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Selective 1,2 addition of polar X–H bonds to the Ga–P double bond of gallaphosphene L(Cl)GaPGaL†

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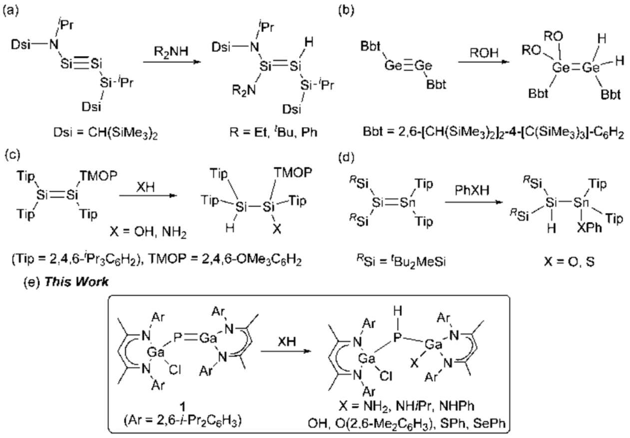
Gallaphosphene L(Cl)GaPGaL **1** (L = HC[C(Me)N(2,6-i-Pr_2-C_6H_3)]$_2$) reacts at ambient temperature with a series of polar X–H bonds, *i.e.* ammonia, primary amines, water, phenol, thiophenol, and selenophenol, selectively with 1,2 addition at the polar Ga–P double bond. The gallium atom serves as electrophile and the phosphorous atom is protonated in all reactions. The resulting complexes L(Cl)GaP(H)Ga(X)L (X = NH_2 **2**, NHi-Pr **3**, NHPh **4**, OH **5**, OXyl **6**, SPh **7**, SePh **8**) were characterized by IR and heteronuclear (^{1}H, ^{13}C {^{1}H}, ^{31}P{^{1}H}) NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction.

Introduction

Activation of polar and non-polar X–H bonds (X = H, N, O,…) by main group element compounds has received increasing interest over the last years with respect to the development of similar reactions as known for transition metals, including catalytic reactions.[1] Homonuclear heavier group 14 element analogues of alkenes (E_2R_4) and alkynes (E_2R_2; E = Si–Pb) received particular attention in the activation of such bonds due to their small and to some extent tunable HOMO–LUMO energy gaps and their biradical type bonding nature.[1,2] In 2005, Power and co-workers reported the H–H bond activation of H_2 using digermyne Ge_2Ar_2 (Ar = 2,6-$(Dipp)_2C_6H_3$, Dipp = 2,6-i-$Pr_2C_6H_3$),[3] which was later extended to other digermynes,[4] and distannynes.[5] Sekiguchi showed that a disilyne (Scheme 1a) activates N–H bonds of secondary amines,[6] while O–H bonds of H_2O and MeOH were activated by a digermyne (Scheme 1b).[7] Heavier group 14 alkene analogues failed to activate such X–H bonds except for disilenes, which were shown to react with H_2,[8] NH_3, and H_2O (Scheme 1c),[9] respectively, whereas a heteronuclear silastannene was found to activate X–H bonds of phenol and thiophenol (Scheme 1d).[10]

Metallapnictenes RMPnR (M = B–Tl; Pn = N–Bi) containing M–Pn double bonds are isovalence-electronic to alkenes and have attracted high interest due to their fascinating electronic structures. Their reactivity is expected to be increased compared to homonuclear heavier group 14 congeners due to the polarity of the heteronuclear M–Pn double bonds.[11]



Scheme 1 (a–d) Selected examples of polar X–H bond activation using homo and heterodiatomic multiply bonded heavier group 14 compounds (isoelectronic to gallaphosphene **1**), and (e) X–H bond activation using gallaphosphene **1** (present work).

While compounds of this type are well known for the lightest elements of both groups, *i.e.* borapnictenes with B–Pn (Pn = N, P, As)[11] and metallaimines with M–N double bonds (M = Al, Ga, In),[12] the heavier congeners with M–Pn (M = Al, Ga; Pn = P, As, Sb) double bonds have been reported only recently,[13–17] and their reactivity studies are in its infancy.[16–20] Such compounds possess polarized double bonds due to the different electronegativities of the group 13 and 15 elements, hence, revealing a chemical reactivity that differs largely from homonuclear heavier group 14 analogues of alkenes. We

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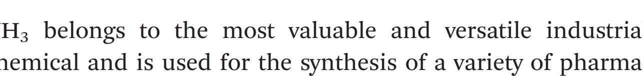
recently reported on a series of reactions of gallaarsenes and -stibenes L(Cl)GaPnGaL (Pn = As, Sb; L = HC[C(Me)N(Dipp)]$_2$, Dipp = 2,6-i-Pr$_2$C$_6$H$_3$) with both electrophilic and nucleophilic reagents,[18] while Goicoechea *et al.* reported on frustrated Lewis pair-type (FLP-type) reactions of phosphanyl-substituted phosphagallene (P′)PGaL (P′ = (H$_2$C)$_2$(NAr)$_2$P) with a variety of small molecules (H$_2$, CO$_2$, NH$_3$, RNH$_2$, H$_2$O *etc.*). The reactions typically occurred at ambient temperature at the 1,3 positions of the Ga–P–P moiety rather than at the Ga–P double bond,[16a,19] however, thermal treatment of some 1,3 addition products resulted in a 1,2 proton migration and subsequent formation of the 1,2 addition products.[19] Very recently, we reported on reversible [2 + 2] and [2 + 2 + 2] cycloaddition reactions of gallaphosphene LGa(Cl)PGaL **1** with heteroallenes (CO$_2$, isocyanates, carbodiimides) at the Ga–P double bond,[17,20] while the reactions with ketones proceeded *via* a C(sp^3)–H bond activation at the Ga–P double bond.[17] This unprecedented C(sp^3)–H bond activation reaction as well as the scarcity of π-bonded metallapnictenes to activate X–H bonds encouraged us to investigate X–H bond activation reactions of gallaphosphene **1** with compounds with different X–H bond polarity, and we herein report on reactions with ammonia, primary amines, water, phenol, thiophenol, and selenophenol, respectively (Scheme 1e).

Results and discussion

NH$_3$ belongs to the most valuable and versatile industrial chemical and is used for the synthesis of a variety of pharmaceuticals, polymer additives, fertilizers and industrial amines. However, functionalization of NH$_3$ is one of the most challenging and important processes in organic chemistry due to the rather strong N–H bonds. Traditionally, the activation of NH$_3$ is dominated by transition metal complexes, while main group element complexes entered this field only in recent years.[1,2] We therefore became interested in the activation of ammonia using gallaphosphene **1**.

Addition of NH$_3$ gas (1 atm) to a red solution of **1** in toluene at ambient temperature instantaneously gave a colorless solution, from which LGa(Cl)PH(NH$_2$)GaL **2** was isolated as colorless solid in 92% isolated yield (Scheme 2). The selective 1,2 addition of the N–H bond to the Ga–P double bond of **1** stands in remarkable contrast to the reaction of phosphanyl–phosphagallene,[19] which reacts at ambient temperature in a FLP-type mechanism at the 1,3 positions of the Ga–P–P unit, and only thermal treatment of this 1,3 addition product to 80 °C resulted in 1,2 proton migration and formation of the 1,2 addition product.[19] Addition of Lewis acidic B(C$_6$F$_5$)$_3$ to the 1,3 addition product proceeded with regeneration of the phosphanyl–phosphagallene.[19]



1 Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$ X = NH$_2$ **2**, *i*-PrNH **3**, PhNH **4**

Scheme 2 Reactions of gallaphosphene **1** with NH$_3$ and primary amines.

The ^{1}H NMR spectrum of **2** shows a broad resonance at 0.48 ppm for the NH$_2$ moiety, which agrees well with that of P′(H)PGa(NH$_2$)L (0.47 ppm, P′ = (H$_2$C)$_2$(NAr)$_2$P),[19] whereas it is shifted to lower field compared to that of LGa(NH$_2$)$_2$ (−0.58 ppm).[21] In addition, **2** displayed the expected doublets in the ^{1}H NMR (−0.84 ppm, $^1J_{\text{P–H}}$ = 174.5 Hz; Fig. S1†) and the proton-coupled ^{31}P NMR spectra (−314.6 ppm, $^1J_{\text{P–H}}$ = 174.5 Hz; Fig. S4†) for the P–H unit. The $^1J_{\text{P–H}}$ coupling constants are similar to those reported for the 1,2 addition products of ketones, which were formed by C(sp^3)–H bond activation.[17] The proton decoupled ^{31}P(^{1}H) NMR spectrum gave a sharp singlet at −314.6 ppm, that is shifted to higher field compared to gallaphosphene **1** (−245.8 ppm).[17] Selected NMR and IR data are given in Table S1.†

Single crystals of **2** suitable for X-ray diffraction analysis were obtained by storage of a saturated toluene solution at −30 °C for 24 h (Fig. 1).[22] **2** crystallizes in the monoclinic space group *P*2$_1$/*c*. The fourfold-coordinated gallium atoms adopt distorted tetrahedral geometries, whereas the phosphorous atom adopts a trigonal pyramidal geometry. The Ga–P–Ga bond angle (107.594(14)°) is smaller than that of the gallaphosphene **1** (113.87(2)°),[17] and the Ga–P bond lengths in **2** (Ga–P1 2.3125(4) Å, Ga2–P1 2.3187(4) Å) are almost equal and agree with the sum of the calculated Ga–P single-bond radii (Ga 1.24 Å; P 1.11 Å).[23] The Ga2–N5 bond length (1.970(7) Å) is slightly longer than that of LGa(NH$_2$)$_2$ (1.852(2) Å, 1.847(2) Å)[21] and (P′H)P(NH$_2$)GaL (1.845(2) Å).[19]

Since NH$_3$ readily reacted with gallaphosphene **1** under mild reaction conditions, we became interested to elucidate if **1** is also capable for N–H bond activation of primary and secondary amines, respectively, which are important reagents in hydroamination reactions. Reactions of **1** with isopropylamine and aniline occurred with 1,2 addition of the N–H bond to the Ga–P double bond and formation of LGa(Cl)PH(NHR)GaL (R = i-Pr **3** and Ph **4**) in almost quantitative (>95%) yields (Scheme 2), whereas no reaction was observed with secondary amines (Me$_2$NH, i-Pr$_2$NH). Compounds **2–4** are colorless crystalline solids and stable for weeks under inert gas atmosphere at ambient temperature, but they decompose rapidly when exposed to air. The ^{1}H NMR spectra of compounds **2–4** exhibit two sets of resonances for the Dipp groups of the β-diketiminate ligand as was reported for LGa-substituted gallapnictenes,[15,17] dipnictanes,[24] dipnictenes,[25] and other complexes.[26,27] The proton coupled ^{31}P NMR spectra of **3** (−313.9 ppm, $^1J_{\text{P–H}}$ = 175.6 Hz) and **4** (−315.0 ppm, $^1J_{\text{P–H}}$ = 177.0 Hz) as well as the ^{1}H NMR spectra of **3** (−0.88 ppm, $^1J_{\text{P–H}}$ = 175.6 Hz) and **4** (−0.58 ppm, $^1J_{\text{P–H}}$ = 177.0 Hz) each display a doublet for the P–H units. Furthermore, the ^{31}P{^{1}H} NMR spectra showed sharp singlets at −313.7 ppm (**3**) and −315.0 ppm (**4**), which are shifted to lower field compared to that reported for gallaphosphene **1** (−245.8 ppm).[17]

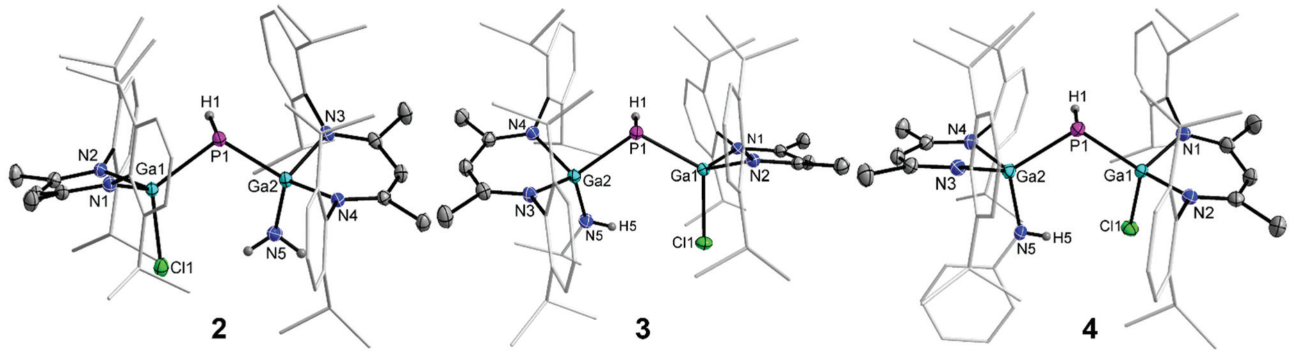
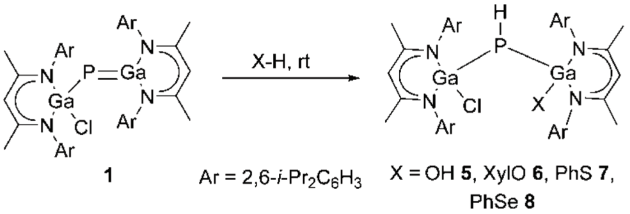


Fig. 1 Molecular structures of compounds **2**, **3**, and **4**. Ellipsoids set at 50% probability; C–H hydrogen atoms, minor disordered atoms (in **2**) and solvent molecules (toluene) are omitted for clarity.

Single crystals of compounds **3** and **4** suitable for X-ray diffraction were obtained either upon storage of saturated toluene solutions at −30 °C or diffusing *n*-hexane into toluene solutions at ambient temperature (Fig. 1).[22] Compounds **3** and **4** crystallize in the orthorhombic space group *Pbca* (**3**) and triclinic space group $P\bar{1}$ (**4**).[22] The Ga atoms adopt distorted tetrahedral, and the P atoms trigonal pyramidal geometries as observed in compound **2**. The Ga–P–Ga bond angles in **3** (112.95(15)°) and **4** (111.07(18)°) are comparable to that observed for **1** (113.87(2)°),[17] but much smaller than those of LGa(Cl)P[μ-C(X)NR]GaL (X = NR, R = i-Pr (131.1(2)°; X = O, (131.1(2)°; X = O, R = Cy (133.1(1)°).[20] The Ga1–P1 bonds in **3** (2.3080(4) Å) and **4** (2.3132(5) Å) are slightly shorter than the Ga2–P1 bonds (2.3445(4) Å **3**, 2.3395(5) Å **4**), but agree well with the sum of the calculated single-bond radii (Ga 1.24 Å; P 1.11 Å)[23] and with Ga–P single bonds reported for $\mathrm{LGa(P_4)}$ (2.340(2), 2.346(2) Å),[28a] $\mathrm{L(H)GaPPh_2}$ (2.363(1) Å),[28b] $\mathrm{LGa(PH_2)_2}$ (2.3286(5), 2.3532(5) Å),[28c] and $\mathrm{L(Cl)GaPH(OC(Ph)CH_2)GaL}$ (2.3068(4), 2.3220(4) Å),[17] respectively, whereas the Ga–P double bond of gallaphosphene **1** (2.16(6) Å) is significantly shorter.[17] The Ga2–N5 bond lengths of **3** (1.8606(12) Å), and **4** (1.8762(14) Å) fairly match to the calculated[23] and experimentally[19,20] observed Ga–N single bond length.

The ease of which gallaphosphene **1** was found to activate N–H bonds of ammonia and primary amines encouraged us to test the reactions of **1** with other reagents containing polar X–H bonds. Reactions of **1** with one equiv. of water or 2,6-dimethylphenol in toluene immediately yielded the O–H bond activation products L(Cl)GaP(H)Ga(X)L (X = OH **5**, OR **6**, R = $\mathrm{2,6\text{-}(CH_3)_2C_6H_3}$), and reactions with thiophenol (PhSH) and selenophenol (PhSeH) occurred with S–H and Se–H bond activation and subsequent formation of L(Cl)GaP(H)Ga(X)L (X = SPh **7**, SePh **8**), respectively, which were isolated in almost quantitative yields (Scheme 3). To the best of our knowledge, this is the first Se–H bond activation by a multiply bonded main-group complex reported to date.



Scheme 3 Reactions of gallaphosphene **1** with water, 2,6-dimethylphenol, thiophenol, and selenophenol.

Compounds **5–8** are soluble in common organic solvents and stable for weeks under argon atmosphere. The ^{1}H NMR spectra of compounds **5–8** exhibit two sets of resonances for the Dipp groups of the β-diketiminate ligand, and the ^{1}H NMR spectrum of **5** showed a characteristic singlet resonance at 1.41 ppm for the O–H group, that is shifted to higher field compared to that of LGa(H)OH (−0.02 ppm)[29] and $\mathrm{LGa(OH)_2}$ (−0.27 ppm).[21] The proton coupled ^{31}P NMR spectra of **5** (−312.9 ppm, $^1J_{\text{P–H}}$ = 173.7 Hz), **6** (−281.6 ppm, $^1J_{\text{P–H}}$ = 189.7 Hz), **7** (−297.0 ppm, $^1J_{\text{P–H}}$ = 177.0 Hz), and **8** (−294.0 ppm, $^1J_{\text{P–H}}$ = 177.2 Hz) as well as the ^{1}H NMR spectra of **5** (−0.71 ppm, $^1J_{\text{P–H}}$ = 174.3 Hz), **6** (= −0.21 ppm, $^1J_{\text{P–H}}$ = 188.9 Hz), **7** (−0.54 ppm, $^1J_{\text{P–H}}$ = 177.3 Hz), and **8** (−0.45 ppm, $^1J_{\text{P–H}}$ = 176.4 Hz) displayed the expected doublets for the P–H units. Moreover, the proton decoupled $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra showed sharp singlets at −312.9 ppm (**5**), −281.3 ppm (**6**), −297.0 ppm (**7**), and −294.0 ppm (**8**), which are shifted to lower field than that of gallaphosphene **1** (−245.8 ppm).[17]

The molecular structures of compounds **6**, **7**, and **8** were determined by single-crystal X-ray diffraction (Fig. 2).[22] Suitable crystals were obtained upon storage of saturated toluene solutions at −30 °C (see ESI† for details). The compounds crystallize in the orthorhombic, and monoclinic space groups *Iba*2 (**6**), *Pbcn* (**7**), and $P2_1/c$ (**8**), respectively.[22] The Ga–P–Ga bond angles in **7** (112.15(2)°) and **8** (113.86(2)°) are almost identical to those of compounds **2–4** and comparable with that reported for **1** (113.87(2)°)[17] but significantly smaller than that of **6** (127.49(3)°), most likely resulting from the bulky 2,6-dimethylphenoxy group in **6**. The Ga1–P1 bonds in **6** (2.3235(8) Å), **7** (2.3144(4) Å), and **8** (2.3132(4) Å) are slightly shorter than the Ga2–P1 bonds in **6** (2.3461(8) Å), **7** (2.3304(4) Å), and **8** (2.3319(5) Å), respectively, but agree with the sum of the calculated single-bond radii (Ga 1.24 Å; P 1.11 Å)[23] as well as with Ga–P single bond

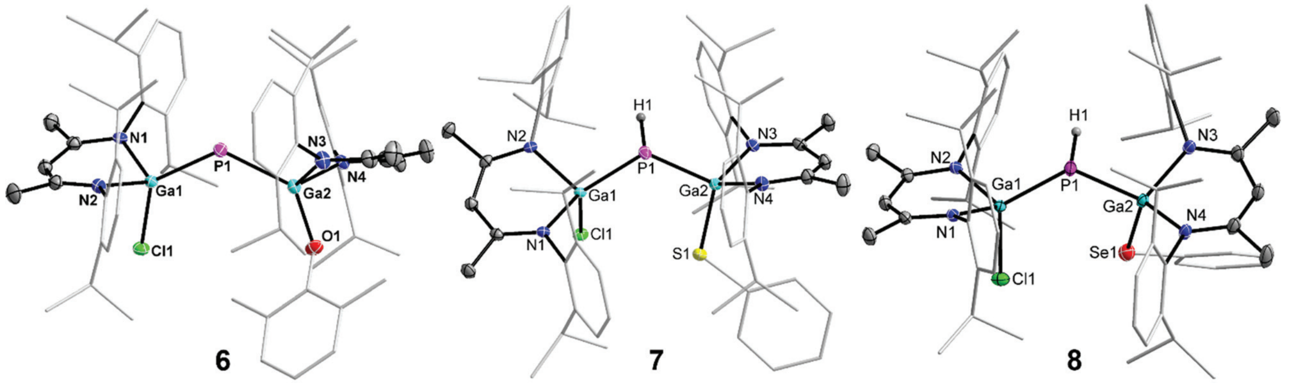


Fig. 2 Molecular structures of compounds **6**, **7**, and **8**. Ellipsoids set at 50% probability; C–H hydrogen atoms, and solvent molecules (toluene in **7** and **8**) are omitted for clarity.

Table 1 Selected bond lengths (Å) and angles (°) of gallaphosphene (**1**) and the X–H bond activation products (**2–8**)

	1	**2** (X = N5)	**3** (X = N5)	**4** (X = N5)	**6** (X = O1)	**7** (X = S1)	**8** (X = Se1)
Ga1–P1	2.2688(5)	2.3125(4)	2.3080(4)	2.3132(5)	2.3235(8)	2.3144(4)	2.3132(4)
Ga2–P1	2.1613(6)	2.3187(4)	2.3445(4)	2.3395(5)	2.3461(8)	2.3304(4)	2.3319(5)
Ga1–X	—	1.970(7)	1.8606(12)	1.8762(14)	1.842(2)	2.2551(4)	2.3898(3)
Ga1–Cl1	2.2360(5)	2.1913(14)	2.2361(4)	2.2322(5)	2.2191(8)	2.2098(3)	2.2143(4)
Ga1–P1–Ga2	113.87(2)	107.59(14)	112.96(15)	111.07(18)	127.49(3)	112.15(15)	113.86(18)
Cl1–Ga1–P1	127.65(2)	120.54(4)	120.233(14)	119.93(18)	128.58(3)	123.69(14)	122.81(17)
X–Ga2–P1	—	119.1(3)	116.86(4)	113.26(5)	134.25(7)	108.41(14)	111.62(12)

lengths observed for compounds **2–4**.[17,28] The Ga–O (1.842(2) Å), Ga–S (2.2551(4) Å), and Ga–Se (2.3898(3) Å) bond lengths of **6**, **7**, and **8** agree with the calculated[23] single bond lengths and compare well with experimentally observed Ga–O,[16a,17] Ga–S,[30] and Ga–Se single bond lengths (Table 1).

Conclusions

We report for the first time on bond activation reactions of polar X–H bonds of ammonia, primary amines, water, phenol, thiophenol and selenophenol in reactions with gallaphosphene L(Cl)GaPGaL **1**. All reactions proceed at ambient temperature with selective 1,2 addition at the Ga–P double bond. The gallium atom serves as electrophilic center, whereas the nucleophilic phosphorous atom is protonated in all reactions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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