Synthesis of the Sterically Related Nickel Gallanediyl Complexes $[\text{Ni}(\text{CO})_3(\text{GaAr}')] \text{ (Ar}' = \text{C}_6\text{H}_3\text{-2,6-(C}_6\text{H}_3\text{-2,6-}i\text{Pr}_2)_2 \text{) and } [\text{Ni}(\text{CO})_3(\text{GaL})]$ (L = $\text{HC}[\text{C}(\text{CH}_3)\text{N}(\text{C}_6\text{H}_3\text{-2,6-}i\text{Pr}_2)]_2$): Thermal Decomposition of $[\text{Ni}(\text{CO})_3(\text{GaAr}')] \text{ to give the Cluster } [\text{Ni}_4(\text{CO})_7(\text{GaAr}')_3]$

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Abstract Reaction of $\text{Ni}(\text{CO})_4$ in toluene at room temperature with one equivalent of GaAr' ($\text{Ar}' = \text{C}_6\text{H}_3\text{-2,6-(C}_6\text{H}_3\text{-2,6-}i\text{Pr}_2)_2$) and GaL ($\text{L} = \text{HC}[\text{C}(\text{Me})\text{N}(\text{C}_6\text{H}_3\text{-2,6-}i\text{Pr}_2)]_2$) formed the mono-substituted $\text{Ni}(\text{CO})_3(\text{GaAr}')$ (**1**) and $\text{Ni}(\text{CO})_3(\text{GaL})$ (**3**), respectively. Compound **1** decomposed under reduced pressure or upon heating in toluene to give the new cluster species $\text{Ni}_4(\text{CO})_7(\text{GaAr}')_3$ (**2**). Reaction of **3** with a second equivalent of GaL in toluene at 95 °C afforded the disubstituted complex $\text{Ni}(\text{CO})_2(\text{GaL})_2$ (**4**). All the compounds were characterized by IR, ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy and X-ray crystallographic studies were undertaken to elucidate the structures of the complexes **2**, **3** and **4**.

Keywords Gallium · Nickel · Steric hindrance · Carbonyl

Introduction

The synthesis and characterization of stable organo group 13 metal (I) species dates from the early 1990s [1–3]. The early compounds were stabilized by $\eta^5\text{-C}_5\text{Me}_5$ and $\text{C}(\text{SiMe}_3)_3$ substituents. Later, the range of available examples was further expanded with use of terphenyl [4–6] and β -diketiminate and related ligands [7–11]. The ability of these low-valent metal (I) compounds to act as strong terminal or bridging σ -donor ligands has been well demonstrated by the experimental studies of Fischer, Jutzi and Uhl and by the theoretical work of Frenking [12–20]. Such species are of interest not only from a fundamental structure/bonding perspective [20, 21], but also from the viewpoint of potential applications of this class of compounds (e.g. in the chemical synthesis of intermetallic nanomaterials) [22–24]. We have shown that low

Dedicated to Malcolm Chisholm, on the occasion of this 65th birthday; friend, mentor and colleague.

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coordination Ga(I) species containing bulky aryl ligands $\text{Ar}'\text{GaGaAr}'$ ($\text{Ar}' = \text{C}_6\text{H}_3\text{-}2,6\text{-}(\text{Dipp})_2$) or GaL ($\text{L} = \text{HC}[\text{C}(\text{Me})\text{N}(\text{Dipp})]_2$, $\text{Dipp} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$) are monomeric in solution and exhibit Lewis base behavior toward iron carbonyl to give monomeric $\text{Ar}'\text{GaFe}(\text{CO})_4$ or $\text{LGaFe}(\text{CO})_4$ complexes [25–27]. Similar to those previously reported for $\text{RMFe}(\text{CO})_4$ ($\text{M} = \text{Al}$, $\text{R} = \eta^5\text{-C}_5\text{Me}_5$ (Cp^*) [For reviews of MR complexes of ligands: 28–32]; $\text{M} = \text{Ga}$, $\text{R} = \text{C}_6\text{H}_3\text{-}2,6\text{-}(2,4,6\text{-}i\text{Pr}_3\text{C}_6\text{H}_2)_2$ [33]). In this context we were interested in studying the reactivity of $\text{Ar}'\text{GaGaAr}'$ or GaL with $\text{Ni}(\text{CO})_4$. Herein we report the synthesis and characterization of four new $\text{Ni}(\text{O})$ carbonyl complexes of these monovalent metal ligands group 13, $\text{Ni}(\text{CO})_3\text{GaAr}'$ (**1**), $\text{Ni}_4(\text{CO})_7(\text{GaAr}')_3$ (**2**), $\text{Ni}(\text{CO})_3(\text{GaL})$ (**3**) and $\text{Ni}(\text{CO})_2(\text{GaL})_2$ (**4**).

Results and Discussion

Reactivity of the Digallene $\text{Ar}'\text{GaGaAr}'$ with $\text{Ni}(\text{CO})_4$: Synthesis and Characterization of $\text{Ni}(\text{CO})_3(\text{GaAr}')$ (**1**) and $\text{Ni}_4(\text{CO})_7(\text{GaAr}')_3$ (**2**)

Treatment of a benzene (or hexane) solution of $\text{Ar}'\text{GaGaAr}'$ with two equivalents of $\text{Ni}(\text{CO})_4$ rapidly led to a discharge of the green color of $\text{Ar}'\text{GaGaAr}'$ and evolution of CO. A solution of the unstable pale yellow derivative $\text{Ni}(\text{CO})_3\text{GaAr}'$ (**1**) was formed (see Scheme 1). But no higher substituted nickel species could be observed

Scheme 1

even when a large excess of gallium aryl was used. This can be rationalized on the basis of the high steric requirement of the Ar' substituent which prevents the coordination of further equivalents of GaAr' . The NMR and IR spectra are in agreement with the formulated monosubstituted structure. Thus, when equimolar quantities of starting materials were reacted in benzene- D_6 solution and investigated spectroscopically, only complexed GaAr' was detected in the ^1H and ^{13}C NMR spectra (^1H NMR 2.88 ppm ($\text{CH}(\text{CH}_3)_2$); ^{13}C NMR (31.4 ($\text{CH}(\text{CH}_3)_2$), 25.3 and 24.6 ($\text{CH}(\text{CH}_3)_2$). The ^{13}C NMR spectrum shows an additional signal at 198.2 ppm which could be assigned to the carbonyls. In the IR spectrum of **1** there are two absorptions in the carbonyl region at 2024 and 1972 cm^{-1} , as expected for an $\text{Ni}(\text{CO})_3\text{L}$ complex with local C_{3v} symmetry [34–36].

Surprisingly, solutions of the pale yellow **1** change color to deep red under reduced pressure or upon storage at room temperature. A red product was isolated from these solutions and spectroscopic studies indicated a structure of considerably higher complexity than **1**. For example, in the CO stretching region of the IR spectrum, four absorption bands were observed, three of these appeared at 2012, 2003 and 1991 cm^{-1} indicating the presence of several terminal CO groups. In addition there was an absorption band at 1820 cm^{-1} which is typical for a bridging CO ligands [37, 38]. The ^1H and ^{13}C NMR spectra of **2** in solution did not establish its structure but indicated high fluxionality on the NMR time scale. Thus, the ^1H

Fig. 1 Thermal ellipsoid (30%) plot of $\text{Ni}_4(\text{CO})_7(\text{GaAr}')_3$, (**2**). The flanking aryl groups of the terphenyl substituents and hydrogen atoms are not shown. A line drawing of the structure is also given

NMR spectrum of a benzene- D_6 solution of **2** at room temperature featured only one septet signal at 2.89 ppm for the $CH(CH_3)_2$ groups. In the ^{13}C NMR spectrum there was just one signal at 201.2 in the carbonyl region could be assigned to the seven carbonyl ligands. An X-ray crystallographic diffraction study of **2** was therefore undertaken to establish its structure. Suitable single crystals of **2** were obtained from a solution in toluene upon cooling for 5 days at ca. -20 °C (Fig. 1). Details of the data collection and refinement parameters are given in Table 1.

The molecular structure of $Ni_4(CO)_7(GaAr')_3$ (**2**) is depicted in Fig. 1. Selected bond lengths and angles are collected in Table 2. The core structure of **2** is similar to compounds of the type $Ni_4(CO)_6L_4$ with $L = PR_3$ ($R = Me$, nBu and C_2H_4CN) or $GaCp^*$ although no analogous example of species of the general formula $Ni_4(CO)_7L_3$

Table 1 Crystallographic data and data refinement summary for **2**, **3**, and **4**

	2	3	4
Empirical formula	$C_{97}H_{111}O_7Ga_3Ni_4$	$C_{32}H_{41}O_3N_2GaNi$	$C_{65}H_{57}O_2N_4Ga_2Ni$
Formula weight	1832.86	630.10	1124.30
Color	Red	Yellow	Orange
Temperature (K)	90(2)	90(2)	90(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P 2_1/n$	$P 2_1/n$	$P 2_1/c$
Unit cell dimensions			
a (Å)	11.9207(7)	12.5415(13)	26.223(4)
b (Å)	25.9542(15)	18.9829(19)	11.949(2)
c (Å)	28.1999(16)	13.7157(14)	37.895(6)
α (°)	90	90	90
β (°)	92.912(1)	102.423(2)	94.149(2)
γ (°)	90	90	90
Volume (Å ³)	8713.6(9)	3188.9(6)	1184.2(3)
Z	4	4	4
d_{calc} (Mg m ⁻³)	1.397	1.312	1.263
Absorption coefficient (mm ⁻¹)	1.813	1.468	1.263
$F(000)$	3816	1320	4808
No of reflns (all data)	5779	20031	21483
No of reflns ($1 > 2(\sigma)I$)	4385	13838	11186
Goodness of fit on F^2	1.07	1.024	0.984
R indices (all data)			
R_1	0.0873	0.0652	0.1684
R_w	0.1751	0.1114	0.2192
Final R indices [$I > 2\sigma(I)$]			
R_1	0.0597	0.0421	0.0758
R_w	0.1534	0.0985	0.1820
Largest diff. peak and hole	1.538 −1.472	0.665 −0.783	1.809 −2.142

Table 2 Selected bond angles (°) for **2**

Ni(1)–Ni(3)–Ni(4)	64.62(3)
Ni(1)–Ni(3)–Ni(2)	62.32(3)
Ni(2)–Ni(4)–Ni(3)	60.91(3)
Ni(2)–Ni(4)–Ni(1)	59.48(3)
Ni(3)–Ni(4)–Ni(1)	54.29(3)
Ni(4)–Ni(3)–Ni(2)	59.19(3)
Ni(3)–Ga(1)–Ni(2)	65.93(3)
Ni(2)–Ga(2)–Ni(1)	65.95(3)
Ni(1)–Ga(3)–Ni(3)	58.38(3)
Ni(1)–Ga(3)–Ni(4)	65.16(3)
Ni(3)–Ga(3)–Ni(4)	62.39(3)
C(31)–Ga(1)–Ni(3)	156.08(16)
C(31)–Ga(1)–Ni(2)	137.18(16)
C(1)–Ga(2)–Ni(2)	152.83(16)
C(1)–Ga(2)–Ni(1)	141.21(16)
C(61)–Ga(3)–Ni(1)	143.85(17)
C(61)–Ga(3)–Ni(3)	139.22(15)
C(61)–Ga(3)–Ni(4)	146.19(16)

is known [13, 37, 38]. Probably, the flanking phenyls rings of the three GaAr' ligands prohibit a coordination of a fourth GaAr' ligand to the Ni₄ cluster.

The cluster **2** possesses a Ni₄ tetrahedron as its central framework, whose structure is distorted from idealized geometry. The Ni–Ni distances are between 2.361(10) and 2.628(11) Å. A similar range of Ni–Ni distances was reported for Ni₄(CO)₆(GaCp*)₄ [13, 17, 39–41]. Two of the six edges of the Ni₄ tetrahedron are bridged by a μ -GaAr' fragment. Two of the remaining four edges are each bridged by a carbonyl ligand and one face (Ni₁, Ni₃, Ni₄) is complexed by a μ_3 GaAr' unit (Ga(3)). All four nickels carry a terminally bound carbonyl and an “extra” terminal carbonyl is bound to Ni₄. The Ni–Ga bond lengths are in the range (Ga–Ni 2.329(9)–2.476(10) Å). The three GaAr' ligands are coordinated similarly to those in Ni₄(CO)₆(GaCp*)₄, with two GaAr' bonded in a μ_2 and one in a μ_3 mode. Additionally, all C–O and Ni–C bond distances are in the expected range (1.104(8)–1.140(7) and 1.748(6)–2.094(6) Å, respectively).

Reactions of GaL with Ni(CO)₄: Synthesis and Structure of Ni(CO)₃(GaL) (**3**) and Ni(CO)₂(GaL)₂ (**4**)

Reaction of GaL with Ni(CO)₄ at room temperature in benzene or hexane led to an immediate evolution of CO and formation of the nickel complex Ni(CO)₃(GaL) (**3**) as a yellow solid in nearly quantitative yield (Scheme 1). The ¹H NMR spectrum revealed two characteristic signals at 5.15 and 1.64 ppm, assignable to the CH and CH₃ hydrogens of the C₃N₂Ga ring, while the signals of the CH(CH₃)₂ substituents appear at 2.99 and 1.48 and 1.06 ppm, respectively. The CO stretching frequencies and the chemical shift, of the carbonyl groups of **3**, 2011 and 2003, respectively, are

similar to these found for **1** and for the silylene and germanediyl complexes $\text{Ni}(\text{L})(\text{CO})_3$ ($\text{L} = [\text{CHN}(\text{Bu}')_2\text{Si}$ or $[\text{CHN}(\text{Bu}')_2\text{Ge}]$) [42, 43]. To unambiguously characterize this compound single crystals were grown for an X-ray diffraction analysis. The structure of compound **3** is shown in Fig. 2. Crystal data and refinement parameters are given in Table 1 and selected bond lengths and angles are collected in Table 3. The structure of **3** displays a very distorted, approximately trigonal bipyramidal geometry at nickel in which an apical position is unoccupied. The coordination geometry of the nickel is similar to that of the silylene–nickel complexes [43]. The Ni–Ga bond is in the known range of bond lengths for nickel–gallanediyl complexes [13] and may be compared to the 2.191(1)–2.210(1) Å range for the terminal Ni–Ga distances in the complex $(\text{tmpGa})_2\text{Ni}(\mu\text{-Ga tmp})_3\text{Ni}(\text{Ga tmp})_2$ ($\text{tmp} = 2,2,6,6\text{-tetramethylpiperidido}$) [44] or the 2.1700(4) Å $\text{Ni}\{\text{C}(\text{SiMe}_3)_3\}_4$ in which the gallium carries a monodentate ligand [45]. The Ni–C bond lengths are in the range 1.78–1.79 Å.

Unsuccessful, attempts were made to synthesize a Ni cluster species analogous to **2** under similar conditions. For example upon treatment of a pale yellow solution of **3** with one equivalent of GaL in toluene at 95 °C under nitrogen flow for 1 day, the proton resonance spectrum shows at 5.15 and 5.14 ppm characteristic of **3** and GaL, respectively, and one new signal at 4.9 ppm attributable to the disubstituted compound **4**. Prolonged heating of this solution gave an intractable mixture of products. For an unambiguous characterization of **4**, single crystals were grown for an X-ray diffraction analysis.

Fig. 2 Thermal ellipsoid (30%) plot of $\text{Ni}(\text{CO})_3(\text{GaL})$ (**3**). The hydrogen atoms are not shown

Table 3 Selected bond lengths (Å) and angles (°) for **3**

Bond lengths (Å)	
Ga(1)–N(1)	1.962(3)
Ga(1)–N(2)	1.970(3)
Ga(1)–Ni(1)	2.289(6)
Ni(1)–C(30)	1.792(5)
Ni(1)–C(31)	1.783(5)
Ni(1)–C(32)	1.798(5)
Bond angles (°)	
N(1)–Ga(1)–N(2)	93.68(11)
N(1)–Ga(1)–Ni(1)	133.89(8)
N(2)–Ga(1)–Ni(1)	132.42(8)
O(1)–C(30)–Ni(1)	178.4(4)
O(2)–C(31)–Ni(1)	178.5(4)
O(3)–C(32)–Ni(1)	178.4(4)
C(31)–Ni(1)–C(30)	111.9(2)
C(31)–Ni(1)–C(32)	115.9(2)
C(30)–Ni(1)–C(32)	116.62(19)
C(30)–Ni(1)–Ga(1)	102.94(13)
C(31)–Ni(1)–Ga(1)	104.21(15)
C(32)–Ni(1)–Ga(1)	102.93(13)

The molecular structure of $\text{Ni}(\text{CO})_2(\text{GaL})_2$ (**4**) is depicted in Fig. 3. Crystal structure parameters are given in Table 1, and selected bond lengths and angles are collected in Table 4. The zero-valent metal atom has an almost ideal tetrahedral coordination geometry. The bond lengths to carbonyl and gallanediyl ligands are similar to these in **3**. The GaN_2C_3 six-membered rings are slightly distorted from planarity as in the free ligand. Interestingly, the nonequivalence of the isopropyl groups in the solid state cannot be observed in solution. The ^{13}C NMR spectra in benzene- D_6 display one signal for carbonyl and also one signal for both isopropyl groups, indicating a high fluxionality in **4** on the NMR time scale, similar to that observed **2** and analogous $\text{Ni}(\text{CO})_2(\text{L})_2$ complexes [42, 43]. The IR showed two characteristic stretching signals at 2039 (A_1) and 1,967 cm^{-1} (B_1), confirming that GaL is a ligand with good σ -donor and poor π -acceptor qualities.

Concluding Remarks

We have shown that the highly sterically encumbered gallanediyls GaAr' and GaL react readily with $\text{Ni}(\text{CO})_4$. The selective, partial substitution of CO in $\text{Ni}(\text{CO})_4$ by GaAr' and GaL yields the monomeric complexes $\text{Ni}(\text{CO})_3(\text{GaAr}')$ (**1**) and $\text{Ni}(\text{CO})_3(\text{GaL})$ (**3**), respectively, which is quite similar to the chemistry of the 1:1:1 reaction of GaCp^* with $\text{Ni}(\text{CO})_4$ to afford $\text{Ni}(\text{CO})_3(\text{GaCp}^*)$ [13]. However, complex **1** decomposes in solution at room temperature to form the cluster $\text{Ni}_4(\text{CO})_7(\text{GaAr}')_3$ (**2**). In contrast, under similar conditions, compound **3** is stable. The reaction of **3** with excess of GaL produced the disubstituted $\text{Ni}(\text{CO})_2(\text{GaL})_2$ (**4**).

Fig. 3 Thermal ellipsoid (30%) plot of $\text{Ni}(\text{CO})_2(\text{GaL})_2$ (**4**). H atoms are not shown

Table 4 Selected bond lengths (Å) and angles (°) for **4**

Bond lengths (Å)	
Ni(1)–Ga(2)	2.271(12)
Ni(1)–Ga(3)	2.280(12)
Ni(1)–C(125)	1.755(9)
Ni(1)–C(126)	1.762(8)
N(1)–Ga(1)	2.001(6)
N(2)–Ga(1)	2.008(6)
N(3)–Ga(4)	1.986(6)
N(4)–Ga(4)	2.016(6)
Bond angles (°)	
C(125)–Ni(1)–C(126)	111.7(4)
C(125)–Ni(1)–Ga(2)	108.4(2)
C(126)–Ni(1)–Ga(2)	105.2(3)
C(125)–Ni(1)–Ga(3)	106.2(2)
C(126)–Ni(1)–Ga(3)	108.9(3)
Ga(2)–Ni(1)–Ga(3)	116.67(5)
N(1)–Ga(1)–N(2)	90.0(2)
N(3)–Ga(4)–N(4)	90.7(2)
O(3)–C(125)–Ni(1)	173.8(7)
O(4)–C(126)–Ni(1)	174.5(8)
N(5)–Ga(3)–Ni(1)	147.05(18)
N(6)–Ga(3)–Ni(1)	121.52(16)

Experimental Section

All manipulations were carried out using modified Schlenk techniques under an atmosphere of N₂ or in a Vacuum Atmospheres HE-43 drybox. All solvents were dried and degassed three times prior to use. The compounds GaAr' [10] and GaL [10] were prepared according to literature procedures. Ni(CO)₄ was used as received from Johnson Matthey. ¹H and ¹³C NMR were recorded on Varian 300 spectrometer and referenced to known standards. Infrared data were recorded in Nujol mulls using a Perkin-Elmer 1430 instrument. Melting points were recorded using a Meltemp apparatus and are uncorrected.

X-ray quality crystals of **2**, **3** or **4** were covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and placed in the cold temperature stream. The data were collected near 90 K using a Bruker SMART 1000 diffractometer and Mo K_α (λ = 0.71073 Å) radiation.

Absorption corrections were applied using SADABS [46]. The structures were solved by use of Direct Methods in SHELXS [47] and refined by the full-matrix least-squares procedure in SHELXL. All non hydrogen atoms were refined anisotropically, while hydrogens were placed at calculated positions and included in the refinement by using a riding model. Some details of the data collection and refinement are given in Table 1. Further details are in the supplementary material. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 773645–773647. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: int code_(1223) 336-033; email: www.ccdc.cam.ac.uk/data/request/cif).

Generation of Ni(CO)₃(GaAr') (**1**) in Solution

To a C₆D₆ solution (0.6 mL) of GaAr' (0.046 g, 0.01 mmol) was added Ni(CO)₄ (18 μL, 0.015 mmol). The deep green color became yellow and evolution of CO was observed. The yellow solution was analyzed by NMR and IR spectroscopy: ¹H NMR (300 MHz, C₆D₆, 25 °C): 7.28–7.08 (m, 9H, CH, Ar), 2.88 (sept, 4H, ³J_{HH} = 6.6 Hz, CH(CH₃)₂), 1.25 (d, 12H, ³J_{HH} = 6.6 Hz, CH(CH₃)₂), 1.05 (d, 12H, ³J_{HH} = 6.6 Hz, CH(CH₃)₂). ¹³C{¹H}NMR (75 MHz, C₆D₆, 25 °C): 198.2 (CO), 144.6 (*o*-Dipp), 136.2 (*p*-C₆H₃), 130.8 (*o*-C₆H₃), 129.7 (*m*-C₆H₃), 128.2 (*i*-Dipp), 125.5 (*m*-Dipp), 123.9 (*p*-Dipp), 30.8 (CH(CH₃)₂), 24.7 (CH(CH₃)₂), 23.9 (CH(CH₃)₂). IR ν_{CO} (cm⁻¹): 2024 (s), 1972 (vs).

Synthesis of Ni₄(CO)₇(GaAr')₃ (**2**)

A deep green toluene solution (10 mL) of GaAr' (0.1 g, 0.214 mmol) was added dropwise to a toluene (5 mL) solution of Ni(CO)₄ (0.038 g, 27 μL, 0.205 mmol). Evolution of CO was observed and the resulting yellow solution was stirred for 1 h, whereupon all volatiles were removed under reduced pressure. The orange solid residue was dissolved in a small volume, ca. 3 mL, of hexane and cooled to a –20 °C. After 5 days deep red crystals of **2** were obtained. Yield: 0.098 g, 65%.

m.p. = 128 °C (decomp. with CO evolution). ^1H NMR (300 MHz, C_6D_6 , 25 °C): 7.28–7.08 (m, 9H, CH, Ar), 2.89 (sept, 4H, $^3J_{\text{HH}} = 6.6$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.25 (d, 12H, $^3J_{\text{HH}} = 6.9$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.05 (d, 12H, $^3J_{\text{HH}} = 6.6$ Hz, $\text{CH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6 , 25 °C): 201.2 (CO), 145.0 (*o*-Dipp), 131.0 (*p*- C_6H_3), 130.4 (*o*- C_6H_3), 129.8 (*m*- C_6H_3), 128.0 (*i*-Dipp), 124.4 (*m*-Dipp), 31.4 ($\text{CH}(\text{CH}_3)_2$), 25.3 ($\text{CH}(\text{CH}_3)_2$), 24.6 ($\text{CH}(\text{CH}_3)_2$). IR ν_{CO} (Nujol, cm^{-1}): 2012, 2003, 1991, 1820.

Synthesis of $\text{Ni}(\text{CO})_3(\text{GaL})$ (**3**)

A yellow toluene (10 mL) solution of GaL (0.1 g, 0.205 mmol) was added dropwise to a toluene (5 mL) solution of $\text{Ni}(\text{CO})_4$ (0.035 g, 27 μL , 0.205 mmol). Evolution of CO was observed. The solution was stirred for 1 h, and all volatiles were removed under reduced pressure. Yellow crystals of **3** were obtained by slow evaporation of a saturated benzene solution. Yield: 0.12 g (92%). m.p. = 203–205 (decomp.) °C. ^1H NMR (300 MHz, C_6D_6 , 25 °C): 7.14 (m, 6H, CH, Ar), 5.15 (s, 1H, methine CH), 2.99 (sept, 2H, $^3J_{\text{HH}} = 6.6$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.64 (s, 6H, $\text{C}(\text{CH}_3)_3$), 1.48 (d, 12H, $^3J_{\text{HH}} = 6.6$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.06 (d, 12H, $^3J_{\text{HH}} = 6.6$ Hz, $\text{CH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6 , 25 °C): 200.3 (CO), 167.8 (CN), 143.4 ($\text{C}(\text{CH}_3)_3$), 141.6 (*o*-Dipp), 138.9 (*p*-Dipp), 125.1 (*m*-Dipp), 100.9 (γ -C), 29.7 ($\text{CH}(\text{CH}_3)_2$), 25.1 (CH_3), 24.57 ($\text{CH}(\text{CH}_3)_2$), 24.52 ($\text{CH}(\text{CH}_3)_2$). IR ν_{CO} (Nujol, cm^{-1}): 2039 (s), 1967 (vs).

Synthesis of $\text{Ni}(\text{CO})_2(\text{GaL})_2$ (**4**)

A yellow toluene solution (20 mL) of $\text{Ni}(\text{CO})_3(\text{GaL})$ (0.63 g, 1 mmol) was added dropwise to a solution of (10 mL) GaL (487 mg, 1 mmol). The solution was stirred for 1 day at 95 °C. All volatiles were removed under reduced pressure. The resulting orange solid was dissolved in hexane (15 mL). Cooling the solution to –20 °C overnight gave yellow crystals which were a mixture of **3** and GaL. The supernatant liquid was separated and after concentration (ca. 10 mL) cooled to –20 °C for 3 days to yield orange crystals of **4**. Yield: 0.085 g (18%, respect to GaL). m.p. = 208–210 °C. ^1H NMR (300 MHz, C_6D_6 , 25 °C): 7.10 (m, 6H, CH, Ar), 4.90 (s, 1H, methine CH), 3.17 (sept, 4H, $^3J_{\text{HH}} = 6.9$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.56 (s, 6H, $\text{C}(\text{CH}_3)_3$), 1.24 (d, 12H, $^3J_{\text{HH}} = 6.6$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.20 (d, 12H, $^3J_{\text{HH}} = 6.6$ Hz, $\text{CH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6 , 25 °C): 202.5 (CO), 166.1 (CN), 143.7 ($\text{C}(\text{CH}_3)_3$), 143.4 (*o*-Dipp), 127.7 (*p*-Dipp), 124.8 (*m*-Dipp), 100.7 (γ -C), 29.5 ($\text{C}(\text{CH}_3)_3$), 25.8 ($\text{CH}(\text{CH}_3)_2$), 24.8 ($\text{CH}(\text{CH}_3)_2$), 24.79 ($\text{CH}(\text{CH}_3)_2$). IR ν_{CO} (Nujol, cm^{-1}): 2038 (s), 1970 (vs).

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