[\text{CpArNi}\{\text{Ga(nacnac)}\}]: \text{An Open-Shell Nickel(I) Complex Supported by a Gallium(I) Carbenoid (CpAr = C5(C6H4-4-Et)5, nacnac = HC(C(Me)N-(C6H3)-2,6-iPr2)2)}

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[Cp^ArNi{Ga(nacnac)}]: An Open-Shell Nickel(I) Complex Supported by a Gallium(I) Carbenoid (Cp^Ar = C_5(C_6H_4-4-Et)_5, nacnac = HC[C(Me)N-(C_6H_3-2,6-iPr_2)_2])

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ABSTRACT: The 17 valence electron (VE) open-shell nickel gallanediyl complex [Cp^ArNi{Ga(nacnac)}] (3, Ar = C_5(C_6H_4-4-Et)_5, nacnac = HC[C(Me)N-(C_6H_3-2,6-iPr_2)_2]), having an unsupported Ni−Ga bond, was synthesized from [CpArNi(μ-Br)]_2 (1) by reducing the adduct [CpArNi(μ-Br){Ga(nacnac)}] (2) or, alternatively, trapping the "CpArNiI" 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_5Me_5 (= Cp^*), C(SiMe_3)_3, terphenyl, nacnac, and related ligands) have been widely used as supporting ligands for metal-to-metal bonded complexes and clusters. 1−11 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_2NiGa-nacnac] (L = C_2H_4, styrene; L_2 = 1,1,3,3-tetramethyl 1,3-divinyl disiloxane (dvds); Figure 1). 2,3 Several other 18 VE electron Ni−Ga(nacnac) complexes such as [L_2NiGa(nacnac)] (L = CO; L_3 = 1,5,9-cyclododecatriene (CDT); Figure 1) were obtained by ligand substitution reactions. 2,4,5 Interestingly, Ga(nacnac) can also insert into metal halide bonds, leading to M−Ga bonded complexes, although only a few examples are known involving transition metals. 6−9 The reaction with [AuCl(PPh_3)] gives the linear complexes [Au{GaCl(nacnac)}-PPh_3] and [Au{Ga(nacnac)}{GaCl(nacnac)}]. 9 A unique observation is the reaction of [RhCl(PPh_3)_3] with Ga(nacnac), which gave the "frozen-insertion intermediate" [Rh(μ-Cl)Ga-nacnac-PPh_3]. 7

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^*])_2(PPh_3)_2][BAr^F], which is an open-shell complex with a single nickel(I) atom supported by two pentamethylycyclopentadienylgallanediyl ligands (Figure 1). 10 For the bimetallic Ni−Ga open-shell complexes, the Ni_2Ga_2 complex [CpNi(μ-Ga[C(SiMe_3)_3])_2] is an especially interesting example, because it can be viewed as the dimer of the hypothetical open-shell monomer [CpNi-Ga(CSiMe_3)_3] (Figure 1). 12,13 Our interest in the chemistry of mononuclear nickel(I) radicals of type [CpNi(NHC)] supported by N-heterocyclic carbenes (NHCs) 12,13 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^ArNi{Ga(nacnac)}] (3), which can be obtained via two routes: (a) reduction of adduct [Cp^ArNi(μ-Br){Ga(nacnac)}] (2) and (b) reduction of 1 with KC_8 and subsequent addition of Ga(nacnac) (see Scheme 1).

The reaction of the half-sandwich complex [Cp^ArNi(μ-Br)]_2 (1) with Ga(nacnac) in THF affords [Cp^ArNi(μ-Br)]Ga-

Figure 1. Examples of previously characterized Ni−Ga complexes.
Scheme 1. Synthesis of Complexes 2 and 3a

![Scheme 1](image)

a) Reagents and conditions: (a) + Ga(nacnac), THF; (b) + KC8/ — KBr, benzene; (c) + KC8/ — KBr, benzene, then + Ga(nacnac).

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 C6H5 are omitted for clarity. Selected average bond distances (Å) and angles (deg): Ni1—Ga 2.6888(8), Ni1—CpAr(centroid) 1.775(5), Ni1—Br1 2.3577(7), Ga1—Br1 2.6861(9); CpAr(centroid)—Ni1—Ga1 151.40(1), Ni1—Br1—Ga1 152.98(3), N1—Ni1—N2 94.3(3).

The triangular arrangement of the Ni, Ga, and Br atoms in 2 is comparable to that of the only known halide-bridged transition metal–gallium bond in [Rh(μ-Cl)(Ga(nacnac))(PPh3)]2.7 The CpBr4(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)3(Ga(nacnac))][2.289(6) Å],8 and considerably shorter than that in [Ni(CDT)(Ga(nacnac))][2.3482(6) Å].9 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 NH).10 The Ga—Br bond (av. 2.6861(9) Å) is significantly longer than those in the Ga(III) complexes [(nacnac)GaBr2] (2.286(1) and 2.330(1) Å) and in [[(Me3Si)3C]GaBr(μ-Br)]15 however the sterically encumbered Ga(II) complex [Cp*5Ga(μ-Br)]2 features a similar Ga—Br distance (2.573(4) – 2.624(4) Å).16 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))(PPh3)]2.7 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 B3LYP17/def2-TZVP18 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 CpBr4 π*-orbital and a p-orbital of the bromine atom (Figure S7, SI).

The 1H NMR spectrum of the diamagnetic complex 2 in C6D6 shows a set of four doublets and two septets for the characteristic diastereotopic methyl and methine groups of the Dipp unit (Dipp = 2,6-iPr2C6H3). The CpBr4 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 CpBr4 unit in solution at room temperature on the NMR timescale. In agreement with that, the 13C{1H} NMR spectrum shows a characteristic ring carbon signal for CpBr4 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.7 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 [CpBr5Ni(Ga(nacnac))](3). The reduction of 2 with one equivalent of KC8 affords 3 in 84% yield (Scheme 1b). Complex 3 can also be obtained by reducing the dimeric complex 1 with two equivalents of KC8 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 “CpBr5Ni(I)” fragment that is trapped by Ga(nacnac).1H 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 η5-coordinated CpBr4 ligand (Figure 3). It is worth noting that the reaction of [GaC(SiMe3)3]4 with [CpNi(CO)]2 yielded the dimeric complex [CpNiμ-Ga-C(SiMe3)3]2 (Figure 1),11 whereas 3 is mononuclear due to the steric demand of the CpBr4 and nacnac ligands. The CpBr4(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—Ni2 (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)3(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...
[CpNi(IDipp)] (IDipp = 1,3-bis(2,6-disopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene). The Ni–Ga bond (2.915(3) Å) and Ni1–CpAr(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(II) cation relative to a Ni(II) cation.

The 1H NMR spectrum of 3 displays broad signals between −3 and 10 ppm in C6D6, which is typical for a paramagnetic Ni(I) complex.13 The solution state magnetic moment of 3 (1.9(1) μB in C6D6 at 300 K according to Evans NMR method) is consistent with a doublet ground state. A slightly higher value of 2.3(1) μB was observed for [CpNi(IDipp)] in CD3THF.13 In accord with the S = 1/2 multiplicity, the EPR spectrum showed a rhombic g-tensor with significant deviations from g⊥ 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⊥ line (AGa = ~130 MHz). The g∥ and g⊥ lines are too broad to give an estimate of the Ga HFIs along these directions. The DFT computed g-tensor of 3 (g∥ = 2.117, g⊥ = 2.291, gz = 2.403) is in reasonable agreement with the experimental one (g∥ = 2.01, g⊥ = 2.28, gz = 2.58), and the DFT property calculations confirm the presence of sizable Ga HFIs (in particular along g∥: AGa = −64 MHz, AGa∥ = −92 MHz, AGa⊥ = 75 MHz).

DFT calculations (B3LYP/def2-TZVP level)17,18 on the truncated model complex [(η3-C5Ph3)Ni{Ga(HC(C=Me)N(p-C6H4))2}] reproduced the experimentally observed structure very well (see SI). A Löwdin population analysis19 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 CpBrNi 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 [CpNi(IDipp)].12 The distorted CpAr(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⋯π bonding between the aryl groups of CpBr and Dipp is not apparent crystallographically or theoretically.

In conclusion, the reaction of the very bulky pentaarylcyclopentadienyl nickel halide complex [CpBrNi(µ-Br)]2 (1) with Ga(nacnac) affords the “arrested Ni–Br bond insertion intermediate” [CpBrNi(µ-Br){Ga(nacnac)}] (2), having a triangular arrangement of the Ni, Ga and Br atoms. Compound 2 is rare example having a halide-bridged transition metal–gallium bond, the only other example being [Rh(µ-Cl){Ga(nacnac)}(PPh3)2].7 The reduction of 2 with KC8 afforded the first 17 VE open-shell gallandiyl complex [CpBrNi{Ga(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 KC8 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 metallo-radical. 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. dimetallocenes of the type [CpBrNi{ECpBr2}] (E = Al – In, CpBr = cyclopentadienyl derivative), is another highly attractive target pursued in our laboratories.

**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 SP800 solvent purification system. NMR spectra were recorded on Bruker/Avance 400 spectrometers at 300 K and internally referenced to residual solvent resonances. The 1H NMR signals of 2 were assigned by a combination of H–H COSY, HSQC, HMBC experiments. The 1H 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. [CpBrNi(µ-Br)]20 and Ga(nacnac)2 were prepared according to the literature procedures.

**Synthesis of [CpBrNi(µ-Br){Ga(nacnac)}] (2).** A solid mixture of [CpBrNi(µ-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 1H NMR spectrum of the product showed the presence of 0.5 equiv of n-hexane per formula unit. Elemental analysis calc. for C57H45BrGaNi0.5C6H4 (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): λmax/nm (εmax/L·mol−1·cm−1) = 346

**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 CpBr are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni1–Ga1 2.9214(3), Ni1–CpBr(centroid) 1.7922(7), CpBr(centroid)–Ni1–Ga1 164.6(1)°, Ni1–Ga1–Ni1 122.14(4), Ni1–Ga1–N1 145.75(4), N1–Ga–N2 92.09(6)°.

**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.19

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A mixture of [CpArNi(Ga(nacnac)] (the Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b02979.

Crystalllographic data for 2 (CIF) NMR, EPR, UV-vis, and crystalllographic data; details of the DFT calculations; and relevant bond lengths and angles. (PDF)

ASSOCIATED CONTENT
Supporting Information

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REFERENCES