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[Cp<sup>Ar</sup>Ni{Ga(nacnac)}]: An Open-Shell Nickel(I) Complex Supported by a Gallium(I) Carbenoid (Cp<sup>Ar</sup> = C<sub>5</sub>(C<sub>6</sub>H<sub>4</sub>-4-Et)<sub>5</sub>, nacnac = HC[C(Me)N-(C<sub>6</sub>H<sub>3</sub>)-2,6-iPr<sub>2</sub>]<sub>2</sub>)

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### DOI

[10.1021/acs.inorgchem.5b02979](https://doi.org/10.1021/acs.inorgchem.5b02979)

### Publication date

2016

### Document Version

Final published version

### Published in

Inorganic Chemistry

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[Link to publication](#)

### Citation for published version (APA):

Chakraborty, U., Mühlendorf, B., van Velzen, N. J. C., de Bruin, B., Harder, S., & Wolf, R. (2016). [Cp<sup>Ar</sup>Ni{Ga(nacnac)}]: An Open-Shell Nickel(I) Complex Supported by a Gallium(I) Carbenoid (Cp<sup>Ar</sup> = C<sub>5</sub>(C<sub>6</sub>H<sub>4</sub>-4-Et)<sub>5</sub>, nacnac = HC[C(Me)N-(C<sub>6</sub>H<sub>3</sub>)-2,6-iPr<sub>2</sub>]<sub>2</sub>). *Inorganic Chemistry*, 55(6), 3075-3078. <https://doi.org/10.1021/acs.inorgchem.5b02979>

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# [Cp<sup>Ar</sup>Ni{Ga(nacnac)}]: An Open-Shell Nickel(I) Complex Supported by a Gallium(I) Carbenoid (Cp<sup>Ar</sup> = C<sub>5</sub>(C<sub>6</sub>H<sub>4</sub>-4-Et)<sub>5</sub>, nacnac = HC[C(Me)N(C<sub>6</sub>H<sub>3</sub>-2,6-*i*Pr<sub>2</sub>)<sub>2</sub>])

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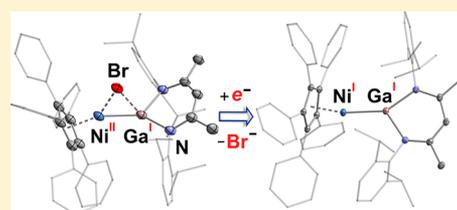
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## S Supporting Information

**ABSTRACT:** The 17 valence electron (VE) open-shell nickel gallanediyl complex [Cp<sup>Ar</sup>Ni{Ga(nacnac)}] (3, Ar = C<sub>5</sub>(C<sub>6</sub>H<sub>4</sub>-4-Et)<sub>5</sub>, nacnac = HC[C(Me)N(C<sub>6</sub>H<sub>3</sub>-2,6-*i*Pr<sub>2</sub>)<sub>2</sub>]), having an unsupported Ni–Ga bond, was synthesized from [Cp<sup>Ar</sup>Ni(μ-Br)]<sub>2</sub> (1) by reducing the adduct [Cp<sup>Ar</sup>Ni(μ-Br){Ga(nacnac)}] (2) or, alternatively, trapping the “Cp<sup>Ar</sup>Ni<sup>I</sup>” synthon with Ga(nacnac); spectroscopic and DFT studies showed that the single unpaired electron in 3 resides mainly at the Ni center.



Low-valent organyl gallium species of the general type Ga-R (R = C<sub>3</sub>Me<sub>5</sub> {= Cp\*}, C(SiMe<sub>3</sub>)<sub>3</sub>, terphenyl, nacnac, and related ligands) have been widely used as supporting ligands for metal-to-metal bonded complexes and clusters.<sup>1–11</sup> Among these, Ga(nacnac), having a bulky nacnac ligand on gallium, has drawn special attention due to its ability to stabilize coordinately unsaturated metal complexes, such as [L<sub>2</sub>NiGa(nacnac)] (L = C<sub>2</sub>H<sub>4</sub>, styrene; L<sub>2</sub> = 1,1,3,3-tetramethyl 1,3-divinylsiloxane (dvds); Figure 1).<sup>2,3</sup> Several other 18 VE electron Ni–Ga(nacnac) complexes such as [L<sub>2</sub>NiGa(nacnac)] (L = CO; L<sub>3</sub> = 1,5,9-cyclododecatriene (CDT); Figure 1) were obtained by ligand substitution reactions.<sup>2,4,5</sup> Interestingly, Ga(nacnac) can also insert into metal halide bonds, leading to M–Ga bonded complexes, although only a few examples are

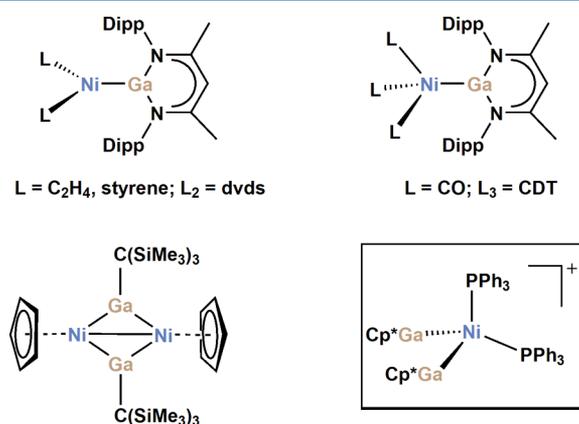


Figure 1. Examples of previously characterized Ni–Ga complexes.

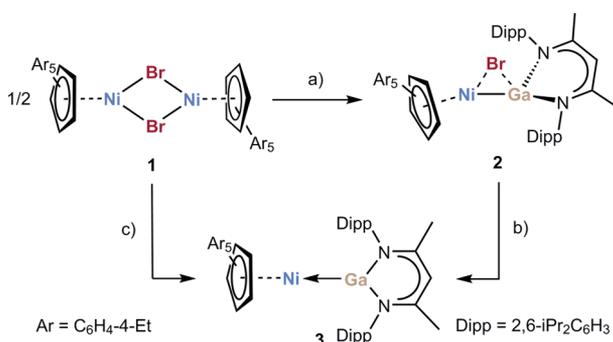
known involving transition metals.<sup>6–9</sup> The reaction with [AuCl(PPh<sub>3</sub>)] gives the linear complexes [Au{GaCl(nacnac)}(PPh<sub>3</sub>)] and [Au{Ga(nacnac)}{GaCl(nacnac)}].<sup>9</sup> A unique observation is the reaction of [RhCl(PPh<sub>3</sub>)<sub>3</sub>] with Ga(nacnac), which gave the “frozen-insertion intermediate” [Rh(μ-Cl)Ga(nacnac)(PPh<sub>3</sub>)<sub>2</sub>].<sup>7</sup>

Interestingly, all complexes derived from the coordination of gallanediyl fragments to transition metals exclusively appear to be closed-shell compounds, except for the very recently published trimetallic complex [Ni(GaCp\*)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>][BAr<sup>F</sup>], which is an open-shell complex with a single nickel(I) atom supported by two pentamethylcyclopentadienylgallanediyl ligands (Figure 1).<sup>10</sup> For the bimetallic Ni–Ga open-shell complexes, the Ni<sub>2</sub>Ga<sub>2</sub> complex [CpNi(μ-GaC(SiMe<sub>3</sub>)<sub>3</sub>)<sub>2</sub>] is an especially interesting example, because it can be viewed as the dimer of the hypothetical open-shell monomer [CpNi{GaC(SiMe<sub>3</sub>)<sub>3</sub>}] (Figure 1).<sup>11</sup> Our interest in the chemistry of mononuclear nickel(I) radicals of type [CpNi(NHC)] supported by N-heterocyclic carbenes (NHCs)<sup>12,13</sup> prompted us to investigate whether analogous nickel(I) complexes containing gallanediyl ligands might also be accessible. Here, we report the synthesis of the new 17 VE complex [Cp<sup>Ar</sup>Ni{Ga(nacnac)}] (3), which can be obtained via two routes: (a) reduction of adduct [Cp<sup>Ar</sup>Ni(μ-Br){Ga(nacnac)}] (2) and (b) reduction of 1 with KC<sub>8</sub> and subsequent addition of Ga(nacnac) (see Scheme 1).

The reaction of the half-sandwich complex [Cp<sup>Ar</sup>Ni(μ-Br)]<sub>2</sub> (1) with Ga(nacnac) in THF affords [Cp<sup>Ar</sup>Ni(μ-Br){Ga-

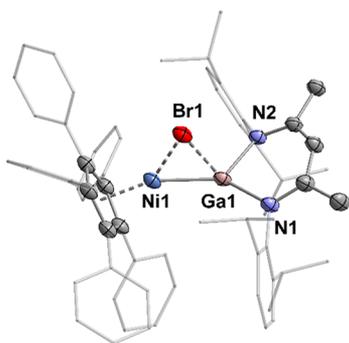
Received: December 27, 2015

Published: March 7, 2016

Scheme 1. Synthesis of Complexes 2 and 3<sup>a</sup>

<sup>a</sup>Reagents and conditions: (a) + Ga(nacnac), THF; (b) + KC<sub>8</sub>/– KBr, benzene; (c) + KC<sub>8</sub>/– KBr, benzene, then + Ga(nacnac).

(nacnac)}] (2) in 82% yield (Scheme 1a and Supporting Information (SI)). The complex was obtained as a red-brown, thermally robust solid; it dissolves well in polar and apolar solvents such as THF, benzene and *n*-hexane. A single-crystal X-ray diffraction study on crystals obtained from *n*-hexane revealed that the asymmetric unit contains three crystallographically independent molecules having very similar structural parameters (see SI). The molecular structure of 2 displays an unusual bonding situation. The nickel atom is surrounded by an η<sup>5</sup>-coordinated Cp<sup>Ar</sup> ligand and a σ-coordinated Ga(nacnac) ligand, while the bromide bridges the Ni–Ga bond (Figure 2).



**Figure 2.** Solid-state molecular structure of 2 (see Table S1 for relevant bond lengths and angles). Thermal ellipsoids are drawn at the 35% probability level. The H atoms and ethyl groups of Cp<sup>Ar</sup> are omitted for clarity. Selected average bond distances (Å) and angles (deg): Ni1–Ga1 2.2688(8), Ni1–Cp<sup>Ar</sup>(centroid) 1.775(5), Ni1–Br1 2.3577(7), Ga1–Br1 2.6861(9); Cp<sup>Ar</sup>(centroid)–Ni1–Ga1 151.40(1), Ni1–Br1–Ga1 52.98(3), N1–Ga1–N2 94.3(3).

The triangular arrangement of the Ni, Ga, and Br atoms in 3 is comparable to that of the only known halide-bridged transition metal–gallium bond in [Rh(μ-Cl){Ga(nacnac)}(PPh<sub>3</sub>)<sub>2</sub>].<sup>7</sup> The Cp<sup>Ar</sup>(centroid)–Ni–Ga linkage in 2 is bent, having an average bond angle of 151.40(1)°. The Ni–Ga bond length (av. 2.2688(8) Å) is slightly shorter than that in [Ni(CO)<sub>3</sub>{Ga(nacnac)}] (2.289(6) Å),<sup>4</sup> and considerably shorter than that in [Ni(CDT){Ga(nacnac)}] (2.3482(6) Å).<sup>2</sup> The Ni–Br bond length (av. 2.3577(7) Å) is similar to that observed for cyclopentadienyl complexes of the type [CpNiBr(L)] (L = phosphine or NHC).<sup>14</sup> The Ga–Br bond (av. 2.6861(9) Å) is significantly longer than those in the Ga(III) complexes [(nacnac)GaBr<sub>2</sub>] (2.286(1) and 2.330(1) Å) and in [{(Me<sub>3</sub>Si)<sub>3</sub>C}GaBr(μ-Br)]<sub>2</sub>,<sup>15</sup> however the sterically encumbered Ga(III) complex [Cp\*<sub>2</sub>Ga(μ-Br)]<sub>2</sub> features a similar Ga–

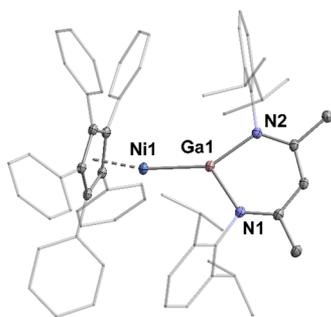
Br distance (2.573(4) – 2.624(4) Å).<sup>16</sup> The average Ni–Br–Ga bond angle amounts to 52.98(3)°, which is slightly smaller than the Rh–Cl–Ga angle (57.83(3)°) observed in [Rh(μ-Cl){Ga(nacnac)}(PPh<sub>3</sub>)<sub>2</sub>].<sup>7</sup> These structural parameters indicate a strong interaction between the Ni and Br atoms, whereas the interaction between Ga and Br is also significant, but much weaker. Thus, complex 2 can be viewed as an arrested intermediate of an insertion reaction of Ga(nacnac) into the Ni–Br bond, where the bromide acts as three valence electron (VE) donor and bridges the electrophilic Ni and Ga centers to attain the 18VE nickel center.

DFT calculations at the B3LYP<sup>17</sup>/def2-TZVP<sup>18</sup> level reproduce the crystallographically determined structure of 2 (Table S2, SI). An inspection of the frontier Kohn–Sham molecular orbitals shows that the LUMO is mainly a combination of the Ni–Br σ\* orbital and an empty p-orbital at the Ga center. The HOMO is nonbonding with respect to Ga(nacnac), featuring an antibonding combination of a Cp<sup>Ar</sup> π\*-orbital and a p-orbital of the bromine atom (Figure S7, SI).

The <sup>1</sup>H NMR spectrum of the diamagnetic complex 2 in C<sub>6</sub>D<sub>6</sub> shows a set of four doublets and two septets for the characteristic diastereotopic methyl and methine groups of the Dipp unit (Dipp = 2,6-iPr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>). The Cp<sup>Ar</sup> ligand gives rise to single set of resonances with a triplet at 1.05 ppm (overlapped with signals of Dipp unit) and a quartet at 2.37 ppm arising from the ethyl groups, whereas the aromatic protons appear as two doublets at 6.69 and 6.98 ppm. This suggests fast rotation of the Cp<sup>Ar</sup> unit in solution at room temperature on the NMR time scale. In agreement with that, the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum shows a characteristic ring carbon signal for Cp<sup>Ar</sup> at 107.2 ppm, whereas the Ga(nacnac) moiety gives rise to the typical set of signals expected for a Ga(nacnac) transition metal complex.<sup>7</sup> The UV/vis spectrum of 2 in cyclohexane features strong charge-transfer type absorptions at λ = 346 and 462 nm with a weak shoulder detected at λ = 590 nm (Figure S3, SI).

Complex 2 is a useful precursor for the preparation of the Ni(I) complex [Cp<sup>Ar</sup>Ni{Ga(nacnac)}] (3). The reduction of 2 with one equivalent of KC<sub>8</sub> affords 3 in 84% yield (Scheme 1b). Complex 3 can also be obtained by reducing the dimeric complex 1 with two equivalents of KC<sub>8</sub> followed by the addition of two equivalents of Ga(nacnac) in 53% yield (Scheme 1c). This reaction presumably leads to an unidentified intermediate, which is a source for the “Cp<sup>Ar</sup>Ni(I)” fragment that is trapped by Ga(nacnac). <sup>1</sup>H NMR monitoring of both reactions showed that 3 is formed as sole product. Complex 3 was isolated as a highly air-sensitive purple-red solid which dissolves well in benzene, diethyl ether and moderately in *n*-hexane.

Single crystal X-ray crystallography (see SI) revealed that the complex adopts a pogo stick structure with an η<sup>5</sup>-coordinated Cp<sup>Ar</sup> ligand (Figure 3). It is worth noting that the reaction of [GaC(SiMe<sub>3</sub>)<sub>3</sub>]<sub>4</sub> with [CpNi(CO)]<sub>2</sub> yielded the dimeric complex [CpNi{μ-GaC(SiMe<sub>3</sub>)<sub>3</sub>}]<sub>2</sub> (Figure 1),<sup>11</sup> whereas 3 is mononuclear due to the steric demand of the Cp<sup>Ar</sup> and nacnac ligands. The Cp<sup>Ar</sup>(centroid)–Ni–Ga linkage is bent with an angle of 164.6(1)°, which is significantly higher than that in complex 2 (*vide supra*). Interestingly, the difference in Ni1–Ga1–N1 (122.12(4)°) and Ni1–Ga1–N2 (145.75(4)°) angles suggest that the Ga(nacnac) lone pair is connected to the Ni center in an askew fashion. By comparison, the Ni–Ga–N angles in [Ni(CO)<sub>3</sub>{Ga(nacnac)}] are approximately the same and close to 133°. These structural features of 3 are quite similar to the analogous N-heterocyclic carbene complex



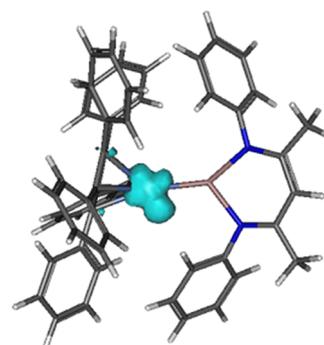
**Figure 3.** Solid-state molecular structure of **3**. Thermal ellipsoids are drawn at the 35% probability level. The H atoms and the ethyl groups of  $\text{Cp}^{\text{Ar}}$  are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni1–Ga1 2.2914(3), Ni1– $\text{Cp}^{\text{Ar}}$ (centroid) 1.7922(7),  $\text{Cp}^{\text{Ar}}$ (centroid)–Ni1–Ga1 164.6(1)°, Ni1–Ga1–N1 122.12(4), Ni1–Ga1–N2 145.75(4), N1–Ga–N2 92.09(6)°.

[ $\text{Cp}^{\text{Ar}}\text{Ni}(\text{IDipp})$ ] (IDipp = 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene).<sup>13</sup> The Ni–Ga bond (2.2915(3) Å) and Ni1– $\text{Cp}^{\text{Ar}}$ (centroid) distance (1.7922(7) Å) in **3** are slightly elongated compared to the starting complex **2** in agreement with the larger ionic radius of a Ni(I) cation relative to a Ni(II) cation.

The  $^1\text{H}$  NMR spectrum of **3** displays broad signals between –3 and 10 ppm in  $\text{C}_6\text{D}_6$ , which is typical for a paramagnetic Ni(I) complex.<sup>13</sup> The solution state magnetic moment of **3** (1.9(1)  $\mu_{\text{B}}$  in  $\text{C}_6\text{D}_6$  at 300 K according to Evans NMR method) is consistent with a doublet ground state. A slightly higher value of 2.3(1)  $\mu_{\text{B}}$  was observed for [ $\text{Cp}^{\text{Ar}}\text{Ni}(\text{IDipp})$ ] in [ $\text{D}_8$ ]THF.<sup>13</sup> In accord with the  $S = 1/2$  multiplicity, the EPR spectrum showed a rhombic  $g$ -tensor with significant deviations from  $g_{\text{e}}$ , pointing to metalloradical character (Figure S6). The X-band EPR spectrum is rather broad, showing a rhombic spectrum without resolved hyperfine interactions (HFIs). However, line shape analysis and spectral simulations suggest the presence of sizable Ga HFIs, in particular for the central  $g_y$  line ( $A_{\text{Ga}_y}^{\text{Ga}} \sim 130$  MHz). The  $g_x$  and  $g_z$  lines are too broad to give an estimate of the Ga HFIs along these directions. The DFT computed  $g$ -tensor of **3** ( $g_x = 2.117$ ,  $g_y = 2.291$ ,  $g_z = 2.403$ ) is in reasonable agreement with the experimental one ( $g_x = 2.01$ ,  $g_y = 2.28$ ,  $g_z = 2.58$ ), and the DFT property calculations confirm the presence of sizable Ga HFIs (in particular along  $g_y$ :  $A_{\text{Ga}_x}^{\text{Ga}} = -64$  MHz,  $A_{\text{Ga}_y}^{\text{Ga}} = -92$  MHz,  $A_{\text{Ga}_z}^{\text{Ga}} = 75$  MHz).

DFT calculations (B3LYP/def2-TZVP level)<sup>17,18</sup> on the truncated model complex [ $(\eta^5\text{-C}_5\text{Ph}_5)\text{Ni}\{\text{Ga}(\text{HC}[\text{C}(\text{Me})\text{N}(\text{C}_6\text{H}_5)_2])\}$ ] reproduced the experimentally observed structure very well (see SI). A Löwdin population analysis<sup>19</sup> indicates that the spin density resides mainly at the nickel atom (see spin density map, Figure 4). This is also reflected by an orbital population analysis of the SOMO, which is located on the  $\text{Cp}^{\text{Ar}}\text{Ni}$  fragment and shows 20% metal character (Figure S8, SI). The spin density has an asymmetric shape with a lobe protruding from the metal center toward one of the phenyl substituents. A very similar situation was found for the NHC complex [ $\text{Cp}^{\text{Ar}}\text{Ni}(\text{IDipp})$ ].<sup>12</sup> The distorted  $\text{Cp}^{\text{Ar}}$ (centroid)–Ni–Ga and Ni–Ga–N angles observed by X-ray crystallography (*vide supra*) might be the result of a Jahn–Teller type distortion. An interaction between the Ni center and aryl rings or C–H $\cdots\pi$  bonding between the aryl groups of  $\text{Cp}^{\text{Ar}}$  and Dipp is not apparent crystallographically or theoretically.

In conclusion, the reaction of the very bulky pentaaryl cyclopentadienyl nickel halide complex [ $\text{Cp}^{\text{Ar}}\text{Ni}(\mu\text{-Br})_2$ ] (**1**) with



**Figure 4.** Spin density map for **3** obtained from a spin-unrestricted DFT calculation (isosurface value is set to 0.005); according to the Löwdin population analysis, 89% of the spin density resides at nickel.<sup>19</sup>

Ga(nacnac) affords the “arrested Ni–Br bond insertion intermediate” [ $\text{Cp}^{\text{Ar}}\text{Ni}(\mu\text{-Br})\{\text{Ga}(\text{nacnac})\}$ ] (**2**), having a triangular arrangement of the Ni, Ga and Br atoms. Compound **2** is rare example having an halide-bridged transition metal–gallium bond, the only other example being [ $\text{Rh}(\mu\text{-Cl})\{\text{Ga}(\text{nacnac})\}(\text{PPh}_3)_2$ ].<sup>7</sup> The reduction of **2** with  $\text{KC}_8$  afforded the first 17 VE open-shell nickel gallandiyl complex [ $\text{Cp}^{\text{Ar}}\text{Ni}\{\text{Ga}(\text{nacnac})\}$ ] (**3**), which contains two electron rich metal atoms in the oxidation state + I. Another route to compound **3** is the reduction of **1** with  $\text{KC}_8$  followed by the addition of Ga(nacnac). The NMR and EPR data in combination with DFT calculations support the notion that complex **3** may be viewed as a nickel-based metalloradical. In future work, we will investigate the reactivity of complex **3**. An extension of the synthetic approach presented here to the synthesis of related group 13 and group 14 element carbenoid complexes, e.g. dimetalloenes of the type [ $\text{Cp}^{\text{Ar}}\text{Ni}\{\text{ECp}^{\text{R}}\}$ ] ( $\text{E} = \text{Al} - \text{In}$ ,  $\text{Cp}^{\text{R}} = \text{cyclopentadienyl derivative}$ ), is another highly attractive target pursued in our laboratories.

## EXPERIMENTAL SECTION

**General Considerations.** All experiments were performed under an atmosphere of dry argon, by using standard Schlenk and glovebox techniques. Solvents were purified, dried, and degassed with an MBraun SPS800 solvent purification system. NMR spectra were recorded on BrukerAvance 400 spectrometers at 300 K and internally referenced to residual solvent resonances. The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR signals of **2** were assigned by a combination of H–H COSY, HSQC, HMBC experiments. The  $^1\text{H}$  NMR signals for complexes **3** were assigned by H–H COSY experiments and the relative integration of the signals. Melting points were measured in sealed capillaries on a Stuart SMP10 melting point apparatus. UV/vis spectra were recorded on a Varian Cary 50 spectrometer. Elemental analyses were determined by the analytical department of Regensburg University. [ $\text{Cp}^{\text{Ar}}\text{Ni}(\mu\text{-Br})_2$ ]<sup>20</sup> and Ga(nacnac)<sup>2</sup> were prepared according to the literature procedures.

**Synthesis of [ $\text{Cp}^{\text{Ar}}\text{Ni}(\mu\text{-Br})\{\text{Ga}(\text{nacnac})\}$ ] (**2**).** A solid mixture of [ $\text{Cp}^{\text{Ar}}\text{Ni}(\mu\text{-Br})_2$ ] (150 mg, 0.21 mmol) and Ga(nacnac) (100 mg, 0.21 mmol) was treated with THF (10 mL). The brown-red solution was stirred for 18 hours. Then the solvent was evaporated completely. The red-brown residue was extracted with *n*-hexane (10 mL). The *n*-hexane extract was evaporated completely to dryness. The red-brown residue was pulverized with a spatula and dried *in vacuo*. Complex **2** was obtained as a red-brown powder. Yield: 205 mg (0.17 mmol, 82%); mp >178 °C (decomp.). The  $^1\text{H}$  NMR spectrum of the product showed the presence of 0.5 equiv of *n*-hexane per formula unit. Elemental analysis calcd. for  $\text{C}_{74}\text{H}_{86}\text{BrGa}_2\text{Ni}_2\text{O}_5\text{C}_6\text{H}_{14}$  (Mw. 1254.93 g/mol): C 73.70, H 7.47, N 2.23; found: C 73.80, H 7.26, N 2.13. UV/vis (cyclohexane):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon_{\text{max}}/\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ) = 346

(47068), 462 (14401), 590 (2228).  $^1\text{H}$  NMR (400.13 MHz,  $\text{C}_6\text{D}_6$ , 300 K): 1.00 (d,  $^3J(\text{H,H}) = 8.0$  Hz, 6H,  $2 \times \text{CH}_3$ , Dipp), 1.03–1.06 (overlapping m, 21H,  $5 \times \text{CH}_3$ ,  $\text{Cp}^{\text{Ar}}$  and  $2 \times \text{CH}_3$ , Dipp), 1.25 (d,  $^3J(\text{H,H}) = 8.0$  Hz, 6H,  $2 \times \text{CH}_3$ , Dipp), 1.47 (s, 6H,  $2 \times$  backbone  $\text{CH}_3$ , nacnac), 1.48 (d, overlapping with the signal at 1.47 ppm, 6H,  $2 \times \text{CH}_3$ , Dipp), 2.37 (q,  $^3J(\text{H,H}) = 8.0$  Hz, 10H,  $5 \times \text{CH}_2$ ,  $\text{Cp}^{\text{Ar}}$ ), 3.19 (sept.  $^3J(\text{H,H}) = 8.0$  Hz, 2H,  $2 \times \text{CH}(\text{CH}_3)_2$ , Dipp), 3.71 (sept.  $^3J(\text{H,H}) = 8.0$  Hz, 2H,  $2 \times \text{CH}(\text{CH}_3)_2$ , Dipp), 4.94 (s, 1H, backbone CH, nacnac), 6.69 (d,  $^3J(\text{H,H}) = 8.0$  Hz, 10H,  $10 \times m\text{-CH}$ ,  $\text{Cp}^{\text{Ar}}$ ), 6.98 (d,  $^3J(\text{H,H}) = 8.0$  Hz, 10H,  $10 \times o\text{-CH}$ ,  $\text{Cp}^{\text{Ar}}$ ), 7.09 (t,  $^3J(\text{H,H}) = 4.4$  Hz, 2H,  $2 \times p\text{-CH}$ , Dipp), 7.28 (d,  $^3J(\text{H,H}) = 4.4$  Hz, 4H,  $2 \times m\text{-CH}$ , Dipp).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.61 MHz,  $\text{C}_6\text{D}_6$ , 300 K): 15.2 (s,  $5 \times \text{CH}_3$ ,  $\text{Cp}^{\text{Ar}}$ ), 24.1 (s,  $2 \times \text{CH}_3$ , Dipp), 24.3 (s,  $2 \times$  backbone  $\text{CH}_3$ , nacnac), 24.4 (s,  $2 \times \text{CH}_3$ , Dipp), 24.8 (s,  $2 \times \text{CH}_3$ , Dipp), 27.8 (s,  $2 \times \text{CH}(\text{CH}_3)_2$ , Dipp), 28.8 (s,  $5 \times \text{CH}_2$ ,  $\text{Cp}^{\text{Ar}}$ ), 28.9 (s,  $2 \times \text{CH}_3$ , Dipp), 30.5 (s,  $2 \times \text{CH}(\text{CH}_3)_2$ , Dipp), 99.7 (s, backbone CH, nacnac), 107.2 (s,  $5 \times \text{Cp}_{\text{ring}}$  atoms of  $\text{Cp}^{\text{Ar}}$ ), 123.9 (s,  $2 \times p\text{-CH}$ , Dipp), 126.0 (s,  $4 \times m\text{-CH}$ , Dipp), 126.9 (s,  $10 \times m\text{-CH}$ ,  $\text{Cp}^{\text{Ar}}$ ), 132.4 (s,  $10 \times o\text{-CH}$ ,  $\text{Cp}^{\text{Ar}}$ ), 132.7 (s,  $5 \times ipso\text{-C}$ ,  $\text{Cp}^{\text{Ar}}$ ), 140.9 (s,  $5 \times p\text{-C}$ ,  $\text{Cp}^{\text{Ar}}$ ), 142.4 (s,  $2 \times o\text{-C}$ , Dipp), 142.8 (s,  $2 \times ipso\text{-C}$ , Dipp), 146.4 (s,  $2 \times o\text{-C}$ , Dipp), 169.7 (s,  $\text{NC}(\text{CH}_3)$ , nacnac).

**Synthesis of  $[\text{Cp}^{\text{Ar}}\text{Ni}(\text{Ga}(\text{nacnac}))]$  (3).** *Procedure 1:* A mixture of 2 (169 mg, 0.14 mmol) and  $\text{KC}_8$  (19 mg, 0.14 mmol) was treated with benzene (10 mL) while stirring. The brown-red mixture was stirred for 6 days. The color of the mixture slowly changed from brown-red to red-purple. The completion of the reaction was confirmed by  $^1\text{H}$  NMR spectroscopy. The turbid solution was filtered, and the red-purple filtrate was evaporated completely to dryness under vacuum. The dark purple residue was pulverized and dried *in vacuo*. Complex 3 was obtained as a purple-red powder. Yield: 132 mg (0.12 mmol, 84%); mp 250–252 °C (decomp.). Elemental analysis calcd. for  $\text{C}_{74}\text{H}_{86}\text{GaN}_2\text{Ni}$  (Mw. 1131.93 g/mol): C 78.52, H 7.66, N 2.47; found: C 78.39, H 7.47, N 2.34. UV/vis (cyclohexane):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon_{\text{max}}/\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ) = 339 (35026), 407 (8867), 531(5459).  $^1\text{H}$  NMR (400.13 MHz,  $\text{C}_6\text{D}_6$ , 300 K):  $-3.02$  (s br, 10H,  $5 \times o/m\text{-CH}$ ,  $\text{Cp}^{\text{Ar}}$ ),  $-0.29$  (s, 12H,  $2 \times \text{CH}(\text{CH}_3)_2$ , Dipp), 0.59 (t,  $^3J = 8.0$  Hz, 15H,  $5 \times \text{CH}_3$ ,  $\text{Cp}^{\text{Ar}}$ ), 1.42 (s, 12H,  $2 \times \text{CH}(\text{CH}_3)_2$ , Dipp), 4.46 ( $2 \times$  backbone  $\text{CH}_3$ , nacnac), 4.56 (s br, 2H,  $2 \times p\text{-CH}$ , Dipp), 4.71 (s br, 4H,  $2 \times m\text{-CH}$ , Dipp), 8.10 (m, 10H,  $5 \times \text{CH}_2$ ,  $\text{Cp}^{\text{Ar}}$ ), 9.02 (s, 10H,  $5 \times o/m\text{-CH}$ ,  $\text{Cp}^{\text{Ar}}$ ), 10.02 (s, 1H, backbone CH, nacnac) (the resonances of the  $\text{CH}(\text{CH}_3)_2$  moieties of the Dipp ligand could not be observed presumably due to the severe broadening of the signal). *Procedure 2:* A mixture of  $[\text{Cp}^{\text{Ar}}\text{Ni}(\mu\text{-Br})_2]$  (100 mg, 0.14 mmol) and  $\text{KC}_8$  (19 mg, 0.26 mmol) was treated with benzene (15 mL). The mixture turned green upon stirring for a few minutes. After stirring for 4 days, the green suspension was filtered to remove graphite, and  $\text{Ga}(\text{nacnac})$  (117 mg, 0.24 mmol) was added to the green filtrate under stirring. The color of the solution slowly turned to purple over 6 days. The mixture was stirred further 2 weeks before it reached completion according to  $^1\text{H}$  NMR spectroscopy. The purple solution was evaporated completely to a dark purple solid and washed with *n*-hexane (3 mL). Complex 3 was obtained as a purple-red solid after drying *in vacuo*. Yield: 83 mg (0.07 mmol, 53%).

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b02979.

Crystallographic data for 2 (CIF)

NMR, EPR, UV–vis, and crystallographic data; details of the DFT calculations; and relevant bond lengths and angles. (PDF)

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## Funding

Deutsche Forschungsgemeinschaft (WO1496/4-1).

## Notes

The authors declare no competing financial interest.

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