

Reactivity of “GaI” Toward *N*-Substituted 1,4-Diazabuta-1,3-dienes: Synthesis and Characterization of Gallium Heterocycles Containing Paramagnetic Diazabutadiene Monoanions

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The paramagnetic heterocycles $\text{N(R)C}_2\text{H}_2\text{N(R)GaI}_2$ ($\text{R} = 2,6\text{-dimethylphenyl}$ (**1**), $2,4,6\text{-trimethylphenyl}$ (**2**), and $2,6\text{-diisopropylphenyl}$ (**3**)) were obtained by reaction of “GaI” with Xyl-dab (*N,N*-bis[2,6-dimethylphenyl]-1,4-diazabuta-1,3-diene), Mes-dab (*N,N*-bis[2,4,6-trimethylphenyl]-1,4-diazabuta-1,3-diene), and Dipp-dab (*N,N*-bis[2,6-diisopropylphenyl]-1,4-diazabuta-1,3-diene), respectively. Compounds **1–3** were characterized structurally by X-ray crystallography. ESR investigations of **3** and quantum chemical calculations for the parent system $\text{NHC}_2\text{H}_2\text{NHGaI}_2$ were carried out to provide information on the bonding. The reaction of **1** with 1 equiv of the 1,4-dilithiated Xyl-dab led to the formation of Ga(Xyl-dab)_2 (**4**) with one singly and one doubly reduced ligand; this compound was also characterized by X-ray crystallography.

Introduction

1,4-Diazabuta-1,3-diene (dab) ligands with bulky substituents in 1,4-position have been used as chelating ligands in the chemistry of gallium(III) compounds. The resulting heterocycles can be classified according to the formal oxidation state of the dab ligand (Figure 1). Whereas in compounds of type I the dab system is present as an ene-diamido dianion, it occurs as a monoanion in type II species. In compounds of type III the dab system acts as a neutral ligand. Heterocycles of type I are well known; they can be prepared by the reaction of organogallium dihalides with the dilithiated dab systems^{1–5} or by oxidative addition of neutral diazabutadienes to $\text{Cp}^*\text{Ga(I)}$.⁶ In contrast, type II and III heterocycles are less well known. The only example of a type II heterocycle is $\text{Ga(Bu}^t\text{-dab)}_2$ ($\text{Bu}^t\text{-dab} = N,N\text{-di-tert-butyl-1,4-diazabuta-1,3-diene}$).^{6,7} In this com-

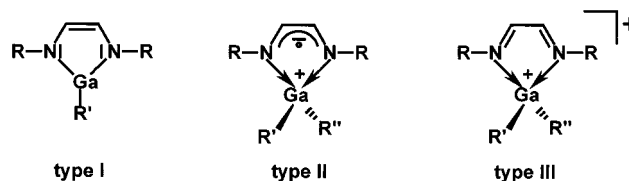


Figure 1. Possible oxidation states of the dab ligand in gallium-dab heterocycles.

pound one dab unit has undergone a two-electron reduction (type I), whereas the other dab unit is singly reduced (type II). Comparable paramagnetic complexes (bpyGaR_2) with the aromatic α -diimine 2,2'-bipyridine were studied by ESR.⁸ The ionic compound $[(\text{Bu}^t\text{-dab})\text{-GaCl}_2][\text{GaCl}_4]$ is the only example of a type III heterocycle.⁹

“Green’s GaI”¹⁰ was employed as a facile starting material for the synthesis of novel gallium compounds during the last years.^{11a–e} We report here the reactions of “Green’s GaI” with differently *N*-substituted 1,4-diazabuta-1,3-dienes in which gallium heterocycles containing paramagnetic diazabutadiene monoanions are formed. ESR studies and quantum chemical calcula-

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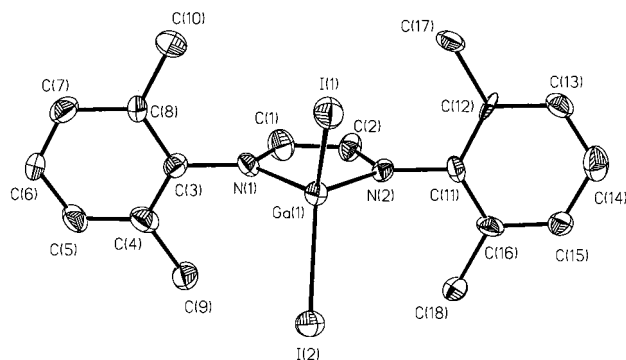
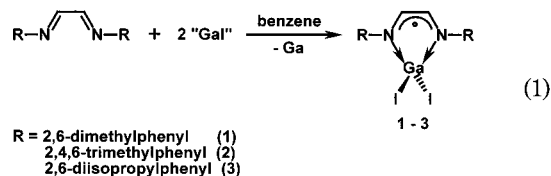


Figure 2. ORTEP plot of **1**, thermal ellipsoids at 50% probability.

tions have served to explain the bonding in the product heterocycles. Furthermore, a derivatization reaction is described which leads to a compound of the type Ga(dab)₂.

Results and Discussion

The reaction of 2 equiv of "Green's GaI" with 1 equiv of Xyl-dab, Mes-dab, or Dipp-dab in benzene at room temperature led to the formation of compounds **1–3** in quantitative yield. The reaction could be followed by the formation of a reddish-brown solution and by the precipitation of gallium metal (eq 1).



Compounds **1–3** were isolated as air-sensitive, brown, crystalline solids, which readily dissolve in aprotic organic solvents such as *n*-hexane, toluene, and tetrahydrofuran (THF).

Single crystals suitable for X-ray crystallography were obtained by recrystallization from a concentrated solution of the respective compound in toluene at room temperature. **1** crystallizes in the space group *P*2₁/*n* (Figure 2). The molecular structure is pseudosymmetric with respect to a mirror plane spanned out by the gallium and the two iodine atoms. Small deviations from the ideal symmetry are caused by the aromatic substituents at the nitrogen atoms; the planes are twisted against each other by approximately 15°. The gallium–iodine distances are 2.5329(16) and 2.5207(15) Å, respectively. The GaN₂C₂ ring is planar within experimental error, and the nitrogen atoms adopt a slightly distorted trigonal planar geometry. The carbon–carbon and the average carbon–nitrogen and gallium–nitrogen distances are 1.421(17), 1.325(16), and 1.954(10) Å, respectively. These values are comparable to those found for the singly reduced dab-unit in Ga(Bu^t-dab)₂ (dab^{•−}: C–C = 1.393(6) Å, C–N = 1.332(5) Å, Ga–N = 1.968(3) Å; dab^{2−}: C=C = 1.344(5) Å, C–N = 1.406(3) Å, and Ga–N = 1.865(2) Å).⁷ For free, nonreduced dab ligands the typical values are C–C ≈ 1.45 Å and C=N ≈ 1.23 Å.¹²

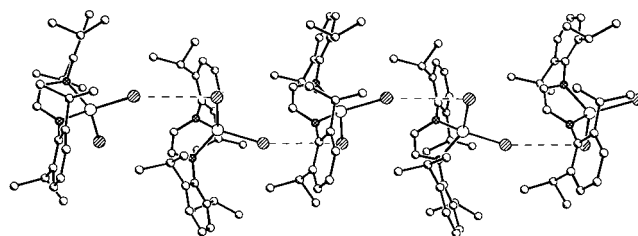


Figure 3. Packing of **3** in the crystal.

The molecular structures of **2** and **3** resemble that of **1**. However, there is a slight tendency from planarity to pyramidal in the geometric environment of the nitrogen atoms from **1** to **3**. This effect is accompanied by a displacement of the gallium atom from the NCCN plane and by a change in gallium–iodine distances, which differ most in **3** (2.4982(2) and 2.5397(2) Å). With respect to the packing of molecules in the crystal, weak iodine–iodine interactions seem possible, the iodine–iodine distance between two adjacent molecules being 4.093 Å (Figure 3). Crystallographic data of compounds **1–3** are given in Table 1, and structural parameters are collected in Table 2.

The observed bond lengths within the heterocycles require the description (dab)^{−1}Ga^{III}I₂ for **1–3**. ESR studies support this assumption. The ESR spectrum of **3** at room temperature in toluene is only partially resolved due to the coupling of the unpaired electron with ¹H, ¹⁴N, ⁶⁹Ga, ⁷¹Ga, and ¹²⁷I nuclei (1320 theoretical lines, excluding the N-substituents).¹³ The smallest observable coupling is found at 0.41 mT, which is a typical value for the coupling of the imine protons in paramagnetic dab complexes.¹⁴ A quartet structure with about 2.7 mT spacing is attributed to the coupling with the ^{69,71}Ga isotopes, both with *I* = 3/2.^{8,13} Assuming a ¹⁴N coupling of about 0.7 mT,¹⁴ and considering the total spectral width of 19.9 mT, we estimate a value of about 0.8 mT for the ¹²⁷I coupling (*I* = 5/2, 100% nat. abundance). A possible hyperconjugative interaction of the gallium–iodine bonds with the π-system of the dab unit would give rise to such a large value.¹⁵ At lower temperatures the ESR spectrum of **3** is less well resolved, revealing only the quartet coupling of about 2.7 mT due to the gallium isotopes (Figure 4). The anisotropy of the *g*-factor is not strongly developed, which is in agreement with a predominantly organic radical. The observed ESR data prove the paramagnetic character of **3** and reveal a considerable influence of the cationic diiodogallium(III) fragment on the dab radical ligand.

Density functional calculations (B3LYP/ECP++g-(d,p))^{16,17} for the parent compound NHC₂H₂NHGaI₂ were performed in order to analyze the bonding in more detail. They yield bonding parameters (Figure 5, left) that are close to the experimentally determined values. The calculations predict C_{2v} symmetry of the structures (distorted tetrahedral shape), in accord with the previous analysis of the main group diazabutadiene com-

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Table 1. Crystallographic Data for 1–3

| | C₁₈H₂₀GaI₂N₂, 1 | C₂₀H₂₄GaI₂N₂, 2 | C₂₆H₃₆GaI₂N₂, 3 |
|---|---|---|---|
| empirical formula | C ₁₈ H ₂₀ GaI ₂ N ₂ , 1 | C ₂₀ H ₂₄ GaI ₂ N ₂ , 2 | C ₂₆ H ₃₆ GaI ₂ N ₂ , 3 |
| fw | 587.88 | 615.93 | 700.09 |
| cryst color, habit | dark red, plate | red, plates | brown, needles |
| cryst size | 0.29 × 0.20 × 0.02 mm ³ | 0.30 × 0.20 × 0.08 mm ³ | 0.30 × 0.30 × 0.15 mm ³ |
| temperature | | 100(2) K | |
| wavelength | | 0.71073 Å | |
| space group | <i>P</i> 2 ₁ / <i>n</i> | <i>P</i> 2 ₁ / <i>c</i> | <i>Pnma</i> |
| unit cell dimensions | <i>a</i> = 8.2030(2) Å <i>b</i> = 14.1840(4) Å <i>c</i> = 16.8650(5) Å <i>β</i> = 94.659(1)° | <i>a</i> = 7.3865(1) Å <i>b</i> = 17.8440(1) Å <i>c</i> = 17.4850(1) Å <i>β</i> = 108.8780(3)° | <i>a</i> = 12.5080(1) Å <i>b</i> = 21.2160(1) Å <i>c</i> = 10.4060(2) Å <i>β</i> = 90° |
| volume | 1955.78(9) Å ³ | 2180.491(17) Å ³ | 2761.44(6) Å ³ |
| <i>Z</i> | 4 | 4 | 4 |
| density (calcd) | 1.997 Mg/m ³ | 1.876 Mg/m ³ | 1.684 Mg/m ³ |
| <i>θ</i> range for data collection | 3 to 25° | 3 to 30° | 3 to 30° |
| no. of reflns collected | 32 769 | 65 899 | 65 299 |
| no. of unique reflns | 3395 (<i>R</i> _{int} = 0.140) | 6351 (<i>R</i> _{int} = 0.111) | 4107 (<i>R</i> _{int} = 0.034) |
| abs corr | | multiscan | |
| final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] | <i>R</i> _F = 0.0666, <i>wR</i> _F ² = 0.1427 | <i>R</i> _F = 0.0250, <i>wR</i> _F ² = 0.0618 | <i>R</i> _F = 0.0150 <i>wR</i> _F ² = 0.0384 |
| no. of reflns [<i>I</i> > 2σ(<i>I</i>)] | 2366 | 5701 | 3906 |
| no. of params | 213 | 233 | 217 |
| largest diff peak and hole | 2.051 (1.07 Å near I(1)) and −1.216 e Å ^{−3} | 1.226 (1.1 Å near I(2)) and −1.025 e Å ^{−3} | 0.780 and −0.556 e Å ^{−3} |
| diffractometer used | | Nonius Kappa CCD | |
| structure refinement | | full-matrix least-squares on <i>F</i> ² (SHELXL-97) | |

Table 2. Selected Bond Lengths (Å) for 1–3

| | C₁₈H₂₀GaI₂N₂, 1 | C₂₀H₂₄GaI₂N₂, 2 | C₂₆H₃₆GaI₂N₂, 3 |
|------|--|--|--|
| C–C | 1.421(17) | 1.408(3) | 1.406(2) |
| C–N | 1.313(15) | 1.337(3) | 1.3386(15) |
| | 1.337(17) | 1.338(3) | |
| Ga–N | 1.952(10) | 1.9384(17) | 1.9449(10) |
| | 1.956(9) | 1.9388(18) | |
| Ga–I | 2.5207(15) | 2.5173(2) | 2.4982(2) |
| | 2.5329(16) | 2.5261(3) | 2.5397(2) |

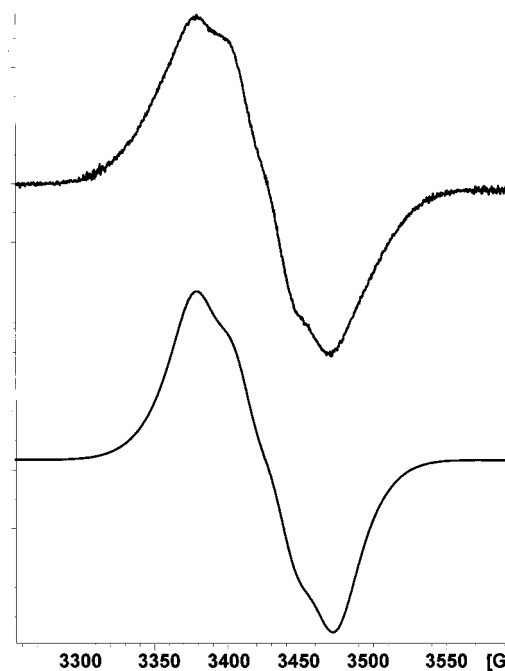
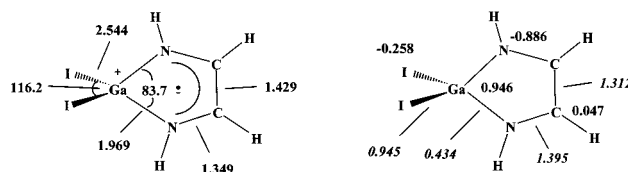
plexes El(dab)₂ with group 13 elements.¹⁸ It is of further interest to inspect the charge distribution within the molecules.¹⁹ The results for the parent compound are as follows (Figure 5, right): the chelated gallium atom carries a positive charge of 0.946, considerably less than computed for Ga(dab)₂ (1.655)¹⁸ with a comparable basis set (and the same density functional). This effect may be attributed to the iodine atoms bonded to the gallium atom, which are less electronegative than the nitrogen atoms. The Wiberg bond indices (values in italics) reveal a fractional bond order between the gallium and the neighboring nitrogen atoms. At the same time the C–N bonds are shortened and between a single and a double bond, while the C–C bond is lengthened toward a single

(16) All calculations were performed with the Gaussian set of programs. All calculations were performed with the Gaussian set of programs. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98* (Revision A.1); Gaussian Inc.: Pittsburgh, PA, 1998.

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**Figure 4.** ESR spectrum of **3** in toluene at 210 K (top) with computer simulation (bottom).**Figure 5.** Equilibrium geometry of NHC₂H₂NHGaI₂ (bond lengths in Å, bond angles in deg [left]; natural atomic charges and Wiberg bond indices [right]).

bond. The Ga–I bonds are single bonds. As a consequence, the unpaired electron resides preferentially in the five-membered ring system. We note that our calculations do not explicitly account for spin–orbit coupling. Hence we cannot give a further analysis of the anisotropy of the *g*-factor in the ESR measurement.

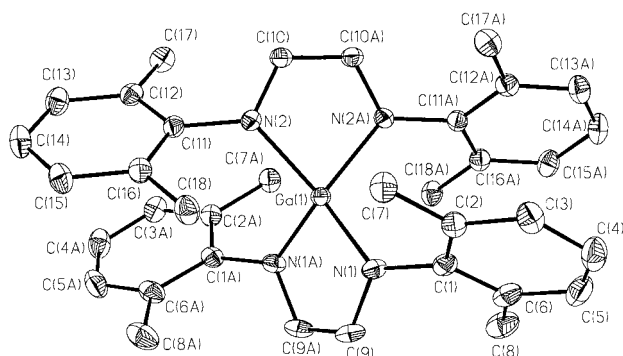
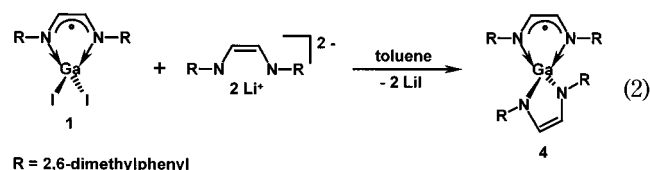


Figure 6. ORTEP plot of **4**, thermal ellipsoids at 50% probability.

The reaction of **1** with 1 equiv of the 1,4-dilithiated Xyl-dab led to the formation of $\text{Ga}(\text{Xyl-dab})_2$ (**4**) (eq 2).



Compound **4** was isolated in high yield as an air-sensitive, dark brown, crystalline solid, which readily dissolves in aprotic organic solvents such as *n*-hexane, toluene, and THF.

Single crystals suitable for X-ray crystallography were obtained by recrystallization from a concentrated solution in toluene at room temperature. **4** crystallizes in the space group *Pbcn* (Figure 6).

The molecule lies on a crystallographic symmetry axis (C_2), which results from the intersecting NCCN planes. As in $\text{Ga}(\text{Bu}^t\text{-dab})_2$,⁷ the bonding in **4** shows all the characteristics of one singly and one doubly reduced dab ligand, the bond lengths being as follows: dab^{2-} : $\text{C}=\text{C} = 1.331(4)$ Å, $\text{C}-\text{N} = 1.413(2)$ Å, $\text{Ga}-\text{N} = 1.8831(13)$ Å; dab^- : $\text{C}-\text{C} = 1.402(3)$ Å, $\text{C}-\text{N} = 1.337(2)$ Å, $\text{Ga}-\text{N} = 1.9678(13)$ Å. Obviously, the orthogonality of the dab ligands precludes any rapid intramolecular electron transfer and delocalization of charge between dab^{2-} and dab^- .

Conclusion

In the reaction of 1,4-diazabutadienes possessing bulky substituents in 1,4-position with "Green's GaI", neither simple complex formation (to type III compounds) nor clean oxidative addition (to type I compounds) is observed. Instead, a more complex reaction sequence takes place, which finally leads to compounds **1–3** of the composition $(\text{dab})^{-1}\text{Ga}^{\text{III}}\text{I}_2$ containing the paramagnetic monoanion of the respective dab species (type II compounds) and to the formation of elemental gallium. ESR measurements and quantum chemical calculations explain the bonding within the novel heterocycles. The diido substituents can be replaced by ene-diamido dianions, as shown by the synthesis of $\text{Ga}(\text{Xyl-dab})_2$ (**4**).

Experimental Section

General Comments. All manipulations were carried out under a purified argon atmosphere using standard vacuum

techniques. The solvents were purified by conventional means and distilled immediately prior to use. Xyl-dab, Mes-dab, and Dipp-dab were prepared according to the literature.²⁰ "GaI" was prepared by a modified procedure according to the literature.¹⁰ Sonication experiments were performed using a Bandelin Sonorex Super 10 P ultrasonic bath (50% power). Elemental analyses were performed by the Microanalytical Laboratory of the Universität Bielefeld. IR data were collected using a Bruker Vektor 22-FT spectrometer. The samples were measured as KBr pellets. The melting point determinations were performed using a Büchi 510 melting point apparatus. The ESR spectrum was recorded on a Bruker ESP 300 system.

Preparation of 1. A mixture of gallium particles (697 mg, 10 mmol) and iodine (1269 mg, 10 mmol) in 50 mL of benzene was sonicated for 12 h at 50 °C. To the resulting suspension of pale green "GaI" in benzene was added 5 mmol of Xyl-dab (1322 mg). Instantaneously a brown solution was formed and gallium metal precipitated. The reaction mixture was stirred for another 2 h. After filtration, all volatile components were removed in vacuo to yield 2675 mg of **1** (4.6 mmol, 91% based on Xyl-dab) as a brown crystalline solid. Single crystals suitable for X-ray crystallography were obtained by recrystallization from toluene at room temperature. Mp: 170–180 °C (dec). IR (cm^{-1} , KBr): 2962(s), 2918(m), 1450(s), 1378(w), 1326(m), 1261(m), 1231(s), 1096(m), 1030(m), 881(w), 801(w), 772(m). Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{GaI}_2\text{N}_2$ ($M = 587.88$ g mol^{-1}): C, 36.78; H, 3.43; N, 4.77. Found: C, 36.70; H, 3.48; N, 4.60.

Preparation of 2. The same procedure was used in the reaction of "GaI" (10 mmol) with Mes-dab (1462 mg, 5 mmol) in benzene (50 mL). Compound **2**, 2864 mg (4.7 mmol, 93% based on Mes-dab), was obtained as a brown crystalline solid. Single crystals suitable for X-ray crystallography were obtained by recrystallization from toluene at room temperature. Mp: 170–180 °C (dec). IR (cm^{-1} , KBr): 2961(s), 2920(m), 1452(s), 1380(w), 1324(m), 1263(m), 1227(m), 1091(m), 1026(m), 881(w), 800(w), 776(m). Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{GaI}_2\text{N}_2$ ($M = 615.93$ g mol^{-1}): C, 39.00; H, 3.93; N, 4.55. Found: C, 38.76; H, 3.91; N, 4.43.

Preparation of 3. The same procedure was used in the reaction of "GaI" (10 mmol) with Dipp-dab (1883 mg, 5 mmol) in benzene (50 mL). Compound **3**, 3290 mg (4.7 mmol, 94% based on Dipp-dab), was obtained as a brown crystalline solid. Single crystals suitable for X-ray crystallography were obtained by recrystallization from toluene at room temperature. Mp: 170–180 °C (dec). IR (cm^{-1} , KBr): 2963(s), 2922(m), 2863(w), 1451(s), 1382(w), 1360(w), 1322(m), 1264(m), 1251(m), 1224(m), 797(m), 786(m), 753(m). Anal. Calcd for $\text{C}_{26}\text{H}_{36}\text{GaI}_2\text{N}_2$ ($M = 700.09$ g mol^{-1}): C, 44.61; H, 5.18; N, 4.00. Found: C, 44.30; H, 5.11; N, 3.94.

Preparation of 4. A suspension of 1,4-dilithio-1,4-bis[2,6-dimethylphenyl]-1,4-diazabuta-1,3-diene in toluene (40 mL), prepared from the diazabutadiene (1322 mg, 5 mmol) and lithium metal (69 mg, 10 mmol), was added to a solution of **1** (2939 mg, 5 mmol) in toluene (40 mL). After filtration, all volatile components were removed in vacuo to yield 2693 mg of **4** (4.5 mmol, 90% based on Xyl-dab) as a brown crystalline solid. Single crystals suitable for X-ray crystallography were obtained by recrystallization from toluene at room temperature. Mp: 190 °C. IR (cm^{-1} , KBr): 2964(s), 1630(w), 1550(w), 1478(m), 1344(m), 1262(m), 1226(s), 1101(s), 781(w). Anal. Calcd for $\text{C}_{36}\text{H}_{40}\text{GaI}_2\text{N}_4$ ($M = 598.44$ g mol^{-1}): C, 72.25; H, 6.74; N, 9.36. Found: C, 72.18; H, 6.45; N, 9.33.

Supporting Information Available: Tables of crystal structure data, positional and thermal parameters, and bond lengths and angles of **1–4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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