## Main Group Chemistry

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

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


#### Abstract

Cycloaddition reactions of gallaphosphene $L(C l) G a P G a L 1 \quad\left(L=H C\left[C(M e) N\left(2,6-i-\mathrm{Pr}_{2} C_{6} H_{3}\right)\right]_{2}\right)$ with carbodiimides $\left[C(N R)_{2} ; \quad R=i-P r, \quad C y\right]$ and isocyanates [RNCO; $R=E t, i-P r, C y]$ yielded four-membered metallaheterocycles $L G a(C l) P[\mu-C(X) N R] G a L \quad(X=N R, R=i-\operatorname{Pr} 2$, Cy 3; $X=O, R=E t$ 4, $i-\operatorname{Pr}$ 5, Cy 6). Compounds 4-6 reversibly react with $\mathrm{CO}_{2}$ via $[2+2]$ cycloaddition at ambient temperature to the six-membered metallaheterocycles LGa(Cl)P[ $-C(O) O]-\mu-C(O) N(R) G a L(R=E t 7$, i-Pr 8, Cy 9). Compounds 2-9 were characterized by IR and heteronuclear $\left({ }^{1} H,{ }^{13} C\left\{{ }^{1} H\right\},{ }^{31} P\left\{{ }^{1} H\right\}\right) \quad N M R$ spectroscopy and elemental analysis, while quantum chemical calculations provided a deeper understanding on the energetics of the reactions.


Thhe 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

[^0]$[2+2+2]$ cycloaddition of ethylene to a distannyne, ${ }^{[3]}$ followed by subsequent reports on reversible [2+2] cycloaddition reactions of unsaturated molecules to digermynes (Scheme $1 \mathrm{a}, \mathrm{b}$ ), ${ }^{[4]}$ ditetrelenes (Scheme $1 \mathrm{c}, \mathrm{d}$ ), ${ }^{[5]}$ 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 $\mathrm{RMPnR}(\mathrm{M}=\mathrm{B}-\mathrm{Tl} ; \mathrm{Pn}=\mathrm{N}-\mathrm{Bi})$ containing $\mathrm{M}-\mathrm{Pn}$ 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 $\mathrm{B}-\mathrm{Pn}(\mathrm{Pn}=\mathrm{N}, \mathrm{P}$, $\mathrm{As}){ }^{[8]}$ and $\mathrm{M}-\mathrm{N}$ double bonds $(\mathrm{M}=\mathrm{Al}, \mathrm{Ga}, \mathrm{In}),{ }^{[9]}$ the heavier congeners with $\mathrm{M}-\mathrm{Pn}(\mathrm{M}=\mathrm{Al}, \mathrm{Ga} ; \mathrm{Pn}=\mathrm{P}, \mathrm{As}, \mathrm{Sb})$ double bonds have been reported only recently, ${ }^{[10-14]}$ and their reactivity is virtually unexplored. ${ }^{[13-15]}$ Since the $\mathrm{M}-\mathrm{Pn}$ 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 $\mathrm{M}^{\delta+}-\mathrm{Pn}^{\delta-}$ 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 $\quad \mathrm{K}\left[\operatorname{In}\left(\mathrm{NON}^{\mathrm{Ar}}\right)(\mathrm{NMes})\right] \quad\left(\mathrm{NON}^{\mathrm{Ar}}=[\mathrm{O}-\right.$ $\left.\left(\mathrm{SiMe}_{2} \mathrm{NAr}\right)_{2}\right]^{2-}, \quad \mathrm{Ar}=2,6-i-\mathrm{Pr}_{2} \mathrm{C}_{6} \mathrm{H}_{3}, \quad \mathrm{Mes}=2,4,6-$ $\left.\mathrm{Me}_{3} \mathrm{C}_{6} \mathrm{H}_{2}\right),{ }^{[17]}$ while we reported on reversible $[2+2+2]$ cyclo-
addition reactions of carbon dioxide to gallaphosphene $\mathrm{LGa}(\mathrm{Cl}) \mathrm{PGaL} 1\left(\mathrm{~L}=\mathrm{HC}[\mathrm{C}(\mathrm{Me}) \mathrm{N}(\mathrm{Ar})]_{2}\right) \cdot{ }^{[14]}$ DFT calculations revealed that the addition of the second equivalent of $\mathrm{CO}_{2}\left(\Delta G_{\left(\text {for } 2 \times \mathrm{CO}_{2} \text { addition }\right)}=-7.5 \mathrm{kcalmol}^{-1}\right)$ is energetically more favored than the addition of the first $\mathrm{CO}_{2}$ molecule $\left(\Delta G_{\text {(for } 1 \times \mathrm{CO}_{2} \text { addition) }}=-1.8 \mathrm{kcalmol}^{-1}\right)$, hence only the $[2+2+2]$ cycloaddition product was isolated. These results as well as the scarcity of $\pi$-bonded metallapnictenes to form $[2+2]$ cycloaddition products prompted us to investigate reactions of gallaphosphene $\mathbf{1}$ with unsaturated organic substrates (Scheme 1e).

Addition of equimolar amounts of carbodiimides [ $i$ $\left.\operatorname{PrN})_{2} \mathrm{C}(\mathrm{DIC}),(\mathrm{CyN})_{2} \mathrm{C}(\mathrm{DCC})\right]$ to red solutions of gallaphosphene $\mathbf{1}$ in toluene at ambient temperature instantaneously gave colorless solutions of the corresponding [2+2] cycloaddition products $\mathrm{LGa}(\mathrm{Cl}) \mathrm{P}[\mu-\mathrm{C}(\mathrm{NR}) \mathrm{NR}] \mathrm{GaL}(\mathrm{R}=i-$ $\operatorname{Pr} 2, \mathrm{Cy} \mathrm{3}$ ), 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$)_{2} \mathrm{C}$ ( $\mathrm{Dipp}=2,6-i-\mathrm{Pr}_{2} \mathrm{C}_{6} \mathrm{H}_{3}$ ) failed to react. In contrast to reactions with $\mathrm{CO}_{2},{ }^{[14]}$ both reactions only yielded the $[2+2]$ cycloaddition products $\mathbf{2}$ and $\mathbf{3}$ even with a large excess of DIC and DCC. The reactions are temperature-dependent and fully reversible upon heating to $90^{\circ} \mathrm{C}$ as shown by in situ ${ }^{1} \mathrm{H}$ and ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ 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 $\mathbf{1}$ with isocyanates to test whether isocyanates undergo $[2+2]$ cycloaddition reactions with either their $\mathrm{C}^{-}-\mathrm{O}$ or $\mathrm{C}^{-} \mathrm{N}$ double bonds. All reactions selectively proceeded at ambient temperature with $[2+2]$ cycloaddition at the $\mathrm{C}-\mathrm{N}$ double bonds and formation of $\mathrm{LGa}(\mathrm{Cl}) \mathrm{P}[\mu-\mathrm{C}(\mathrm{O}) \mathrm{NR}] \mathrm{GaL}(\mathrm{R}=\mathrm{Et} 4, i-\mathrm{Pr} 5$ and Cy 6) in quantitative ( $>98 \%$ ) yields (Scheme 3), whereas no reaction occurred with sterically more hindered isocyanates ( $\mathrm{R}=t-\mathrm{Bu}$, 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 $\mathrm{CO}_{2}$ 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 ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ 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 ${ }^{31} \mathrm{P}$ $\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra display sharp singlets $(\mathbf{2}-108.6 ; \mathbf{3}-105.3$;
 field compared to $\mathbf{1}(-245.8 \mathrm{ppm})$, but to higher field than $\mathrm{L}(\mathrm{Cl}) \mathrm{GaP}[\mu-\mathrm{C}(\mathrm{O}) \mathrm{O}]_{2} \mathrm{GaL}(-52.1 \mathrm{ppm}) .{ }^{[14]}$

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


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 $\mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{Ga} 2$ ring. The gallium atoms adopt distorted tetrahedral and the phosphorous atoms trigonal pyramidal geometries. The Ga1-P1-Ga2 bond angles in 2 $\left(131.1(2)^{\circ}\right)$ and $6\left(133.1(1)^{\circ}\right)$ are significantly larger compared to that of $\mathbf{1}\left(113.87(2)^{\circ}\right)^{[14]}$ and $\left[\mathrm{L}(\mathrm{Br}) \mathrm{Ga}_{2} \mathrm{PBr}(118.94-\right.$ $\left.(8)^{\circ}\right) .{ }^{[19 \mathrm{c}]}$ The $\mathrm{Ga}-\mathrm{P}$ bond lengths in $2(\mathrm{Ga} 1-\mathrm{P} 12.3084(4) \AA$, $\mathrm{Ga} 2-\mathrm{P} 12.3115(4) \AA$ Å) and 6 (Ga1-P1 2.296(2) Å, Ga2-P1 $2.266(2) \AA$ ) agree with the sum of the calculated single-bond radii ( $\mathrm{Ga} 1.24 \AA ; \mathrm{P} 1.11 \AA)^{[23]}$ and with $\mathrm{Ga}-\mathrm{P}$ single bonds in related systems, ${ }^{[24]}$ but are elongated compared to the $\mathrm{Ga}-\mathrm{P}$ double bonds of neutral gallaphosphene $\mathbf{1}(2.16(6) \AA)^{[14]}$ and cationic gallaphosphene $\left[\mathrm{LGaP}\left({ }^{\mathrm{Me}} \mathrm{cAAC}\right)\right](2.2393(6) \AA) .{ }^{[25]}$

Strained ring systems are valuable synthons in organic synthesis. ${ }^{[26]]}$ Introducing heteroatoms in such rings led to charge-induced asymmetry, hence providing reactive reaction
sites. ${ }^{[266]}$ 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 $\mathrm{CO}_{2}$ at ambient temperature as is indicated by a slight color change of the reaction solution. Reactions of $\mathbf{2}$ and $\mathbf{3}$ yielded a mixture of single and double ${ }^{[14]}$ $\mathrm{CO}_{2}$ 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 $\mathrm{CO}_{2}$ to $\mathrm{L}(\mathrm{Cl}) \mathrm{GaP}[\mu-\mathrm{C}(\mathrm{O}) \mathrm{O}][\mu-\mathrm{C}-$ (O)NR]GaL ( $\mathrm{R}=\mathrm{Et} 7, i-\operatorname{Pr} 8$, and Cy 9), respectively (Scheme 4). The reactions are temperature-dependent and fully reversible upon heating to $90^{\circ} \mathrm{C}$ as shown by in situ ${ }^{1} \mathrm{H}$


Scheme 4. Temperature-dependent binding/release reactions of compounds 4,5 , and 6 with $\mathrm{CO}_{2}$.
and ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy (Figures $\mathrm{S} 45-\mathrm{S} 50$ ), allowing for the quantitative regeneration of compounds 4-6 with the release of $\mathrm{CO}_{2}$. The reversible binding of $\mathrm{CO}_{2}$ in main group chemistry was previously observed with frustrated Lewis pairs, organic Lewis bases, ${ }^{[27]}$ and for gallaphosphene $\mathbf{1},{ }^{[14]}$ but to the best of our knowledge was only reported once for a metallaheterocycle. The calix[4]pyrrolato aluminate anion featuring a square-planar $\mathrm{Al}^{\text {III }}$ cation was found to reversibly bind $\mathrm{CO}_{2}$ and aldehydes. ${ }^{[28]}$ Moreover, temperature-dependent ring expansion/contraction reactions are unprecedented in main group metal chemistry.

Compounds 7, 8, and $\mathbf{9}$ are colorless crystalline solids and soluble in common organic solvents. The ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra each exhibit two doublets of the NCO and OCO moieties, and the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ 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 $4(-112.0 \mathrm{ppm}), 5(-114.8 \mathrm{ppm})$, and $\mathbf{6}$ $(-115.4 \mathrm{ppm})$ as well as $\mathrm{L}(\mathrm{Cl}) \mathrm{GaP}-[\mu-\mathrm{C}(\mathrm{O}) \mathrm{O}]_{2}-\mathrm{GaL}$ $(-52.1 \mathrm{ppm}) .{ }^{[14]}$

The molecular structures of compounds $\mathbf{8}$ 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 $\mathbf{8}(2.3272(15) \AA)$ and $9(2.3215(5) \AA)$ 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) À) bond lengths of $\mathbf{8}$ and $\mathbf{9}$ as well as the $\mathrm{Ga} 2-\mathrm{O} 2$ bond lengths $1.840(4) \AA(\mathbf{8})$ and $1.8337(12) \AA(9)$ 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 $\mathrm{CO}_{2}$, 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 $i-\operatorname{PrNCN} i-\mathrm{Pr}$ (DIC) to the corresponding four-membered metallaheterocycles 2, 4, and 10-12 (Scheme 5 a ). 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 $\mathbf{2}, \mathbf{4}, \mathbf{1 0}$, and $\mathbf{1 2}$ with $\mathrm{CO}_{2}$ to the sixmembered metallaheterocycles $\mathbf{7}$ and 13-15 (Scheme 5b).

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



Scheme 5. a) Calculation of the $[2+2]$ cycloaddition reactions of gallaphosphene 1 with $\mathrm{CO}_{2}$, isocyanate EtNCO and two carbodiimides DMC and DIC to the four-membered metallaheterocycles 2, 4, and 1012. b) Calculation of the addition of $\mathrm{CO}_{2}$ to the metallaheterocycles $\mathbf{2}$, 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 $\mathrm{kcal}_{\mathrm{mol}}{ }^{-1}$.
$\mathrm{mol}^{-1}$ than the $\mathrm{C}^{-} \mathrm{O}$ cycloaddition. The reaction with the carbodiimides is energetically the most favorable, with values ranging from -33.4 to $-35.7 \mathrm{kcal} \mathrm{mol}^{-1}$.

A different order is found for the calculated Gibbs free energies $(\Delta G)$. Here the $\mathrm{C}-\mathrm{N}$ cycloaddition of DIC is even less favorable $\left(-8.3 \mathrm{kcalmol}^{-1}\right)$ than that of EtNCO $\left(-10.2 \mathrm{kcalmol}^{-1}\right)$. This means that starting from 1 the formation of $\mathbf{2}$ is less favorable than the formation of $\mathbf{4}$ due to entropic reasons. Presumably, the free rotation of the large groups in $\mathbf{2}$ is severely restricted and the entropy loss during the cycloaddition is correspondingly high. This also explains the fact that the formation of $\mathbf{2}$ and $\mathbf{1 3}$ is reversible, while $\mathbf{4}$ is irreversibly formed starting from $\mathbf{1}$. Note that the reversibility of the formation of $\mathbf{1 3}$ is due to enthalpic reasons, whereas in the case of $\mathbf{2}$ 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 $\mathrm{CO}_{2}\left(\mathbf{T S}_{\mathbf{1} \rightarrow \mathbf{1 0}}\right)$ and EtNCO ( $\mathbf{T S}_{1 \rightarrow 4}$ ) to $\mathbf{1}$ 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 $14.0\left(\mathbf{T S}_{\mathbf{1} \rightarrow \mathbf{1 0}}\right)$ and 8.8 kcal $\mathrm{mol}^{-1}\left(\mathbf{T S}_{\mathbf{1 \rightarrow 4}}\right)$. Due to the highly polarized bonds, the distances between the reaction centers in the transition states differ significantly: The $\mathrm{Ga}-\mathrm{O}$ and $\mathrm{Ga}-\mathrm{N}$ distances ( $\mathbf{T S}_{\mathbf{1 \rightarrow 1 0}}: 2.376 \AA ; \mathbf{T S}_{\mathbf{1} \rightarrow 4}: 2.272 \AA$ ) are by far smaller than the $\mathrm{P}-\mathrm{C}$ distances ( $\mathbf{T S}_{\mathbf{1}_{\rightarrow 10}}: 2.698 \AA ; \mathbf{T S}_{\mathbf{1 \rightarrow 4}}: 3.173 \AA$ ).

We also determined the thermodynamic parameters for the addition of $\mathrm{CO}_{2}$ to the four-membered metallaheterocycles 2, 4, $\mathbf{1 0}$ and $\mathbf{1 2}$ (Scheme 5b). The reaction energies $(\Delta E)$ for the $\mathrm{CO}_{2}$ and EtNCO adducts $\mathbf{4}$ and $\mathbf{1 0}$ vary between -13.4 and $-13.9 \mathrm{kcal} \mathrm{mol}^{-1}$, which roughly corresponds to the energy obtained by the cycloaddition of $\mathrm{CO}_{2}$ to the gallaphosphenes $1\left(-15.4 \mathrm{kcalmol}^{-1}\right)$. The values for the Gibbs energy for the addition of $\mathrm{CO}_{2}$ to the four-membered rings 4 and $\mathbf{1 0}$ are even lower than that for the addition of $\mathrm{CO}_{2}$ to the $\mathrm{P}-\mathrm{Ga}$ double bond of $\mathbf{1}$; that is, the first step (addition of $\mathrm{CO}_{2}$ or EtNCO to 1) leads to an activation of the resulting system regard to a $\mathrm{CO}_{2}$ addition. The calculated Gibbs free energies $(\Delta G)$ for the formation of $\mathbf{7}$ and $\mathbf{1 3}$ amount to $-5.1 \mathrm{kcal} \mathrm{mol}^{-1}$ and $-5.7 \mathrm{kcalmol}^{-1}$, respectively. Accordingly, the absolute value is quite small and explains the experimentally found reversibility of the $\mathrm{CO}_{2}$ addition to $\mathbf{4}$ and $\mathbf{1 0}$. The cycloaddition of $\mathrm{CO}_{2}$ to the RNCNR adducts $\mathbf{2}$ and $\mathbf{1 2}$ is significantly unfavored compared to the cycloaddition of $\mathrm{CO}_{2}$ to the previously mentioned systems. Both are endergonic reactions. This agrees with the experimentally found behavior of 2 in the presence of $\mathrm{CO}_{2}$, according to which products $\mathbf{1 5}$ and $\mathbf{1 3}$ 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 $\mathbf{1}$ selectively reacts with $\mathrm{C}-\mathrm{N}$ double bonds of carbodiimides and isocyanates at ambient temperature, affording four-membered metallaheterocycles 2-6. The reactions with carbodiimides are fully reversible, yielding gallaphosphene $\mathbf{1}$ and the corresponding carbodiimides upon heating. Compounds 2-6 are promising synthons for $\mathrm{CO}_{2}$ activation reactions. Reactions of compounds 4-6
with $\mathrm{CO}_{2}$ yielded compounds $\mathbf{7}, \mathbf{8}$, and $\mathbf{9}$, respectively. The reactions are fully reversible, and $\mathrm{CO}_{2}$ is released upon heating of $\mathbf{7 - 9}$ to $90^{\circ} \mathrm{C}$. DFT calculations show that the addition of $\mathrm{CO}_{2}$ 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 $\mathbf{1}$ 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.
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[22] Full crystallographic data of all structurally characterized compounds described herein as well as central bond lengths and angles (Tables S1 and Figures S47-S51) are given in the Supporting Information. Deposition numbers 2089048 (2), 2089049 (6), 2089050 (8), and 2089051 (9) contain 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 www.ccdc.cam.ac.uk/structures.
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