Inorg. Chem. **2008**, *47*, 11398−11404

Inorganic Chemistry
Article

2,2,6,6-Tetramethylpiperidinogallium as a Terminal and Bridging Ligand in Homo- and Heteroleptic Chromium, Nickel, and Cobalt Complexes

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Received July 31, 2008

By reaction of the gallium(I) derivative Ga_4tmp_4 (tmp = 2,2,6,6-tetramethylpiperidino) with $Cr(CO)_5$(*cyclo*-octene), $Co_2(CO)_8$, and Ni(cyclooctadiene)$_2$, respectively, the Gatmp complexes [$Cr(CO)_5$Gatmp], $(CO)_3Cr(\mu^2\text{-Gatmp})_3Cr(CO)_3$, $(CO)_3Co(\mu^2\text{-Gatmp})_2Co(CO)_3$, and $(tmpGa)_2Ni(\mu^2\text{-Gatmp})_3Ni(Gatmp)_2$ were obtained. The latter are described as derivatives of the binuclear metal carbonyls $Cr_2(CO)_9$, $Co_2(CO)_8$, and $Ni_2(CO)_7$, where some or all carbonyls are replaced by the amino gallylene group. All compounds are characterized by spectroscopy and crystal structure analysis. The change of the bonding situation from localized two-center gallium metal bonds in the chromium derivative to three-center bonds in the cobalt complex is discussed by means of density functional theory calculations.

Introduction

The chemistry of low-valent gallium compounds has gained broad interest during the last years.[1−3] Gallium(I) derivatives tend to aggregate to cluster compounds. With bulky substituents, dimer and even monomer species could be stabilized, i.e., Ga_2Aryl_2 [Aryl = 2,6-(2,6-$^iPr_2C_6H_3)_2$-C_6H_3],[4] Ga{(2,6-$^iPr_2C_6H_3$)NC(CH_3)}$_2$CH,[5] and GaN($SiMe_3$)-(2,6-$Mes_2C_6H_3$).[6] GaCp*[7−9] is a hexamer in the solid state but a monomer in solution and the gas phase. Because of the lone pair and the empty π-type p orbitals, GaCp* and other GaR derivatives [R = C($SiMe_3)_3$, Si($SiMe_3)_3$] are considered as CO analogue ligands.[8,10−13] Recently, even a complex with GaI as a ligand was prepared.[14] Here, the biatomic ligand GaI allows one to best compare CO and gallylenes. The cationic complex $[(Cp^*Ga)_4Rh(GaCH_3)]^+$ [15] demonstrates that this chemistry is not confined to bulky substituents. Even naked Ga^+ ions can act as ligands.[16] Heterocyclic gallylenes are useful ligands also,[17] and those complexes have been studied as analogues to diboration catalysts.[18]

The gallylenes act as terminal and bridging ligands. This area has been reviewed several times.[3,19−21] The degree of M−Ga π back-bonding in transition-metal gallylene complexes is still under discussion and is dependent on the nature of R and M.[16] Contrary to CO, the GaR ligands are

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10.1021/ic801437n CCC: $40.75

Table 1. Crystallographic Data for **2**−**5**

	2	**3**	**4**	**5**
empirical formula	$C_{14}H_{18}CrGaNO_5$	$C_{33}H_{54}Cr_2Ga_3N_3O_6$	$C_{24}H_{36}Co_2Ga_2N_2O_6$	$C_{63}H_{126}Ga_7N_7Ni_2$
M_r (g mol^{-1})	402.01	901.95	705.85	1587.17
temperature (K)	200	200	200	200
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$	$P2_1$	$C2/c$
a [pm]	1104.8(2)	1055.4(2)	967.1(2)	6128.1(6)
b [pm]	1243.2(3)	3915.0(8)	1062.9(2)	1316.4(2)
c [pm]	1279.7(3)	1015.0(2)	1465.5(3)	3155.9(4)
β [deg]	95.78(3)	103.09(3)	96.64(3)	116.24(3)
V [Å^3]	1748.7(6)	4085.0(14)	1496.2(5)	22835(8)
Z	4	4	2	12
ρ_{calcd} [g cm^{-3}]	1.527	1.467	1.567	1.385
μ [mm^{-1}]	2.181	2.509	2.908	2.958
F(000)	816	1848	716	9912
2θ range [deg]	3−48	4−48	4−48	3−48
index range	±12, ±14, ±14	±12, ±44, ±11	±11, ±12, ±16	±70, ±14, ±35
no. of param	203	238	333	1114
reflns, collected	10 972	12 870	9615	71 435
reflns, unique	2614 (R_{int} = 0.070)	3179 (R_{int} = 0.075)	4669 (R_{int} = 0.098)	17872 (R_{int} = 0.13)
reflns [$I > 2\sigma(I)$]	1900	2401	4211	10 831
GOF on F^2	0.920	0.891	0.992	0.842
final R indices [$I > 2\sigma(I)$]^a	R1 = 0.044, wR2 = 0. 100	R1 = 0.036, wR2 = 0.089	R1 = 0.040, wR2 = 0.105^b	R1 = 0.049, wR2 = 0.111
R indices (all data)	R1 = 0. 062, wR2 = 0.109	R1 = 0.051, wR2 = 0.094	R1 = 0.045, wR2 = 0.108	R1 = 0.085, wR2 = 0.123
min/max res. el. density [e Å^{-3}]	1.18/−0.92	0.76/−0.59	0.92/−0.95	1.15/−0.98

^{a} R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$; wR2 = $[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. ^{b} Flack parameter: −0.02(2).

predominantly σ-donor ligands.[22] Fe(CO)$_4$GaAryl′[23] [Aryl′ = 2,6-bis(2,4,6-triisopropylphenyl)phenyl)] has a very short Ga−Fe bond. The Ga−Fe bond in Fe(CO)$_4$GaCp*[8] is longer, which was explained by the higher coordination number and blocking of the p orbitals at the gallium atom. In the coordination chemistry of borylenes, it was demonstrated that the nature of R [^{t}Bu, N(SiMe$_3$)$_2$ has a large influence on the M−B bond.[24,25]

The synthesis of transition-metal complexes with GaR ligands can be accomplished in several ways.[3,19−21] These include (a) substitution of CO or labile ligands like alkenes of transition-metal complexes by gallium(I) derivatives, (b) reaction of carbonyl metallates with gallium(II) and gallium(III) halide derivatives, and (c) insertion of metal fragments into Ga−Ga bonds. Starting from GaCp*, the complexes Co$_2$(CO)$_6$(μ^2-GaCp*)$_2$,[8] Ni$_4$(μ^2-GaCp*)$_4$(CO)$_6$,[8] Cr(CO)$_5$GaCp*,[8] and Fe(CO)$_5$GaCp*[8] with bridging and terminal GaCp* units have been prepared via pathway a, for example. Using [GaC(SiMe$_3$)$_3$]$_4$,[26] Fe$_2$(CO)$_6${μ^2-GaC(SiMe$_3$)$_3$}$_3$[12,13] and the remarkable homoleptic complex Ni{GaC(SiMe$_3$)$_3$}$_4$[12,27] have been synthesized. The series of cluster compounds Fe$_2$(CO)$_{9-x}${μ^2-GaSi(SiMe$_3$)$_3$}$_x$[11] (x = 1−3) and Fe(CO)$_4$GaAryl[23] demonstrate the utility of pathway b.

Here, we describe the use of Gatmp as the ligand starting from the tetramer cluster Ga$_4$tmp$_4$.[28] The bonding of this ligand to transition-metal fragments is discussed in comparison with gallium organyl ligands.

Experimental Section

All procedures were performed under purified argon or in vacuum using Schlenck techniques. Starting materials were prepared according to the literature [**1**[28] and Cr(CO)$_5$(cyclooctene)[29]] or were used as purchased. IR spectra were recorded from a benzene-d_6 solution on a Perkin-Elmer Spectrum 100 FTIR spectrometer. Elemental analyses were done in the microanalytical laboratory of the Insitute of Inorganic Chemistry, University of Heidelberg, Heidelberg, Germany. Mass spectra (electron impact, EI; for m/z, the most intense peak of the isotopic pattern is reported) were recorded on a Finnegan MAT3830 machine. NMR spectra were recorded on a Bruker Advance II 400 instrument. X-ray crystallography: suitable crystals were mounted with a perfluorated polyether oil on the tip of a glass fiber and cooled immediately on the goniometer head. Data collection was performed on a STOE IPDS I diffractometer with Mo Kα radiation (λ = 0.710 73 Å). Structures were solved and refined with the Bruker AXS *SHELXTL 5.1* program package. Refinement was in full matrix against F^2. All hydrogen atoms were included as riding models with fixed isotropic U values in the final refinement. For further data, refer to Table 1. Quantum chemical calculations: All DFT calculations have been performed with the *TURBOMOLE* package[30,31] using an RI approximation with a BP86 functional and a def-SV(P) basis.

Synthesis of 2 and 3. A total of 0.43 g (0.47 mmol) of Ga$_4$tmp$_4$·THF (**1**) was dissolved in 30 mL of a toluene/n-hexane mixture (1:2). This solution was added to 0.58 g (1.9 mmol) of Cr(CO)$_5$(cyclooctene), and the reaction mixture was heated to 80 °C for 1 h. During this time, the solution turned dark blue. After cooling to room temperature, all volatiles were removed in vacuum.

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Table 2. IR Data (Carbonyl Region) of Gatmp Complexes **2**−**4** and Related Compounds (Experimental[a] and Calculated Values)[b]

		CO stretching vibrations [cm^{-1}][c]
$(CO)_5CrGatmp$	**2**	2019 (s, $\nu_s(CO)_4$), 1980 (w, $\nu(CO)_4$), 1924 (sh, $\nu(CO)_{ax}$), 1883 (vs, $\nu_{as}(CO)_4$)
$(CO)_3Cr(Gatmp)_3Cr(CO)_3$	**3**	2021, 1987, 1895
$(CO)_5CrGaNMe_2$	**6**	*2080* (s, $\nu_s(CO)_4$), *2011* (w, $\nu(CO)_4$), *2008* (s, $\nu(CO)_{ax}$), *1992* (vs, $\nu_{as}(CO)_4$)
$(CO)_5CrGaMe$	**7**	*2076* (s, $\nu_s(CO)_4$), *2011* (w, $\nu(CO)_4$), *2006* (s, $\nu(CO)_{ax}$), *1990* (vs, $\nu_{as}(CO)_4$)
$(CO)_5CrGaCp^*$[8]		2052 (s, $\nu_s(CO)_4$), 1982 (w, $\nu(CO)_4$), 1918 (sh, $\nu(CO)_{ax}$), 1902 (vs, $\nu_{as}(CO)_4$)
$(CO)_5CrGa(2,5\text{-}^tBuC_4H_2P)$[32]		2022 (s, $\nu_s(CO)_4$), 1936 (sh, $\nu(CO)_{ax}$), 1870 (vs, $\nu_{as}(CO)_4$)
$(CO)_5CrGaCp$	**8**	*2080* (s, $\nu_s(CO)_4$), *2009* (w, $\nu(CO)_4$), *1999* (s, $\nu(CO)_{ax}$), *1987* (vs, $\nu_{as}(CO)_4$)
$(CO)_5CrGaMe(tmeda)$[33]		2013, 1920, 1844
$(CO)_5CrGaCl(tmeda)$[34]		2033, 1944, 1900
$(CO)_3Co(Gatmp)_2Co(CO)_3$	**4**	2046, 2007, 1974, 1863
$(CO)_3Co(GaCp^*)_2Co(CO)_3$[8]		2023, 1989, 1953, 1948

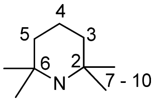
[a] In benzene-d_6 as the solvent. [b] RI-DFT, BP86 functional, def-SV(P) basis. [c] ax: ligand trans to GaR. ν_{as}: asymmetric vibrational mode.

The residue was extracted twice with 10 mL of *n*-hexane. From this solution, dark-blue crystals of **3** (0.40 g, 70%) precipitated upon cooling to −30 °C. The mother liquor was reduced in volume, and colorless crystals of **2** (0.16 g, 21%) were obtained at −30 °C.

2. ^1H NMR (C_6D_6): δ 1.26 (m, 4 H, H-3,5), 1.04 (s, 12 H, H-7−10), 0.90 (m, 2 H, H-4). ^{13}C NMR (C_6D_6): δ 223.0 ($(CO)_{ax}$), 217.8 (CO), 55.7 (C-2,6), 39.1 (C-3,5), 33.7 (C-7−10), 18.2 (C-4). MS (70 eV, EI): *m/z* (%) 401 ($M^{\bullet+}$, 50), 373 ($[M - CO]^{\bullet+}$, 5), 345 ($[M - 2CO]^{\bullet+}$, 8), 317 ($[M - 3CO]^{\bullet+}$, 10), 289 ($(M - 4CO]^{\bullet+}$, 25), 261 ($[M - 5CO]^{\bullet+}$ or $[M - tmp]^+$, 75), 209 ($[Gatmp]^{\bullet+}$, 51), 177 ($[Cr(CO)_2Ga]^+$, 100). IR (C_6D_6, CsBr plates, cm^{-1}): 2019 (m), 1987 (w), 1924 (sh), 1883 (b). Anal. Calcd for $C_{14}H_{18}NCrGaO_5$ (402.01): C, 40.82; H, 4.51; N, 3.48. Found C, 41.01; H, 4.63; N, 3.36.

3. ^1H NMR (C_6D_6): δ 1.26 (m, 4 H, H-3,5), 1.06 (s, 12 H, H-7−10), 0.91 (m, 2 H, H-4). ^{13}C NMR (C_6D_6): δ 216.5 (CO), 53.8 (C-2,6), 40.4 (C-3,5), 34.5 (C-7−10), 18.2 (C-4). IR (C_6D_6, CsBr plates, cm^{-1}): 2021 (s), 1987 (m), 1895 (b), 1466 (s), 1378 (s). Anal. Calcd for $C_{33}H_{54}N_3Cr_2Ga_3O_6$ (901.95): C, 43.94; H, 6.02; N, 4.65. Found C, 43.55; H, 5.36; N, 4.35.

The following is the numbering scheme for tmp groups:



Synthesis of 4. A total of 0.42 g (0.45 mmol) of **1** was dissolved in 15 mL of *n*-hexane, and the solution was cooled to 0 °C. A total 0.31 g (0.9 mmol) of $Co_2(CO)_8$ dissolved in *n*-hexane was added. This solution was allowed to warm up to room temperature within 90 min and stirred for an additional 1 h. The color changed from dark violet to orange during this time. The solution was concentrated to a volume of 5 mL in vacuum. Upon cooling to −30 °C, orange crystals of **4** (0.38 g, 60%) were obtained.

^1H NMR (C_6D_6): δ 1.40 (m, 2 H, H-4), 1.33 (s, 12 H, H-7−10), 1.14 (t, 4 H, H-3,5). ^{13}C NMR (C_6D_6): δ 55.4 (C-2,6), 39.6 (C-4), 34.1 (C-7−10), 18.3 (C-4). IR (C_6D_6, CsBr plates, cm^{-1}): 2046 (w), 2007 (s), 1974 (b), 1863 (w), 1618 (s), 1453 (s), 1330 (s), 1162 (s). Anal. Calcd for $C_{24}H_{36}N_2Co_2Ga_2O$ (705.85): C, 40.83; H, 5.13; N, 3.96. Found: C, 41.44; H, 5.71; N, 3.62.

Synthesis of 5. A total of 0.14 g (0.51 mmol) of Ni(cyclooctadiene)$_2$ was dissolved in 10 mL of a toluene/*n*-hexane mixture (1:1), and the solution was cooled down to 0 °C. A total of 0.22 g (0.23 mmol) of **1** dissolved in 20 mL of a toluene/*n*-hexane mixture (1:1) was added. After warming to room temperature, the mixture was heated for 1 h to 60 °C. The color changed to dark brown. All of the volatiles were removed in vacuum at room temperature. The oily residue was dissolved in *n*-hexane. Upon storage at 4 °C, black crystals of **5** (0.05 g, 23%) were isolated.

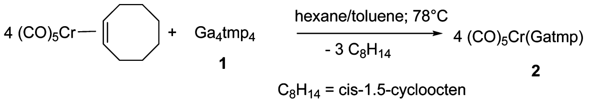
^1H NMR (C_6D_6): δ 1.72 (s, 84 H, H-7−10), 1.49 (m, 42 H, H-3,5), 1.24 (m, 14 H, H-4). ^{13}C NMR (C_6D_6): δ 55.5 (C-2,6), 40.6 (C-3,5), 34.2 (C-7−10), 19.2 (C-4).

Results and Discussion

Synthesis. In a hexane solution, Ga_4tmp_4 (**1**) and $Cr(CO)_5(C_8H_{14})$ react upon heating to form complexes **2** and **3** (eqs 1a and 1b). This means that not only *cis*-cyclooctene but also CO are exchanged under these conditions.

If $Co_2(CO)_8$ is used (eq 2), evolution of CO is observed already at 0 °C. The reaction completes at ambient temperatures within 1 h, and **4** is obtained. If the mixture is heated to 80 °C, the ligand Gatmp is cleaved and $Co_4(CO)_{12}$ is formed.

The homoleptic dinuclear complex **5** (eq 3) is synthesized by the reaction of Ni(1.5-cyclooctadiene)$_2$ with **1** at 60 °C. Only if the nickel complex is used in excess is **5** formed in notable amounts.



(1a)

$$2\ (CO)_5Cr(Gatmp) \xrightarrow[-\ 4\ CO]{+\ Gatmp} Cr_2(CO)_6(Gatmp)_3 \qquad (1b)$$

2 **3**

$$2\ Co_2(CO)_8 \ +\ Ga_4tmp_4 \xrightarrow[-\ 4\ CO]{hexane} 2\ Co_2(CO)_6(Gatmp)_2 \qquad (2)$$

1 **4**

$$8\ Ni(COD)_2 \ +\ 7\ Ga_4tmp_4 \xrightarrow[-\ 16\ COD]{hexane/toluene;\ 60\ °C} 4\ Ni_2(Gatmp)_7 \qquad (3)$$

1 **5**

COD = 1.5-cyclooctadiene

Spectroscopic Characterization. The ^1H and ^{13}C NMR spectra of **2** and **3** show single sets of signals for the tmp groups. The carbonyl carbon atoms in **2** give rise to two signals at δ 217.8 [$(CO)_4$] and 223.0 ($(CO)_{ax}$). For **3**, only one resonance for the carbonyl carbon atoms (δ 216.5) is observed. This is similar for the tmp signals of **4**, but the CO signals could not be observed in this case. The ^1H and ^{13}C NMR spectra of **5** show only one set of signals for the tmp groups. This indicates that **5** is not retained as a rigid bridged molecule in solution.

The IR spectrum of **2** exhibits four C−O stretching vibrations for the carbonyl groups at 2019, 1980, 1924, and

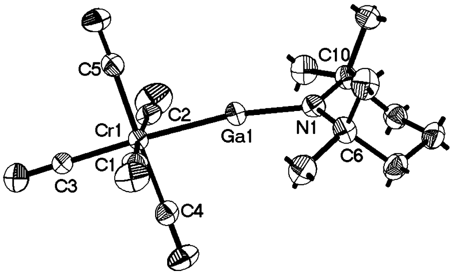


Figure 1. Molecular structure of **2**. The thermal ellipsoids are given at the 30% probability level. Selected bond lengths [pm] and angles [deg]: Cr1−Ga1 237.4(1), Ga1−N1 184.2(3), Cr1−C1 189.7(5), Cr1−C2 191.5(6), Cr1−C3 188.7(4), Cr1−C4 190.2(6), Cr1−C5 191.3(6); Cr1−N1−Ga1 170.1(1), C6−N1−C10 120.3(4), Ga1−Cr1−C3 176.2(3).

1883 cm^{-1}. For complex **3**, these are observed at 2021, 1987, and 1845 cm^{-1}. These are at similar wavenumbers compared to other Cr(CO)$_5$GaR complexes (see Table 2). In the IR spectrum of **4**, four bands are observed in the carbonyl region. Compared with Co$_2$(CO)$_6$(GaCp*)$_2$,[8] they are shifted to higher wavenumbers.

If π back-bonding from the chromium atom to the gallium ligand is assumed, the axial carbonyl vibration should be affected most. In **2**, it is observed at 1924 cm^{-1}. Compared to the corresponding GaCp*,[8] Ga(2,5-^{t}BuC$_4$H$_2$P),[32] and GaX(tmeda)[33,34] (X = Cl, Me) complexes, no markable shift is observed. Calculated vibrations for model compounds **6**−**8** give the same trend but are all shifted to higher wavenumbers. This would mean that a GaNR$_2$ ligand should be a σ donor only. Computational studies[35] showed GaR ligands to be much worse π-acceptor ligands than CO. [36] It was stated before[22] that a discussion on grading of the π-back-bonding abilities of ligands on the basis of wavenumbers is not unambiguous because of the effects of polarization. However, it can be concluded at this point that terminal Gatmp groups seem to be bad π-acceptor ligands, but as bridging ligands, this ability might be improved, especially if no CO ligands are present.[36]

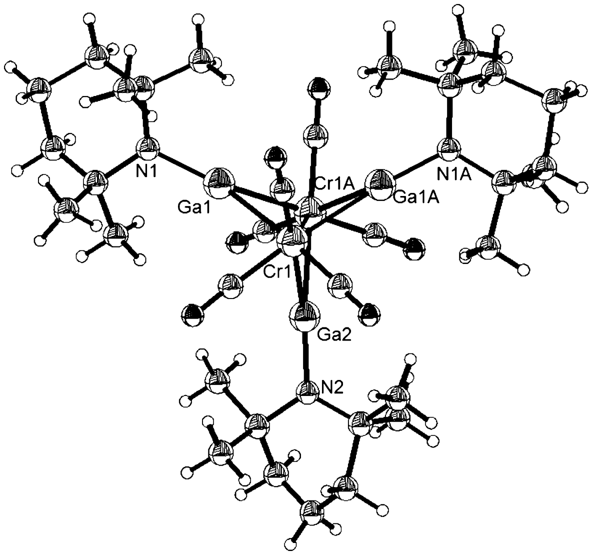


Figure 2. Molecular structure of **3**. The thermal ellipsoids are given at the 30% probability level. Selected bond lengths [pm] and angles [deg]: Cr1−Cr1 245.8(1), Ga1−Cr1 248.43(9), Ga1−Cr1A 248.75(8), Ga2−Cr1 248.99(8), Ga2−Cr1A 248.99(8), Ga1−N1 182.8(3), Ga2−N2 182.7(5), Cr1−C1 186.7(4), Cr1−C2 187.0(4), Cr1−C3 187.0(5); Cr1−Ga1−Cr1A 59.26(2), Cr1−Ga2−Cr1A 59.16(2), Cr1−Ga1−N1 153.5(1), Cr1A−Ga1−N1 147.2(1), Cr1−Ga2−N2 150.4(2).

Crystal Structure Determination. 2 is obtained as colorless crystals, space group $P2_1/c$ (Table 1). The chromium atom in **2** (Figure 1) is coordinated octahedrally by five CO ligands and a Gatmp ligand. The Ga−Cr distance is 237.4(1) pm. This is shorter than those in Cr(CO)$_5$GaCp*[8] [$d_{\mathrm{Ga-Cr}}$ = 240.47(7) pm] and (CO)$_5$CrGaX(tmeda)[33,34] complexes [245.6(1) pm, X = Cl; 247.9(1) pm, X = CH$_3$]. The Cr−C distances vary from 188.7(5) to 191.4(6) pm, where the CO ligand in the trans position to Gatmp [further called (CO)$_{\mathrm{ax}}$] has the shortest Cr−C bond. Compared with the GaCp* complex the axial CO ($d_{\mathrm{Cr-C}}$ = 186.9 pm) has a longer Cr−C distance. This hints to a better π back-bonding from chromium to carbon in the corresponding GaCp* complex and thus a weaker Cr−Ga π bonding. The Ga−N bond [$d_{\mathrm{Ga-N}}$ = 184.2(4) pm] is shortened compared to **1** ($d_{\mathrm{Ga-N}}$ = 188.5 pm). This is in line with the nearly coplanar arrangement of the NC$_2$ plane and the line C1−Cr1−C2.

In **3**, crystallizing in dark-blue prisms of the monoclinic system, space group $C2/c$, three Gatmp groups bridge two Cr(CO)$_3$ units (Figure 2). The molecule lies on a 2-fold axis. The tmp group belonging to Ga2 shows disorder of the carbon atoms. This was modeled using split positions with occupational factors of 0.5 for the carbon atoms. The Cr(CO)$_3$ units are in an eclipsed conformation. The Ga−Cr distances [$d_{\mathrm{Ga-Cr}}$ = 248.43(8)−248.99(9) pm] are longer than those in **2**, as expected. The Ga−N bonds [$d_{\mathrm{Ga-N}}$ = 182.8(3) pm] are even shorter than those in **2**. This does not imply an increased Ga−N π bond. A weak Cr−Ga π back-bonding is in line with short Cr−C bonds [$d_{\mathrm{Cr-C}}$ = 186.7(5)−187.0(5) pm]. The Cr1−Ga−Cr2 and Ga−Cr−Ga bond angles are nearly equal (60 ± 1°). In other complexes with bridging GaR units, like (CO)$_3$Fe(GaR′)$_3$Fe(CO)$_3$ [R′ = Si(SiMe$_3$)$_3$],[11] the M−Ga−M angles (approximately 74°) and Ga−M−Ga angles (approximately 87°) are wider. The lone pair of GaR is slightly antibonding[37] regarding the Ga−N bond. Upon coordination to a metal fragment, this orbital should be slightly depopulated and thus the Ga−N bond is shortened. These more obtuse angles are in line with the idea of three-center interactions, while the even more acute angles in **3** hint to more individual ligand−chromium interactions. This has been discussed for Cr$_2$(CO)$_9$ also.[38] The ground state of Cr$_2$(CO)$_9$ is unsymmetrically bridged. **3** might be viewed upon as an isolobal derivative of hypothetical Cr$_2$(CO)$_9$, for which by DFT calculations a Cr≡Cr triple bond ($d_{\mathrm{Cr-Cr}}$ 230

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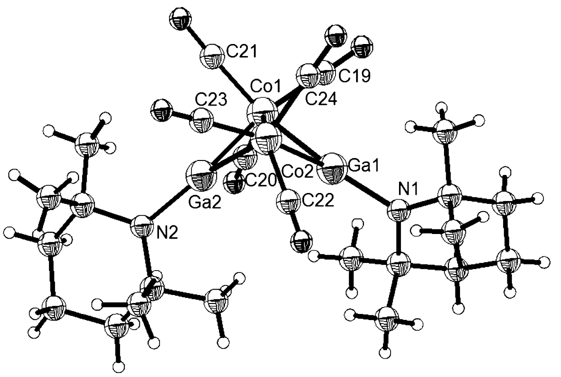

Figure 3. Molecular structure of **4**. The thermal ellipsoids are given at the 30% probability level. Selected bond lengths [pm] and angles [deg]: Co1−Co2 283.6(1), Ga1−Co1 234.7(1), Ga1−Co2 239.1(1), Ga2−Co1 235.4(1), Ga2−Co2 236.0(1), Ga1−N1 185.2(6), Ga2−N2 183.8(5), Co1−C19 179.3(8),Co1−C21 179.2(8);Co1−Ga1−Co2 73.54(3),Co1−Ga2−Co2 73.98(4), Co1−Ga1−N1 145.0(2), Co2−Ga1−N1 141.5(2), Co1−Ga2−N2 142.8(2), Co2−Ga2−N2 143.0(2), C1−N1−C5 120.2(5).

pm) was established. The Cr−Cr distance in **3** [d_{Cr-Cr} = 245.8(1) pm] is longer, which is due to the longer Ga−Cr bonds in **3** compared to the C−Cr bonds in $Cr_2(CO)_9$. Nevertheless, the eclipsed conformation hints to qualitatively similar but weaker interactions between the chromium atoms in $Cr_2(CO)_9$. The Gatmp groups bridge the Cr_2 core symmetrically. This might be due to the bulky tmp groups. A symmetric bridging is observed in $Fe_2(CO)_9$ and its gallium derivatives, i.e., $(CO)_3Fe\{\mu^2\text{-GaSi(SiMe}_3)_3\}Fe(CO)_3$ also.

Yellow crystals of **4** were obtained, and the structure was solved in the monoclinic space group $P2_1$. **4** (Figure 3) is best described as a derivative of $Co_2(CO)_8$, where the bridging CO ligands are substituted for [μ^2-Gatmp] units. The Co1−Co2 distance [d_{Co-Co}=283.6(1) pm] is elongated by 30 pm compared to $Co_2(CO)_8$. This is similar to the values observed for $(CO)_3Co(\mu^2\text{-GaCp*})_2Co(CO)_3$[8] ($d_{Co-Co}$= 282.7 pm) and $(CO)_3Co\{\mu^2\text{-InC(SiMe}_3)_3\}_2Co(CO)_3$[39] ($d_{Co-Co}$ = 280.1 pm). Ga2 bridges the two cobalt atoms symmetrically [d_{Ga-Co} = 235.4(1) and 236.0(1) pm], while the Ga1 bridge is unsymmetrical [d_{Ga-Co} = 234.7(1) and 239.1(1) pm]. The Ga−N bonds (d_{Ga-N} = 184.5 pm on average) are similar to those in **2**. The Co_2Ga and NC_2 planes intersect at angles of 59 and 69°, which is in line with steric requirements. The $Co(CO)_3$ groups are in a staggered conformation. The Co_2Ga planes intersect at an angle of 71°, which allows the bulky aminogallylene groups enough space. The bond angles at the gallium atoms are 73.8° on average. This is a wider angle than that observed in **3** and might be a clue to a three-center bonding description. For a more detailed discussion, see the Quantum Chemical Calculations section of this paper.

5 (Figure 4) is isolated as black crystals of the monoclinic system, space group $C2/c$ with $Z = 12$. That means that two independent molecules of **5** are in the asymmetric unit. One of them has crystallographic 2-fold symmetry and shows disorder of the tmp group, whose nitrogen atom is on this axis. Regardless of this symmetry restriction, both molecules have very similar bond parameters. Here only the complete molecule is discussed. **5** is a homoleptic complex built by two nickel atoms and seven Gatmp groups. Three of the ligands bridge a Ni_2 core; four are ligated in a terminal mode. The Ni−Ni distance is 252.2(1) pm. The terminal Gatmp groups have Ga−Ni distances of 220.0 pm on average. Of the bridging ones, only one Gatmp group is bridging symmetrically [d_{Ga5-Ni} = 234.5(1) and 236.01(1) pm]; the others are shifted from the center to one or the other nickel atom (d_{Ga-Ni} = 228.2 and 245.0 pm).

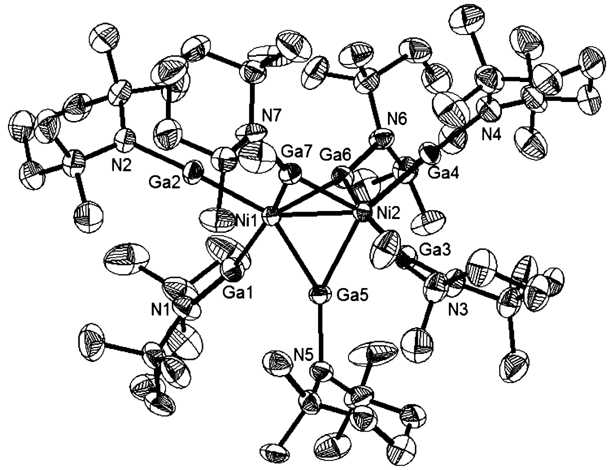

Figure 4. Structure of one independent molecule of **5**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are given at the 30% probability level. Selected bond lengths [pm] and angles [deg]: Ni1−Ni2 252.2(1), Ga1−Ni1 219.1(1), Ga2−Ni1 221.0(1), Ga3−Ni2 219.7(1), Ga4−Ni2 220.2(1), Ga5−Ni1 234.5(1), Ga5−Ni2 236.0(1), Ga6−Ni1 229.1(1), Ga6−Ni2 244.9(1), Ga7−Ni1 245.2(1), Ga7−Ni2 227.4(1), Ga1−N1 185.0(7), Ga2−N2 186.7(5), Ga3−N3 186.7(7), Ga4−N4 186.6(6), Ga5−N5 190.4(5), Ga6−N6 191.3(3), Ga7−N7 188.4(5); Ga1−Ni1−Ga2 88.02(3), Ga3−Ni2−Ga4 88.13(4), Ni1−Ga5−Ni2 64.82(3), Ni1−Ga6−Ni2 64.18(3), Ni1−Ga7−Ni2 64.37(4), Ga5−Ni1−Ga6 93.69(3).

The homoleptic nickel complexes $Ni(GaR)_4$[12,27] possess terminal Ga−Ni bonds of comparable lengths [R = $C(SiMe_3)_3$, d_{Ga-Ni} = 217.00(4) pm; R = Cp*, d_{Ga-Ni} = 221.88(5) pm]. Thus, **5** has a different structure than that calculated for a hypothetical $Ni_2(CO)_7$, in which the minimum structure is a single-bridged one.[40] In **5**, the Ga−N distances of terminal (d_{Ga-N} = 186.2 pm) and bridging (d_{Ga-N} = 190.1 pm) Gatmp groups are longer than those in the chromium complexes **2** and **3**. Especially, the Ga−N bonds of the gallylene groups are elongated by 8 pm compared to **3** and are even longer than those in **1**. Similar to **3**, the C_2N planes are nearly orthogonal to the Ni_2Ga planes (angles between planes: 82−87°). This large discrepancy cannot be explained with different π-bond participation, obviously. For monomeric Gatmp, a Ga−N bond of 193 pm has been calculated. This long bond is explained by the effect of the lone pair at the gallium atom, which is slightly antibonding for the Ga−N bond. In **5**, this electron pair is involved in Ga−Ni bonds and should not cause a bond elongation. On the other hand, for tmp_2GaX derivatives, the Ga−N bond lengths were found to be dependent on the electronegativities of X and cover a range from approximately 182 to 192 pm.[41] Transferred to **3** and **5**, this would mean polar Cr−Ga and less polar Ni−Ga covalent bonds. This is in line with the calculated charges on the metal atoms (−1.78 at Cr

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Table 3. Selected Structural Data as a Result of RI-DFT Calculations with the BP86 Functional and def-SV(P) Basis Sets for **5**−**13**[a]

		M−Ga	Ga−N	M−C	M−M
$GaNMe_2$			190.9		
Gatmp			193.8		
$(CO)_5CrGaNMe_2$	**6**	234.0	184.4	186.4_{ax}, 189.2	
$(CO)_5CrGaMe$	**7**	231.7		187.2_{ax}, 189.0	
$(CO)_5CrGaCp$	**8**	240.3		185.2_{ax}, 188.9	
$(CO)_5CrCO$				190.2	
$(CO)_3Cr(GaNMe_2)_3Cr(CO)_3$	**9**	246.3	183.5	185.7	241.4
$(CO)_3Co(GaNMe_2)_2Co(CO)_3$	**10**	232.6−233.5	183.3	177.2	286.8
$Ni_2(GaNMe_2)_7$	**11**	terminal: 218.6, 219.3	186.4		249.7
		symmetrical bridge: 235.0, 234.2	186.8		
		235.0, 234.2			
		2 × unsymmetrical: 228.6, 238.7	186.8		
$Ni(GaNMe_2)_4$	**12**	219.0	187.0		
$Ni_2(Gatmp)_7$	**5**	terminal: 222.9	190.9		254.3
		symmetrical bridge: 234.5, 239.4	190.9		
		2 × unsymmetrical: 228.0, 248.8	190.9		
$(CO)_2Ni(GaNMe_2)_3Ni(CO)_2$	**13**	symmetrical bridge: 233.2, 233.8	184.8	177.8	271.9, $276.7_{(Ga-Ga)}$
		2 × unsymmetrical: 226.8, 264.0	184.7		

[a] ax: CO trans to GaR.

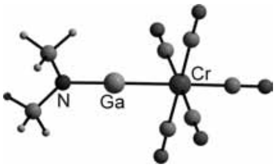

Figure 5. RI-DFT-calculated molecular structure of **6**.

and −0.39 at Ni; see below). On the other hand, bonds involving gallium atoms generally have a shallow potential surface,[42] which might mean that the sterical overload in **5** accounts for longer Ga−N bonds. Noteworthy for **5** are short Ga−Ga contacts. The terminal ligated gallium atoms are separated by only 305 pm; the shortest distance between terminal and bridging gallium atoms is 300.5 pm. This is longer than two-center, two-electron Ga−Ga bonds, which are in the range of 245 ± 10 pm, but comparable to long Ga−Ga interactions on the edges of subvalent gallium clusters.[1] In **5**, these short contacts might be due to the bulky ligands. For a more detailed discussion, see the Quantum Chemical Calculations section.

Quantum Chemical Calculations. To gain better insight into the different bonding modes of Gatmp as a ligand, several model compounds with $GaNMe_2$ groups as well as related compounds and **5** have been studied with DFT methods. For all optimization calculations, the RI-DFT method applying the Becke−Perdew functional with def-SV(P) basis sets for all atoms has been used (Table 3).

For $(CO)_5CrGaNMe_2$ (**6**; Figure 5), a Ga−Cr distance of 234.0 pm and a Ga−N distance of 184.4 pm are calculated. The $GaNMe_2$ plane is parallel to a $Cr(CO)_2$ line. Compared to the monomer $GaNMe_2$, the Ga−N bond is shortened by 6.5 pm. In $(CO)_5CrGaMe$ (**7**; $d_{Cr-Ga} = 231.7$ pm), the Cr−Ga bond is shorter by 2 pm and in $(CO)_5CrGaCp$ (**8**) longer by 6 pm. For $EN(SiH_3)_2$ complexes (E = B, Al, Ga), nearly no effect on the E−N bond was observed by quantum chemical calculations.[35] This might be due to the very polarized E−N bonds in $EN(SiH_3)_2$.[43]

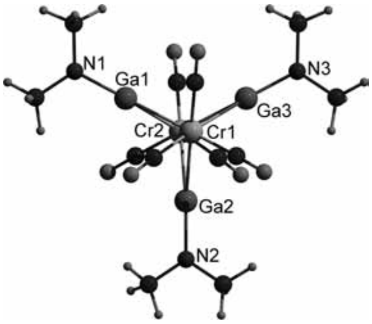

Figure 6. RI-DFT-calculated molecular structure of **9**.

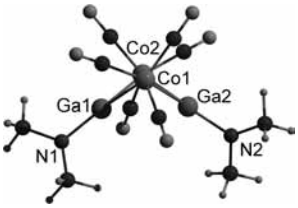

Figure 7. RI-DFT-calculated molecular structure of **10**.

If this is caused by various degrees of back-bonding, the respective axial carbonyl ligands should be influenced. Indeed, while the $Cr(CO)_4$ unit is nearly unaffected by the change of the GaR ligand, the $Cr-C_{ax}$ distance in **6** is longer by only 1 pm than that in **8** and shorter by 1 pm than that in **7**. $Cr(CO)_6$ has considerably longer Cr−C bonds, calculated on the same level. This is in line with an interpretation with only slightly increasing π-acceptor ability from GaCp* to GaMe. This assumption is supported by the calculated vibrational data also. Here **8** has the lowest wavenumber for the axial carbonyl vibration.

The dinuclear $GaNMe_2$ complexes **9**−**11** (Figures 6−8) have structural features that are in good agreement with those observed for **3**−**5**. In **9**, the Ga−Cr bonds of the symmetrically bridging $GaNMe_2$ groups are longer by 12 pm than those in **6**. The N_2C and Cr_2Ga planes are nearly orthogonal. Nevertheless, the Ga−N bonds ($d_{GaN} = 183.5$ pm) are slightly shortened compared to **6**.

In the cobalt complex **10**, the $GaNMe_2$ groups bridge two cobalt atoms nearly symmetrically also. Here, the N_2C planes are tilted by 58° and 68° to the $GaCo_2$ planes, respectively. The Co−Co distance is 45 pm longer than the Cr−Cr distance

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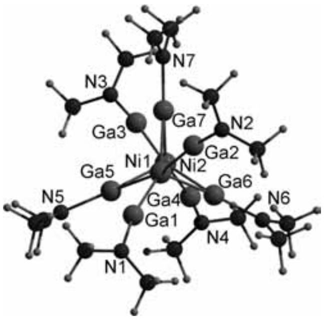

Figure 8. RI-DFT-calculated molecular structure of **11**.

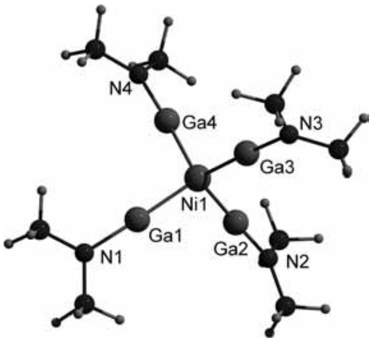

Figure 9. RI-DFT-calculated molecular structure of **12**.

in **9**. This means a weaker metal−metal interaction and as a consequence the M−Ga−M angles in **10** (Co−Ga−Co 73.8°) are more obtuse than those in **9** (Cr−Ga−Cr 59.2°). When the bonding situation is inspected by means of an Ahlrichs−Heinzmann population analysis,[44] the Cr−Cr bond is quite strong (shared electron number SEN 2.1), which is in line with a Cr≡Cr triple bond. The Co−Co interaction (SEN 0.87) is very weak. For a normal Co−Co single bond, an SEN of approximately 1.2 is expected. The wider M−Ga−M angles in **10** indicate a change in the bonding situation. The Cr−Ga−Cr interaction can be viewed as two-center two-electron bonds (SEN 1.30) with negligible three-center participation (3c-SEN < 0.2). In **10**, on the contrary, Co−Ga−Co three-center interactions are dominating (3c-SEN 0.45; 2c-SEN 1.46).

11 with terminal and bridging $GaNMe_2$ ligands has a short M−M distance also. The Ni−Ga−Ni angles are 64.5°, which is intermediate to **9** and **10**. One of the bridging $GaNMe_2$ groups is a symmetric bridge ligand and two are nonsymmetric. This is comparable to the experimentally determined and RI-DFT-calculated structure of **5**, regardless of the more bulky Gatmp ligands. The difference lies in the orientation of the NR_2 groups with respect to Ni_2Ga planes. With the bulky tmp groups, the N_2C and Ni_2Ga planes are nearly orthogonal; in **11**, these planes are nearly coplanar (interplane angles: 5°).

In the homoleptic mononuclear complex **12** (Figure 9), the Ga−Ni (d_{Ga-Ni} = 219.0 pm) and Ga−N (d_{GaN} = 187.0 pm) bonds are comparable to the terminal ones in **11** (d_{Ga-Ni} = 219.3 pm; d_{Ga-N} = 186.4 pm). In **12**, the central nickel atom is coordinated nearly ideally tetrahedral; in **11**, the nickel atoms have a coordination number of six. Some of the Ga−Ga distances in **11** are quite short. This means that the terminal and bridging gallium atoms have shortest contacts of 305 pm (d_{Ga-Ga} = 303−310 pm). This was observed for the more bulky substituted **5** also. The 2c-SEN (0.58−0.73) for these close contacts indicate only weak interactions, but there are strong three-center Ga−Ga−Ni interactions (3c-SEN 0.49). The terminal Ga−Ni bonds are tighter (SEN 1.78−1.92; indicated double bond) than the bridging ones (2c-SEN 1.42−1.53). Here, large three-center Ni_2Ga interactions (3c-SEN 0.39) indicate a delocalized bonding. The Ga−Ni bonds in **12** have an SEN of 2.0, which is in line with the lower coordination number compared to **11**. The M−Ga bond in **6** has an SEN of 1.5. This is weaker than that in the homoleptic nickel complexes because of the strong π-acceptor ligands, which make $GaNR_2$ solely a σ-donor ligand, while in **11** and **12**, Ni−Ga π-bond participation can be anticipated.

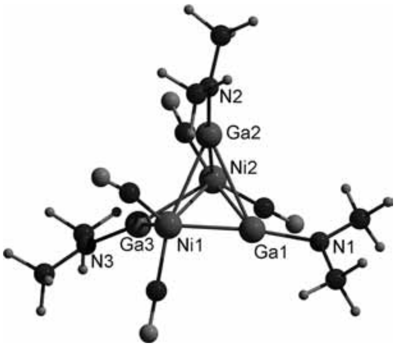

Figure 10. RI-DFT-calculated structure of **13**.

If the terminal $GaNMe_2$ ligands in **11** are substituted for CO, the structure changes to form the distorted tetrahedral Ni_2Ga_2 cluster **13** (Figure 10). Here, Ga3 is symmetrically bridging a Ni−Ni edge (d_{Ga-Ni} = 233.5 pm; 2c-SEN 1.42, 3c-SEN 0.49). Of the other two gallium atoms, each has a short (d_{Ga-Ni} = 226.8 pm) and a long (d_{Ga-Ni} = 264.0 pm) nickel contact, with large and small SEN, respectively (1.64 and 1.15).

Conclusion

By the reaction of **1** with transition-metal complexes with labile ligands, a series of complexes with the aminogallylene ligand Gatmp could be prepared. In addition to **2**, the binuclear complexes **3**−**5** as potential structural analogues to the carbonyl complexes $M_2(CO)_n$ (n = 7−9) were prepared. This is true for **3** and **4**, while the triply bridged structure observed for **5** is not the minimum structure for $Ni_2(CO)_7$. Structural, spectroscopic, and quantum-chemical data for these complexes indicate that $GaNR_2$ groups act as good σ-donor ligands. If no stronger π-acid ligand is present, the gallium atom may become a π acceptor also. Further work has to verify those complexes as potential sources for other gallium transition-metal derivatives and has to explore their reactivity, which will give further insight into bonding modes.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft for financial support. We also thank P. Butzug for assistance in collecting the data sets.

Supporting Information Available: X-ray crystallographic files in CIF format for compounds **2**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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