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Synthesis and structure of (carbonyl){μ-η^5: η^1-[2-(*N*,*N*-dimethylamino)ethyl]cyclopentadienyl}(dichlorogallio)nickel(II)

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Abstract

The synthesis of a nickel–gallium complex with the [2-(*N*,*N*-dimethylamino)ethyl]cyclopentadienyl ligand (Cp^N; $Cp^N = \eta^5$-$C_5H_4CH_2CH_2NMe_2$) is described. The compound is characterized by elemental analysis, IR ν(CO) spectroscopy, NMR, and mass spectroscopy. A single crystal diffraction revealed a short σ(Ni–Ga) bond of 227.9(7) pm. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Organonickel complexes; Nickel gallium bond; [2-(*N*,*N*-dimethylamino)ethyl]cyclopentadienyl ligand (Cp^N)

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1. Introduction

The coordination chemistry of functionalized cyclopentadienyl ligands was recently enriched by the introduction of the (dimethylamino)ethyl group at the Cp ring [1,2]. Jutzi et al. have been studying in detail a number of metal complexes bearing this Lewis base functionalized ligand and its tetramethyl ring-substituted derivative [3–12]. The potential of such a hemilabile ligand, capable of stabilizing both soft and hard metal centers by intramolecular adduct formation [13,14], is also interesting for the synthesis of organometallic single molecule precursors for OMCVD of mixed metal thin films. Metallic alloys of selected combinations of Group 13 elements with d-metals, especially with nickel, e.g. NiGa [15] and NiIn [16], have been discussed as thermodynamically stable metal contacts to III/V semiconductor surfaces [17,18]. In this paper we report on the synthesis and structural characterization of the Ni–Ga complex **1** (Scheme 1) that is intramolecularly stabilized by the *N*-donor functionalized [2-(dimethylamino)ethyl]cyclopentadienyl ligand (Cp^N; $Cp^N = \eta^5$-$C_5H_4CH_2CH_2NMe_2$).

2. Results and discussion

2.1. Synthesis and properties

We have previously reported the synthesis of adduct stabilized Ni–Ga complexes via the salt elimination route, employing K[Cp(CO)Ni] and $ClGaR_2$ (R = CH_2^tBu) or the intramolecularly adduct stabilized organogallium halides $ClGa(R)[(CH_2)_3NMe_2]$ (Scheme 1) [19]. As σ(M–Ga) bonds can vary over a wide range [20], we were interested in establishing a lower limit for Ni–Ga bonds with tetra-coordinated Ga(III) centers. The treatment of metal–metal bonded transition metal–carbonyl compounds with low valent Group 13 halides EX or E_2X_4, leads typically to compounds of the type M_aEX_{3-a} ($a = 1$–2) [21–24]. In the absence of additional Lewis donors these compounds are usually dimeric in the solid state. Following this strategy, the reaction of bis[(carbonyl){2-(*N*,*N*-dimethylamino)-ethyl]cyclopentadienyl}]nickel(I) with Ga_2Cl_4 was investigated; consequently forming the gallium–nickel complex (μ-η^5:η^1-Cp^N)(CO)Ni–$GaCl_2$ (**1**) with an intramolecular coordination of the dimethylamino group of the Cp^N-ligand to the gallium center (Scheme 1). Compound **1** sublimes slowly at 60°C, 10^{-3} Torr. Aiming at a better volatile derivative of **1** to be useful as precursor for OMCVD, we tried out alkylation of **1**

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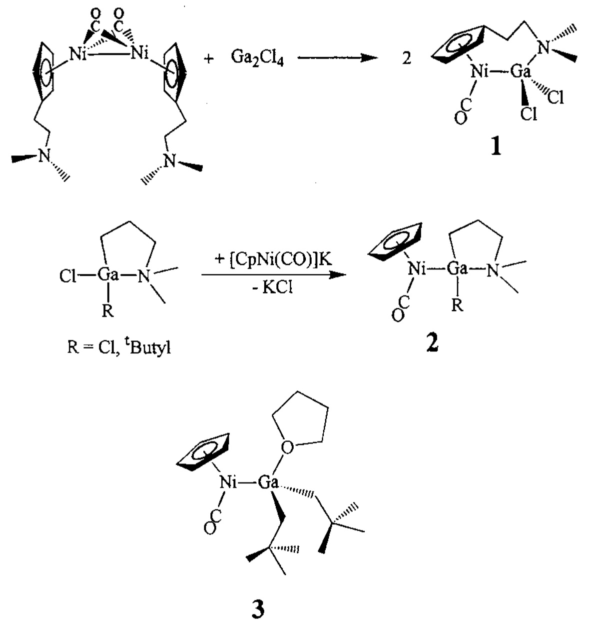
with conventional methods (e.g. methyl-, ethyl-, phenyllithium or Grignard reagents). The products were formed as indicated by the expected shifts of the ν(CO) band to lower wavenumbers at 1958 cm^{-1}, but is was not possible to isolate pure compounds in satisfactory yields. Preliminary OMCVD studies using **1** gave Ni/Ga films but no attempt was made to optimize the conditions and the accessible film properties.



Scheme 1. Synthesis of intramolecularly adduct stabilized Ni–Ga compounds.

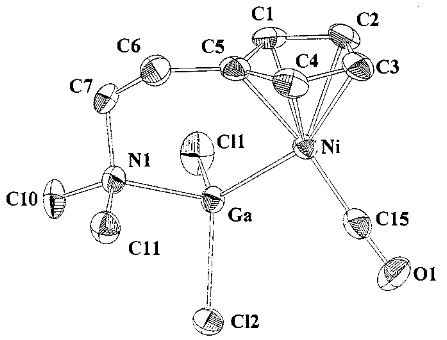


Fig. 1. Molecular structure of **1** in the solid state (PLATON drawing; the thermal ellipsoids are represented at a 50% probability level). Hydrogen atoms are omitted for clarity.

Table 1
Structurally characterized nickel–gallium complexes to date

Compound	CN [b]	Ni–Ga (pm)	Reference
(Cp^N)(CO)Ni–GaCl$_2$ (**1**)	4	227.9(7)	This work
(Cp)(CO)Ni–Ga-(CH$_2^t$Bu)$_2$(THF) (**3**)	4	240.6(1)	[19]
Ni$_4$(Cp*Ga)$_4$(CO)$_6$ (**4**) [a]	4	245.3 (av.)	[25]
	3	244.1 (av.)	[25]

[a] The Cp* ligand counted as one coordination site.

[b] CN = coordination number at the Ga center.

2.2. Spectroscopic characterization

The formation of **1** is proved by NMR, mass spectroscopy and X-ray single-crystal diffraction analysis. The ^{1}H-NMR spectra clearly show the features indicative for an intramolecular adduct of the dimethylaminoethyl side chain involving the gallium center. The methylene groups exhibit two partly resolved AA′BB′ spin systems, similar to those reported in the literature for similar cases [14]. The electron impact mass spectrum exhibits the molecular peak (363 *m*/*z*, 1% relative intensity) and the fragment GaCl$_2^+$ (141 *m*/*z*, 100% relative intensity) as base peak.

2.3. Structure of compound 1

Fig. 1 shows the molecular structure of **1** in the solid state. Crystallographic and structural data are given in Tables 2 and 3. The only other examples of structurally characterized compounds with nickel–gallium bonds are the complex $\{(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Ni–Ga}[\text{CH}_2\text{C}(\text{CH}_3)_3]_2\text{-}(\text{OC}_4\text{H}_8)\}$ (**3**) [19] and the cluster Ni$_4$(Cp*Ga)$_4$(CO)$_6$ (**4**) [25]. The structure determination confirms the presence of an intramolecular Lewis base adduct in the solid state and reveals a rather short σ(Ni–Ga) bond of 227.9(7) pm. The Ni–C(15) 171.1(4) pm and Ni–C(1–5) bond lengths 208.2(4) up to 211.8(4) pm are within the expected range. The coordination of the Cp ring is distinctly off-center with the Ni closest to C(5). The angle Cp–C(5)–C(6) of 174.02° (Cp denote the centroid of the Cp^N-ring) indicates that the coordination of the dimethylamino-group does not impose significant steric stress on the system. The coordination of the nickel center is trigonal planar, if one counts the Cp^N as one coordination site. The angle Ga–Ni–C(15) of 88.92(14)° is somewhat wider as the corresponding angle of **3** with 78.6(2)°. This reflects a less polarized σ(Ni$^{\delta-}$–Ga$^{\delta+}$) bond of **1** with respect to **3**. The GaCl$_2^+$ group can be regarded to be a better Lewis acid as GaR$_2^+$ thus reducing the negative charge of the nickel center as compared with the neopentyl derivative (Table 1). A similar dependence of σ(M–E) bond distances from the substitution pattern at the center E has been established for the series (CO)$_5$M–E(X)L$_2$. The M–E bonds were shorter for X = Cl and longer for X = H, alkyl [26]. Compounds **1** and **3** differ by the 13 pm shorter Ni–Ga bond of **1**. Complex **3** exhibits a σ(Ni–Ga) bond distance of 240.6(1) pm. The latter distance corresponds well with the sum of the estimated covalent radii of Ni and Ga (240 pm) [27]. This shortened bond of **1** can be rationalized as being a

Table 2
Crystallographic data for compound **1**

Empirical formula	$C_{20}H_{28}Cl_4Ga_2N_2Ni_2O_2$
Formula weight	727.10
Crystal color	Orange
Crystal system	Monoclinic
Space group	$P2_1$
Crystal size (mm)	$0.30 \times 0.40 \times 0.30$
Temperature (K)	200 ± 1
Unit cell dimensions	
a (Å)	10.967(2)
b (Å)	9.004(2)
c (Å)	14.190(2)
V (10^6 Å^3)	1333.8(4)
Z	2
$D_{calc.}$(g cm^{-3})	1.810
Wavelength (Å)	0.71073 Mo–K$_\alpha$ (graphite monochromator)
Absorption coefficient (mm^{-1})	3.809
F(000)	728
θ Range for data collection (°)	2.72–25.00
Reflections collected	2471
Independent reflections	2342 [$R_{int} = 0.0172$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2342/0/150
Goodness-of-fit on F^2	0.942
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0296$, $wR_2 = 0.0708$
R indices (all data)	$R_1 = 0.0375$, $wR_2 = 0.0753$
Largest difference peak and hole (e Å^{-3})	0.593 and -0.510

consequence of the more contracted bonding orbitals of the $GaCl_2^+$ unit as compared with the GaR_2^+ unit of **3** [26]. The cluster **4** containing tri-coordinated and tetra-coordinated Ga centers (Table 1), exhibits an average Ni–Ga distance of 245.5(1) pm (from 229.3 to 258.2 pm). The sum of the angles around the gallium center of **1** Ni–Ga–Cl1, Cl1–Ga–Cl2 and Cl2–Ga–Ni of 340.25° and Ni–Ga–N, Cl1–Ga–N and Cl2–Ga–N of 314.13° characterize the deviation from the ideal tetrahedral coordination at the Ga center. The Ga–N bond length of 205.9(3) pm is within the range of rather strong sterically unhindered dative Ga–N bonds thus shorter than in $Me_3Ga–NMe_3$, 220(3) pm, which reflects the enhanced acceptor strength of the $GaCl_2$ unit with respect to the dialkylgallium moieties [28].

Taken together, the results show that bonding Ni–Ga contacts can be as short as 227 pm, which appears to be the shortest σ(Ni–Ga) bond to date. It must be pointed out, however, that M–E bond distances (also Ni–Ga) depend strongly on substituents at the Ga center, as well as on coordination number (CN). Compounds with a *terminal* coordination of a Cp*Ga to a nickel center are thus expected to exhibit Ni–Ga distances below 227 pm.

3. Experimental

All manipulations were undertaken with standard Schlenk and glove box techniques under an inert gas atmosphere (purified N_2) using dried (< 2 ppm H_2O) oxygen-free solvents. All samples for NMR spectra were contained in vacuum-sealed NMR tubes. A Bruker AC 200 spectrometer and routine data collection parameters were used for ^{1}H- and ^{13}C-NMR spectroscopy. ^{1}H- and ^{13}C-NMR spectra were referenced to an internal solvent and corrected to TMS. All J values are reported in Hz. Measurement frequencies of 200.132 (^{1}H) and 50.323 (^{13}C) MHz were applied. Mass spectra were recorded with a Finnigan MAT 8230 instrument; m/z values are reported for ^{31}Ga and ^{59}Ni, normal isotope distribution observed. The starting compounds were prepared as described in the literature [14,29]. Elemental analysis was provided by the Microanalytic Laboratory of the Ruhr-University Bochum and of the University of Heidelberg.

3.1. Synthesis of (carbonyl){μ-η^5:η^1-[2-(N,N-dimethylamino)ethyl]cyclopentadienyl}(dichlorogallio)nickel(II) (1)

A THF solution (20 ml) of bis[(carbonyl){[2-(*N*,*N*-dimethylamino)ethyl]cyclopentadienyl}]nickel(I) (0.892 g, 2 mmol) was added at − 78°C to a stirred solution of 0.844 g (3 mmol) of Ga_2Cl_4 in THF. The resulting mixture was allowed to warm up to room temperature, and stirred for 3 days. After evaporation of the solvent, the residue was extracted with toluene. The crude product was purified by crystallization from saturated toluene solutions at − 30°C. Compound **1** was obtained as orange crystals. Yield: 0.727 g (50%).

1: ^{1}H-NMR (C_6D_6, 25°C): $\delta = 1.61$ (AA′BB′, 2H, $N(CH_2C\underline{H_2})$); 1.95 (AA′BB′, 2H, $N(C\underline{H_2}CH_2)$); 1.98 (s, 6H, $(NC\underline{H_3})$; 4.79 (t, $^3J_{H-H} = 2.2$ Hz, 2H, $C_5\underline{H_4}$); 5.20 (t, $^3J_{H-H} = 2.2$ Hz, 2H, $C_5\underline{H_4}$). ^{13}C{^{1}H}-NMR (C_6D_6, 25°C): $\delta = 22.8$ ($\underline{C}H_2CH_2N$); 44.1 ($N\underline{C}H_3$); 55.5 ($CH_2\underline{C}H_2N$); 89.6–92.0 ($\underline{C_5}H_4$); 93.3 (C_{ipso} of $\underline{C_5}H_4$). IR (toluene), ν(CO): 2012.8 cm^{-1}. MS(CI): m/z (%) = 363 (1) [M^+], 141 (100) [$GaCl_2^+$]. Anal. calc. for $C_{10}H_{14}Cl_2GaNNiO$ (363.54): Calc. C, 33.3; H, 3.88; N, 3.88; Ga, 19.17; Cl, 19.50; Ni, 16.14. Found: C, 33.26; H, 3.84; N, 3.60; Ga, 19.3; Cl, 19.39; Ni, 15.19.

3.2. X-ray single-crystal structure determination of 1

Crystals of compound **1** were obtained from toluene at − 30°C. Preliminary examination and data collection were carried out on a STOE-AED2 (Siemens, Nicolet-Syntex) diffractometer. Crystal data together with details of the data collection and structure refinement are listed in Table 2, while selected bond distances and angles for compound **1** are listed in Table 3.

4. Supplementary material

Supplementary material including full crystallo-

Table 3
Selected bond distances (pm) and angles (°) for compound **1**

Bond lengths			
Ni–C(15)	171.1(4)	N(1)–C(11)	148.4(5)
Ni–C(5)	208.2(4)	N(1)–C(10)	148.9(5)
Ni–C(1)	208.9(4)	N(1)–C(7)	149.5(5)
Ni–C(3)	208.7(4)	C(5)–C(6)	150.4(6)
Ni–C(2)	211.1(4)	C(6)–C(7)	152.0(6)
Ni–C(4)	211.8(4)	Ga–Cl(1)	221.55(11)
Ni–Ga	227.90(7)	Ga–Cl(2)	222.20(11)
Ga–N(1)	205.9(3)	O(1)–C(15)	114.0(5)
Bond angles			
C(15)–Ni–C(5)	165.9(2)	N(1)–Ga–Cl(1)	102.03(9)
C(15)–Ni–C(1)	153.4(2)	N(1)–Ga–Cl(2)	100.05(9)
C(15)–Ni–C(3)	113.8(2)	Cl(1)–Ga–Cl(2)	104.91(5)
C(15)–Ni–C(2)	123.2(2)	N(1)–Ga–Ni	112.05(9)
C(15)–Ni–C(4)	131.9(2)	Cl(1)–Ga–Ni	115.06(4)
C(15)–Ni–Ga	88.92(14)	Cl(2)–Ga–Ni	120.28(3)
C(5)–Ni–Ga	91.61(12)	C(11)–N(1)–C(10)	108.2(3)
C(1)–Ni–Ga	93.71(13)	C(11)–N(1)–C(7)	111.3(3)
C(10)–N(1)–C(7)	108.0(3)	C(11)–N(1)–Ga	109.7(2)
C(7)–N(1)–Ga	109.7(2)	C(5)–C(6)–C(7)	117.0(4)
N(1)–C(7)–C(6)	116.1(3)	O(1)–C(15)–Ni	178.5(4)

graphic and experimental data, hydrogen positional parameters, thermal parameters, interatomic distances, and bond angles may be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (E-mail: deposit@ccdc.cam.ac.uk), on quoting the depository number CCDC-116288, the names of the authors, and the journal citation.

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