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# Interaction of Multiple Bonds with NacNacGa: Oxidative Cleavage vs **Coupling and Cyclization**

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**S** Supporting Information

ABSTRACT: The reactivity of the gallium(I) compound NacNacGa (4) to a variety of unsaturated compounds has been studied. Whereas 4 proved surprisingly unreactive toward olefins, ketones, guanidines, and thioureas, it reacts with isocyanates and carbodiimides to furnish the products of coupling of two heterocumulenes. With isothiocyanate, the



C=S cleavage occurs, leading to the dimer (NacNacGa)<sub>2</sub>( $\mu$ -S)( $\mu$ -CNPh) and the cyclization product NacNacGa(S<sub>2</sub>C=NPh). These compounds were characterized by multinuclear NMR spectroscopy and X-ray crystal structure analyses. Oxidative addition of S=PPh<sub>3</sub> occurs at elevated temperatures and results in the known dimer [NacNacGa( $\mu$ -S)]<sub>2</sub>.

# INTRODUCTION

Oxidative cleavage of  $\sigma$  bonds on reduced main group centers<sup>1</sup> has received significant attention in the context of developing main group analogues of the common catalysts based on transition metal complexes.<sup>2</sup> Much less is known about the reactivity of main group compounds toward multiple bonds, although examples of coordination, cyclization, and oxidative cleavage have been documented.<sup>3</sup> In particular, the groups of Power and Baceiredo demonstrated reversible addition of ethylene to distannyne,<sup>4</sup> silylene,<sup>5,6</sup> and stannylene.<sup>7</sup> Rieger et al. further documented the instance of ethylene coordination to silvlene and insertion into the silvl-silvlene bond, as well as butadiene cyclization with a silylamidosilylene.<sup>8</sup> The groups of Roesky and Driess reported that alkynes form  $\pi$ -complexes with the Al(I) compound NacNacAl (1, NacNac = [ArNC- $(Me)CHC(Me)NAr]^{-}$  and  $Ar = 2_{1}6^{-i}Pr_{2}C_{6}H_{3})^{9}$  and with silylene NacNac'Si (2, NacNac' = [ArNC(Me)CHC(=  $(CH_2)NAr]^{2-}$ .<sup>10</sup> Likewise, compound 1 has been recently shown to reversibly coordinate norbornene.<sup>11</sup> On the other hand, cyclization products were observed in reactions of 1 and 2 with azides.<sup>12</sup> Related addition and cyclization reactions of diimine supported digallene and dialumene compounds with olefins and alkynes have been described by the groups of Fedushkin<sup>13</sup> and Yang.<sup>14</sup> Power et al. reported reactions of monomeric Ar\*Ga (Ar\* =  $C_6H_3$ -2,6- $(C_6H_2$ -2,4,6- $iPr_3)_2$ ) and dimeric Ga(I) species Ar'GaGaAr' (Ar' =  $C_6H_3$ -2,6-( $C_6H_3$ - $2,6-iPr_2)_2$  with two alkene molecules resulting in cyclization into digalocycles.<sup>15</sup> Reactions of digallene with azides and diimines leading to monomeric and dimeric gallium imides and  $\begin{bmatrix} 2 + 2 \end{bmatrix}$  addition products also were described.<sup>16</sup>

We have previously shown that compound 1 cleaves the C=S bond of thioureas and the P=S bond of phosphine

sulfides to give terminal aluminum sulfide derivatives, such as 3 in Scheme 1,<sup>17</sup> and also oxidatively adds the C=N bond of



guanidine.<sup>18</sup> The cleavage of the O=P bond of phosphine oxides was accomplished as well and was accompanied by deprotonation of a Me group of the NacNac backbone to give an aluminum hydroxyl compound.<sup>19</sup> In contrast, a reaction of 1 with urea resulted in isomerization to the urea-complexed hydride NacNac'Al(H)( $O = C(NMeCH_2)_2$ ) having the O = Cbond intact. How this reactivity pattern changes down group 13 remains to be unveiled. For example, the propensity of NacNacGa (4) to cleave single bonds is well documented,<sup>20</sup>

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whereas its reactivity toward multiple bonds has been probed only in reactions with azides.<sup>21</sup> Here we disclose our efforts to study this problem.

# RESULTS AND DISCUSSION

Unlike the aluminum congener 1,<sup>11</sup> the gallium compound 4 does not show any sign of olefin coordination in reactions with cyclohexene and ethylene, even at low temperature (-20 °C). Neither is there a [1 + 4] cycloaddition with butadiene, which is in contrast to the reactivity of the isolobal silylene  $2^{22}$  On the other hand, the  $\alpha$ , $\beta$ -unsaturated aldehyde, methacrolein, easily cyclizes with 4 to give the gallium enolate 5 (Scheme 2).

# Scheme 2. Reactions of 4 with Methacrolein



The identity of this product was established by NMR spectroscopy and confirmed by X-ray analysis (Figure 1). In



Figure 1. Molecular structure of 5 (thermal ellipsoids are shown at 30%; hydrogen atoms, except those on C32 and C30, are omitted for clarity). Selected bond lengths (Å) and angles (deg): Ga(1)-N(1) 1.942(3), Ga(1)-N(2) 1.943(3), Ga(1)-O(1) 1.884(2), Ga(1)-C(30) 1.979(3), C(31)-C(32) 1.339(5), C(30)-C(31) 1.516(5); N(1)-Ga(1)-N(2) 96.3(1), O(1)-Ga(1)-C(30) 93.0(1), Ga(1)-O(1)-C(32) 105.4(2), Ga(1)-C(30)-C(31) 100.3(2).

particular, the olefinic proton gives rise to a resonance at 6.88 ppm and the backbone methine of NacNac is seen at 4.86 ppm. The methyl signal of the enolate part was observed at 1.45 ppm. X-ray study revealed a spiro structure formed as a result of [1 + 4] cycloaddition. The Ga–O bond of 1.884(2) Å and the Ga-C bond of 1.979(3) Å are normal for the respective single bonds. The C(31)-C(30) distance, corresponding to the C=C bond in the parent methacrolein, is elongated to 1.516 (5) Å, whereas the C(31)-C(32) distance is contracted to 1.339 (5) Å, indicating the formation of an enolate moiety. Interestingly, the spiro structure is distorted in such away that the C(30)-Ga(1)-N(1)-N(2) fragment is close to planarity (the sum of bond angles around Ga of  $345.37^{\circ}$ ), whereas the oxygen atom forms rather acute angles with the GaN<sub>2</sub> fragment,  $109.7(1)^{\circ}$  and  $107.7(1)^{\circ}$ . The C(32)-Ga(1)-O(1) angle is almost right, 93.0(1)°. This feature indicates that a significant s character of Ga is spent on the bond to the carbon atom, whereas more p-character goes

to the bond with oxygen, in agreement with the relative electronegativity of these two groups.

Unexpectedly, there was no reaction between 4 and diphenylketone, which also stands in contrast to the easy addition of this ketone to the silylene  $2^{23}$ . This difference in reactivity between 2 and 4 likely stems from the greater stabilization of the lone pair of gallium vs the lone pair of silicon, which results in a larger singlet-to-triplet gap in  $4^{24}$ .

We then looked at the possibility of multiple bond cleavage at gallium. Oxidative addition of a multiple bond X=Y to a group 13 NacNac compound NacNacM is possible if one of the partners, X or Y, is stable in the subvalent state. The possible candidates are, therefore, CO<sub>2</sub>, CS<sub>2</sub>, isocyanates, isothiocyanates, and diimines, to name just some.

Unlike the reactions of the aluminum analogue 1 shown in Scheme 1, compound 4 does not react with cyclic urea, thiourea, guanidine, and phosphine oxides ( $Ph_3P=O$  and  $Et_3P=O$ ). Neither was there any cleavage of the P=S bond of  $Et_3P=S$ , even upon heating to 80 °C. With  $Ph_3P=S$ , however, a slow reaction (2 days) happens upon heating to 80 °C to furnish the known sulfide (NacNacGa-S)<sub>2</sub> (6 in Scheme 3).<sup>25</sup>





Nevertheless, 4 readily reacts with 2 equiv of isothiocyanate PhNCS to give the product of C=S cleavage and cyclization 7 and the dimer (NacNacGa)<sub>2</sub>( $\mu$ -S)( $\mu$ -CNPh) (8) in the ratio 5:1 (Scheme 4). Dropwise addition of only 1 equiv of this reagent to a toluene solution of 4 produced a mixture containing products 7 and 8 in the ratio 1:1. The reaction likely proceeds via intermediate formation of the sulfide cyanide complex (NacNacGa)(=S)(CNPh) that either reacts with another equivalent of PhNCS to give 7 or is intercepted by the starting complex 4 to furnish 8. The first reaction is thus analogous to the reaction of aluminum compound 3 with isothiocyanate to give NacNacAl( $\kappa^2$ -S<sub>2</sub>C=NPh) (9).<sup>17</sup>

In the <sup>1</sup>H NMR spectrum, compound 7 gives rise to a  $C_s$ symmetric pattern featuring the backbone signals at 4.79 and 1.51 ppm, two septets (at 3.17 and 3.10 ppm) for the methine part of <sup>i</sup>Pr groups, and four doublets for their methyl groups. Crystals suitable for X-ray diffraction analysis were grown from a 1:2 mixture of toluene and hexanes, and the molecular structure is shown in Figure 2. The gallium atom has a distorted tetrahedral environment comprised of the chelating NacNac ligand and the  $\kappa^2(S,S)$ -coordinated dithioazacarbonate. The Ga-S bonds have slightly differing distances 2.2639(7) and 2.2561(7) Å and are comparable to the Ga-S distances (2.2511(7) and 2.2736(7) Å) in the sulfide dimer 6 produced from the reaction of 4 with elemental sulfur. The S-C–S bond angle of  $112.5(1)^{\circ}$  is significantly wider than angles at sulfur  $(82.54(9)^\circ)$  or gallium  $(81.78(3)^\circ)$  making the GaS<sub>2</sub>C ring kite-shaped. Similar metrics, e.g., the S-C-S bond angle of 112.21(14)° and the S-Al-S bond angle of  $82.91(4)^{\circ}$ , were found in the aluminum congener 9.

The chemistry of Scheme 3 is reminiscent of the C=S bond cleavage and cyclization observed by Jutzi et al. in the reaction of silylene Cp\*<sub>2</sub>Si with MeNCS to give Cp\*<sub>2</sub>Si(S<sub>2</sub>CNMe),<sup>26</sup>

S=CNPh





Figure 2. Molecular structure of 7 (thermal ellipsoids are shown at 30%; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Ga(1)–N(1) 1.912(3), Ga(1)–N(2) 1.909(2), Ga(1)–S(1) 2.2639(7), Ga(1)–S(2) 2.2561(7), S(1)–C(30) 1.787(2), S(2)–C(30) 1.772(2); N(1)–Ga(1)–N(2) 99.28(8), S(1)–Ga(1)–S(2) 81.78(3), S(1)–C(30)–S(2) 112.5(1), Ga(1)–S(1)–C(30) 82.54(8), Ga(1)–S(2)–C(30) 83.09(8).

and to the reaction of Kira's dialkylsilylene, 2,2,5,5-tetrakis-(trimethylsilyl)-silacyclopentane-1,1-diyl, with isothiocyanate.<sup>27</sup> These authors suggested initial [2 + 1] cycloaddition of the C=S bond to the silicon center to form a highly strained three-membered ring. Subsequent extrusion of isocyanide generates an intermediate silanthione, which then undergoes cycloaddition reaction with isothiocyanate. In the course of our of studies, the groups of Fedushkin and Yang reported on the first instance of the cleavage of the C=S bond of isothiocyanates on a subvalent digallane supported by a noninnocent diimine ligand.<sup>28</sup> It is also noteworthy that the Ga(II) dimer  $[(Me_{3}Si)_{2}HC)_{2}Ga-]_{2}$  (10) does not react with isothiocyanates, whereas its aluminum analogue cleaves the C=S bond quite readily.<sup>29</sup> Uhl et al. however showed that the digallane 10 reacts with phosphorus chalcogenides  $R_3P = X$  (X = S, Se, Te) to give the chalcogen-bridged species  $[(Me_3Si)_2HC)_2Ga]_2(\mu - X).^{30}$ 

The formation of dimeric species 8, having the sulfide and cyanide bridges (Figure 3), in the reaction mixture of 4 and SCNPh serves as indirect evidence that the reaction proceeds via the oxidative addition of the S=C bond of isothiocyanate. Compound 8 then can be considered as the result of a reaction between the immediate product of C=S oxidative addition, the sulfide NacNacGa(=S)(CNPh), and the starting



Ph

Figure 3. Molecular structure of 8 (thermal ellipsoids for the core elements are shown at 30%; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Ga1–N2 1.9988(18), Ga1–N3 1.9890(19), Ga2–N4 2.0225(18), Ga2–N5 2.0099(19), Ga1–C1 2.045(2), Ga2–C1 2.086(2), Ga1–S1 2.2844(6), Ga2–S1 2.2648(6), N1–C1 1.276(3), N3–Ga1–N2 93.86(7), N5–Ga2–N4 92.95(8), C1–Ga1–S1 90.73(6), C1–Ga2–S1 90.24(6), Ga2–S1–Ga1 84.04(2), Ga1–C1–Ga2 94.98(9).

NacNacGa. Red crystals of **8**, grown from ether, were manually isolated from the yellow crystals of 7.

The molecular structure of 8 is shown in Figure 3. The structure is to a great degree symmetric except that the C(1) =N(1) imine moiety has the bent geometry, so that the Nbound phenyl group is oriented to Ga(2). Apart from this, the metrics associated with the bridging atoms as well as the coordination of NacNac ligands are very similar for both parts of the dimer. Thus, the Ga-N distances fall in the narrow range 1.989-2.023(2), albeit the bonds to Ga(2) appear to be slightly longer, likely in order to accommodate the phenyl group located in the pocket comprised by two bulky Ar groups attached to N(4) and N(5). The gallium-sulfide bonds are very similar at 2.2844(6) and 2.2648(6) Å for Ga(1) and Ga(2), respectively; as are the gallium-cyanide distances to the bridging carbon atom, 2.045(2) and 2.086(2) Å, respectively. The somewhat longer distance from C(1) to Ga(2) again may reflect the need to accommodate the phenyl substituent of the bridging isocyanide. The central Ga<sub>2</sub>SC cycle is almost planar, with the dihedral of  $0.29(6)^{\circ}$ . The Ga(1)-C(1)-Ga(2) bond angle of 94.98(9) is quite acute for a expected sp<sup>2</sup>-hybridized carbon, whereas the C(1)-N(1)-C(2) angle is normal  $(122.2(2)^{\circ})$  for an imine, as is the N(1)-C(1) bond length of 1.276(3) Å. On the other had, the similarly acute bond angle at the sulfur atom, Ga(2)-S(1)-Ga(1) of 84.04(2)°, is normal for a heavy main group element and indicative of a high degree of 3p character in the bonds to gallium atoms. The Ga Ga separation of 3.0452(4) Å is similar to other known gallium sulfide dimers<sup>25,28</sup> and is significantly larger than the doubled covalent radius of Ga  $(2 \times$ 

1.22 Å = 2.44 Å),<sup>31</sup> suggesting that there is no interaction between two gallium centers.

Encouraged by this result, we then studied the possibility of C=O cleavage in isocyanates.  $(3,5-Me_2C_6H_3)NCO$  and PhNCO readily react with 4 giving the coupling products shown in Scheme 5. The preservation of the C=O bond





agrees well with its strength (799 kJ/mol) and the lack of C= O oxidative addition in the related aluminum chemistry (Scheme 1). The xylyl derivative, complex 11, was fully characterized by multinuclear NMR spectroscopy and X-ray analysis. The <sup>1</sup>H NMR spectrum displays a  $C_s$  symmetric pattern, with two sets of methine signals at 3.44 and 3.22 ppm and four sets of methyl signals for the <sup>i</sup>Pr groups (1.50, 1.36, 1.15, and 1.04 ppm). The molecular structure is shown in Figure 4, which reveals a bicyclic spiro structure with the



Figure 4. Molecular structure of 11 (thermal ellipsoids for the core elements are shown at 30%; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Ga(1)-N(1) 1.909(2), Ga(1)-N(2) 1.899(2), Ga(1)-O(1) 1.886(2), Ga(1)-C(4) 1.997(3); N(1)-Ga(1)-N(2) 99.8(1), O(1)-Ga(1)-C(4) 87.4(1), Ga(1)-O(1)-C(16) 112.8(2), Ga(1)-C(4)-N(3) 104.7(2), O(1)-C(16)-N(3) 115.9(3), C(4)-N(3)-C(16) 119.1(2).

Scheme 6. Possible Mechanism of Addition of Isocyanate to 4

gallium atom in the bridgehead position. The newly formed OGaCNC ring is almost planar, with the dihedral angle C(4)–Ga(1)-O(1)-C(16) being  $0.5(2)^\circ$ . The Ga–O distance of 1.886(2) and Ga–C distance of 1.997(3) are very close to the respective values in the enolate **5**. The OGaC bond angle at 87.4(1)° is considerably smaller than other bond angles within the OGaCNC cycle.

The regioselectivity of cyclization is such that the C==N bond of one isocyanate adds to the C==O bond of another isocyanate to form a new C-N bond and a cyclic alkoxy alkyl gallium fragment. While we have no mechanistic data of this reaction, the reaction may start by coordination of the C==O end of isocyanate to the ambiphilic gallium center,<sup>32</sup> acting as a Lewis acid (Scheme 6). Such a coordination enhances the nucleophilicity of the gallium-centered lone pair and polarizes the carbonyl fragment of isocyanate. The regioselectivity of subsequent [3 + 2] addition of the second molecule of the substrate is dictated by this polarity and not by the strengths of Ga-X bonds (i.e., Ga-O + Ga-N vs Ga-O + Ga-C), so that the more nucleophilic nitrogen atom adds to the first carbonyl center activated by gallium, whereas the gallium atom adds to the second carbonyl.

Given the ability of the aluminum compound 1 to cleave the C=N in guanidines but the lack of the corresponding reactivity for the gallium compound 4, we reckoned that the more accessible linear carbodiimides RN=C=NR could be better candidates for oxidative addition of C=N. There has been no reaction between 4 and bulky <sup>i</sup>PrN=C=NPr<sup>i</sup> or (*o*-Tol)N=C=N(*o*-Tol), but (*p*-Tol)N=C=N(*p*-Tol) reacted at room temperature in the course of 5 h to give the coupling product 13, similar to compound 11 (Scheme 7). The product

Scheme 7. Addition of Carbodiimide (*p*-Tol)N=C=N(*p*-Tol) to 4



was characterized by NMR and by X-ray diffraction analysis (Figure 5). As expected, the Ga(1)-N(3) bond of 1.893(2) Å is slightly longer than the Ga(1)-O(1) distance in 11. The Ga(1)-C(52) bond is also slightly longer (2.004(2) Å), likely because of the need to accommodate more sterically encumbered iminyl-guanidide ligand.





Figure 5. Molecular structure of 13 (thermal ellipsoids are shown at 30%; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Ga(1)–N(1) 1.930(2), Ga(1)–N(2) 1.936(2), Ga(1)–N(3) 1.893(2), Ga(1)–C(52) 2.004(2); N(1)–Ga(1)–N(2) 96.72(7), N(3)–Ga(1)–C(52) 86.81(8), Ga(1)–N(3)–C(37) 114.2(1), Ga(1)–C(52)–N(5) 105.9(1), N(3)–C(37)–N(5) 113.0(2), C(37)–N(5)–C(52) 120.1(2).

# CONCLUSION

In comparison to its aluminum analogue 1, the Ga(I) compound 4 shows much reduced reactivity, which reflects the greater stabilization of the oxidation state +1 for gallium relative to aluminum. It does not react with olefins, urea, thiourea and phosphine oxides, and reacts only sluggishly with Ph<sub>3</sub>P=S with the P–S bond cleavage. On the other hand, it easily reacts with a conjugated unsaturated aldehyde to afford the product of [4 + 1] cycloaddition. 4 also easily affects oxidative addition of the C=S bond of phenyl isothiocyanate to give the cycloaddition product [NacNacGa( $\kappa^2$ -S<sub>2</sub>CNPh)] (7) or the sulfur/isocyanide-bridged dimer 8. Related reactions with isocyanates and carbodiimides result in [1 + 2+3] cycloaddition products.

#### EXPERIMENTAL SECTION

**General Information.** All manipulations were performed using standard inert atmosphere ( $N_2$  gas) glovebox and Schlenk techniques. Toluene, hexanes, and diethyl ether were dried using a Grubbs-type solvent purification system.  $d_6$ -Benzene was predried and distilled from K/Na alloy and stored in a glass vessel in the glovebox. NMR spectra were obtained with a Bruker AVANCE III HD 400 and 600 MHz spectrometer (<sup>1</sup>H, 400 and 600 MHz; <sup>13</sup>C, 101 and 151 MHz; <sup>31</sup>P, 162 MHz) at room temperature, unless stated otherwise, then processed and analyzed with MestReNova software (v10.0.2–15465). Elemental analyses were obtained by the analytical laboratories of Universite de Montreal and University of Toronto. Reagents were purchased from Sigma-Aldrich. Compound **4** was prepared according to a literature procedure.<sup>33</sup>

Preparation of NacNacGa(OCH=CHMeCH<sub>2</sub>) (5). To a solution of NacNacGa (0.099 g, 0.20 mmol) in Et<sub>2</sub>O was added methacrolein (0.017 mL, 0.20 mmol). The reaction mixture was stirred for 10 min at room temperature. Volatiles were removed. The resulting yellow solid was washed with hexanes to give NacNacGa(-OCH= C(CH<sub>3</sub>) $-CH_2-$ ) (0.084 g, 0.15 mmol, 74%). The product was dissolved in minimum amount of Et<sub>2</sub>O and recrystallized at -30 °C to give white crystals. <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.10–7.01 (m, 6H, C<sub>6</sub>H<sub>3</sub>), 6.88 (s, 1H, OCHC(CH<sub>3</sub>)CH<sub>2</sub>), 4.86 (s, 1H, CH), 3.69 (hept, 2H, CH(CH<sub>3</sub>)<sub>2</sub>) <sup>3</sup>J<sub>H-H</sub> = 6.7 Hz), 3.18 (hept, 2H, CH(CH<sub>3</sub>)<sub>2</sub>)

<sup>3</sup>*J*<sub>H-H</sub> = 6.8 Hz), 1.56 (s, 6H, NCCH<sub>3</sub>), 1.45 (s, 3H, OCHC(*CH*<sub>3</sub>)-CH<sub>2</sub>), 1.43 (d, 6H, CH(*CH*<sub>3</sub>)<sub>2</sub>, <sup>3</sup>*J*<sub>H-H</sub> = 6.7 Hz), 1.29 (d, 6H, CH(*CH*<sub>3</sub>)<sub>2</sub>, <sup>3</sup>*J*<sub>H-H</sub> = 6.8 Hz), 1.16 (d, 6H, CH(*CH*<sub>3</sub>)<sub>2</sub>, <sup>3</sup>*J*<sub>H-H</sub> = 6.7 Hz), 1.11 (d, 6H, CH(*CH*<sub>3</sub>)<sub>2</sub>, <sup>3</sup>*J*<sub>H-H</sub> = 6.8 Hz), 0.66 (s, 2H, OCHC(CH<sub>3</sub>)CH<sub>2</sub>). <sup>13</sup>C{1H} NMR (151 MHz, C<sub>6</sub>D<sub>6</sub>): δ 169.6 (NCCH<sub>3</sub>), 148.4 (OCHC(CH<sub>3</sub>)CH<sub>2</sub>), 145.7, 142.6, 140.38, 127.8, 125.3, 123.7 (C<sub>6</sub>H<sub>3</sub>), 105.5 (OCHC(CH<sub>3</sub>)CH<sub>2</sub>), 96.3 (CH), 29.0, 28.1 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.8, 24.6, 24.6, 24.2 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.4 (NCCH<sub>3</sub>), 19.4 (OCHC(CH<sub>3</sub>)CH<sub>2</sub>), 7.1 (OCHC(CH<sub>3</sub>)2), 23.4 (NCCH<sub>3</sub>), 19.4 (OCHC(CH<sub>3</sub>)CH<sub>2</sub>), 7.1 (OCHC(CH<sub>3</sub>)CH<sub>2</sub>). Anal. Calcd for C<sub>33</sub>H<sub>47</sub>GaN<sub>2</sub>O: C, 71.10; H, 8.50; N, 5.03. Found: C, 70.87; H, 8.51; N, 4.93.

Preparation of NacNacGa( $S_2CNPh$ ) (7). To a solution of phenyl isothiocyanate (0.046 mL, 0.38 mmol) in toluene was slowly added a toluene solution of NacNacGa(0.093 g, 0.19 mmol). The reaction was stirred for 10 min at room temperature. Volatiles were removed under vacuo. A pale orange solid produced was washed with cold hexanes to yield 7 (0.114 g, 0.16 mmol, 84%) as light-yellow powder. The product was recrystallized from a 1:2 mixture of toluene and hexanes at -30 °C to give light yellow crystals of 7.

<sup>1</sup>H NMR (600 MHz,  $C_6D_6$ ):  $\delta$  7.18–7.14 (m, 2H,  $C_6H_3$ ), 7.13–7.08 (m, 4H,  $C_6H_3$ ), 6.99 (t, 2H,  $C_6H_5$ ,  ${}^{3}J_{H-H}$  = 7.6 Hz), 6.80 (d, 2H,  $C_6H_5$ ,  ${}^{3}J_{H-H}$  = 7.3 Hz), 6.74 (t, 1H,  $C_6H_5$ ,  ${}^{3}J_{H-H}$  = 7.3 Hz), 4.79 (s, 1H, CH), 3.17 (hept, 2H, CH(CH<sub>3</sub>)<sub>2</sub> ${}^{3}J_{H-H}$  = 6.7 Hz), 3.10 (hept, 2H, CH(CH<sub>3</sub>)<sub>2</sub> ${}^{3}J_{H-H}$  = 6.7 Hz), 1.46 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H}$  = 6.7 Hz), 1.36 (d, 6H, CCH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H}$  = 6.7 Hz), 1.07 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H}$  = 6.7 Hz). 1.37(1H) NMR (151 MHz,  $C_6D_6$ ):  $\delta$  171.9 (NCCH<sub>3</sub>), 155.6 (NCS), 144.3, 144.3, 138.7, 128.6, 128.4, 125.0, 125.0 (C<sub>6</sub>H<sub>3</sub>), 152.5, 128.7, 123.3, 121.3 (C<sub>6</sub>H<sub>5</sub>), 97.1 (CH), 29.3, 29.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.3, 25.1, 25.0, 25.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.9 (NCCH<sub>3</sub>). Anal. Calcd for C<sub>36</sub>H<sub>46</sub>GaN<sub>3</sub>S<sub>2</sub>·0.6 toluene: C, 68.01; H, 7.21; N, 6,03. Found: C, 67.94; H, 7.15; N, 5.69.

Preparation of  $(NacNacGa)_2(\mu-S)(\mu-PhNC)$  (8). A toluene solution of phenyl isothiocyanate (0.023 mL, 0.19 mmol) was slowly added to a solution of NacNacGa (0.095 g, 0.19 mmol). The reaction mixture was stirred for 10 min at room temperature. A 1:1 mixture of compound 7 and 8 was observed by NMR. The resulting orange solution was concentrated to the state of a viscous oil, which was then dissolved in diethyl ether. Red crystals of 8 (0.030 g, 0.025 mmol, 26%) were produced by slow concentration of the solution by evaporation of solvent in the glovebox and manually separated from compound 7. <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ ):  $\delta$  7.78 (d, 2H,  $C_6H_{53}J_{H-H}$ = 8.1 Hz), 7.27 (t, 2H,  $C_6H_5$ ,  ${}^3J_{H-H}$  = 8.1 Hz), 7.10 (m, 6H,  $C_6H_3$  and  $C_6H_5$ ), 7.04 (m, 3H,  $C_6H_3$ ), 6.91 (dd, 2H,  $C_6H_3$ , J = 7.8 Hz, J = 1.5Hz), 6.80 (t, 2H,  $C_6H_3$ ,  ${}^{3}J_{H-H}$  = 4.5 Hz), 4.85 (s, 1H, CH), 4.79 (s, 1H, CH), 3.73 (hept, 2H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7$  Hz), 3.68 (hept, 2H,  $CH(CH_3)_2$   ${}^{3}J_{H-H} = 6.8$  Hz), 3.22 (hept, 2H,  $CH(CH_3)_2$   ${}^{3}J_{H-H} =$ 6.7 Hz), 2.30 (hept, 2H,  $CH(CH_3)_2$ ,  ${}^3J_{H-H} = 6.8$  Hz), 1.71 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.8$  Hz), 1.62 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7$  Hz) 1.34 (s, 6H, NCCH<sub>3</sub>), 1.22 (s, 6H, NCCH<sub>3</sub>), 1.15 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.8 \text{ Hz}$ ), 1.11 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7 \text{ Hz}$ ), 1.07 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7 \text{ Hz}$ ), 0.74 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.8 \text{ Hz}$ ), 0.57 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7 \text{ Hz}$ ), 0.74 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7 \text{ Hz}$ ), 0.74 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7 \text{ Hz}$ ), 0.757 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7 \text{ Hz}$ ), 0.767 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7 \text{ Hz}$ ), 0.767 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7 \text{ Hz}$ ), 0.767 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7 \text{ Hz}$ ), 0.767 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7 \text{ Hz}$ ), 0.767 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7 \text{ Hz}$ ), 0.767 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7 \text{ Hz}$ ), 0.767 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7 \text{ Hz}$ ), 0.767 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7 \text{ Hz}$ ), 0.767 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7 \text{ Hz}$ ), 0.767 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7 \text{ Hz}$ ), 0.767 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7 \text{ Hz}$ ), 0.767 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7 \text{ Hz}$ ), 0.767 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7 \text{ Hz}$ ), 0.767 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7 \text{ Hz}$ ), 0.767 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7 \text{ Hz}$ ), 0.767 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7 \text{ Hz}$ ), 0.767 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7 \text{ Hz}$ ), 0.767 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>) (d, 6H, CH(CH<sub>3</sub>)<sub>3</sub>) (d, 6H, CH(C MHz, C<sub>6</sub>D<sub>6</sub>): δ 169.7 (NCCH<sub>3</sub>), 169.0 (NCCH<sub>3</sub>), 151.5 (CN), 146.10, 145.01, 143.84, 143.79, 143.45, 127.38, 127.29, 124.80, 124.70, 124.20, 123.89 (C<sub>6</sub>H<sub>3</sub>), 143.90, 128.99, 126.40, 120.30 (C<sub>6</sub>H<sub>5</sub>), 97.50 (CH), 97.32 (CH), 29.40, 29.16, 27.86, 27.67 (CH(CH<sub>3</sub>)<sub>2</sub>), 27.14, 25.40, 25.30, 24.46, 24.31, 24.26, 23.37 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.92, 24.82 (NCCH<sub>3</sub>). Anal. Calcd for C<sub>65</sub>H<sub>87</sub>Ga<sub>2</sub>N<sub>5</sub>S·toluene: C, 71.94; H, 7.97; N, 5.83. Found: C, 72.72; H, 7.34; N, 5.85.

Preparation of NacNacGa[ $(3,5-CH_3)_2C_6H_3NCO]_2(11)$ . To a solution of NacNacGa(0.094 g, 0.19 mmol) in diethyl ether (5 mL) was added 3,5-dimethylphenyl isocyanate (0.054 mL, 0.39 mmol), and the mixture was left overnight at room temperature. The resulting yellow solution was concentrated to give yellow crystals of NacNacGa[ $(3,5-CH_3)_2C_6H_3NCO]_2$  (0.012 g, 0.015 mmol). The remaining solution was placed in a -30 °C freezer to give a yellow precipitate that was filtered to yield the product (0.115 g, 0.15 mmol, 76%). <sup>1</sup>H NMR

(400 MHz,  $C_6D_6$ ):  $\delta$  7.14 (s, 1H,  $C_6H_3$ ), 7.11 (m, 5H,  $C_6H_3(CH_3)_2$ and  $C_6H_3$ ), 7.06 (dd, 2H,  $C_6H_3$ , J = 6.6, 2.6 Hz), 6.63 (s, 1H,  $C_6H_3(CH_3)_2$ ), 6.62 (s, 2H,  $C_6H_3(CH_3)_2$ ), 6.59 (s, 1H,  $C_6H_3(CH_3)_2$ ), 4.75 (s, 1H, CH), 3.44 (hept, 2H,  $CH(CH_3)_2^{3}J_{H-H} = 6.8$  Hz), 3.22 (hept, 2H,  $CH(CH_3)_2^{3}J_{H-H} = 6.8$  Hz), 2.21 (s, 6H,  $C_6H_3(CH_3)_2$ ), 1.90 (s, 6H,  $C_6H_3(CH_3)_2$ ), 1.50 (d, 6H,  $CH(CH_3)_2$ ,  $^{3}J_{H-H} = 6.7$  Hz), 1.48 (s, 6H, NCCH<sub>3</sub>), 1.36 (d, 6H,  $CH(CH_3)_2$ ,  $^{3}J_{H-H} = 6.8$  Hz), 1.15 (d, 6H,  $CH(CH_3)_2$ ,  $^{3}J_{H-H} = 6.8$  Hz), 1.04 (d, 6H,  $CH(CH_3)_2$ ,  $^{3}J_{H-H} = 6.8$  Hz), 1.15 (d, 6H,  $CH(CH_3)_2$ ,  $^{3}J_{H-H} = 6.8$  Hz), 1.04 (d, 6H,  $CH(CH_3)_2$ ,  $^{3}J_{H-H} = 6.8$  Hz), 1.35 (d, 6H,  $CH(CH_3)_2$ ,  $^{3}J_{H-H} = 6.8$  Hz), 1.04 (d, 6H,  $CH(CH_3)_2$ ,  $^{3}J_{H-H} = 6.8$  Hz), 1.15 (d, 6H,  $CH(CH_3)_2$ ,  $^{3}J_{H-H} = 6.8$  Hz), 1.04 (d, 6H,  $CH(CH_3)_2$ ,  $^{3}J_{H-H} = 6.8$  Hz), 1.35 (d, 6H,  $CH(CH_3)_2$ ),  $^{3}J_{H-H} = 6.8$  Hz), 1.04 (d, 6H,  $CH(CH_3)_2$ ,  $^{3}J_{H-H} = 6.8$  Hz), 1.36 (<sup>1</sup>H) NMR (101 MHz,  $C_6D_6$ ):  $\delta$  171.8 (NCCH<sub>3</sub>), 153.1 (NCO), 148.8 (NCO), 145.0, 143.5, 138.7, 125.1, 124.8 ( $C_6H_3$ ), 138.4, 137.4, 136.8, 128.7, 128.7, 123.7, 123.3 ( $C_6H_3(CH_3)_2$ ), 97.8 (CH), 29.4, 28.5 (CH(CH\_3)\_2), 25.6, 24.7, 24.6, 24.4 (CH(CH<sub>3</sub>)\_2), 23.3 (NCCH<sub>3</sub>), 21.7, 21.1 ( $C_6H_3(CH_3)_2$ ). Anal. Calcd for  $C_{47}H_{59}GaN_4O_2:C$ , 72.21; H, 7.61; N, 7.17; found: C, 72.03; H, 7.54; N, 7.09.

Preparation of NacNacGa[4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NCN(4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)]<sub>2</sub>(13). To a solution of NacNacGa (0.094 g, 0.19 mmol) in Et<sub>2</sub>O (5 mL) was added 1,3-di-p-tolylcarbodiimide (0.054 mL, 0.39 mmol). The reaction mixture was left overnight at room temperature, after which time yellow crystals of NacNacGa[(TolNCNTol]<sub>2</sub> started to form. After collecting crystals (0.015 g, 0.016 mmol) volatiles were removed, and the product was washed with cold hexanes to give 0.126 g (0.13 mmol, 70%) of product. <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ ):  $\delta$  7.71 (d, 2H,  $C_6H_4CH_3$ ,  ${}^3J_{H-H}$  = 8.3 Hz), 7.21 (m, 2H,  $C_6H_3$ ), 6.10 (d, 2H,  $C_6H_4CH_3$ ,  ${}^3J_{H-H} = 8.3$  Hz), 6.99, (m, 2H,  $C_6H_3$ ) 6.96 (d, 2H,  $C_6H_4CH_3$ ,  ${}^3J_{H-H} = 8.2$  Hz), 6.91 (d, 2H,  $C_6H_4CH_3$ ,  ${}^3J_{H-H} = 8.2$  Hz), 6.41 (d, 2H,  $C_6H_4CH_3$ ,  ${}^3J_{H-H}$  = 8.0 Hz), 6.30 (d, 2H,  $C_6H_4CH_3$ ,  ${}^{3}J_{H-H} = 8.0 \text{ Hz}), 6.26 \text{ (d, 2H, } C_{6}H_{4}\text{CH}_{3}, {}^{3}J_{H-H} = 8.1 \text{ Hz}), 5.92 \text{ (d,}$ 2H, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>,  ${}^{3}J_{H-H} = 8.1$  Hz), 4.25 (s, 1H, CH), 3.69 (hept, 2H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7$  Hz), 2.69 (hept, 2H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7$ Hz), 2.17 (s, 3H, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 2.08 (s, 3H, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 1.95 (s, 3H,  $C_6H_4CH_3$ ), 1.89 (s, 3H,  $C_6H_4CH_3$ ), 1.78 (d, 6H,  $CH(CH_3)_2$ ,  ${}^3J_{H-H} =$ 6.7 Hz), 1.36 (s, 6H, NCCH<sub>3</sub>), 1.28 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7$ Hz), 0.91 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7$  Hz), 0.79 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{H-H} = 6.7$  Hz).  ${}^{13}C{}^{1}H{}$  NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ 172.2 (NCCH<sub>3</sub>), 153.8, 150.3 (NCN), 145.6, 143.6, 140.4, 125.2, 124.6 (C<sub>6</sub>H<sub>3</sub>), 147.2, 142.6, 138.7, 134.8, 132.6, 130.5, 129.4, 128.7, 126.8, 121.7, 121.5 (C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 100.9 (CH), 28.9, 28.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.3, 25.6, 24.8, 24.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.9 (NCCH<sub>3</sub>), 21.1, 20.8, 20.7, 20.7 (C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>). Anal. Calcd for C<sub>59</sub>H<sub>69</sub>GaN<sub>6</sub>: C, 76.04; H, 7.46; N, 9.02. Found: C, 76.29; H, 6.09; N, 8.63.

X-ray Crystallography. Crystals of 8, 11, and 13 were grown by slow evaporation of ether solution at room temperature. Crystals of 5 were gown from Et<sub>2</sub>O solution at -30 °C. Crystals of 7 were grown from a 1:2 mixture of toluene and hexanes at -30 °C. The crystals were mounted in a film of perfluoropolyether oil on a glass fiber and transferred to a diffractometer. Prior to data collection crystals were cooled to 173 K for 5, 8, and 13, 200 K for 7, and 100 K for 8. Single crystal X-ray diffraction data for 5, 7, 8, and 13 were collected on a Bruker APEX II single crystal diffractometer equipped with a sealed Mo tube source (wavelength 0.71073 Å) and APEX II CCD detector. Semiempirical absorption correction was applied using redundant data. Raw data collection and processing were performed with APEX II software package from BRUKER AXS.<sup>34</sup> Single crystal X-ray diffraction data for compound 11 were collected using a Bruker D8Venture equipped with a Cu  $(I\mu S)$  microfocus source, Photon II CMOS detector, and an Oxford Cryosystems 800. Cell refinement and data reduction were performed using Apex 3 and Saint,<sup>35</sup> respectively. Semiempirical multiscan absorption correction and merging of data was performed using SADABS.<sup>36</sup> Raw data was processed, using XPREP, and solved by direct methods (SHELXS97).<sup>37</sup> The structures were completed by difference Fourier synthesis and refined with full-matrix least-squares procedures based on F2. Refinement was done using Olex2.<sup>38</sup> All structural models were refined with a full set of anisotropic thermal displacement coefficient for all non-hydrogen atoms. All hydrogen atom positions were calculated based on the geometry of related non-hydrogen atoms and were treated as idealized contributions during the refinement. All scattering factors are contained in several versions of the SHELXTL

program library, with the latest version used being v.6.12.<sup>39</sup> Crystal and structure refinement data are given in Table S1.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b01005.

Additional NMR spectra and crystal and structure refinement data (PDF)

# Accession Codes

CCDC 1908463–1908467 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

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