

Main Group Chemistry

Reversible and Irreversible [2+2] Cycloaddition Reactions of Heteroallenes to a Gallaphosphene

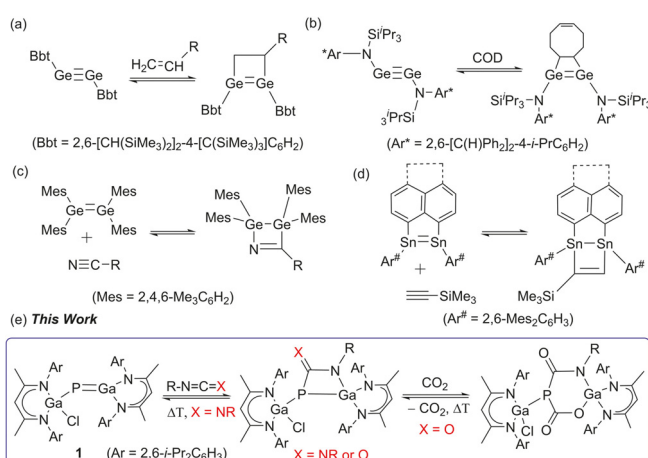
Mahendra K. Sharma, Christoph Wölper, Gebhard Haberhauer, and Stephan Schulz*

Dedicated to Professor Matthias Driess on the occasion of his 60th birthday

Abstract: [2+2] Cycloaddition reactions of gallaphosphene $L(Cl)GaPGaL$ **1** ($L = HC[C(Me)N(2,6-i-Pr_2C_6H_3)]_2$) with carbodiimides $[C(NR)_2]$; $R = i-Pr, Cy$) and isocyanates $[RNCO]$; $R = Et, i-Pr, Cy$) yielded four-membered metallaheterocycles $LGa(Cl)P[\mu-C(X)NR]GaL$ ($X = NR, R = i-Pr$ **2**, Cy **3**; $X = O, R = Et$ **4**, $i-Pr$ **5**, Cy **6**). Compounds **4–6** reversibly react with CO_2 via [2+2] cycloaddition at ambient temperature to the six-membered metallaheterocycles $LGa(Cl)P[\mu-C(O)O]-\mu-C(O)N(R)GaL$ ($R = Et$ **7**, $i-Pr$ **8**, Cy **9**). Compounds **2–9** were characterized by IR and heteronuclear ($^1H, ^{13}C\{^1H\}, ^{31}P\{^1H\}$) NMR spectroscopy and elemental analysis, while quantum chemical calculations provided a deeper understanding on the energetics of the reactions.

The activation of unsaturated molecules by reversible addition to reactive metal centers is a domain of transition metal chemistry and of central importance in catalytic processes. In contrast, comparable reactions at main-group element centers are far less developed and have only recently received increasing interest, not only because of fundamental curiosities but also in order to develop transition metal-like behavior including catalytic reactivity for main group metal complexes.^[1,2] Among others, reversible cycloaddition of unsaturated small molecules to multiply bonded main group element compounds is of particular interest and attracted much attention due to their small, sometimes tunable HOMO–LUMO gaps and their biradical-type bonding nature.^[1] In 2009, Power et al. reported on the first reversible

[2+2+2] cycloaddition of ethylene to a distannyne,^[3] followed by subsequent reports on reversible [2+2] cycloaddition reactions of unsaturated molecules to digermynes (Scheme 1 a,b),^[4] ditetrelenes (Scheme 1 c,d),^[5] and digallene,^[6] respectively. In contrast, comparable reactions at heterodiatomic multiply bonded main group element compounds have rarely been encountered.^[7]



Scheme 1. a–d) Selected examples of reversible [2+2] cycloaddition reactions of multiply bonded compounds (isoelectronic to gallaphosphene **1**) containing heavier main group elements. e) [2+2] Cycloaddition reactions of gallaphosphene **1** with heteroallenes.

Metallapnictenes $RMPnR$ ($M = B-Tl$; $Pn = N-Bi$) containing $M-Pn$ double bonds are isovalence-electronic to alkenes and have attracted significant interest due to their fascinating electronic structures and reactivity.^[8–15] In remarkable contrast to compounds containing $B-Pn$ ($Pn = N, P, As$)^[8] and $M-N$ double bonds ($M = Al, Ga, In$),^[9] the heavier congeners with $M-Pn$ ($M = Al, Ga$; $Pn = P, As, Sb$) double bonds have been reported only recently,^[10–14] and their reactivity is virtually unexplored.^[13–15] Since the $M-Pn$ double bonds are expected to be highly polarized,^[16] they are promising candidates for bond activation reactions of a variety of small molecules as well as unsaturated substrates.^[13–16] However, the addition of unsaturated small molecules at the polarized $M^{\delta+}-Pn^{\delta-}$ double bonds is limited to a recent report by Coles et al. on the irreversible [2+2] cycloaddition of carbon dioxide to an anionic indium imide complex $K[In(NON^{Ar})(NMe_3)]$ ($NON^{Ar} = [O-(SiMe_2NAr)_2]^{2-}$, $Ar = 2,6-i-Pr_2C_6H_3$, $Mes = 2,4,6-Me_3C_6H_2$),^[17] while we reported on reversible [2+2+2] cyclo-

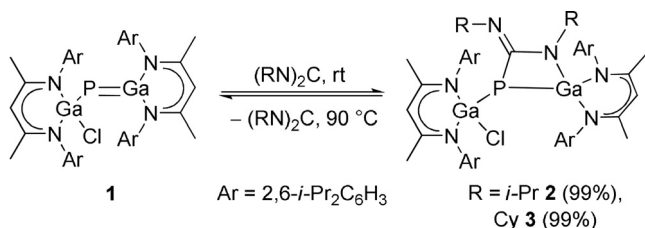
[*] Dr. M. K. Sharma, Dr. C. Wölper, Prof. Dr. S. Schulz
Institute of Inorganic Chemistry
and Center for Nanointegration Duisburg-Essen (CENIDE)
University of Duisburg-Essen
Universitätsstrasse 5–7, 45141 Essen (Germany)
E-mail: stephan.schulz@uni-due.de
Homepage: https://www.uni-due.de/ak_schulz/index_en.php
Prof. Dr. G. Haberhauer
Institute of Organic Chemistry
University of Duisburg-Essen
Universitätsstrasse 5–7, 45141 Essen (Germany)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
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addition reactions of carbon dioxide to gallaphosphene LGa(Cl)PGaL **1** (L = HC[C(Me)N(Ar)]₂).^[14] DFT calculations revealed that the addition of the second equivalent of CO₂ ($\Delta G_{\text{(for } 2 \times \text{CO}_2 \text{ addition)}} = -7.5 \text{ kcal mol}^{-1}$) is energetically more favored than the addition of the first CO₂ molecule ($\Delta G_{\text{(for } 1 \times \text{CO}_2 \text{ addition)}} = -1.8 \text{ kcal mol}^{-1}$), hence only the [2+2] cycloaddition product was isolated. These results as well as the scarcity of π -bonded metallapnictenes to form [2+2] cycloaddition products prompted us to investigate reactions of gallaphosphene **1** with unsaturated organic substrates (Scheme 1e).

Addition of equimolar amounts of carbodiimides [*i*-PrN)₂C (DIC), (CyN)₂C (DCC)] to red solutions of gallaphosphene **1** in toluene at ambient temperature instantaneously gave colorless solutions of the corresponding [2+2] cycloaddition products LGa(Cl)P[μ -C(NR)NR]GaL (R = *i*-Pr **2**, Cy **3**), which were isolated in almost quantitative (> 99%) yields (Scheme 2), whereas the sterically hindered

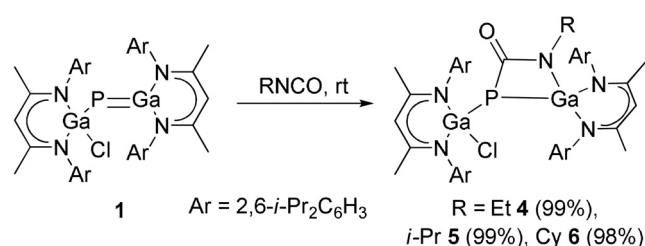


Scheme 2. Reversible [2+2] cycloaddition reactions of carbodiimides to gallaphosphene **1**.

carbodiimide (DippN)₂C (Dipp = 2,6-*i*-Pr₂C₆H₃) failed to react. In contrast to reactions with CO₂,^[14] both reactions only yielded the [2+2] cycloaddition products **2** and **3** even with a large excess of DIC and DCC. The reactions are temperature-dependent and fully reversible upon heating to 90 °C as shown by in situ ¹H and ³¹P{¹H} NMR spectroscopy, allowing the quantitative regeneration of gallaphosphene **1** and the corresponding carbodiimides (Figures S9–S12). To the best of our knowledge, this is the first report on a reversible, temperature-dependent [2+2] cycloaddition of a heavier group 13/15 multiply bonded compound.

We then reacted gallaphosphene **1** with isocyanates to test whether isocyanates undergo [2+2] cycloaddition reactions with either their C–O or C–N double bonds. All reactions selectively proceeded at ambient temperature with [2+2] cycloaddition at the C–N double bonds and formation of LGa(Cl)P[μ -C(O)NR]GaL (R = Et **4**, *i*-Pr **5** and Cy **6**) in quantitative (> 98%) yields (Scheme 3), whereas no reaction occurred with sterically more hindered isocyanates (R = *t*-Bu, Dipp), again revealing the influence of steric bulk on the reaction process. Compounds **4–6** also formed in the presence of an excess of the isocyanate, and in contrast to reactions of **1** with CO₂ and carbodiimides, the isocyanate cycloaddition reactions are fully irreversible.

Compounds **2–6** are colorless crystalline solids, which can be stored without decomposition under inert gas atmosphere at ambient temperature for months, whereas they decompose upon exposure to air. The ¹H and ¹³C NMR spectra (see



Scheme 3. [2+2] cycloaddition reactions of isocyanates to gallaphosphene **1**.

Supporting Information (SI) for details) are comparable to those of LGa-substituted gallapnictenes,^[12,14] dipnictanes,^[18] dipnictenes,^[19] radicals,^[20] and other complexes.^[21] The ³¹P{¹H} NMR spectra display sharp singlets (**2** –108.6; **3** –105.3; **4** –112.0; **5** –114.8; **6** –115.4 ppm), which are shifted to lower field compared to **1** (–245.8 ppm), but to higher field than L(Cl)GaP[μ -C(O)O]₂GaL (–52.1 ppm).^[14]

The solid-state molecular structures of compounds **2** and **6** were determined by single-crystal X-ray diffraction (Figure 1).^[22] Single crystals were obtained upon storage of saturated toluene/*n*-hexane solutions at –30 °C (see SI for details). Compound **2** crystallizes in the monoclinic space group *P*2₁ and compound **6** in the orthorhombic space group *P*2₁2₁2₁.^[22]

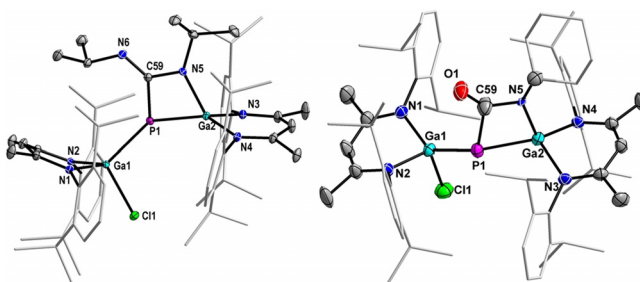
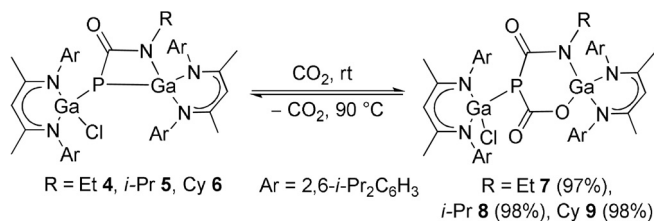


Figure 1. Molecular structures of compounds **2** (left) and **6** (right). Ellipsoids set at 50% probability; hydrogen atoms, alternate positions of the minor disordered parts of **6**, and solvent molecules (toluene in **2** and *n*-hexane in **6**) are omitted for clarity.

Both compounds exhibit planar four-membered GaPCN heterocycles, which adopt almost perpendicular orientations to the six-membered C₃N₂Ga₂ ring. The gallium atoms adopt distorted tetrahedral and the phosphorous atoms trigonal pyramidal geometries. The Ga1–P1–Ga2 bond angles in **2** (131.1(2)°) and **6** (133.1(1)°) are significantly larger compared to that of **1** (113.87(2)°)^[14] and [L(Br)Ga]₂PBr (118.94(8)°).^[19c] The Ga–P bond lengths in **2** (Ga1–P1 2.3084(4) Å, Ga2–P1 2.3115(4) Å) and **6** (Ga1–P1 2.296(2) Å, Ga2–P1 2.266(2) Å) agree with the sum of the calculated single-bond radii (Ga 1.24 Å; P 1.11 Å)^[23] and with Ga–P single bonds in related systems,^[24] but are elongated compared to the Ga–P double bonds of neutral gallaphosphene **1** (2.16(6) Å)^[14] and cationic gallaphosphene [LGaP^{(Me)cAAC)] (2.2393(6) Å).^[25]}

Strained ring systems are valuable synthons in organic synthesis.^[26a] Introducing heteroatoms in such rings led to charge-induced asymmetry, hence providing reactive reaction

sites.^[26b] The strained four-membered metallaheterocycles in compounds **2–6** are therefore promising candidates for bond activation reactions of small molecules. Compounds **2–6** immediately react with CO₂ at ambient temperature as is indicated by a slight color change of the reaction solution. Reactions of **2** and **3** yielded a mixture of single and double^[14] CO₂ addition products with concomitant release of the corresponding carbodiimides (Scheme S1), from which pure products could not be isolated due to their almost equal solubilities (Figures S29–S32). In contrast, compounds **4–6** cleanly reacted with CO₂ to L(Cl)GaP[μ-C(O)O][μ-C(O)NR]GaL (R=Et **7**, *i*-Pr **8**, and Cy **9**), respectively (Scheme 4). The reactions are temperature-dependent and fully reversible upon heating to 90 °C as shown by in situ ¹H



Scheme 4. Temperature-dependent binding/release reactions of compounds **4**, **5**, and **6** with CO₂.

and ³¹P{¹H} NMR spectroscopy (Figures S45–S50), allowing for the quantitative regeneration of compounds **4–6** with the release of CO₂. The reversible binding of CO₂ in main group chemistry was previously observed with frustrated Lewis pairs, organic Lewis bases,^[27] and for gallaphosphene **1**,^[14] but to the best of our knowledge was only reported once for a metallaheterocycle. The calix[4]pyrrolato aluminate anion featuring a square-planar Al^{III} cation was found to reversibly bind CO₂ and aldehydes.^[28] Moreover, temperature-dependent ring expansion/contraction reactions are unprecedented in main group metal chemistry.

Compounds **7**, **8**, and **9** are colorless crystalline solids and soluble in common organic solvents. The ¹³C{¹H} NMR spectra each exhibit two doublets of the NCO and OCO moieties, and the ³¹P{¹H} NMR spectra show singlets at –40.0 ppm (**7**), –34.5 ppm (**8**), and –35.0 ppm (**9**), respectively, which are downfield shifted compared to the starting reagents **4** (–112.0 ppm), **5** (–114.8 ppm), and **6** (–115.4 ppm) as well as L(Cl)GaP–[μ-C(O)O]₂–GaL (–52.1 ppm).^[14]

The molecular structures of compounds **8** and **9** were determined by single-crystal X-ray diffraction (Figure 2).^[22] Crystals were obtained upon storage of saturated toluene solutions at ambient temperature. The Ga1–P1 bond lengths in **8** (2.3272(15) Å) and **9** (2.3215(5) Å) are comparable to those in compounds **2** and **6**. The P–C (1.8524(18)–1.861(5) Å) and Ga2–N5 (1.887(5)–1.8963(14) Å) bond lengths of **8** and **9** as well as the Ga2–O2 bond lengths 1.840(4) Å (**8**) and 1.8337(12) Å (**9**) are almost identical.

Further, we performed DFT calculations at the B3LYP-D3BJ/def2-TZVP level of theory^[29] to determine the energetics of the [2+2] cycloaddition reactions of gallaphosphene **1** with CO₂, isocyanate EtNCO, as well as carbodiimides

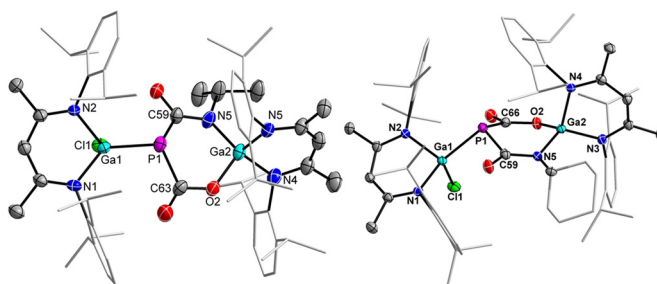
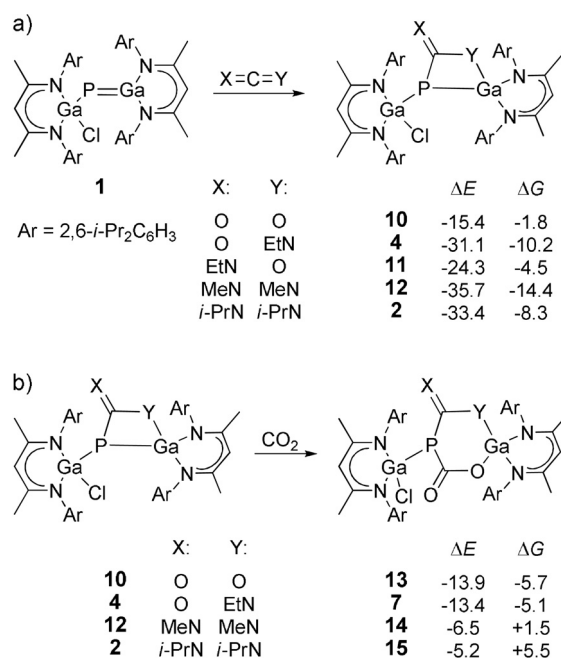


Figure 2. Molecular structures of **8** (left) and **9** (right). Ellipsoids set at 50% probability; hydrogen atoms and solvent molecules (toluene in **9**) are omitted for clarity.

MeNCNMe (DMC) and *i*-PrNCN*i*-Pr (DIC) to the corresponding four-membered metallaheterocycles **2**, **4**, and **10–12** (Scheme 5a). The two carbodiimides were chosen to investigate the influence of the alkyl group of the carbodiimide (small methyl vs. large isopropyl group) in the cycloaddition reaction. In a second step, we calculated the energetic parameters of the cycloaddition reaction of the four-membered metallaheterocycles **2**, **4**, **10**, and **12** with CO₂ to the six-membered metallaheterocycles **7** and **13–15** (Scheme 5b).

The reaction energy (ΔE) for the [2+2] cycloaddition reaction of the gallaphosphenes **1** with CO₂ is the most unfavorable and amounts to –15.4 kcal mol^{–1}. The addition of EtNCO can either proceed via the C–N (**4**) or C–O (**11**) double bond. However, the calculations show that the C–N cycloaddition to **1** is energetically more favorable by 6.8 kcal



Scheme 5. a) Calculation of the [2+2] cycloaddition reactions of gallaphosphene **1** with CO₂, isocyanate EtNCO and two carbodiimides DMC and DIC to the four-membered metallaheterocycles **2**, **4**, and **10–12**. b) Calculation of the addition of CO₂ to the metallaheterocycles **2**, **4**, **10**, and **12** yielding the six-membered metallaheterocycles **7** and **13–15**. The calculations were performed using B3LYP-D3BJ/def2-TZVP and the energy values are given in kcal mol^{–1}.

mol⁻¹ than the C–O cycloaddition. The reaction with the carbodiimides is energetically the most favorable, with values ranging from –33.4 to –35.7 kcal mol⁻¹.

A different order is found for the calculated Gibbs free energies (ΔG). Here the C–N cycloaddition of DIC is even less favorable (–8.3 kcal mol⁻¹) than that of EtNCO (–10.2 kcal mol⁻¹). This means that starting from **1** the formation of **2** is less favorable than the formation of **4** due to entropic reasons. Presumably, the free rotation of the large groups in **2** is severely restricted and the entropy loss during the cycloaddition is correspondingly high. This also explains the fact that the formation of **2** and **13** is reversible, while **4** is irreversibly formed starting from **1**. Note that the reversibility of the formation of **13** is due to enthalpic reasons, whereas in the case of **2** it is mainly due to entropy.

In order to examine whether the [2+2] cycloaddition reactions proceed in a concerted or stepwise fashion, the transition states for the addition of CO₂ (**TS**_{1–10}) and EtNCO (**TS**_{1–4}) to **1** were calculated using B3LYP-D3BJ/def2-TZVP//B3LYP-D3BJ/6-31G* level of theory. The results show that both addition reactions take place in one step, whereby the Gibbs free energies amount to 14.0 (**TS**_{1–10}) and 8.8 kcal mol⁻¹ (**TS**_{1–4}). Due to the highly polarized bonds, the distances between the reaction centers in the transition states differ significantly: The Ga–O and Ga–N distances (**TS**_{1–10}: 2.376 Å; **TS**_{1–4}: 2.272 Å) are by far smaller than the P–C distances (**TS**_{1–10}: 2.698 Å; **TS**_{1–4}: 3.173 Å).

We also determined the thermodynamic parameters for the addition of CO₂ to the four-membered metallaheterocycles **2**, **4**, **10** and **12** (Scheme 5b). The reaction energies (ΔE) for the CO₂ and EtNCO adducts **4** and **10** vary between –13.4 and –13.9 kcal mol⁻¹, which roughly corresponds to the energy obtained by the cycloaddition of CO₂ to the gallaphosphenes **1** (–15.4 kcal mol⁻¹). The values for the Gibbs energy for the addition of CO₂ to the four-membered rings **4** and **10** are even lower than that for the addition of CO₂ to the P–Ga double bond of **1**; that is, the first step (addition of CO₂ or EtNCO to **1**) leads to an activation of the resulting system regard to a CO₂ addition. The calculated Gibbs free energies (ΔG) for the formation of **7** and **13** amount to –5.1 kcal mol⁻¹ and –5.7 kcal mol⁻¹, respectively. Accordingly, the absolute value is quite small and explains the experimentally found reversibility of the CO₂ addition to **4** and **10**. The cycloaddition of CO₂ to the RNCNR adducts **2** and **12** is significantly unfavored compared to the cycloaddition of CO₂ to the previously mentioned systems. Both are endergonic reactions. This agrees with the experimentally found behavior of **2** in the presence of CO₂, according to which products **15** and **13** are obtained. The latter is formed by the release of DIC.

In summary, we reported on the first [2+2] cycloaddition reactions of a heavier group 13/15 metallapnictene with heteroallenes. Gallaphosphene **1** selectively reacts with C–N double bonds of carbodiimides and isocyanates at ambient temperature, affording four-membered metallaheterocycles **2–6**. The reactions with carbodiimides are fully reversible, yielding gallaphosphene **1** and the corresponding carbodiimides upon heating. Compounds **2–6** are promising synthons for CO₂ activation reactions. Reactions of compounds **4–6**

with CO₂ yielded compounds **7**, **8**, and **9**, respectively. The reactions are fully reversible, and CO₂ is released upon heating of **7–9** to 90°C. DFT calculations show that the addition of CO₂ to the four-membered metallaheterocycles is reversible due to the low reaction energy. In contrast, the reversibility of the addition of carbodiimides showing large substituents to **1** is due to the loss of entropy in the cyclization reaction.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: [2+2] cycloaddition reactions · CO₂ activation · gallaphosphene · heteroallenes · main group elements

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