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Synthesis and Structure of [Ni{Ga−C(SiMe$_3$)$_3$}$_4$] and Quantum-Chemical Verification of Strong π Back-Bonding in the Model Compounds [Ni(EMe)$_4$] (E = B, Al, Ga, In, Tl)

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Summary: The reaction of bis(cyclooctadiene)nickel with $Ga_4[C(SiMe_3)_3]_4$ (**1**) *yields a coordination compound analogous to* [Ni(CO)$_4$], [Ni{Ga−C(SiMe$_3$)$_3$}$_4$], *which shows a tetrahedral coordination of the central nickel atom, linear Ni−Ga−C groups, and very short Ni−Ga distances. Quantum-chemical DFT calculations on the model complexes* [Ni(EMe)$_4$] *(E = B, Al, Ga, In, Tl) verify strong* π *back-donation of electron density from nickel to the empty* $p(\pi)$ *orbitals of the group 13 elements, which is more effective than in tetracarbonylnickel itself.*

Organoelement compounds of the monovalent elements Al, Ga, and In tend to form tetrahedral clusters E_4R_4 in the solid state,[1−5] while in solution or in the gas phase they often dissociate to give the monomeric fragments. In the particular case of the element(I) alkyl compounds $E_4\{C(SiMe_2R)_3\}_4$ (E = Ga, In) the coordinatively and electronically strongly unsaturated species $E{-}C(SiMe_2R)_3$ are formed,[2−6] which have frontier orbitals with a lone electron pair and two empty $p(\pi)$ orbitals that are similar to those of carbon monoxide. Guided by this analogy, we were able to synthesize numerous transition-metal complexes of gallium or indium, which are analogues of carbonyl compounds in which the GaR or InR groups frequently occupy bridging positions between two metal atoms.[7] Recently, we reported on the synthesis and characterization of the first transition-metal indium complex [Ni{In−C(SiMe$_3$)$_3$}$_4$] (**1**), which is a remarkable analogue of [Ni(CO)$_4$] and which possesses a nickel atom exclusively coordinated by terminal InR groups in an undistorted tetrahedral coordination sphere.[8] However, despite a very short Ni−In bond, the significance of π back-bonding from Ni to In remained undetermined. Quantum-chemical calculations verified weak iron−aluminum π interactions in [(CO)$_4$Fe(AlCp*)],[9] while significant tungsten−aluminum π bonding was found in HAlW(CO)$_5$.[10] Such calculations would be of particular interest for compound **1**, because it has no other π-acceptor ligands such as carbonyl groups in competition with InR. Besides the results of these quantum-chemical calculations we report here on the synthesis of the gallium analogue of **1**, which is only the second example of a homoleptic group-13 diyl complex.

Treatment of tetragallane **2** (eq 1) with bis(cyclooctadienyl)nickel gave the light red NiGa$_4$ compound **3** in a yield of 70%.[11] **3** shows a surprisingly high thermal stability and does not decompose below 320 °C. In comparison to compounds with trivalent gallium atoms (δ <30 ppm), the C atoms attached to gallium have a quite unusual downfield shift in the ^{13}C NMR spectrum to δ 53.6 ppm, similar to that of **1**. Even stronger shifts

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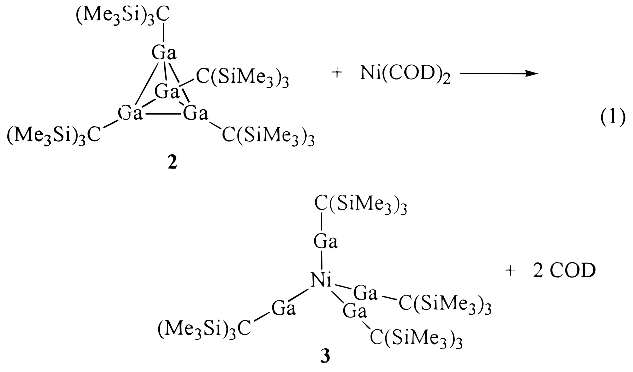
(11) Experimental procedures: All procedures were carried under under purified argon. *n*-Hexane and cyclopentane were predried over LiAlH$_4$ and further distilled over *n*-butyllithium. Ni(COD)$_2$ (107 mg, 0.391 mmol) was treated with a solution of 470 mg (0.391 mmol) of **2**[3] in 80 mL of *n*-hexane and heated at reflux for 2 h. The color changed from red to yellow. A small quantity of a black solid precipitated, which was filtered off. All volatile components were distilled off in vacuo, and the residue was recrystallized from cyclopentane (+20/−30 °C): yield 340 mg (70%); red crystals, which include up to four molecules of cyclopentane each formula unit; due to partial loss of solvent molecules only the ratio of Ni to Ga could be determined satisfactorily by elemental analysis. Dec pt (argon, sealed capillary): 320 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.49 (SiMe$_3$). ^{13}C NMR (75 MHz, C$_6$D$_6$): δ 53.6 (GaC), 6.3 (SiMe$_3$). IR (paraffin, CsBr plates, cm^{-1}): 1304 m, 1250 s δ(CH$_3$); 1169 w, 1117 w, 1080 w, 1040 m ν(CC) (cyclopentane); 860 vs, 842 vs, 775 m, 721 s ρ(CH$_3$(Si)); 673 m, 646 m ν(SiC); 610 s, 521 w, 463 w ν(GaC); 380 vw, 341 w δ(SiC). UV/vis (*n*-hexane; λ_{max}, nm (log ϵ)): 360 (4.2), 380 (4.1). MS (CI, isobutane; *m*/*z* (%)): 1260.4 (15), 1262.4 (25), 1264.4 (25), all M$^+$, in accordance with a calculated isotope pattern.

10.1021/om990417h CCC: $18.00



(1)

(COD = cyclooctadiene)

were observed for the In_4 and Ga_4 starting compounds (δ 72 and 62 ppm, respectively), which for the indium derivative was explained by strong spin–orbit interactions.[5] **3** (Figure 1) crystallizes in the cubic space group $Fd\bar{3}$.[12] The nickel atoms are terminally coordinated by four GaR ligands with an ideally tetrahedral coordination geometry. The angles Ga–Ni–Ga are 109.5°, and the coordinatively unsaturated gallium atoms are linearly coordinated with bond angles Ni–Ga–C of 180°. The Ga–C bond lengths (2.014(4) Å) are shortened in comparison with those of the cluster compound **2** (2.08 Å)[2] but are still longer than in derivatives with tricoordinated, trivalent gallium atoms. This shortening may be caused by an enhancement of the positive charge at gallium or by a smaller steric stress in the coordination compound due to the enlargement of the Ga–Ga separation from 2.68 Å in **2** to 3.544 Å in **3**. The Ga–Ni distance (2.1700(4) Å) is to the best of our knowledge shorter by 0.12 Å than the shortest value reported before in the literature.[13]

We calculated the equilibrium geometries and the Ni–EMe bond energies of the model compounds $[Ni(EMe)_4]$ with E = B, Al, Ga, In, Tl using gradient-corrected DFT methods in conjunction with effective core potentials (ECPs) for the heavy atoms.[14] The bonding situation was then analyzed with the help of the CDA[21,22] and NBO[23] partitioning schemes. Table 1

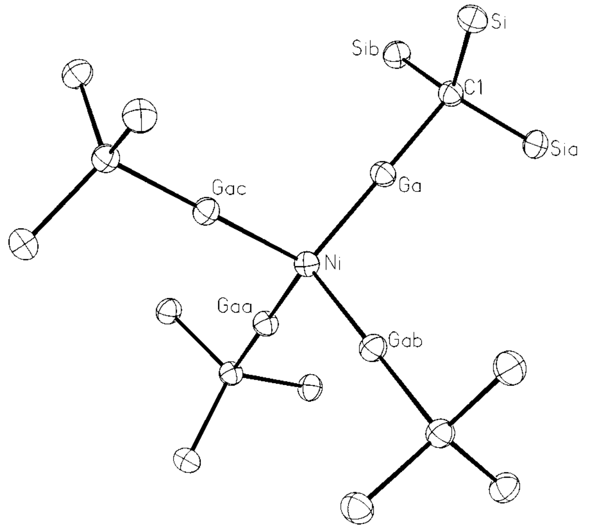


Figure 1. Molecular structure of **3**. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups are omitted for clarity. Important bond lengths (Å) and angles (deg): Ni–Ga = 2.1700(4), Ga–C1 = 2.014(4); Ga–Ni–Ga = 109.5, Ni–Ga–C1 = 180.00(5).

Table 1. Calculated (B3LYP/II) Bond Lengths *R*(A–B) (Å), First Ni–EMe and Ni–CO Dissociation Energies D_e, and ZPE-Corrected Values D_o (kcal/mol) of the Complexes $[Ni(EMe)_4]$ and $[Ni(CO)_4]$[a]

	R(Ni–E)	*R*(E–C)	D_e	D_o
$[Ni(BMe)_4]$	1.764	1.548	83.8	79.7
$[Ni(AlMe)_4]$	2.142	1.987	55.6	53.2
$[Ni(GaMe)_4]$	2.210 (2.217)[b]	2.037 (2.014)[b]	43.2	40.7
$[Ni(InMe)_4]$	2.341 (2.310)[c]	2.182 (2.195)[c]	45.4	43.4
$[Ni(TlMe)_4]$	2.452	2.281	28.4	27.0
$[Ni(CO)_4]$	1.842 (1.817)[d]	1.145 (1.127)[e]	21.9	20.0 (25.0 ± 2)[e]

[a] Experimental values are given in parentheses. [b] This work. [c] Reference 8. [d] Reference 30. [e] Reference 24.

shows the calculated and experimental bond distances and the theoretically predicted bond energies for $[Ni(EMe)_4]$ and $[Ni(CO)_4]$. The theoretical values for the

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(12) Crystal structure of **3**: single crystals from a solution in cyclopentane at −30 °C; the crystals were directly taken from solution and embedded in perfluorinated polyether; $C_{40}H_{108}Ga_4NiSi_{12}\cdot 4C_5H_{10}$, cubic, space group $Fd\bar{3}$, $a = 25.569(1)$ Å, $V = 16\,717(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.195$ g/cm^3, crystal size 1.0 × 0.8 × 0.6 mm, Stoe IPDS diffractometer, radiation Mo Kα, 193 K, range $4.5 < 2\theta < 52°$, 180 exposures, $\Delta\varphi = 1.0°$, 1373 independent reflections, 1213 reflections with $F > 4\sigma(F)$, $\mu = 1.696$ mm^{-1}, numerical absorption correction, programs SHELXTL PLUS, release 4.1, and SHELXL-93, solution by direct methods, refinement with all independent structure factors based on F^2, 55 parameters, R1 = 0.033 and wR2 (all data) = 0.116, max/min residual $+0.58 \times 10^{30}/-1.05 \times 10^{30}$ e/m^3. The structure of the nickel indium compound **1** was redetermined; the better data obtained now at low temperature showed that this compound is isotypic with **3**; distances and angles remained almost unchanged in comparison to those published before.[8] Crystal structure of **1**: $C_{40}H_{108}In_4NiSi_{12}\cdot 4C_5H_{10}$, cubic, space group $Fd\bar{3}$, $a = 25.812(1)$ Å, $V = 17198(1)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.301$ g/cm^3, crystal size 0.30 × 0.22 × 0.09 mm, radiation Mo Kα, 193 K, range $4.4 < 2\theta < 52°$, 120 exposures, $\Delta\varphi = 1.5°$, 1432 independent reflections, 1002 reflections with $F > 4\sigma(F)$, $\mu = 1.468$ mm^{-1}, numerical absorption correction, programs SHELXTL PLUS, release 4.1, and SHELXL-93, 59 parameters, R1 = 0.055 and wR2 (all data) = 0.165, max/min residual 1.46×10^{30}(near the indium atoms)/-1.81×10^{30} e/m^3. The cyclopentane molecules are located on special positions and are strongly disordered; their atoms were refined isotropically, and hydrogen atoms were not considered.

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Ni−Ga, Ga−C, Ni−In, and In−C distances of the model compounds are in very good agreement with the experimental data. The largest difference is only 0.03 Å.

A comparison of the theoretically predicted (D_o = 20.0 kcal/mol) and experimentally observed (D_o = 25 ± 2 kcal/mol)[24] values for the first CO dissociation energy of $[\mathrm{Ni(CO)_4}]$ shows that the calculated bond energies for $[\mathrm{Ni(EMe)_4}]$ may be slightly too small. More important, however, is the trend of the bond energies. The calculations predict that the gallium complex $[\mathrm{Ni(GaMe)_4}]$ has a slightly weaker Ni−E bond than the indium complex $[\mathrm{Ni(InMe)_4}]$ (D_o = 43.4 kcal/mol). The Tl compound $[\mathrm{Ni(TlMe)_4}]$ has a significantly weaker bond (D_o = 27.0 kcal/mol), and it will be more difficult to isolate. The Ni−E bond of the aluminum complex $[\mathrm{Ni(AlMe)_4}]$, however, is clearly stronger (D_o = 53.2 kcal/mol). The strongest Ni−E bond is calculated for the boron complex $[\mathrm{Ni(BMe)_4}]$ (D_o = 79.7 kcal/mol). Previous studies indicate, however, that boron compounds are particularly sensitive to the degree of p(π) saturation. The recently isolated first borylene complexes with terminal BR ligands have strong π donor groups (R = Cp*,[25] $\mathrm{N(SiMe_3)_2}$[26]) as substituents.

Table 2 shows the results of the CDA and NBO analysis. The CDA data clearly indicate that the Ni→EMe π back-donation significantly contributes to the Ni−ER interactions in $[\mathrm{Ni(EMe)_4}]$. The *b*/*d* ratio varies only slightly between 0.68 for E = Ga and 0.78 for E = Tl. This means that the contributions of the π bonding to the metal−ligand interactions in $[\mathrm{Ni(EMe)_4}]$ are even higher than in $[\mathrm{Ni(CO)_4}]$, which has a *b*/*d* ratio of only 0.46. This can be explained by the nature of the acceptor orbitals of E, which are empty p(π) AOs. Without significant nickel→EMe π back-donation in $[\mathrm{Ni(EMe)_4}]$ there would only be an electron quartet in the valence shell of E, which is a very unlikely description for a stable group 13 compound. A similar bonding situation exists in the recently synthesized $[\mathrm{(CO)_4Fe(GaR)}]$,[27] which has an aryl group R as substituent. We want to point out, however, that the metal−ligand bonds in these complexes have a large ionic character.[28,29]

Table 2. Results of the CDA and NBO Analyses of $[\mathrm{Ni(EMe)_4}]$ and $[\mathrm{Ni(CO)_4}]$[a]

	d	*b*	*b*/*d*	*r*	$p_{x,y}$(E)	p_z(E)
$[\mathrm{Ni(BMe)_4}]$	0.670	0.482	0.72	−0.272	0.39 (0.02)	0.73 (0.71)
$[\mathrm{Ni(AlMe)_4}]$	0.597	0.461	0.77	−0.199	0.31 (0.01)	0.33 (0.37)
$[\mathrm{Ni(GaMe)_4}]$	0.604	0.410	0.68	−0.242	0.26 (0.01)	0.34 (0.39)
$[\mathrm{Ni(InMe)_4}]$	0.526	0.384	0.73	−0.234	0.27 (0.01)	0.30 (0.38)
$[\mathrm{Ni(TlMe)_4}]$	0.470	0.368	0.78	−0.153	0.21 (0.01)	0.30 (0.39)
$[\mathrm{Ni(CO)_4}]$	0.439	0.201	0.46	−0.220		

[a] Definitions: *d*, donation Ni←L; *b*, back-donation Ni→L; *r*, repulsive polarization Ni↔L; *p*(E), occupation of the p AO's in E. The Ni−E bond lies on the *z* axis; values in parentheses give the occupation in the free ligands EMe.

The NBO analysis also predicts a significant π contribution to the Ni−EMe bonding in $[\mathrm{Ni(EMe)_4}]$. Table 2 shows that the p(π) orbitals of E, which are nearly empty in free EMe, become significantly occupied in the complexes. We want to point out that the p(π) population agrees nicely with the trend of the calculated Ni−EMe bond energies (Table 1). The same trend B > Al > Ga ≈ In > Tl has also been found for the bond energies of other group 13 diyl complexes.[29]

In summary, there are two conclusions which arise from the theoretical calculations. (1) The complexes $[\mathrm{Ni(EMe)_4}]$ have rather high Ni−EMe bond dissociation energies. (2) The Ni−EMe bonds have significant contributions from Ni→EMe π back-donation.

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Supporting Information Available: Tables of atomic coordinates, isotropic and anisotropic displacement parameters, and all bond lengths and angles for **3** and **1**. This material is available free of charge via the Internet at http://pubs.acs.org. Further details of the crystal structure determinations are available from the Cambridge Crystallographic Data Center on quoting the depository numbers CCDC-114211 (**3**) and CCDC-114212 (**1**).

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(21) (a) The CDA (charge decomposition analysis) decomposes the wave function or the Kohn−Sham determinant of a complex [ML] in terms of fragment orbitals of the chosen ligand L and the metal fragment [M]. The [M]←L donation *d* is then given by the mixing of the occupied orbitals of L and vacant orbitals of [M]. The [M]→L back-donation *b* is given by the mixing of the occupied orbitals of [M] and vacant orbitals of L. Mixing of occupied orbitals of both fragments gives the repulsive polarization *r*: Dapprich, S.; Frenking, G. *J. Phys. Chem.* **1995**, *99*, 9352. (b) Frenking, G.; Pidun, U. *J. Chem. Soc., Dalton Trans.* **1997**, 1653.

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