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Nickel Olefin Complexes Supported by Ga$^{\mathrm{I}}$(DDP)[†]

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The reactions of the low-valent group 13 bis-imidinate ligand Ga(DDP) [DDP = 2-{(2,6-diisopropylphenyl)amino}-4-{(2,6-diisopropylphenyl)imino}-2-pentene] with Ni(0) olefin complexes are reported. Treatment of [Ni(cdt)] (cdt = 1,5,9-cyclododecatriene) with Ga(DDP) yields the adduct [(cdt)Ni{Ga-(DDP)}] (**1**). Substitution of the cdt moiety in **1** with olefins (ethylene, styrene, or dvds (dvds = 1,3-divinyl-(1,1,3,3-tetramethyl)disiloxane)) gives a series of olefin complexes, i.e., [{(DDP)Ga}Ni(C_2H_4)$_2$] (**2**), [(DDP)GaNi(styrene)$_2$] (**3**), and [{(DDP)Ga}Ni(dvds)] (**4**). The reaction of Ga(DDP) with excess [Ni(C_2H_4)$_3$] yields the clusters [{(ethylene)$_2$Ni}$_2$(μ^2-Ga(DDP)] (**5**), [{(ethylene)Ni}$_2$(μ^2-Ga(DDP))(μ^2-ethylene)] (**6**), and [{{μ^2-Ga(DDP)}Ni(ethylene)}$_2$Ni(μ^2-CH=CH$_2$)(H)] (**7**). While an agostic interaction of a bridging ethylene molecule is observed in **5** and **6**, a C−H activation takes place in the formation of **7**. Finally, the reaction of [Ni(cod)$_2$] (cod = 1,5-cyclooctadiene) with Ga(DDP) in the presence of Ph−C≡C−Ph yields the dimeric complex [{{μ^2-Ga(DDP)}Ni$_2$(μ^2-PhCCPh)}$_2$(PhCCPh)(1,5-cod)] (**8**). Compounds **1**−**8** were fully characterized by C/H analysis, NMR spectroscopy, and X-ray single-crystal diffraction studies.

Introduction

The ability of low-valent group 13 organyls E$^{\mathrm{I}}$R to effectively bridge two or three transition metal centers via μ^2- or μ^3-coordination modes, respectively, is a specific feature of this novel ligand class and has led to the characterization of a wide variety of mixed metal clusters of different nuclearities and structures.[1−3] The preparation of these mixed metal clusters most often involves replacement of olefins from a transition metal−olefin precursor, e.g., [Pt(cod)$_2$], [Ni(cod)$_2$], [Pd$_2$(dvds)$_3$] (cod = 1,5-cyclooctadiene; dvds = 1,3-divinyl-(1,1,3,3-tetramethyl)-disiloxane)), by the more strongly binding ligands E$^{\mathrm{I}}$R. The direct formation and isolation of larger clusters, e.g., [Pd$_2$(GaCp*)$_5$] or [Pd$_3$(GaCp*)$_8$], is possible by precisely controlling the molar ratios of the employed transition metal precursor to the E$^{\mathrm{I}}$R ligand.[4,5] The detailed understanding of this chemistry is important for the use of GaCp* and AlCp* together with all-hydrocarbon transition metal complexes as precursors for soft chemical synthesis of the respective intermetallic nanophases, i.e., NiAl, in nonaqueous media.[6] Moreover, apart from potential applications in materials science,[7−16] the close proximity of very electrophilic metals E and highly nucleophilic transition metals is an intrinsically interesting feature of the [L$_n$M(E$^{\mathrm{I}}$R)] complexes. Classical organometallic reactions, such as the activation of small molecules with rather inert chemical bonds (e.g., C−H, Si−H, and C−C activation reactions), have been observed in certain mononuclear complexes of the type [M(E$^{\mathrm{I}}$R)$_n$].[17,18] From this point of view it is interesting to introduce the rather exotic monovalent group 13 species E$^{\mathrm{I}}$R as novel ancillary ligands for mixed metal *cluster cores*. In particular, we are interested in extending the classical organometallic activation chemistry from mononuclear, homoleptic complexes [M(E$^{\mathrm{I}}$R)$_n$] to clusters [M$_a$(E$^{\mathrm{I}}$R)$_b$]. Conceptually these clusters are sometimes regarded as molecular models of transition metal main group metal alloys M/E, which are known for tunable properties in heterogeneous or nano catalysis.[19,20] A major synthetic problem, however, is the thermodynamically favorable formation of electronically and sterically saturated clusters such as those stated above with ECp* as the typical ligand, which prevents further reactivity. One strategy to overcome this problem is a tailored increase of the steric bulk of E$^{\mathrm{I}}$R, leading to electronically unsaturated clusters that can additionally coordinate the desired small molecules. This strategy has already been successfully applied in the preparation

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[†] Organo Group 13 Complexes of Transition Metals XLVII; for Part XLVI, see ref 2.

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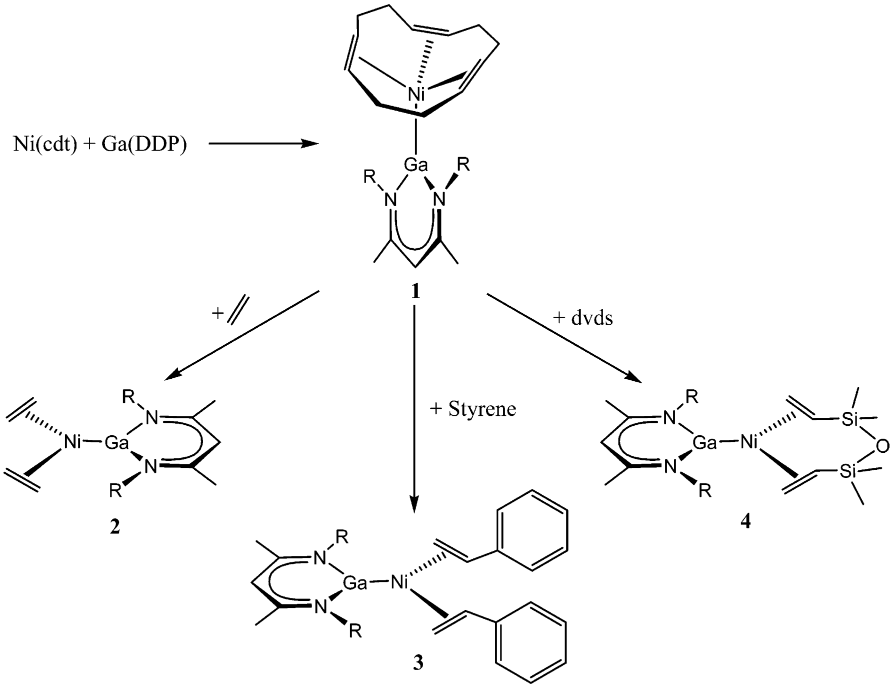
Scheme 1. Synthesis of 1 and Reaction Path for the Formation of 2, 3 and 4



of the Pd/Ga cluster [$Pd_3(GaCp^{*Ph})_4(dvds)$][5] and the Pd/Al cluster [$Pd_2\{Al(DDP)\}(dvds)_2$].[21]

The bulky Ga^I ligands Ga(DDP) [DDP = 2-{(2,6-diisopropylphenyl)amino}-4-{(2,6-diisopropylphenyl)imino}-2-pentene],[2,21−25] [$Ga\{[N(Ar)C(H)]_2\}]^-$,[26−29] and Ga[(Ar)NC(NCy$_2$)N(Ar)][30] have been thoroughly studied as ligands for transition metals by us and others in the past few years. The very high steric bulk of these compounds allows the isolation of unsaturated mononuclear transition metal complexes such as [Pt{Ga(DDP)}$_2$(cod)] and [Pd{Ga(DDP)}(dvds)].[2,21] However, thus far only a few cluster complexes with bridging Ga(DDP) units could be isolated, a notable example of which is the dihydride [$Pt_2\{Ga(DDP)\}_2H_2$].[2] In this paper we now report the reactions of the nickel(0) olefin complexes [Ni(cdt)] (cdt = 1,5,9-cyclododecatriene), [Ni(cod)$_2$], and [$Ni(C_2H_4)_3$] with Ga(DDP), leading to various Ni/Ga compounds and in particular to novel Ni/Ga clusters containing ethylene as co-ligand. Two clusters with a Ni_2Ga core contain bridging ethylene units with π-interactions to one and an agostic C−H bond to the second nickel center, whereas a Ni_3Ga_2 cluster incorporates a bridging vinyl unit originating from a C−H activation of an ethylene molecule.

Results and Discussion

Mononuclear Complexes. The reaction of Ga(DDP) with an equimolar amount of [Ni(cdt)][31] yields the 18 VE complex [(cdt)Ni{Ga(DDP)}] (**1**) as deep red crystals in 88% yield. Analogous to [Ni(cdt)(PMe$_2$R)] (R = Me, menthyl),[32,33] **1** represents a simple coordination compound of a 2*e* donor ligand to the unsaturated Ni(cdt) fragment, where the cdt ligand is still bound in an η^6-coordination mode (Scheme 1). Compound **1** is air- and moisture-sensitive in solution as well as in the solid state, but can be stored at room temperature for several weeks in an inert gas atmosphere. It readily dissolves in nonpolar organic solvents such as hexane or benzene. The NMR spectrum in benzene at room temperature shows one set of signals for the Ga(DDP) ligand, which is only slightly different from free Ga(DDP).[25] Four signals are found for the cdt ring, indicating the coordination of the Ga(DDP) moiety to the Ni(cdt) fragment. This splitting of the cdt-hydrogen atoms can be best explained by two different conformation modes for the ethylene bridges (*syn* or *anti* with respect to the Ga(DDP) ligand). Similar spectra with splitting of the cdt signals were reported for the phosphane analogue [(cdt)Ni(PMe$_3$)].[33] The ^{13}C NMR spectrum is in accordance with this result, showing one set of signals for the Ga(DDP), one signal for the C═C double bonds, and two distinct signals for the CH_2 groups of the bridges.

Crystals, suitable for single-crystal X-ray analysis, could be obtained by cooling a saturated solution of **1** in hexane to −30 °C overnight. A mercury plot of **1** is depicted in Figure 1.

Compound **1** crystallizes in the triclinic space group $P\bar{1}$. The coordination geometry around the Ni center is nearly tetrahedral, with angles in the range 108.8° to 115.2° (the C═C centroids are taken for the calculations of the angles in the case of cdt). The Ni−C bond distances of 2.01 to 2.20 Å are significantly longer than in [Ni(cdt)][34] (av 2.02 Å), but similar to the

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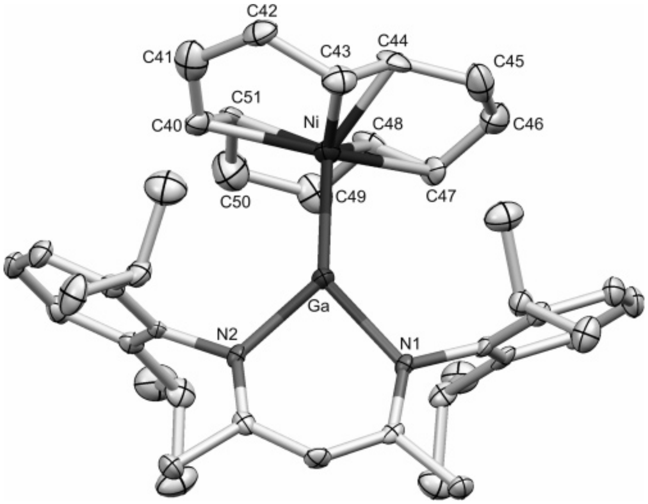

Figure 1. Mercury plot of [(cdt)Ni{Ga(DDP)}] (**1**) with thermal ellipsoids set at 50% probability. Protons are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ga−N2 2.041(3), Ga−N1 2.060(3), Ga−Ni 2.3482(6), Ni−C47A 2.006(11), Ni−C48A 2.023(12), Ni−C40A 2.078(6), Ni−C43A 2.144(10), Ni−C51A 2.185(8), Ni−C44A 2.200(13), C1−N1 1.334(4), N2−C3 1.326(4), C40A−C41 1.555(9), C41−C42 1.515(5), C42−C43A 1.484(14), C43A−C44A 1.39(3), C44A−C45 1.559(15), C45−C46 1.488(5), C46−C47A 1.478(14), C47A−C48A 1.33(3), C48A−C49 1.515(16), C49−C50 1.513(5), C50−C51A 1.392(10), C51A−C40A 1.366(14); N2−Ga−N1 87.38(10), C40A−C51A−C50 127.53, C43A−C44A−C45 121.35, C47A−C48A−C49 129.22.

phosphine compound [(cdt)Ni(PMe$_2$R′)] (R′ = menthyl).[31] The C═C bond lengths in **1** are very similar to those in [Ni(cdt)] (1.33 to 1.39 Å in **1** vs 1.37 to 1.38 Å in [Ni(cdt)]), but significantly longer than in [(cdt)Ni(PR$_2$R′)] (1.28 to 1.33 Å), possibly an effect of the strong electron-donating ability of Ga(DDP), as already discussed in previous publications.[2] The Ni−Ga distance of 2.35 Å is *significantly* longer than in [Ni(GaCp*)$_4$] (2.218 Å)[35] or [Ni(GaCSiMe$_3$)$_4$] (2.17 Å)[36] and can be attributed to the high sterical demand of the DDP moiety. Similarly long Ni−Ga bond distances can be found only in the compound [Ni{Ga[N(Ar)C(H)]$_2$}$_2${C[N(Me)C(Me)$_2$]$_2$}$_2$] (Ar = C$_6$H$_3$Pr$^i_2$-2,6) (2.32 Å),[26] where the square-planar Ni(II) center shows *trans* coordination of the two formally anionic Ga moieties. Interestingly, the Ga−N distances in **1** of 2.041 and 2.059 Å lie in the same range as observed for free Ga(DDP) (2.053 and 2.056 Å) and, therefore, are significantly longer than in other compounds with coordinated Ga(DDP) (e.g., 1.95 Å in [{(DDP)Ga}Au{Cl−Ga(DDP)}][22] or 1.99 Å in [{Ga(DDP)}Pd(dvds)][2]). This observation suggests that coordination of Ga(DDP) to the Ni(cdt) moiety does not increase the electrophilicity of the Ga(I) center as much as observed in other d^{10}-Ga(DDP) complexes (*vide supra*).

When monitoring the reaction of [Ni(cod)$_2$] and Ga(DDP) by ^{1}H NMR (C$_6$D$_6$), signals for free as well as coordinated cod were observed on heating the mixture to reflux for several minutes. However, a black precipitate starts to form almost immediately, and complete decomposition is observed overnight at room temperature. Several attempts to reproduce this reaction in order to isolate a pure product on a preparative level failed.

Following Wilke's route for the preparation of [Ni(ethylene)$_3$],[31] we treated a solution of [Ni(cdt)] in hexane at −10 °C with ethylene, whereupon the color of the solution turned yellowish-brown. After addition of a cooled solution of Ga(DDP) (1 equiv with respect to Ni(cdt)) in hexane, insoluble impurities were filtered off. Cooling the filtrate to −30 °C afforded deep red single crystals of [{(DDP)Ga}Ni(C$_2$H$_4$)$_2$] (**2**), which could be isolated in yields around 40% (Scheme 1). Alternatively, **2** can be prepared by substitution of the cdt ligand in **1** by ethylene, simply by applying increased pressure (3 bar) or bubbling ethylene through a solution of **1** in organic solvents in similar yields and purity. Compound **2** is very air-, moisture-, and temperature-sensitive and decomposes in an inert gas atmosphere at −30 °C after several days. The ^{1}H NMR spectrum of **2** shows one signal set of a C_{2v} symmetric Ga(DDP) (s, 5.20 ppm; sep, 3.11 ppm; s, 1.68 ppm; d, 1.21 ppm; d, 1.09 ppm) as well as one signal for coordinated ethylene (2.29 ppm). Also the ^{13}C NMR spectrum is in good agreement with the solid-state structure.

The crystal structure of **2** shows an almost ideally trigonal planar coordinated Ni center with angles close to 120° (Ga−Ni−C30/C31$_{centr}$ 115.7°, C30/C31$_{centr}$−Ni−C32/C33$_{centr}$ 129.0°, and C32/C33$_{centr}$−Ni−Ga 115.3°). The DDP backbone is slightly twisted, with a torsion angle of 16.8°. The Ni−Ga bond distance in **2** of 2.28 Å is again longer than in [Ni(GaCp*)$_4$][35] (2.22 Å), but *shorter* than in **1** (2.35 Å). The rather strong donor capabilities of Ga(DDP) are reflected in the C═C double-bond lengths in **2** (1.42 and 1.40 Å), which are similar to those found in [(Cy$_3$P)Ni(C$_2$H$_4$)$_2$][37] (1.41 and 1.39 Å) or the Fischer carbene complex [(C$_2$H$_4$)$_2$Ni(CPh(NR$_2$))][38] (1.40 and 1.39 Å). The Ga−N bond distances in **2** of 1.99 Å are significantly shorter than in **1** (av 2.05 Å) or free Ga(DDP) (av 2.055 Å) (*vide supra*).

According to the synthesis of **2**, the cdt ligand in **1** can be readily replaced by other olefins such as styrene and 1,3-divinyl-(1,1,3,3-tetramethyl)disiloxane (dvds), leading to the complexes [{(DDP)Ga}Ni(styrene)$_2$] (**3**) and [{(DDP)Ga}Ni(dvds)] (**4**), respectively. The new complexes **3** and **4** are soluble in common organic solvents such as hexane and benzene and distinctly more stable than **2**. The ^{1}H NMR spectrum of **3** exhibits only C_s symmetry in the DDP moiety, indicating an asymmetric and static coordination of the styrene molecules. The ^{13}C NMR spectrum also displays the expected signals for **3**. The ^{1}H NMR spectrum of **4** is similar to that of the previously reported Pd analogue [{(DDP)E}Pd(dvds)],[2,21] with a C_s symmetric DDP ligand and two distinct signals for the dvds methyl groups. The ^{13}C NMR spectrum does not bear any unusual features. Mercury plots of **3** and **4** as well as tables containing important bond lengths and angles are given in the Supporting Information.

Cluster Complexes. The reaction of Ga(DDP) with excess [Ni(ethylene)$_3$] leads to Ni clusters with bridging Ga(DDP) ligands. A ratio of Ni:Ga of 2:1 yields [{(ethylene)$_2$Ni}$_2$(μ^2-Ga(DDP)] (**5**) and [{(ethylene)Ni}$_2$(μ^2-Ga(DDP))(μ^2-ethylene)] (**6**). However, the cluster [{{μ^2-Ga(DDP)}Ni(ethylene)}$_2$Ni(μ^2-CH═CH$_2$)(H)] (**7**) with a Ni to Ga ratio of 3:2 seems to be the thermodynamic product in these cluster formation processes (*vide infra*). Thus, 2 equiv of Ga(DDP) was added to a cooled solution of 3 equiv of [Ni(ethylene)$_3$] (−5 to −10 °C) in hexane in an ethylene atmosphere. When the reaction mixture was allowed to warm to room temperature, heated to ca. 60 °C for several minutes, and cooled to room temperature again, the formation of a deep red solid occurred after 1−2 h. Recrystallization from hot hexane led to the formation of deep red needles of **7** (Scheme 2). It should be noted that the reaction of [Ni-

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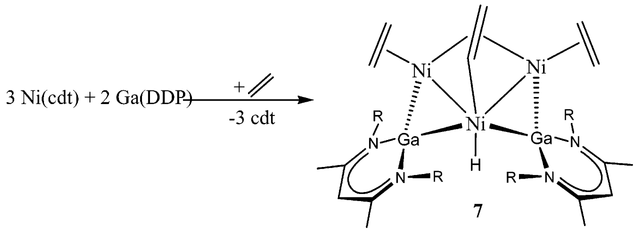
Scheme 2. Synthesis of 7



(ethylene)$_3$] and Ga(DDP) always led to the formation of **7** upon heating to ca. 60 °C, independent of the ratio of the reactants (1:1, 2:1, 3:2). Alternatively, **7** can also be prepared by reaction of [Ni(cdt)] and **2** (3:2) in an ethylene atmosphere upon warming to ca. 60 °C, as shown by ^{1}H NMR spectroscopy.

The ^{1}H NMR spectrum of **7** shows asymmetrically (C_1) coordinated Ga(DDP), whereas the two ethylene ligands are equivalent. The two terminally coordinating ethylene ligands appear as a multiplet signal centered at 3.26 ppm (8H). The bridging vinyl ligand gives rise to three distinct signals in the expected regions, and the hydrid signal is found at −5.06 ppm. The ^{13}C NMR spectrum also shows the expected signals. Compound **7** was found to be rather stable in solution as well as in the solid state. Also, variable-temperature NMR spectroscopy does not show any changes in the NMR spectra in the range −60 to +70 °C.

Deep red needles of **7** suitable for X-ray single-crystal diffraction studies could be obtained by cooling a hot saturated solution of **7** in hexane to room temperature. Complex **7** crystallizes in the orthorhombic space group *Pccn*. The molecular structure in the solid state consists of a triangular arrangement of the Ni atoms (Ni−Ni−Ni: 90.0°), with two short (2.5531(5) Å) and one longer Ni−Ni contact (3.611 Å). The two short Ni−Ni bonds are bridged by Ga(DDP) ligands, the Ga−Ni bond distances of 2.29 Å (to the central Ni2) and 2.38 Å (to the terminal Ni1) being distinctly longer than the terminal Ni−Ga distances found in [Ni(GaCp*)$_4$] (Ni−Ga: 2.21 Å), but also considerably longer than the distances for bridging ligands found in [{(C(SiMe$_3$)$_3$)Ga}$_2$(NiCp)$_2$][39] (Ga−Ni: 2.28 Å). Each terminal Ni center (Ni1 and its symmetry equivalent) are coordinated by an ethylene molecule with a C═C double-bond distance of 1.40 Å, which is similar to those found in **2** or [(Cy$_3$P)Ni(C$_2$H$_4$)$_2$][37] (1.41 and 1.39 Å). The hydride ligand could not be located in the refinement. The vinyl group is σ-bound to the central Ni2, which presumably also bears the hydride ligand, which is suggested by the open space *trans* to the vinyl group. The vinyl group is π-coordinated by both terminal nickel atoms, placing it exactly in between these two metal centers, with a relatively long C−C distance of 1.44 Å, being a result of the strong π-back-bonding. The vector of the vinylic C═C bond is tilted toward the Ni$_3$ plane by an angle of 28°, which leads to the C_1 symmetry of the Ga(DDP) ligands found in the ^{1}H NMR spectrum.

The two clusters **5** and **6** (Figure 4) with a Ni:Ga ratio of 2:1 could be isolated in single crystalline form (see Experimental Section) and were analyzed by X-ray diffraction. However, both complexes are not stable in solution in the absence of ethylene. In both cases, substantial amounts of **7** are found in the NMR spectra, which is quantitatively formed on heating the solutions above room temperature. Additionally, as a result of the presence of unidentified species, the NMR spectra of **5** and **6** are quite complex and not readily interpretable.

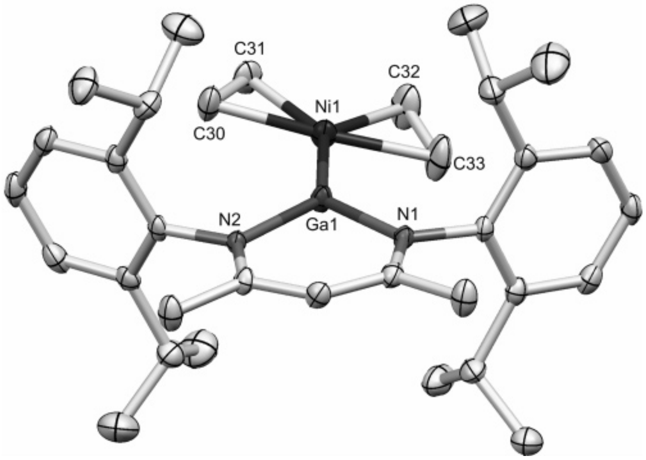


Figure 2. Mercury plot of [{(DDP)Ga}Ni(C$_2$H$_4$)$_2$] (**2**) with thermal ellipsoids set at 50% probability. Protons are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ga1−N2 1.992(2), Ga1−N1 1.992(2), Ga1−Ni1 2.2839(6), Ni1−C31 1.962(3), Ni1−C32 1.974(3), Ni1−C30 1.991(3), Ni1−C33 1.998(3), C30−C31 1.416(4), C32 C33 1.406(5), C3−N2 1.331(4), C1−N1 1.332(4); C30−Ni1−Ga1 94.88(9), C30−Ni1−C31 41.97(12), C31−Ni1−C32 87.10(14), C32−Ni1−C33 41.46(13), C33−Ni1−Ga1 94.83(10), N1−Ga1−N2 89.80(10).

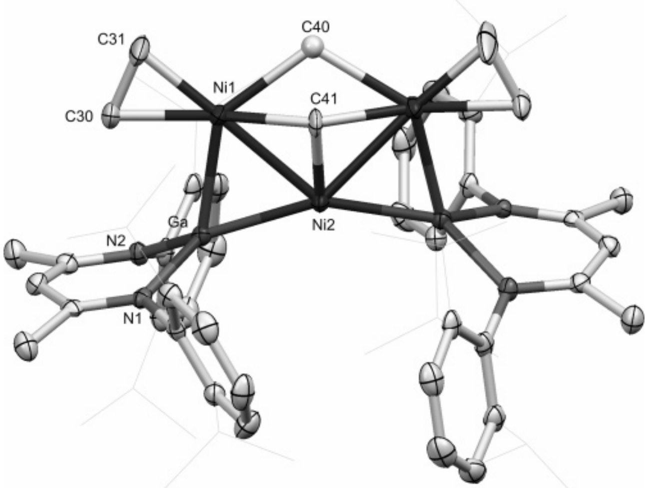


Figure 3. Mercury plot of [{{μ^2-Ga(DDP)}Ni(ethylene)}$_2$Ni(μ^2-CH═CH$_2$)(H)] (**7**) with thermal ellipsoids set at 50% probability. Protons are omitted for clarity (also the hydrido group at Ni2 is not shown). Selected bond lengths (Å) and angles (deg): Ga−Ni1 2.3796(5), Ga−Ni2 2.2889(3), Ni1−Ni2 2.5531(5), Ni1−C30 1.999(3), Ni1−C31 1.932(4), Ni1−C40 2.161(7), Ni1−C41 1.888(6), Ni2−C41 1.941(6), Ga−N1 1.996(2), Ga−N2 1.989(2), C30−C31 1.400(5), C40−C41 1.443(7), N1−C1 1.327(3), N2−C3 1.346(4); N1−Ga−N2 93.13(9), Ni1−Ga−Ni2 66.274(18), Ni1−Ni2−Ni1* 90.02(2), C40−C41−Ni2 124.0(4).

The molecular structures of **5** and **6** both consist of two Ni centers bridged by a Ga(DDP) moiety (Ga−Ni bond distances: 2.33 Å in both cases). Both compounds contain an ethylene molecule in a “bridging” position, i.e., π-coordinated to one Ni center and an agostic C−H interaction to the second Ni center. A comparable bridging mode of ethylene has recently been described by R. R. Schrock in a W−W dimeric complex.[40] In the case of **5**, each Ni center is stabilized by two ethylene molecules, with the two (ethylene)$_2$Ni planes perpendicular to each other (torsion angle: ∼93°). The Ni−Ni distance

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(40) Schrock, R. R.; Lopez, L. P. H.; Hafer, J.; Singh, R.; Sinha, A.; Mueller, P. *Organometallics* **2005**, *24*, 5211.

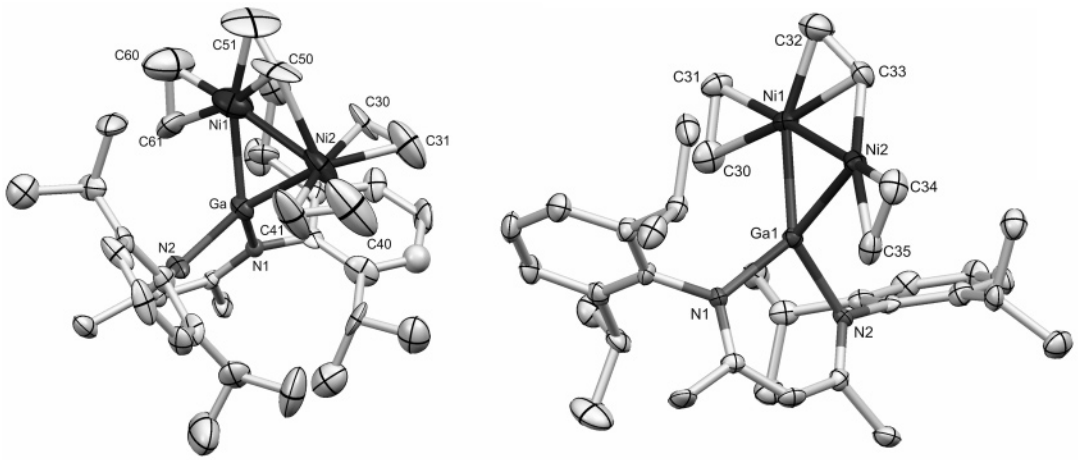

Figure 4. Mercury plot of [{(ethylene)$_2$Ni}$_2$(μ^2-Ga(DDP)] (**5**) (left) and [{(ethylene)Ni}2(μ^2-Ga(DDP))(μ^2-ethylene)] (**6**) (right) with thermal ellipsoids set at 50% probability. Protons are omitted for clarity. Selected bond lengths (Å) and angles (deg) of **5**: Ga−Ni1 2.3332(14), Ga−Ni2 2.3231(11), Ni1−Ni2 2.5051(18), Ni1−C50 2.011(9), Ni1−C51 1.992(8), Ni1−C60 1.881(9), Ni1−C61 2.016(7), Ni2−C30 2.031(8), Ni2−C31 2.061(9), Ni2−C40 1.968(10), Ni2−C41 2.011(8), Ni2−C50 2.454(10), Ni2−C31 2.061(9), Ni2−C40 1.968(10), Ni2−C41 2.011(8), Ni2−C50 2.454(10), C30−C31 1.417(11), C40−C41 1.337(11), C50−C51 1.383(12), C60−C61 1.407(9), Ga−N1 2.029(5), Ga−N2 1.970(6), C1−N1 1.335(8), C3−N2 1.348(8); N1−Ga−N2 92.56(19), Ni1−Ga−Ni2 65.10(5), C51 C50 Ni2 127.9(7). Selected bond lengths (Å) and angles (deg) of **6**: Ga1−N1 1.965(3), Ga1−N2 2.000(3), Ga1−Ni1 2.3200(11), Ga1−Ni2 2.3314(10), Ni1−Ni2 2.4830(14), Ni1−C30 1.993(5), Ni1−C31 1.941(4), Ni1−C32 1.959(5), Ni1−C33 1.976(5), Ni2−C33 1.980(5), Ni2−C34 1.909(4), Ni2−C35 1.991(4), N1−C1 1.354(4), C3−N2 1.329(5), C32−C33 1.374(6), C34−C35 1.392(6), C30−C31 1.392(5); N1−Ga1−N2 92.50(13), Ni1−Ga1−Ni2 64.53(4).

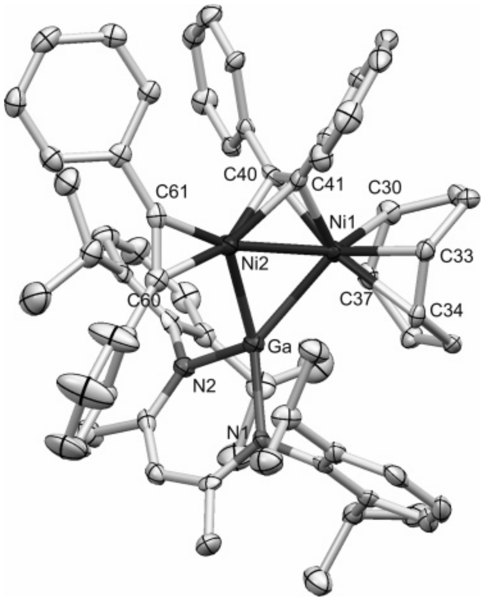

Figure 5. Mercury plot of [(cod)Ni$_2${μ^2-Ga(DDP)}{μ^2-(PhC≡CPh)}(PhC≡CPh)] (**8**) with thermal ellipsoids set at 50% probability. Protons are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ga−Ni1 2.4556(4), Ga−Ni2 2.4129(4), Ni1−Ni2 2.4680(4), Ni1−C30 2.075(2), Ni1−C33 2.128(2), Ni1−C34 2.193(2), Ni1−C37 2.099(2), Ni1−C40 1.950(2), Ni1−C41 2.035(2), Ni2−C40 2.044(2), Ni2−C41 1.937(3), Ni2−C60 1.919(2), Ni2−C61 1.865(2), C33−C34 1.380(3), C30−C37 1.383(3), C40−C41 1.304(3), C60−C61 1.279(3), Ga−N1 2.0018(18), Ga−N2 2.0377(18), N2−C3 1.340(3), N1−C1 1.353(3); N1−Ga−N2 90.69(8), Ni1−Ga−Ni2 60.912(12).

(2.50 Å) is only slightly longer than the Ni^I−Ni^I bond in [(CpNi)$_2${GaC(SiMe$_3$)$_3$}$_2$][36] (Ni−Ni: 2.45 Å) and in the range of Ni−Ni interactions in the Ni−Ga carbonyl cluster [Ni$_4$(μ^2-GaCp*)$_4$(CO)$_5$(μ^2-CO)].[41] The Ni−C bond distances to the terminal ethylenes of 1.88 to 2.05 Å (av 2.01 Å) are slightly longer than in **2** (1.96−1.99 Å) but comparable to those found in the phosphine compound [(Cy$_3$P)Ni(ethylene)$_2$][37] (1.99−2.04 Å). The C=C bond distance of the terminal ethylenes are all between 1.34 and 1.42 Å, indicating the strong donor properties of the Ga(DDP) moiety, as already discussed in the case of **2**. The orientation of the bridging ethylene suggests an agostic interaction between the ethylene-C−H bond and the Ni center (Ni−C bond distance: 2.454(10) Å, Ni−C−C angle: 128°). However, the agostic proton could not be located in the refinement, and thus no other structural parameters of the agostic interaction can be given.The molecular structure of **6** is very similar to that of **5**, with the coordination of three instead of four ethylene ligands. The Ni−Ni distance is slightly shorter than in **5** (2.48 Å). Each Ni center is coordinated by one terminal ethylene with Ni−C bond distances of 1.91 to 1.99 Å. The third ethylene is located in a bridging position between the two Ni centers, again showing a π-bond/agostic coordination mode. However, the Ni−C bond distance of the bridging ethylene moiety (1.980(5) Å) is significant shorter than in **5** (2.454(10) Å).

Notably, preliminary DFT calculations at the B3LYP/LANL2DZ level of theory confirm the experimental observation that both Ni$_2$Ga clusters **5** and **6** show agostic C−H interactions to the bridging ethylene, while the Ni$_3$Ga$_2$ cluster **7** contains a C−H activated ethylene ligand. [Ga{(MeNCMe)$_2$CH}] was used as the model ligand in these calculations. Thus, the corresponding zero-point energy differences between activated and non-activated species are positive and relatively high for **5** (19.8 kcal/mol) and only slightly lower for **6** (13.8 kcal/mol), while **7** shows a preference for the C−H-activated species by 20.1 kcal/mol. Depictions, coordinates, and energies of all the calculated species are provided in the Supporting Information.

Reaction of [Ni(cod)$_2$],[42] Ga(DDP), and PhC≡CPh in a ratio 2:1:2 in hexane yields the Ni$_2$Ga cluster [(cod)Ni$_2${μ^2-Ga-(DDP)}{μ^2-(PhC≡CPh)}(PhC≡CPh)] (**8**) as a dark red solid

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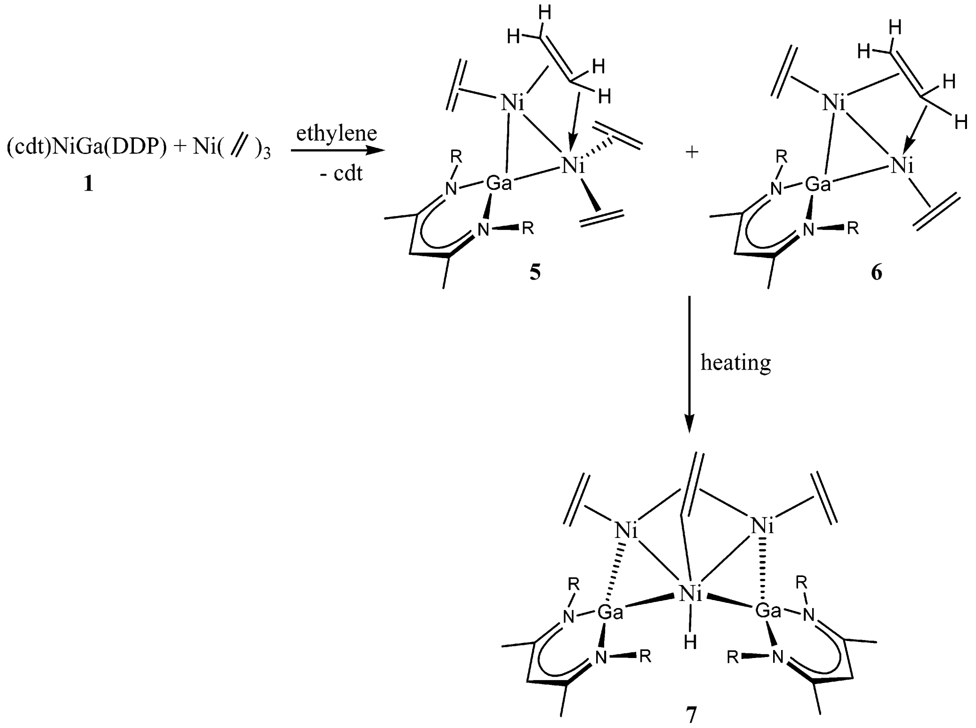
[41] Jutzi, P.; Neumann, B.; Reumann, G.; Stammler, H.-G. *Organometallics* **1998**, *17*, 1305.

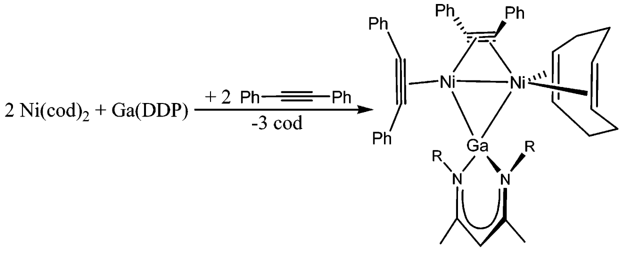
[42] Macchi, P.; Proserpio, D. M.; Sironi, A. *J. Am. Chem. Soc.* **1998**, *120*, 1447.

Scheme 3. Reaction Path for the Formation of 5, 6, and 7



(Scheme 4). Compound **8** is stable in an inert gas atmosphere for several weeks without decomposition and can be redissolved in common organic solvents such as hexane, benzene, or toluene.

Scheme 4. Synthesis of 8



The ^1H NMR spectrum of **8** shows the expected signals for a C_s symmetric Ga(DDP) ligand. The cod ligand gives rise to two broad signals at 5.57 and 5.49 ppm (2H each) for the olefinic protons as well as a multiplet at 1.85 ppm (8H) for the aliphatic protons. Signals for the acetylenic carbons can be found at 96.6 and 91.4 ppm in the ^{13}C NMR spectrum.

Crystals suitable for single-crystal X-ray analysis were obtained from a saturated solution of **8** in hexane by cooling to −30 °C overnight. Compound **8** crystallizes in the orthorhombic space group $P2_12_12_1$. Similar to **5** and **6**, the molecular structure of **8** consists of two Ni centers bridged by a Ga(DDP) moiety. The cod ligand is coordinated to Ni1 in a η^4-mode, whereas the second Ni center (Ni2) bears a terminally coordinated PhC≡CPh ligand. In addition, the two Ni centers are bridged by a PhC≡CPh moiety. The Ni−Ga bond distances in **8** are rather long, 2.41 and 2.46 Å. A similar Ni−Ga bond length could be found only for the μ^2-bridging GaCp* moiety in the cluster compound $[(\mu^2\text{-CO})(CO)_5\{(Cp^*Ga)Ni\}_4]$[41] (2.44 Å). The C=C double-bond distance of the coordinated cod ligand is, at 1.38 Å, similar to the parent compound $[Ni(cod)_2]$.[42] The C≡C distance of the bridging PhC≡CPh (1.31 Å) is somehow shorter than in $(\mu^2\text{-PhC}{\equiv}\text{CPh})(\mu^2\text{-tetraphenylbutadienyl})(Cp^*)_2Ni_3$ (1.33 Å)[43] or in $[(\mu^2\text{-PhC}{\equiv}\text{CPh})\{Ni(cod)\}_2]$[44] (1.388 Å), whereas the terminal PhC≡CPh ligand (1.279 Å) shows a bond distance similar to those reported for other terminal diphenylacetylene compounds (e.g., $[(^tBuNC)_2Ni(PhC{\equiv}CPh)]$[45] (1.276 Å) or $[(cod)Ni(PhC{\equiv}CPh)]$[46] (1.28 Å)).

Conclusion

In this paper we reported on the chemistry of Ni(0) olefin complexes with Ga(DDP) as a ligand. The high steric demand of the DDP moiety prevents the formation of kinetically inert homoleptic Ni/Ga complexes or clusters and thus allows the coordination of additional olefin ligands. Complexes of the type $[Ni\{Ga(DDP]\}(olefin)_2]$ (where "olefin" represents two monodentate or one chelating diolefin ligand) are thermodynamically rather stable species, with the exception of $[Ni\{Ga(DDP]\}(C_2H_4)_2]$, which decomposes at room temperature in the absence of ethylene. Two nickel−gallium clusters with a Ni_2Ga cluster have been isolated, where one ethylene molecule is bridging the two nickel centers in a π/agostic mixed coordination mode, while in the case of a cluster with a Ni_3Ga_2 composition, the bridging ethylene is C−H-activated, resulting in a vinyl hydride cluster.

The concept of tuning the reactivity of mixed metal cluster complexes by an increase of the steric bulk of the ligands E^IR has been successfully applied. The strongly electron donating character and the ability to bridge two metal centers are key attributes of the Ga(DDP) ligand. Such properties of Ga(DDP) allow the formation of reactive clusters that induce bond activation reactions. The reported preparative and structural chemistry of novel Ni/Ga mixed metal clusters indicate a

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(43) Pasynkiewicz, S.; Pietrzykowski, A.; Kryza-Niemiec, B.; Zachara, J. *J. Organomet. Chem.* **1998**, *566*, 217.

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potential for further studies directed toward the activation of small molecules such as olefins at transition metal centers supported by carbenoid group 13 metal ligands. Moreover, these mixed metal cluster compounds can serve as model complexes for alloy materials and thus lead toward tailored alloy compositions for more controlled and selective reactivities of heterogeneous catalysts.

Experimental Section

General Remarks. All manipulations were carried out in an atmosphere of purified argon using standard Schlenk and glovebox techniques. Hexane was dried using an mBraun solvent purification system. The final H_2O content in all solvents was checked by Karl Fischer titration and did not exceed 5 ppm. [Ni(cod)$_2$],[47] [Ni(cdt)],[31] and Ga(DDP)[25] were prepared according to literature methods. Elemental analyses were performed by the Microanalytical Laboratory of the Ruhr-Universität Bochum. NMR spectra were recorded on a Bruker Avance DPX-250 spectrometer (^{1}H, 250.1 MHz; ^{13}C, 62.9 MHz) in C_6D_6 at 298 K, if not stated otherwise. Chemical shifts are given relative to TMS and were referenced to the solvent resonances as internal standards.

All crystal structures were measured on an Oxford Excalibur 2 diffractometer using Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS-97 and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.

Computational Details. All calculations were performed with the Gaussian98 (rev A11) program package. DFT calculations were carried out using the hybrid exchange−correlation functional B3LYP together with the Los Alamos National Laboratory double-ζ LanL2DZ basis set. All structures were fully optimized without symmetry constraints. Vibrational frequencies were calculated for all stationary points to ensure that local minima were located. In order to verify that the overall picture is not affected by the choice of the comparably small LANL2DZ basis set, single-point calculations were performed using a significantly larger basis (6-311G** for C, H, Ga and Stuttgart RSC 1997 ECP for Ni). The results indicate that the qualitative trends in energies and activation barriers are reasonably well reproduced by the LANL2DZ basis set. A respective comparative table is given in the Supporting Information.

Syntheses. [{(DDP)Ga}Ni(cdt)] (1). A mixture of Ni(cdt) (91 mg, 0.41 mmol) and Ga(DDP) (200 mg, 0.41 mmol) was dissolved in hexane (5 mL) and stirred for 1 h at room temperature. Cooling the reaction mixture to −30 °C overnight gave deep red crystals of **1**. Yield: 256 mg (88%). ^{1}H NMR (C_6D_6, 25 °C): δ 7.15 (m, 6H), 5.17 (s, 1H, γ-CH), 4.96 (br, 4H, olefinic H), 4.30 (m, 4H, olefinic H), 3.17 (sept, 4H, C*H*(Me)$_2$), 2.15 (d, 4H, cdt-CH$_2$), 1.99 (s, 8H, cdt-CH$_2$), 1.71 (s, 6H, CH$_3$), 1.32 (d, 12H, CH(*Me*)$_2$), 1.13 (d, 12H, CH(*Me*)$_2$). ^{13}C NMR (C_6D_6, rt): δ 164.2 (*C*N), 144.3 (*C*Me), 142.8 (Ar), 131.6 (Ar), 126.5 (Ar), 124.2 (Ar), 99.4 (C=C), 98.1 (γ-C), 40.2 (CH$_2$CH$_2$), 32.7 (CH$_2$CH$_2$), 28.9 (*C*HMe$_2$), 25.1 (CH*Me*$_2$), 24.1 (C*Me*), 23.8 (CH*Me*$_2$). Aanl. Calcd (found) for $C_{41}H_{59}GaN_2Ni$: C, 69.52 (69.67); H, 8.40 (8.58); N, 3.95 (4.15).

[{(DDP)Ga}Ni(C_2H_4)$_2$] (2). Method A: A cooled solution (−30 °C) of Ga(DDP) (200 mg, 0.41 mmol) in hexane was added to Ni(ethylene)$_3$, synthesized *in situ* by bubbling ethylene through a solution of Ni(cdt) (90.6 mg, 0.41 mmol) in hexane at −10 °C for ca. 30 min. The color of the solution turned deep red. Solid residue was removed by means of cannulation, and deep red crystals of **2** were obtained by crystallization overnight at −30 °C. Yield: 88 mg (35.63%). Method B: Ga(DDP) (200 mg, 0.41 mmol) and Ni(cdt) (90.6 mg, 0.41 mmol) were dissolved in 5 mL of hexane and stirred for 30 min. Ethylene was bubbled through this solution for 20 min and the deep red solution stored under ethylene atmosphere (∼1 bar) at −30 °C overnight. Deep red crystals of **2** could be obtained in 45% yield (110 mg). The same yield is obtained by applying ethylene pressure (2−3 bar) to a solution of **1** in hexane for approximately 20 min ^{1}H NMR (rt, C_6D_6): δ 5.20 (s, 1H, γ-C*H*), 3.11 (sept, 4H, C*H*Me$_2$), 2.29 (s, 8H, *ethylene-H*), 1.68 (s, 6H, C*H*$_3$), 1.21 (d, 12H, *Me*$_2$CH), 1.09 (d, 12H, *Me*$_2$CH); ^{13}C NMR (rt, C_6D_6): δ 166.4 (CN), 142.9 (Ar), 124.4 (Ar), 100.0 (γ-C), 42.5 (C_2H_4), 31.9 (CH(*C*H$_3$)$_2$), 29.0 (CH(*C*H$_3$)$_2$), 24.5 (*C*H(CH$_3$)$_2$), 24.0 (*C*H(CH$_3$)$_2$), 23.9 (C*Me*). Aanl. Calcd (found) for $C_{33}H_{49}GaN_2Ni$: C, 65.82 (64.75); H, 8.20 (8.06); N, 4.65 (4.94).

[{(DDP)Ga}Ni(styrene)$_2$] (3). Method A: A mixture of Ni(cdt) (68 mg, 0.307 mmol) and Ga(DDP) (150 mg, 0.307 mmol) was dissolved in hexane (5 mL) and stirred for 1 h. After addition of styrene (1 mL) the solution turned orange-yellow. On stirring the reaction mixture for 1 h at room temperature, an orange precipitate was formed. Removal of the solvent by cannulation and recrystallization from hexane (−30 °C overnight) gave orange-yellow crystals. Yield: 166 mg (71%). Method B: Ni(cod)$_2$ (84 mg, 0.307 mmol), Ga(DDP) (150 mg, 0.307 mmol), and styrene (1 mL) were dissolved in 5 mL of hexane. Stirring the solution for 1 h and removal of the solvent *in vacuo* yielded a yellow solid. Recrystallization out of hexane gave orange-yellow crystals. Yield: 110 mg (47%). ^{1}H NMR (C_6D_6, 25 °C): δ 7.15 (m, 12H), 6.68 (m, 4H), 5.18 (s, 1H, γ-CH), 3.39 (dd, 2H, *H*C=CH$_2$, J = 9.3 Hz), 3.07 (sept, 4H, C*H*(Me)$_2$), 2.48 (dd, 2H, HC=C*H*$_2$, ^2J(gem) = 2.7 Hz, ^3J(E) = 12.38 Hz), 2.25 (dd, 2H, HC=C*H*$_2$, ^2J(gem) = 2.7 Hz, ^3J(Z) = 9.25 Hz), 1.67 (s, 6H, CH$_3$), 1.30 (d, 6H, CH(*Me*)$_2$), 1.09 (d, 6H, CH(*Me*)$_2$), 1.07 (d, 6H, CH(*Me*)$_2$), 1.04 (d, 6H, CH(*Me*)$_2$). ^{13}C NMR (C_6D_6, rt): δ 166.9 (CN), 146.3 (Ar), 143.1 (Ar), 142.6 (Ar), 142.2 (Ar), 124.8 (Ar), 124.6 (Ar), 124.1 (Ar), 123.3 (Ar), 100.2 (γ-C), 67.4 (C=C), 41.2 (C=C), 29.2 (*C*HMe$_2$), 24.9 (CHMe$_2$), 24.3 (C*Me*), 23.9 (CH*Me*$_2$), 23.8 (CH*Me*$_2$). Anal. Calcd (found) for $C_{45}H_{57}GaN_2Ni$: C, 71.65 (70.70); H, 7.62 (7.94); N, 3.71 (3.80).

[{(DDP)Ga}Ni(dvds)] (4). Ni(cdt) (90.6 mg, 0.41 mmol) and Ga(DDP) (200 mg, 0.41 mmol) were dissolved in hexane (5 mL), and an excess of dvds was added (ca. 0.2 mL, ca. 0.87 mmol). After stirring the reaction mixture for 1 h, the solvent was removed *in vacuo*. Recrystallization from hexane (−30 °C overnight) gave yellow needles. Yield: 196 mg (65%). ^{1}H NMR (C_6D_6, 25 °C): δ 7.15 (m, 6H), 5.20 (s, 1H, γ-C*H*), 3.06 (sept, 4H, C*H*Me$_2$), 2.30−2.40 (complex spin system, 6H, olefinic H), 1.66 (s, 6H, C*H*$_3$), 1.21 (d, 12H, *Me*$_2$CH), 1.06 (d, 12H, *Me*$_2$CH), 0.50 (s, C*H*$_3$Si, 6H), −0.27 (s, 6H, C*H*$_3$Si). ^{13}C NMR (C_6D_6, rt): δ 166.5 (CN), 142.4 (Ar), 124.0 (Ar), 99.8 (γ-C), 49.2 (*C*H$_2$CH), 44.5 (CH$_2$*C*H), 28.6 (*C*H(CH$_3$)$_2$), 24.1 (CH(CH$_3$)$_2$), 23.7 (CH(*C*H$_3$)$_2$), 2.1 (Si*Me*), −0.9 (Si*Me*). Anal. Calcd (found) for $C_{37}H_{59}GaN_2OSi_2Ni$: C, 60.67 (60.12); H, 8.12 (8.13); N, 3.82 (3.83).

[{{μ^2-Ga(DDP)}Ni(ethylene)}$_2$Ni(μ^2-CH=CH$_2$)(H)] (7). Method A: Ni(ethylene)$_3$ was prepared *in situ* by dissolving 68 mg (0.307 mmol) of Ni(cdt) in 5 mL of cold hexane (−10 °C) and applying 3 bar of ethylene for 1 h. Meanwhile, the color of the solution turned from deep red to pale yellow. To this solution was added a cooled hexane solution of Ga(DDP) (100 mg, 0.205 mmol), and the solution turned deep red. Heating the solution for several minutes to ca. 60 °C yielded a deep red precipitate after cooling to room temperature. Recrystallization by repeated heating of the solution to ca. 60 °C and slowly cooling to room temperature gave deep red crystals in 83% yield (105 mg). Method B: The addition of 0.5 equiv of Ni(cdt) (4 mg, 0.018 mmol) to **2** (22 mg, 0.036 mmol) in C_6D_6 and heating the solution to ∼60 °C gave **7** in high yields, as proven by NMR spectroscopy.

^{1}H NMR (C_6D_6, 25 °C): δ 9.70 (dd, 1H, ethylene-CH, $J_{H,H1}$ = 10.3 Hz, $J_{H,H2}$ = 16.6 Hz), 7.01 (m, 4H, ar), 6.91 (t, 4H, ar), 6.85 (d, 2H, ar), 6.72 (d, 2H, ar), 4.98 (s, 2H, γ-CH), 4.49 (dd, 1H, ethylene-CH$_2$, $J_{H,H}$ = 10.3 Hz), 3.82 (d, 1H, ethylene-CH$_2$, $J_{H,H}$ =

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16.86 Hz), 3.26 (m, 8H, ethylene-CH$_2$, $J_{\mathrm{H,H}} = 12.96$ Hz), 3.15 (m, 4H, ^{i}Pr-CH), 1.50 (s, 12H, CH$_3$), 1.19 (d, 6H, ^{i}Pr-CH$_3$), 1.13 (d, 6H, ^{i}Pr-CH$_3$), 1.03 (d, 6H, ^{i}Pr-CH$_3$), 1.01 (d, 6H, ^{i}Pr-CH$_3$), 1.00 (d, 6H, ^{i}Pr-CH$_3$), 0.90 (d, 6H, ^{i}Pr-CH$_3$), 0.61 (d, 6H, ^{i}Pr-CH$_3$), 0.07 (d, 6H, ^{i}Pr-CH$_3$), −5.06 (s, 1H, Ni-H). ^{13}C NMR (C$_6$D$_6$, rt): δ 167.7 (CN), 167.4 (CN), 144.3 (Ar), 144.1 (Ar), 143.2 (Ar), 143.1 (Ar), 142.9 (Ar), 129.3 (Ar), 128.5 (Ar), 128.2 (Ar), 127.9 (Ar), 126.6 (Ar), 126.5 (Ar), 124.6 (Ar), 124.4 (Ar), 124.2 (Ar), 100.8 (γ-C), 44.9 (C═C), 44.1 (C═C), 29.0, 28.5, 28.4, 28.2, 26.2, 26.1, 26.0, 24.5, 24.4, 24.2, 24.1, 23.8. Anal. Calcd (found) for C$_{63}$H$_{92}$Ga$_2$N$_4$Ni$_3$: C, 61.97 (61.66); H, 7.56 (7.49); N, 4.59 (5.02).

[{μ^2-Ga(DDP)}Ni$_2$(μ^2-PhCCPh)}$_2$(PhCCPh)(1,5-cod)] (8). Ni(cod)$_2$ (225 mg, 0.82 mmol), Ga(DDP) (200 mg, 0.41 mmol), and PhCCPh (150 mg, 0.84 mmol) were dissolved in hexane and heated to reflux for several minutes. Additional stirring of the solution for 1 h at room temperature and cooling to −30 °C overnight yielded deep red, octahedral crystals of **8** in 90% yield (395 mg).

^{1}H NMR (C$_6$D$_6$, rt): δ 7.75 (d, 2H, ar), 7.62 (d, 2H, ar), 7.56 (d, 4H, ar), 7.50 (d, 2H, ar), 7.06 − 6.86 (m, 16H, ar), 5.57 (br s, 2H, C═C); 5.49 (br s, 2H, C═C), 5.26 (s, 1H, γ-CH), 3.81 (sept, 2H, ^{i}Pr-CH), 3.18 (sept, 2H, ^{i}Pr-CH), 1.85 (m, 8H, CH$_2$), 1.59 (s, 6H, CH$_3$), 1.24 (d, 6H, ^{i}Pr-CH$_3$), 0.82 (d, 6H, ^{i}Pr-CH$_3$), 0.52 (d, 6H, ^{i}Pr-CH$_3$). ^{13}C NMR (C$_6$D$_6$, rt): δ 166.9 (CN), 145.0 (Ar), 144.8 (Ar), 142.7 (Ar), 137.8 (Ar), 136.2 (Ar), 133.7 (Ar), 131.9 (Ar), 129.9 (Ar), 129.7 (Ar), 129.0 (Ar), 128.9 (Ar), 128.7 (Ar), 128.6 (Ar), 127.1 (Ar), 126.5 (Ar), 126.3 (Ar), 125.8 (Ar), 123.6 (Ar), 101.6 (γ-C), 96.6 (acetylene), 91.4 (acetylene), 33.3 (cod), 31.9 (cod), 30.4 (*C*H$_3$), 30.1 (*C*HCH$_3$), 28.7 (cod), 28.6 (cod) 28.4 (*C*HCH$_3$), 26.0 (CH*C*H$_3$), 25.7 (CH*C*H$_3$), 25.1 (CH*C*H$_3$), 25.0 (CH*C*H$_3$), 23.7 (CH*C*H$_3$). Anal. Calcd (found) for C$_{65}$H$_{73}$GaN$_2$Ni$_2$: C, 73.00 (72.03); H, 6.88 (6.92); N, 2.62 (2.75).

Synthesis of [{(ethylene)$_2$Ni}$_2$(μ^{2-}Ga(DDP)] (5) and [{(ethylene)Ni}$_2$(μ^{2-}Ga(DDP))(μ^2-ethylene)] (6). Ni(ethylene)$_3$ was prepared *in situ* by dissolving 91 mg (0.41 mmol) of Ni(cdt) in 5 mL of cold hexane (−10 °C) and applying 3 bar of ethylene for 1 h. Meanwhile, the color of the solution turned from deep red to pale yellow. To this solution was added a cooled hexane solution of Ga(DDP) (100 mg, 0.205 mmol) and the deep red solution stirred at −10 °C for 1 h. Slowly warming to room temperature forms a mixture of deep red single crystals of **5** and **6**. Unfortunately, neither **5** nor **6** could be synthesized individually.

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Supporting Information Available: Crystallographic data tables and CIF files for compounds **1**−**8**, Mercury plot of compounds **3** and **4**, pictures, *xyz*-coordinates of the calculated structures (**1a**−**3b**), and a table for basis set evaluation. This material is available free of charge via the Internet at http://pubs.acs.org.

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