



Main-Group Elements Hot Paper

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Multi-Talented Gallaphosphene for Ga–P–Ga Heteroallyl Cation Generation, CO₂ Storage, and C(sp³)–H Bond Activation

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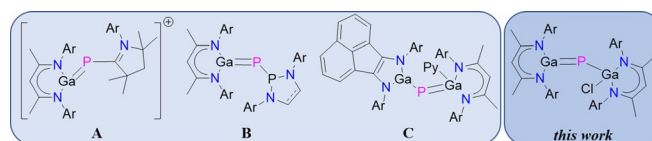
Dedicated to Professor Frank-Gerrit Klärner on the occasion of his 80th birthday

Abstract: Gallaphosphene L(Cl)GaPGaL (**2**; L = HC[C(Me)N(2,6-*i*-Pr₂C₆H₃)₂]), which is synthesized by reaction of LGa(Cl)PCO (**1**) with LGa, reacts with [Na(OCP)(dioxane)_{2.5}] to LGa(OCP)PGaL (**3**), whereas chloride abstraction with LiBAR^F₄ yields [LGaPGaL][BAR^F₄] (**4**; BAR^F₄ = B(C₆F₅)₄). **4** represents a heteronuclear analog of the allyl cation according to quantum chemical calculations. Remarkably, **2** reversibly reacts with CO₂ to yield L(Cl)Ga–P[μ-C(O)O]₂GaL (**5**), while reactions with acetophenone and acetone selectively give compounds **6** and **7** by C(sp³)–H bond activation.

Introduction

Heteronuclear group 13–15 compounds RMER' with M–E double bond (M = B–Tl; E = N–Bi) are isovalence-electronic to alkenes.^[1] While compounds of this type are well known for the lightest elements of both groups, that is, borapnictenes with B–E (E = N, P, As)^[1] and metallaimines with M–N π-bonding contribution (M = Al, Ga, In),^[2] heavier congeners are rare due to a less effective pπ–pπ orbital overlap. [[Li(thf)₃]₂Ga₂{As(Si-Pr₃)₄}] was the only structurally characterized species^[3] until we established a general route to gallaarsenes and -stibenes LGaEGa(X)L (E = As, X = Cl, Br; E = Sb, X = F, Cl, Br, I) and LGaER (ER = AsCp*, SbTer; Ter = 2,6-Mes₂C₆H₃; Mes = 2,4,6-Me₃C₆H₂).^[4] We also prepared [LGaP^{(Me)cAAC}][An] (An = B(C₆H₃(CF₃)₂)₄, B(C₆F₅)₄, Al(OC(CF₃)₃)₄; type **A**) by halide abstraction of LGa(X)–P^{(Me)cAAC}.^[5a] Cation [LGaP^{(Me)cAAC}]⁺ shows substantial Ga–P π-bonding contribution and can be

considered as heteronuclear analogue of an allyl cation.^[5b,c] Goicoechea et al. recently synthesized phosphanyl-substituted phosphagallenes (P')PGaL (P' = (HC)₂(NAr)₂P, (H₂C)₂(NAr)₂P; type **B**) and reported on their frustrated Lewis pair-type (FLP-type) reaction with CO₂ on the 1,3 positions of the P–P–Ga moiety.^[6a] They furthermore reported on the reaction of a pyridine-stabilized gallium phosphaketene L'(pyr)GaPCO (L' = Dipp-Bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene; pyr = C₅H₅N) with LGa, yielding L'(pyr)GaPGaL (type **C**), whose electronic situation resembles that of carbodiphosphorane.^[6b] Apart from these studies, the reactivity of heavier heteroalkene analogues, which are expected to be reactive species due to the presence of a strongly polarized M–E double bond (M^{δ+}–E^{δ-}), is almost unknown.^[4f] We herein report on the synthesis of gallaphosphene L(Cl)GaPGaL (**2**) and its reactions with halide abstraction reagents, CO₂, as well as acetophenone and acetone (Scheme 1).



Scheme 1. Structurally characterized compounds with Ga–P π-bonding contribution; compounds **B** and L(Cl)GaPGaL (**2**; this work) can be considered as true gallaphosphenes.

Results and Discussion

2-Phosphaethynolate-substituted compounds are promising starting reagents for the synthesis of low-valent phosphorus compounds.^[7] While group 14^[8] and group 15 element phosphaketenes^[9] are well established, reports on group 13 metal phosphaketenes are limited.^[6b,10,11] We therefore became interested in the synthesis of gallium phosphaketene L(Cl)GaPCO (**1**) and its capability to serve as precursor for the gallaphosphene L(Cl)GaPGaL (**2**) by reaction with LGa. Salt elimination reaction of LGaCl₂^[12] with [Na(OCP)(dioxane)_{2.5}] yielded LGa(Cl)PCO (**1**), which was isolated as a pale yellow solid in 95% yield of isolated product (Scheme 2). Subsequent reaction of compound **1** with LGa almost quantitatively yielded gallaphosphene L(Cl)GaPGaL (**2**) as a crystalline red solid. Compounds **1** and **2** are soluble in common organic solvents and stable under inert gas atmosphere at ambient temperature.

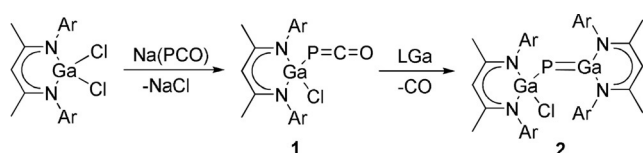
The ¹H NMR spectrum of compound **1** exhibits two sets of resonances for the Dipp groups of the β-diketiminato ligand

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Scheme 2. Synthesis of gallium phosphaketene LGa(Cl)PCO (**1**) and gallaphosphene L(Cl)GaPGaL (**2**).

as was previously observed for LGa-substituted gallapnicthenes,^[4] dipnictanes,^[13] dipnictenes,^[14] radicals,^[15] and other complexes,^[16] whereas that of compound **2** shows one set of signals for the β -diketiminato ligand, indicating a dynamic chloride ion shifting between two Ga atoms in solution. This was proven by variable-temperature (VT) ^1H NMR studies (Figure S34). Cooling a solution of compound **2** in $[\text{D}_8]\text{toluene}$ to -50°C led to a broadening of the resonances, whereas further cooling to -80°C resulted in two signals for the $\gamma\text{-C-H}$ protons and three broad signals for the *i*-Pr groups of the β -diketiminato ligands in a relative intensity of 2:2:4. This finding not only proves the magnetically inequivalent nature of the two β -diketiminato ligands, but the occurrence of the two smaller signals points to a hindered rotation of the Ga–P double bond. We furthermore calculated the activating barrier for the chloride ion shifting between two Ga atoms in compound **2** to $\Delta E^\ddagger = 8.3 \text{ kcal mol}^{-1}$ (see Figure S49), which is in accordance with the fact that only a single set of resonances for the β -diketiminato ligands is found in the NMR spectra at room temperature. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **1** shows the expected doublet for the phosphaketenylic carbon atom at 181.6 ppm ($^1J_{\text{P-C}} = 100 \text{ Hz}$), and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum displays a sharp singlet at -371.4 ppm as observed in gallium phosphaketenes (-354.9 to -394.6 ppm),^[6b,11] but upfield shifted compared to boron phosphaketenes (-337.1 and -289.7 ppm).^[10] The singlet at -245.8 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of compound **2** is shifted to lower field compared to compound **1** (-371.4 ppm) and $\text{L}'(\text{pyr})\text{GaPGaL}$ (-319.0 ppm),^[6b] but occurs at higher field than phosphanylphosphagallenes (-43.0 , -61.3 ppm).^[6a] The IR spectrum of compound **1** shows a strong absorption band at 1936 cm^{-1} of the PCO stretching vibration, comparable to that observed for a gallium phosphaketene (1910 cm^{-1}).^[11]

The solid-state molecular structures of compounds **1** and **2** were determined by single-crystal X-ray diffraction studies (Figure 1). **1** crystallizes in the orthorhombic space group $Pnma$ and **2** in the monoclinic space group $P2_1/n$, respectively.^[17] Unfortunately, the PCO moiety in compound **1** is disordered over two positions, which are each disordered over a mirror plane. The PCO groups are also biased by restraints, hence the bond lengths and angles can't be discussed. The Ga1 atom in compound **2** is fourfold-coordinated and adopts a distorted tetrahedral geometry, whereas the Ga2 atom is threefold-coordinated and adopts a distorted trigonal-planar geometry (sum of bond angles 357.3°). The Ga–P–Ga bond angle in gallaphosphene **2** ($113.87(2)^\circ$) is comparable with those reported for gallapnicthenes L(X)GaEGaL ($\text{E} = \text{As, Sb}$; $\text{X} = \text{halide}$) which were found to range from 111° to 113° .^[4] The Ga–P bond lengths in gallaphosphene **2** (Ga1–P1 $2.2688(5) \text{ \AA}$, Ga2–P1 $2.1613(6) \text{ \AA}$) differ by almost 0.1 \AA .

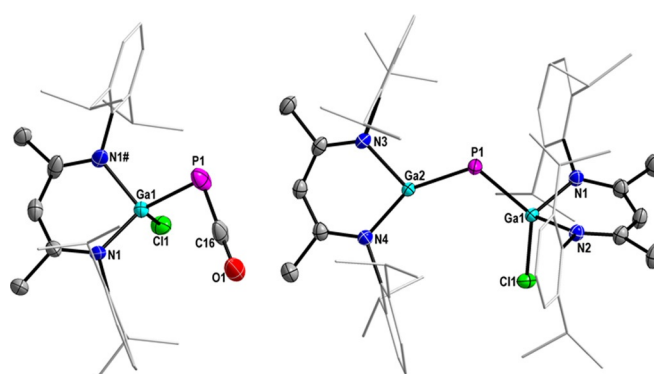
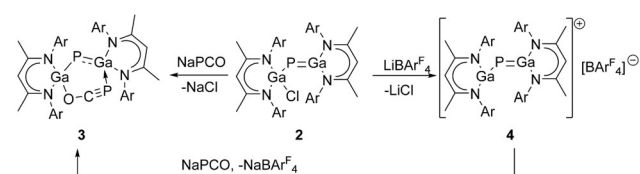


Figure 1. Molecular structures of the phosphaketenylic-gallane **1** (left) and gallaphosphene **2** (right).^[17] Ellipsoids set at 50% probability; hydrogen atoms and alternate positions of the disordered parts are omitted for clarity.

The Ga1–P1 bond length agrees with sum of the calculated single-bond radii (Ga 1.24 \AA ; P 1.11 \AA),^[18a] but is shorter than Ga–P single bonds in $\text{LGa}(\text{O}_3\text{SCF}_3)(\text{PPh}_2)$ ($2.312(3) \text{ \AA}$),^[19a] $\text{LGa}(\text{P}_4)$ ($2.340(2)$, $2.346(2) \text{ \AA}$),^[19b] $\text{LGa}(\text{H})\text{PPh}_2$ ($2.363(1) \text{ \AA}$),^[19c] $\text{LGa}(\text{PH}_2)_2$ ($2.3286(5)$, $2.3532(5) \text{ \AA}$),^[19d] and 7-galla-1,4-diphosphanorbornadiene ($2.4240(9)$, $2.4585(9) \text{ \AA}$).^[19e] The Ga2–P1 bond is virtually identical with previously reported Ga–P double bonds ($2.1650(7)$, $2.1766(3)$, and $2.207(1) \text{ \AA}$)^[6] and also agrees with the sum of the calculated double-bond radii (Ga 1.17 \AA ; P 1.02 \AA),^[18b] respectively.

Reaction of gallaphosphene **2** with $[\text{Na}(\text{OCP})(\text{dioxane})_{2.5}]$ yielded $\text{L}(\text{OCP})\text{GaPGaL}$ (**3**), whereas chloride abstraction with $\text{LiBAR}^{\text{F}_4}$ ($\text{BAR}^{\text{F}_4} = \text{B}(\text{C}_6\text{F}_5)_4$) gave $[\text{LGaPGaL}][\text{BAR}^{\text{F}_4}]$ (**4**). Compound **3** was also formed by reaction of compound **4** with $[\text{Na}(\text{OCP})(\text{dioxane})_{2.5}]$ (Scheme 3). Compounds **3** and **4** are stable under inert gas atmosphere, but rapidly decompose when exposed to air. Compound **3** is soluble in common organic solvents (Et_2O , benzene, toluene, THF), while compound **4** only dissolves in toluene and THF.

Compounds **3** and **4** show one set of signals for the β -diketiminato ligand in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3** shows two singlets (-290.5 , -320.8 ppm), which are shifted to higher field compared to phosphagallene **2** (-245.8 ppm). Notably, the latter resonance corresponds fairly well with the chemical shifts reported for boryl–OCP (-285.9 ppm)^[20] and Al–OCP complexes (-336.8 , -335.2 ppm),^[11] indicating that the 2-phosphaethynolate anion binds via the oxygen (–OCP) rather than by the phosphorous atom (–PCO). Moreover, the $^1J_{\text{P-C}}$ coupling constant observed for compound **3** (40.1 Hz) is smaller than those observed for compound **1** (100 Hz) and the related



Scheme 3. Synthesis of $\text{L}(\text{OCP})\text{GaPGaL}$ (**3**), and $[\text{LGaPGaL}][\text{BAR}^{\text{F}_4}]$ (**4**).

gallaphosphaketenes (85.4–101.0 Hz).^[6b,11] The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of compound **4** shows a signal at -267.0 ppm due to the phosphagallene unit, which is upfield shifted in comparison to those of phosphagallene **2** (-245.8 ppm) and cAAC-coordinated Ga–P=C allyl cations (-56.6 , -56.7 ppm).^[5a] The spectroscopic findings point to an increased electron density transfer from the gallium atoms to the phosphorous atom. The ^{19}F NMR spectrum of compound **4** shows the expected three resonances (-137.7 , -163.1 , -166.7 ppm) for the BAR^{F}_4 anion. The IR spectrum of compound **3** supports the –OCP coordination mode with a C–O stretching vibration at 1739 cm^{-1} , which is comparable to that observed for $\text{Na}(\text{OCP})\cdot(\text{dioxane})_{2.5}$ (1755 cm^{-1})^[21a] but smaller than the “free” OCP^- anion (1791 cm^{-1}).^[21b] The ^1H , ^{13}C , and ^{31}P NMR spectra of compound **4** dissolved in $[\text{D}_8]$ toluene and two drops of THF show largely shifted signals due to THF coordination, whereas the ^{19}F NMR spectrum is virtually identical with that in $[\text{D}_8]$ toluene (Figures S35–S38). These findings prove the electrophilic character of the cation of compound **4**, which was revealed in its reaction with 4-dimethylaminopyridine (dmap; Figures S39–S42).

The molecular structures of compounds **3** and **4**, which crystallize in the monoclinic and triclinic space groups Pn (**3**) and $P\bar{1}$ (**4**), were determined by single-crystal X-ray diffraction (Figure 2).^[17] Suitable crystals were grown from saturated benzene/toluene solutions upon storage at ambient temperature. The Ga atoms in compound **3** are fourfold-coordinated and adopt distorted tetrahedral geometries, whereas both Ga atoms in the cation of compound **4** adopt distorted trigonal-planar geometries. The Ga–P–Ga bond angle in compound **3** ($99.86(7)^\circ$) is significantly smaller compared to that observed for gallaphosphene **2** ($113.87(2)^\circ$) as well as the cation of compound **4** ($117.32(2)^\circ$), respectively. The Ga–P bonds in the cation of **4** are almost equidistant ($2.2026(4)$ and $2.1860(4)$ Å), indicating a delocalized Ga–P–Ga π -electron system, whereas the significantly longer Ga1–P1 ($2.2943(16)$ Å) and Ga2–P1 bonds ($2.297(2)$ Å) of gallaphosphene **3** rather represent short Ga–P single bonds. These structural findings most likely result from the binding mode of the phosphathynolate substituent, which binds to Ga1 through the oxygen atom (O1) and to Ga2 by a donor–acceptor bond from the phosphorous atom (P2). As a result, a short Ga1–O1 bond ($1.977(4)$ Å) and a long Ga2–P2 bond ($2.4798(16)$ Å) is

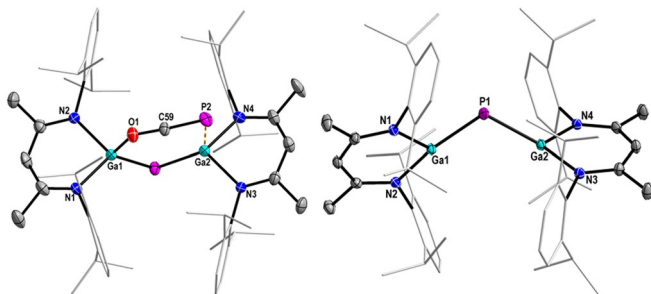


Figure 2. Molecular structures of compound **3** (left) and cationic part of compound **4** (right).^[17] Ellipsoids set at 50% probability; hydrogen atoms, alternate positions of the disordered parts of **3** and anion of **4** are omitted for clarity.

observed.^[19e] Phosphane–gallane adducts $\text{R}_3\text{P–GaR}'_3$ show Ga–P bond lengths ranging from 2.347 to 2.719 Å (mean 2.448 Å).^[22]

To gain a better understanding of the electronic structures of phosphagallene **2** and the cation of compound **4**, DFT calculations were performed at the B3LYP-D3BJ/def2-TZVP level of theory.^[23] The optimized geometries are in good agreement with their solid-state structures. To investigate the bonding nature, NBO analyses^[24a] were performed and the Mayer bond orders^[24b] were calculated. The analysis of the wavefunctions revealed that the HOMO of **2** corresponds to the Ga2–P1 π -bond (Figures 3 and S50), which is considerably high in energy (-4.65 eV). The calculated HOMO–LUMO energy gap for compound **2** (2.94 eV) is remarkably small. We therefore performed CASSCF(2/2) and CASSCF(4/4) calculations. The occupation numbers of the orbitals in the active space amount to 2.00 and 0.00 for the CASSCF(2/2) calculation (Figure S51) as well as to 2.00, 1.96, 0.00, and 0.04 for the CASSCF(4/4) approximation (Figure S52), thus proving that compound **2** has almost no open-shell singlet diradical character. The HOMO of compound **4** (-7.58 eV) is the π -type orbital located at the Ga–P–Ga moiety (Figure S53), which is consistent with an allyl system. The LUMOs of compounds **2** and **4** are the π^* orbitals of the β -diketiminato ligand, whereas the LUMOs + 2 represent the π^* orbitals of the Ga=P and Ga–P–Ga unit, respectively (Figures 3, S50, and S53). The calculated Mayer’s bond orders for the Ga1–P1 bond (1.077) and the Ga2–P1 bond (1.709) strongly support the presence of both a localized single and double bond in compound **2**, respectively, whereas the Mayer’s bond orders calculated for compound **4** (Ga2–P1 1.411; Ga1–P1 1.397) are in between, indicating a delocalized π -electron system as is expected for a heteroallyl cation. The distribution of the positive charge over all three centers (Ga–P–Ga) in the cation of compound **4** furthermore supports this description. The increase of the positive charges going from compound **2** to the cation of compound **4** at Ga1 ($+0.075$) and Ga2 ($+0.115$) is greater than that at P1 ($+0.032$) (Table S3), which proves that the positive charge is shifted via mesomerism and confirm the description of $[\text{LGa=P–GaL}]^+$ as a heteroallylic cation.

Low-valent main-group element compounds have been demonstrated in the last decade to be able to mimic reactions known for transition metal complexes, including small-molecule activation reactions, that is, of H_2 , CO, or CO_2 . Therefore, oxidative addition and reductive elimination

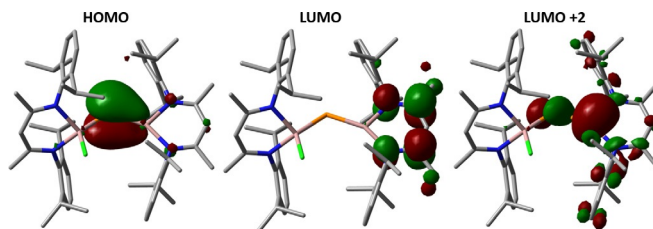
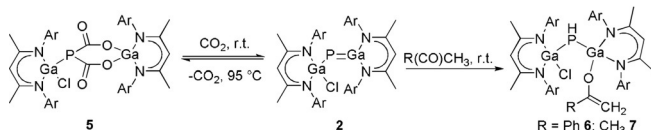


Figure 3. HOMO, LUMO, and LUMO + 2 of compound **2** calculated at B3LYP-D3BJ/def2-TZVP level of theory (isovalue 0.04). Hydrogen atoms are omitted for clarity.

reactions at main group metal centers have emerged as an important tool in organic synthesis^[25] and have also been extended to catalytic reactions.^[26] Moreover, Stephan's cooperative approach of a set of sterically encumbered Lewis acid/Lewis base, termed "frustrated Lewis pairs" (FLPs), has also substantially added to this area.^[27] However, the capability of π -bonded heavier main group element compounds to activate small molecules with rather inert bonds is still very limited,^[25] and the reactivity of heavier group 13 and group 15 multiply bonded compounds is almost unknown.^[4f,6] Therefore, we sought to probe the reactivity of gallaphosphene **2** in bond activation reactions.

At ambient temperature, gallaphosphene **2** reacts with CO₂ at the Ga–P double bond with subsequent formation of L(Cl)GaP- $[\mu$ -C(O)O]₂-GaL (**5**; Scheme 4). DFT calculations (B3LYP-D3BJ/def2-TZVP) reveal that the addition of the second equivalent of CO₂ ($\Delta G = -7.5$ kcal mol⁻¹) to **2** is significantly favored compared to the addition of the first equivalent ($\Delta G = -1.8$ kcal mol⁻¹). Accordingly, only the double CO₂ addition product (**5**) is experimentally found. Remarkably, this reaction is fully reversible and compound **2** is quantitatively regenerated upon heating a solution of compound **5** in benzene to 95 °C as was proven by in situ ¹H and ³¹P{¹H} NMR spectroscopy (Figures S32 and S33). The reversible binding of CO₂ was previously reported for FLPs and organic Lewis bases,^[28] but to the best of our knowledge, this has never been observed for main group multiply bonded compounds to date.^[29] In contrast to gallaphosphene **2**, Goicoechea's phosphanyl-phoshaallene irreversibly reacted as a frustrated Lewis pair in 1,3 position.^[6a]

The unprecedented reaction of gallaphosphene **2** with CO₂ encouraged us to expand our studies to C(sp³)–H bond activation reactions, which belong to the most important processes in organic chemistry.^[30] This reaction is a typical domain of transition metal complexes, but very rare in main group chemistry^[25] and almost limited to intramolecular insertion of low-valent main group elements into adjacent C(sp³)–H bonds.^[31] In contrast, intermolecular C(sp³)–H bond activation reactions on main group elements or multiply bonded group 13 and/or group 15 element compounds are virtually unknown.^[32] To the best of our knowledge, iminoborane (TMP)B=NAr* and diboryne (SIDip)B=B(SIDip) are the only complexes capable of C(sp³)–H bond activation of acetone (SIDip = 1,3-bis(2,6-diethylphenyl)-4,5-(dihydro)imidazolidine-2-ylidene; Ar* = (2,6-(CHPh)₂-4-*t*BuC₆H₂); TMP = 2,6-tetramethyl piperidyl).^[33] While the iminoborane required 70 °C for this reaction, the diboryne already reacted at ambient temperature with acetone.^[33] We therefore reacted gallaphosphene **2** with acetophenone and acetone to test



Scheme 4. Temperature-dependent reaction of gallaphosphene **2** with CO₂ and C(sp³)–H bond activation reactions of acetophenone and acetone.

whether it undergoes C–H bond activation, either C(sp²)–H or C(sp³)–H, or 2 + 2 cycloaddition reactions. Remarkably, both reactions already occurred at ambient temperature as is indicated by an immediate color change from red to colorless, and selectively proceeded with C(sp³)–H bond activation and formation of compounds **6** and **7** in quantitative yields.

Compounds **5–7** are colorless crystalline solids, which are soluble in common organic solvents and stable under an inert gas atmosphere at ambient temperature. The ¹H NMR spectra of compounds **5–7** exhibit two sets of signals for the Dipp groups of the β -diketiminato ligand. The ¹³C{¹H} NMR spectrum of compound **5** exhibits the expected doublet at 175.0 ppm (d, ¹J_{P–C} = 15.1 Hz) due to the carbonyl carbon atom (Figure S19), and the ³¹P{¹H} NMR spectrum shows a strong singlet at –52.1 ppm, which is downfield shifted with respect to the gallaphosphene **2** (–245.8 ppm). The ¹H NMR spectra of compounds **6** (–0.63 ppm, d, ¹J_{P–H} = 181.0 Hz; Figure S22) and **7** (–0.75 ppm, d, ¹J_{P–H} = 178.9 Hz; Figure S27) as well as the proton-coupled ³¹P NMR spectra of compounds **6** (–313.3 ppm, d, ¹J_{P–H} = 181.0 Hz; Figure S25) and **7** (–316.3 ppm, d, ¹J_{P–H} = 178.9 Hz; Figure S30) exhibit the expected doublets for the P–H unit. These coupling constants agree with the ¹J_{P–H} coupling constants observed for LGa(PH₂)₂ (¹J_{P–H} = 168.0 Hz)^[19d] and IDipp-GaH₂PH₂ (¹J_{P–H} = 170.8 Hz, IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolidine-2-ylidene).^[34] The ³¹P{¹H} NMR spectra of **6** (–313.3 ppm; Figure S24) and **7** (–316.2 ppm; Figure S29) show sharp singlets which are shifted to higher field compared to gallaphosphene **2** (–245.8 ppm).

The solid-state molecular structures of compounds **5** and **6** were determined by single-crystal X-ray diffraction (Figure 4).^[17] Suitable single crystals were obtained by cooling a saturated toluene solution of compound **5** at –30 °C for several days or by diffusing *n*-hexane into a benzene solution of compound **6** at ambient temperature. Both compounds **5** and **6** crystallize in the orthorhombic space group *Pbca*. The gallium atoms within the boat-type six-membered PC₂O₂Ga as well as in the C₃N₂Ga rings possess distorted tetrahedral geometries, whereas the phosphorous atoms adopt a trigonal-pyramidal geometry. The Ga–P bond length (2.3319(12) Å) in compound **5** is comparable to LGa-substituted derivatives.^[19a–d] The P–C_{CO} (1.865(4), 1.871(4) Å), and Ga–O (1.826(3), 1.832(3) Å) bond lengths are almost identical and in line with experimental^[6a] and calculated^[18a] C–P and Ga–O single

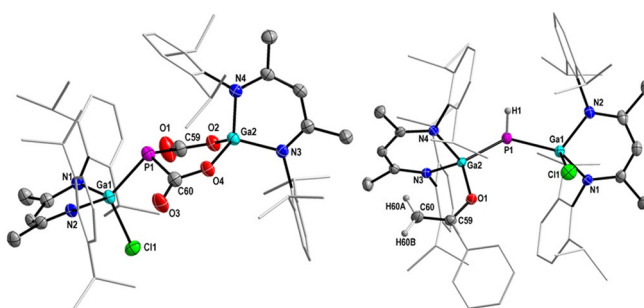


Figure 4. Molecular structures of compounds **5** (left) and **6** (right).^[17] Ellipsoids set at 50% probability; hydrogen atoms and solvent molecules (toluene in **5** and benzene in **6**) are omitted for clarity.

bond lengths, respectively. However, the Ga–O bond is shorter than the Ga–O single bond (1.9061(18) Å) reported by Goicoechea.^[6a] The Ga–P bonds (2.3068(4) and 2.3220(4) Å) in compound **6** are longer than the Ga–P double bonds, however they fall in the typical Ga–P single bond range.^[19a–d] Moreover, the Ga–O bond length (1.8523(10) Å) is also comparable to Ga–O single bonds. The Ga–P–Ga bond angle (116.793(17)°) is slightly larger than that of compound **2** (113.87(2)°) but almost identical to that of compound **4** (117.32(2)°).

Conclusion

Reaction of gallium phosphaketene **1** with LGa yielded gallaphosphene **2**, which reacted with [Na(OCP)(dioxane)_{2.5}] to compound **3** with an unusual OCP bridging unit. Halide abstraction of **2** with LiBAR₄^F gave compound **4** containing the cation [LGaPGaL]⁺, whose electronic situation resembles that of an allyl cation based on quantum chemical calculations. Moreover, compound **2** is a promising reagent for bond activation reactions as shown in reactions with CO₂, acetophenone, and acetone, yielding compounds **5–7**. Remarkably, the reaction with CO₂ is fully reversible, whereas reactions with acetophenone and acetone selectively proceeded with C(sp³)–H bond activation at ambient temperature.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: CO₂ activation · double bonds · gallium · main-group elements · phosphorous

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