Main-Group Elements Hot Paper

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Multi-Talented Gallaphosphene for Ga–P–Ga Heteroallyl Cation Generation, CO_2 Storage, and C(sp^3)–H Bond Activation

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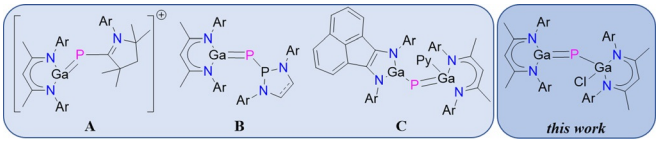
Dedicated to Professor Frank-Gerrit Klärner on the occasion of his 80th birthday

Abstract: *Gallaphosphene L(Cl)GaPGaL (**2**; L = HC[C(Me)N(2,6-i-Pr$_2$C$_6$H$_3$)]$_2$), 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$^F_4$ yields [LGaPGaL][BAr$^F_4$] (**4**; BAr$^F_4$ = B(C$_6$F$_5$)$_4$). **4** represents a heteronuclear analog of the allyl cation according to quantum chemical calculations. Remarkably, **2** reversibly reacts with CO_2 to yield L(Cl)Ga–P[μ-C(O)O]$_2$GaL (**5**), while reactions with acetophenone and acetone selectively give compounds **6** and **7** by C(sp^3)–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)$_3$}$_2$Ga$_2${As(Si*i*-Pr$_3$)}$_4$] 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-Mes$_2$C$_6$H$_3$; Mes = 2,4,6-Me$_3$C$_6$H$_2$).[4] We also prepared [LGaP(^{Me}cAAC)][An] (An = B(C$_6$H$_3$(CF$_3$)$_2$)$_4$, B(C$_6$F$_5$)$_4$, Al(OC(CF$_3$)$_3$)$_4$; 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] Goichoechea et al. recently synthesized phosphanyl-substituted phosphagallenes (P′)PGaL (P′ = (HC)$_2$(NAr)$_2$P, (H$_2$C)$_2$(NAr)$_2$P; type **B**) and reported on their frustrated Lewis pair-type (FLP-type) reaction with CO_2 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 = C$_5$H$_5$N) 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$^{\delta+}$–E$^{\delta-}$), is almost unknown.[4f] We herein report on the synthesis of gallaphosphene L(Cl)GaPGaL (**2**) and its reactions with halide abstraction reagents, CO_2, 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 LGaCl$_2$[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 ^{1}H NMR spectrum of compound **1** exhibits two sets of resonances for the Dipp groups of the β-diketiminate ligand

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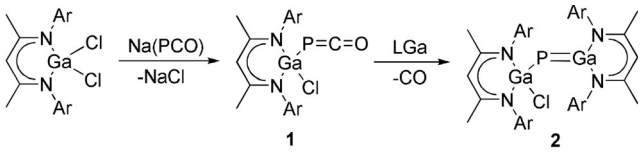


Scheme 2. Synthesis of gallium phospaketene LGa(Cl)PCO (**1**) and gallaphosphene L(Cl)GaPGaL (**2**).

as was previously observed for LGa-substituted gallapnictenes,[4] dipnictanes,[13] dipnictenes,[14] radicals,[15] and other complexes,[16] whereas that of compound **2** shows one set of signals for the β-diketiminate ligand, indicating a dynamic chloride ion shifting between two Ga atoms in solution. This was proven by variable-temperature (VT) ^{1}H NMR studies (Figure S34). Cooling a solution of compound **2** in [D$_8$]toluene to −50 °C led to a broadening of the resonances, whereas further cooling to −80 °C resulted in two signals for the γ-C−H protons and three broad signals for the *i*-Pr groups of the β-diketiminate ligands in a relative intensity of 2:2:4. This finding not only proves the magnetically inequivalent nature of the two β-diketiminate 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 $\Delta E^{\#} = 8.3$ kcal mol^{-1} (see Figure S49), which is in accordance with the fact that only a single set of resonances for the β-diketiminate ligands is found in the NMR spectra at room temperature. The ^{13}C{^{1}H} NMR spectrum of compound **1** shows the expected doublet for the phosphaketenyl carbon atom at 181.6 ppm ($^1J_{P-C} = 100$ Hz), and the ^{31}P{^{1}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}P-{^{1}H} NMR spectrum of compound **2** is shifted to lower field compared to compound **1** (−371.4 ppm) and L′(pyr)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)°) is comparable with those reported for gallapnictenes L(X)GaEGaL (E = As, Sb; X = halide) which were found to range from 111° to 113°.[4] The Ga−P bond lengths in gallaphosphene **2** (Ga1−P1 2.2688(5) Å, Ga2−P1 2.1613(6) Å) differ by almost 0.1 Å.

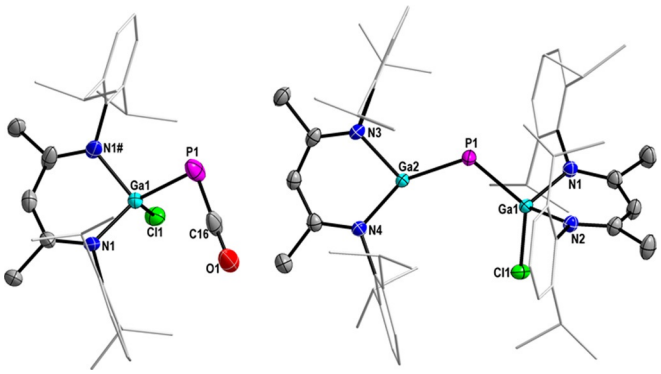
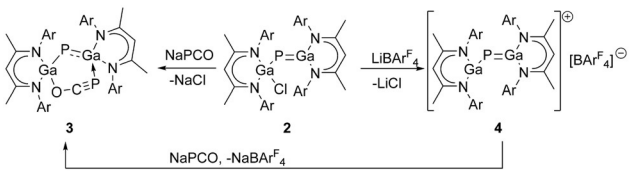


Figure 1. Molecular structures of the phosphaketenyl-gallane **1** (left) and gallaphosphene **2** (right).[17] Ellipsoids set at 50% probability; hydrogen atoms and alternate positions of the disordered parts are omitted for clarity.

The Ga1−P1 bond length agrees with sum of the calculated single-bond radii (Ga 1.24 Å; P 1.11 Å),[18a] but is shorter than Ga−P single bonds in LGa(O$_3$SCF$_3$)(PPh$_2$) (2.312(3) Å,),[19a] LGa(P$_4$) (2.340(2), 2.346(2) Å),[19b] LGa(H)PPh$_2$ (2.363-(1) Å),[19c] LGa(PH$_2$)$_2$ (2.3286(5), 2.3532(5) Å)),[19d] and 7-galla-1,4-diphosphanorbornadiene (2.4240(9), 2.4585(9) Å).[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) Å)[6] and also agrees with the sum of the calculated double-bond radii (Ga 1.17 Å; P 1.02 Å),[18b] respectively.

Reaction of gallaphosphene **2** with [Na(OCP)(dioxane)$_{2.5}$] yielded L(OCP)GaPGaL (**3**), whereas chloride abstraction with LiBAr$^F_4$ (BAr$^F_4$ = B(C$_6$F$_5$)$_4$) gave [LGaPGaL][BAr$^F_4$] (**4**). Compound **3** was also formed by reaction of compound **4** with [Na(OCP)(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$_2$O, benzene, toluene, THF), while compound **4** only dissolves in toluene and THF.

Compounds **3** and **4** show one set of signals for the β-diketiminate ligand in the ^{1}H and ^{13}C{^{1}H} NMR spectra. The ^{31}P{^{1}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 $^1J_{P-C}$ 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 L(OCP)GaPGaL (**3**), and [LGaPGaL][BAr$^F_4$] (**4**).

gallaphosphaketenes (85.4–101.0 Hz).[6b,11] The $^{31}P\{^1H\}$ 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 Na(OCP)·(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 [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 [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)°) is significantly smaller compared to that observed for gallaphosphene **2** (113.87(2)°) as well as the cation of compound **4** (117.32(2)°), 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 phosphaethynolate 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 observed.[19e] Phosphane–gallane adducts $R_3P{-}GaR'_3$ 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-diketiminate 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 $[LGa{=}P{-}GaL]^+$ 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

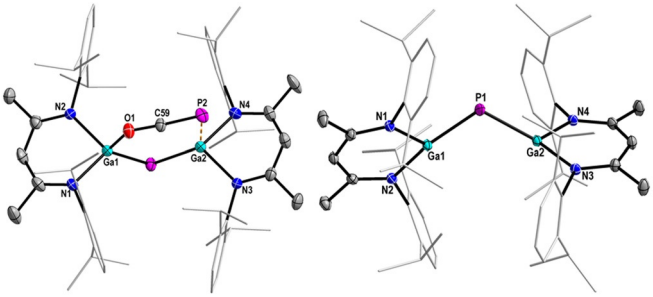


Figure 2. Molecular structures of compound **3** (left) and cationic part of compound **4** (right).[17] Ellipsoids set at 50% probability; hydrogen atoms, alternate positions of the disordered parts of **3** and anion of **4** are omitted for clarity.

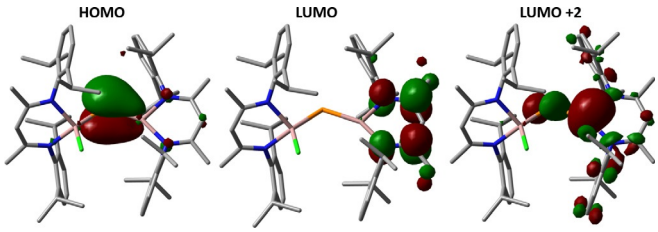


Figure 3. HOMO, LUMO, and LUMO + 2 of compound **2** calculated at B3LYP-D3BJ/def2-TZVP level of theory (isovalue 0.04). Hydrogen atoms are omitted for clarity.

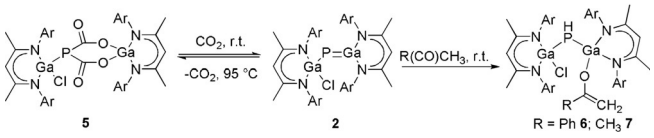
reactions at main group metal centers have emerged as an important tool in organic synthesis[25] and have also been extended to catalytic reactions.[26] Moreover, Stephan's cooperative approach of a set of sterically encumbered Lewis acid/Lewis base, termed "frustrated Lewis pairs" (FLPs), has also substantially 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 CO_2 at the Ga–P double bond with subsequent formation of L(Cl)GaP-[μ-C(O)O]$_2$-GaL (**5**; Scheme 4). DFT calculations (B3LYP-D3BJ/def2-TZVP) reveal that the addition of the second equivalent of CO_2 ($\Delta G = -7.5$ 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 CO_2 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 ^{1}H and ^{31}P{^{1}H} NMR spectroscopy (Figures S32 and S33). The reversible binding of CO_2 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-phoshagallene irreversibly reacted as a frustrated Lewis pair in 1,3 position.[6a]

The unprecedented reaction of gallaphosphene **2** with CO_2 encouraged us to expand our studies to C(sp^3)–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(sp^3)–H bonds.[31] In contrast, intermolecular C(sp^3)–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 our knowledge, iminoborane (TMP)B≡NAr*) and diboryne (SIDip)B≡B(SIDip) are the only complexes capable of C(sp^3)–H bond activation of acetone (SIDip = 1,3-bis(2,6-diethylphenyl)-4,5-(dihydro)imidazolidine-2-ylidene; Ar* = (2,6-(CHPh$_2$)$_2$-4-*t*BuC$_6$H$_2$); 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 whether it undergoes C–H bond activation, either C(sp^2)-H or C(sp^3)-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(sp^3)–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 ^{1}H NMR spectra of compounds **5**–**7** exhibit two sets of signals for the Dipp groups of the β-diketiminate ligand. The ^{13}C{^{1}H} 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 ^{31}P{^{1}H} NMR spectrum shows a strong singlet at −52.1 ppm, which is downfield shifted with respect to the gallaphosphene **2** (−245.8 ppm). The ^{1}H 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 ^{31}P 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(PH$_2$)$_2$ ($^1J_{P-H} = 168.0$ Hz)[19d] and IDipp·GaH$_2$PH$_2$ ($^1J_{P-H} = 170.8$ Hz, IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazoline-2-ylidene).[34] The ^{31}P{^{1}H} 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 PC$_2$O$_2$Ga as well as in the C$_3$N$_2$Ga 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



Scheme 4. Temperature-dependent reaction of gallaphosphene **2** with CO_2 and C(sp^3)–H bond activation reactions of acetophenone and acetone.

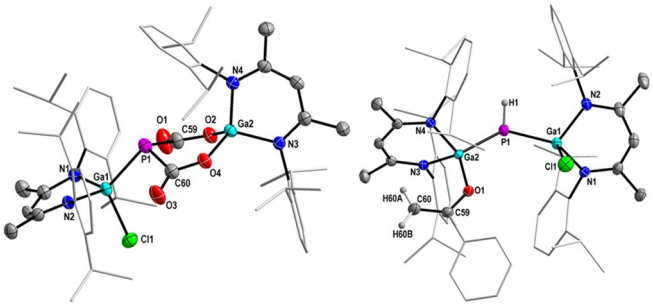


Figure 4. Molecular structures of compounds **5** (left) and **6** (right).[17] Ellipsoids set at 50% probability; hydrogen atoms and solvent molecules (toluene in **5** and benzene in **6**) are omitted for clarity.

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 $LiBAr^F{}_4$ 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 CO_2, acetophenone, and acetone, yielding compounds **5**–**7**. Remarkably, the reaction with CO_2 is fully reversible, whereas reactions with acetophenone and acetone selectively proceeded with $C(sp^3)$–H bond activation at ambient temperature.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: CO_2 activation · double bonds · gallium · main-group elements · phosphorous

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