreover, they also show remarkable stability in the solid state (\( T_L = 127 \) °C for 3a, 176 °C for 3b).

The molecular structure of compound 3b in the solid state was determined by sc-XRD, further confirming the Ga–OCP binding mode of the phosphaketynolate substituent (Figure 3).\textsuperscript{[10]} Compound 3b crystallizes in the orthorhombic space group Pbc\( a \). The OCP unit in 3b binds via the oxygen atom (O1) to the gallium atom (Ga1), while the indium atom (In1) is datively coordinated by the phosphorus atom P2. This finding is consistent with the HSAB principle, according to which the “hard” Ga atom prefers binding to the oxygen atom and the rather “soft” In atom prefers P-coordination. The In1-Ga1 bond angle in compound 3b (98.09(4)°) is slightly smaller than the Ga1-P2-Ga2 bond angle reported for 3a (99.86(7)°),\textsuperscript{[8a]} however, considering the rotational disorder of the central P(OCP) moiety between the two gallium atoms in 3a, the difference is likely insignificant. The In1–P1 (2.3813(12) Å) bond length in 3b perfectly agrees with sum of the calculated In–P double bond radii (1.36 Å; P 1.02 Å),\textsuperscript{[15]} however, the short Ga1–P1 (2.2370(12) Å) bond points toward a partly delocalized \( \pi \)-electron system within the In–P–Ga unit.

The –OCP binding mode leads to a rather short Ga1–O1 bond (2.054(3) Å) and a long In1–P2 bond (2.7177(12) Å), which is close to the mean In–P bond distance of 2.64(10) Å reported in the CSD.\textsuperscript{[16]}

To gain a deeper understanding of the electronic structures of 3a and 3b, DFT calculations were performed. Geometry optimizations of 3a and 3b gave two minima for both compounds, one of which corresponds to the phosphaketynolate isomers observed by sc-XRD, LGa(OCP)PML (M = Ga 3a, In 3b), while the second are represented by the corresponding phosphaketenyl isomers, LGaP(OCP)ML (M = Ga 3a’, In 3b’), respectively (Figure S46). The phosphaketenyl isomers, 3a and 3b, are both slightly more stable by 3.6 kcal mol\(^{-1} \) (M = Ga) and 0.7 kcal mol\(^{-1} \) (M = In), respectively. However, the small energy differences and slight geometric changes between both isomers suggest that both structures can co-exist in solution (Scheme 2), which is consistent with the observed reactivity (see below). Variable-temperature (VT) \(^1\)H NMR spectroscopy studies with 3a and 3b did not allow freezing the equilibrium, indicating a very small activation barrier for the interconversion.

The HOMOs of 3a and 3b are reflected by the phosphorus-centered electron lone pairs (Figures 4, S47, S48), which are of pure p-orbital character (3a 99.4 % p, 3b 99.3 % p) according to NBO analysis. In addition, electron lone pairs at the central P atom with high s-orbital character (3a 66.8 % s, 33.0 % p

**Figure 3.** Molecular structures of compounds 3a\textsuperscript{[8a]} and 3b. Ellipsoids set at 50% probability; hydrogen atoms and alternate positions of the disordered parts (in 3a) are omitted for clarity. Selected bond lengths (Å) and angles (°): 3a: Ga1–P1 2.2943(16), Ga2–P1 2.2972(16), Ga1–O1 1.977(4), O1–C59 1.223(7), C59–P2 1.592(6), Ga2–P2 2.4798(16), Ga1–P1–Ga2 99.86(7), O1–C59–P2 176.9(7), 3b: In1–P1 2.3813(12), Ga1–P1 2.2370(12), In1–P2 2.7177(12), P2–C59 1.609(5), O1–C59 1.204(5), Ga1–O1 2.054(3); P1–In1–P2 125.60(4), O1–C59–P2 177.7(4).

**Figure 4.** HOMOs of 3a and 3b. Hydrogen atoms are omitted for clarity.

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(HOMO-2); 3b 74.7% s, 25.1% p (HOMO-3)) were also found. Second order perturbation theory (SOPPT) analysis disclosed strong additional π-type interactions of both phosphorus electron lone pairs with the antibonding ω∗(M–N) orbitals of the LM fragments accounting to 72.3 kcal mol⁻¹ (s(P)→ω∗(Ga–N)) and 56.2 kcal mol⁻¹ (p(P)→ω∗(Ga–N)) for 3a. In 3b the P–M backdonation is slightly stronger to the Ga center (s(P)→ω∗(Ga–N)) 31.7 kcal mol⁻¹, p(P)→ω∗(Ga–N) 26.4 kcal mol⁻¹) than to the In center (s(P)→ω∗(In–N) 31.8 kcal mol⁻¹, p(P)→ω∗(In–N) 15.0 kcal mol⁻¹), respectively. The P–M π interactions thus result in increased Wiberg bond indices (WBIs; 3a Ga–P 1.13, 1.14; 3b Ga–P 1.16, In–P 0.97) and Mayer Bond Orders (MBO; 3a Ga–P 1.31, 1.38; 3b Ga–P 1.37, In–P 1.28), as observed for other gallaphenenes. 9,21 However, these values suggest less strongly localized M–P single and double bonds in 3a and 3b compared to Li(Cl)GaPΔGaL. The WBIs between the Ga and In centers and the PCO unit (3a Ga–P 0.41, Ga–O 0.19; 3b In–P 0.31, Ga–O 0.19) rather suggest ionic/electrostastic interactions, while three P–C bonds and one C–O bond were found within the PCO unit, consistent with the phosphaethynolate bonding mode of the PDO moiety. Considering the NBO analyses of isomers 3a' and 3b', only slight alterations in the bonding were observed, as the WBIs (3a' Ga–P 1.07, 1.18; 3b' Ga–P 1.20, In–P 0.95) and MBOs (3a' Ga–P 1.22, 1.43; 3b' Ga–P 1.39, In–P 1.21) within the central MPGa units are comparable to those of 3a and 3b, respectively. Similarly, the π-type P–M interactions in the PCO-bonded isomers 3a' (s(P)→ω∗(Ga–N) 72.4 kcal mol⁻¹; p(P)→ω∗(Ga–N) 56.6 kcal mol⁻¹) and 3b' (s(P)→ω∗(Ga–N) 35.0 kcal mol⁻¹; p(P)→ω∗(Ga–N) 29.0 kcal mol⁻¹; s(P)→ω∗(In–N) 32.7 kcal mol⁻¹; p(P)→ω∗(In–N) 15.3 kcal mol⁻¹) disclosed by SOPPT analyses are comparable to those of the OCP-bonded isomers 3a and 3b, respectively.

Low-valent main group element compounds have attracted enormous interest in the activation of polar and non-polar X–H bonds (X=H, O, N, C, etc.) of small molecules including the development of catalytic reactions similar to those of transition metal complexes. 8,15 We recently expanded such studies to gallaphosphene Li(Cl)GaPΔGaL, demonstrating that polar X–H bonds are readily activated via 1,2 addition to the Ga–P double bond. 29 We therefore probed the reactivity of 3a and 3b toward X–H bond activation and reacted compounds 3a and 3b with equimolar amounts of aniline in toluene at ambient temperature, immediately resulting in N–H bond activation and formation of 4a and 4b, respectively. Analogous reactions with phenol gave the O–H bond activation products 5a and 5b in almost quantitative yields (Scheme 3).

Compounds 4 and 5 are colorless crystalline solids, which are soluble in common organic solvents and stable under an inert gas atmosphere at ambient temperature in both solution and solid state. The ¹H NMR spectra of compounds 4 and 5 exhibit two sets of signals for the Ar groups of the β-diketiminate ligand as was previously reported for LGa-substituted gallaphenenes, 13,14 dipnictenes, 14,15 and other complexes. 12,21,22 The ¹3C(H) NMR spectra of 4a (185.9 ppm, ¹JPC = 96.5 Hz), 4b (183.8 ppm, ¹JPC = 102.7 Hz), 5a (188.0 ppm, ¹JPC = 94.6 Hz), and 5b (185.4 ppm, ¹JPC = 101.9 Hz) each exhibit the expected doublet due to the PCO carbon atom. The ¹JPC coupling constants compare well with those of the phosphaetynolates but are larger than those of 3a (¹JPC = 40.1 Hz) and 3b (¹JPC = 48.1 Hz), respectively, suggesting a switch in coordination of the phosphaethynolate substituents from –OCP to –PCO in compounds 4 and 5. Base induced –OCP to –PCO coordination switching was previously reported by Grützmacher and Goicoechea et al. 4b,24 The ¹31P(H) NMR spectra of 4a (–291.1, –363.8 ppm), 4b (–314.7, –373.3 ppm), 5a (–296.1, –362.5 ppm), and 5b (–232.6, –371.9 ppm) each showed two sharp singlets, which are shifted to lower field than those of the starting compounds 3a (–290.5, –320.8 ppm) and 3b (–313.1, –333.1 ppm). However, the latter resonances in 4 and 5 are similar to those observed for phosphaetynolates 14,15 and support the switch in coordination of the phosphaethynolate substituent. The proton coupled ¹31P NMR spectra of 4a (–291.1 ppm, ¹JPH = 176.9 Hz), 4b (–314.7 ppm, ¹JPH = 162.8 Hz), 5a (–296.1 ppm, ¹JPH = 173.9 Hz), and 5b (–232.6 ppm, ¹JPH = 163.1 Hz) each display a doublet for the P–H units, and the coupling constants agree with the ¹JPH coupling constants observed for the 1,2 addition products of reagents containing X–H bonds (X=C, N, O etc.) to gallaphosphene LGa(Cl)PΔGaL (¹JPH = 178.9–181.0 Hz). 8a,b

The solid-state molecular structures of compounds 4a (Figure 5), 4b (Figure 5), and 5b (Figure S45) were determined by sc-XRD. All compounds crystallize in the monoclinic space group C2/c, and the structures confirmed the –PCO bonding mode of the phosphaethynolates substituents. 16

Figure 5. Molecular structures of compounds 4a and 4b. Ellipsoids set at 50% probability; hydrogen atoms, solvent molecules (benzene in 4a, and toluene in 4b), and alternate positions of the disordered parts are omitted for clarity. Selected bond lengths (Å) and angles (°): 4a: Ga1–P1 2.3396(6), Ga1–P2 2.3859(6), Ga2–N3 1.9803(18), Ga2–P1 2.3369(6); Ga2–P1 1.16, Ga2–P1 1.14. 4b: In1–P1 2.4877(4), In1–P2 2.5447(5), Ga1–NS 1.8771(10), Ga1–P1 2.3230(4), Ga1–P1–In1 108.646(17).
The four-coordinate Ga/In atoms adopt distorted tetrahedral geometries and the P atoms trigonal pyramidal geometries. The Ga1–P1–Ga2 bond angle in 4a (113.14(2)°) is comparable to that observed for LGa(Cl) PH(OC(Ph) CH2)2GaL (116.8(2)°),[18] but much larger than that of 3a (99.86(7)°).[19] The Ga1–P1 (2.3396(6) Å) and Ga2–P2 (2.3369(6) Å) bond lengths are equi-


distant and compare well with the Ga–P single bond lengths mentioned previously.[15] Interestingly, the molecular structures of compounds 4b and 5b confirm the selective addition of the N–H and O–H bonds to the Ga1–P1 bond rather than to the In1–P1 double bond in 3b, which is most likely caused by the higher nitro- and oxophilicity of gallium than indium. The In1–P1 bond lengths in 4b (2.4887(4) Å) and 5b (2.4896(10) Å) are consistent with the In–P single bonds[13] and agree with the calculated In–P single bond radii (In 1.42 Å; P 1.11 Å),[11] whereas they are significantly elongated compared to the corresponding In–P double bond 3b (2.3813(12) Å). Similarly, the Ga1–P1 bond lengths in 4b (2.3230(4) Å) and 5b (2.3085(10) Å) agree with experimental[11] and calculated[11] Ga–P single bond lengths, and the In1–P2 bond lengths in 4b (2.5447(5) Å) and 5b (2.5273(11) Å) are comparable to the In–P single bond lengths.

Conclusion

In summary, the syntheses and single crystal X-ray structures of the first bis-phosphaketenes 2a and 2b and their reactions with LGa to –OCP coordinated metallaphosphenes 3a and 3b is reported. Even though the π-electron system in 3a and 3b is rather delocalized within the M–P–Ga units (M = Ga, In), compound 3b represents the first structurally characterized compound with a substantial In–P π-bonding contribution. Compounds 3a and 3b are promising starting reagents for the activation of polar X–H bonds as was shown in reactions with aniline and phenol, which selectively occurred at the Ga–P bond with formation of compounds 4 and 5.

Supporting Information

Supporting Information Available: Detailed synthetic procedures and analytical data (H, 13C, 31P NMR and IR spectra) of 1–5, plots of DFT calculated optimized geometries and coordinates, WBI and NBO charges as well as selected molecular orbitals of 3a and 3b, and cif files of 2–5.

Deposition Number(s) 2038995 (for 2a), 2132670 (for 2b), 2038997 (for 3a), 2132671 (for 3b), 2132672 (for 4a), 2132673 (for 4b), and 2132674 (for 5b) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: bond activation · double bonds · gallium · indium · main-group elements · phosphorus

[1] a) X. Chen, S. Aldiord, F. F. Puschmann, G. Santiso-Quinones, Z. Benkó, Z. Li, G. Becker, H.-F. Grützmacher, H. Grützmacher, Angew. Chem. Int. Ed. 2014, 53, 1641–1645; Angew. Chem. 2014, 126, 1667–1671; b) M. Goicoechea, H. Grützmacher, Angew. Chem. Int. Ed. 2018, 57, 16989–16994; Angew. Chem. 2018, 130, 17214–17220; c) L. Weber, Eur. J. Inorg. Chem. 2018, 2175–2227.

[2] D. Heift, Z. Benkó, H. Grützmacher, Dalton Trans. 2014, 43, 5920–5928.

[3] Transition metal phosphaketenes: a) S. Aldiordi, D. Heift, G. Santiso-Quinones, Z. B. H. Grützmacher, M. Caporali, L. Gonsalvi, A. Rossin, M. Peruzzini, Chem. Eur. J. 2012, 18, 14805–14811; b) L. Liu, D. A. Ruiz, F. Dahcheh, G. Bertrand, R. Suter, A. M. Tondreacu, H. Grützmacher, Chem. Sci. 2016, 7, 2335–2341; c) A. R. Jupp, M. B. Geeson, M. E. Dow, A. V. Protchenko, P. Vasko, J. Campos, E. L. Kolychev, S. Aldridge, Chem. Eur. J. Inorg. Chem. 2016, 639–648; d) L. N. Grant, J. Krystek, B. Pinter, J. Telsert, H. Grützmacher, D. J. Mindiola, Chem. Commun. 2019, 55, 5966–5969.

[4] Group 13 element phosphaketenes: a) S. Hagspiel, F. Fantuzzi, R. D. Dewhurst, A. Gartner, F. Lindl, A. Lamprecht, H. Braunschweig. Angew. Chem. Int. Ed. 2021, 60, 13666–13670; Angew. Chem. 2021, 133, 13780–13784; b) D. W. N. Wilson, M. P. Franco, W. K. Myers, J. E. McGrady, J. M. Goicoechea, Chem. Soc. Rev. 2020, 49, 3971–3975; Angew. Chem. 2020, 132, 3999–4003; d) D. Wilson, W. Myers, J. M. Goicoechea, Dalton Trans. 2020, 49, 15249–15255; e) Y. Mei, J. E. Borger, D. J. Wu, H. Grützmacher, Dalton Trans. 2019, 48, 4370–4374.

[5] Group 14 element phosphaketenes: a) N. Del Rio, A. Baceiredo, N. Saffon-Merconer, D. Hashizume, D. Lutters, T. Muller, T. Kato, Angew. Chem. Int. Ed. 2016, 55, 4753–4758; Angew. Chem. 2016, 128, 4831–4836; b) S. Yao, Y. Xiong, T. Szilvási, H. Grützmacher, M. Dries, Angew. Chem. Int. Ed. 2016, 55, 4781–4785; Angew. Chem. 2016, 128, 4859–4863; c) Y. Wu, L. Liu, J. Su, J. Zhu, Z. Ji, Y. Zhao, OrganoMetals 2016, 25, 1593–1596; d) Y. Xiong, S. Yao, T. Szilvási, E. Ballerston-Martínez, H. Grützmacher, M. Dries, Angew. Chem. Int. Ed. 2017, 56, 4333–4336; Angew. Chem. 2017, 129, 4397–4400; e) A. Hinz, J. M. Goicoechea, Chem. Eur. J. 2018, 24, 7358–7363; f) D. Heift, Z. Benkó, H. Grützmacher, Chem. Eur. J. 2014, 20, 11326–11330; g) A. Hinz, J. M. Goicoechea, Dalton Trans. 2018, 47, 8879–8883; h) S. Bestgen, M. Mehta, T. C. Johnstone, P. W. Roeksy, J. M. Goicoechea, Chem. Eur. J. 2020, 26, 9024–9031; i) D. C. H. Do, A. V. Protchenko, P. Vasko, J. Campos, E. L. Kolychev, S. Aldridge, Z. Anorg. Allg. Chem. 2018, 644, 1238–1242.

[6] Group 15 element phosphaketenes: a) M. Mehta, J. E. McGrady, J. M. Goicoechea, Chem. Eur. J. 2019, 25, 5445–5450; b) Z. Li, X. Chen, M. Bergeler, M. Reher, C. V. Su, H. Grützmacher, Dalton Trans. 2015, 44, 6431–6438; c) L. Liu, D. A. Ruiz, D. Munz, G. Bertrand, Chem. Eur. J. 2016, 1, 147–153; d) M. M. Hansmann, D. A. Ruiz, L. Liu, R. Jazgar, G. Bertrand, Chem. Sci. 2017, 8, 3720–3725; e) J. E. Walley, L. S. Waring, E. Kertész, G.
Full crystallographic data of all structurally characterized compounds described herein as well as central bond lengths and angles (Tables S2–S3 and Figures S39–S45) are given in the Supporting Information.

In single bonds yielded 158 hits (459 bonds) ranging from 2.48 to 3.055 Å (mean bond length is 2.64(10) Å). Five compounds with bond distances above 3.1 Å were excluded. Cambridge Structural Database, Version 5.41 Update 3 (Aug 2021); see also: F. H. Allen, Acta Cryst. 2002, 58, 380–388.

Cutsail III, S. Schulz, Wang, D. A. Dickie, Z. Anorg. Allg. Chem. 2018, 644, 1028–1033; c) L. Tuscher, C. Helling, C. Wölper, Y. Schulte, G. Cutsail III, S. Schulz, Angew. Chem. Eur. J. 2018, 59, 10323–10332; d) J. Schoening, L. John, C. Wölper, S. Schulz, Dalton Trans. 2019, 48, 17729–17734.

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Chem. Eur. J. 2020, 59, 11142–11151; b) C. Helling, C. Wölper, G. E. Cutsail III, S. Schulz, Chem. Eur. J. 2020, 26, 3241–3250.

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