www.elsevier.nl/locate/jorganchem
Journal of Organometallic Chemistry 606 (2000) 132–140

Synthesis and structure of adduct stabilized Group III metal transition metal carbonyl complexes: new examples for Fe–Ga, Fe–In, W–Al, Cr–Al and Cr–Ga bonds

Holger Fölsing, Oliver Segnitz, Ursula Bossek, Klaus Merz, Manuela Winter, Roland A. Fischer *

Lehrstuhl für Anorganische Chemie II, Ruhr Universität Bochum, Universitaetsstraße 150, D-44780 Bochum, Germany

Received 21 January 2000; accepted 19 April 2000

Abstract

The carbonylmetallate dianions Fe(CO)$_4^{2-}$, Cr(CO)$_5^{2-}$ and W(CO)$_5^{2-}$ react in THF with the Group III halogenides EX$_3$ (E = Al, Ga, In; X = Cl, Br, I) and X$_2$ER (E = Al, Ga; X = Cl R = Me, ^{t}Bu). After the addition of chelating Lewis base [tmpda, pmdeta (tmpda = *N*,*N*,*N*′,*N*′-tetramethylpropylenediamine, pmdeta = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine)] and solvent exchange with dichloromethane, the primary products undergo a second salt elimination reaction, yielding the following complexes: [(CO)$_4$Fe–Ga(X)(tmpda)] (X = I, Me) (**1** and **2**), [(CO)$_n$M–Al(X)(tmpda)] (M = Fe, W; $n = 4$, 5; X = Cl, ^{t}Bu) (**3** and **4**), [(CO)$_4$Fe–In(Br)(tmpda)] (**5**), [(CO)$_5$Cr–E(Cl)(tmpda)] (E = Al, Ga) (**6** and **7**), [(CO)$_4$Fe–In(Br)(pmdeta)] (**8**) and cationic complex [(CO)$_4$Fe–Ga(pmdeta)]$^+$I$^-$ (**9**). The new compounds were fully characterized by means of elemental analysis, IR and NMR spectroscopy. The structures of [(CO)$_4$Fe–Ga(Me)(tmpda)] (**1**), [(CO)$_4$Fe–Ga(I)(tmpda)] (**2**), [(CO)$_5$W–Al(^{t}Bu)(tmpda)] (**4**), [(CO)$_4$Fe–In(Br)(tmpda)] (**5**), [(CO)$_5$Cr–Al(Cl)(tmpda)] (**6**), [(CO)$_4$Fe–In(Br)(pmdeta)] (**8**) and [(CO)$_4$Fe–Ga(pmdeta)]$^+$I$^-$ (**9**) have been studied by single-crystal X-ray diffraction. Compound **1**: orthorhombic space group *Pnma*, $Z = 4$. $a = 13.240(16)$, $b = 11.623(14)$, $c = 10.316(13)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90°$, $V = 1588(3)$ Å^3, and $R = 0.0364$ ($R_w = 0.1037$). Compound **2**: triclinic space group $P\bar{1}$, $Z = 2$. $a = 8.2059(13)$, $b = 8.2783(13)$, $c = 14.348(2)$ Å, $\alpha = 75.155(3)$, $\beta = 83.953(3)$, $\gamma = 62.117(3)°$, $V = 832.7(2)$ Å^3, and $R = 0.0346$ ($R_w = 0.0828$). Compound **4**: monoclinic space group $P2_1/n$, $Z = 4$. $a = 8.780(5)$, $b = 14.284(4)$, $c = 16.339(5)$ Å, $\alpha = 90$, $\beta = 96.91(2)$, $\gamma = 90°$, $V = 2034.2(14)$ Å^3, and $R = 0.0577$ ($R_w = 0.1303$). Compound **5**: orthorhombic space group $P2_12_12_1$, $Z = 4$. $a = 7.534(3)$, $b = 14.978(9)$, $c = 15.192(9)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90°$, $V = 1714.4(16)$ Å^3, and $R = 0.0409$ ($R_w = 0.1363$). Compound **6**: monoclinic space group $C2/c$, $Z = 10$. $a = 26.458(5)$, $b = 8.998(5)$, $c = 15.567(3)$ Å, $\alpha = 90$, $\beta = 115.83(5)$, $\gamma = 90°$, $V = 3336(2)$ Å^3, and $R = 0.0343$ ($R_w = 0.0650$). Compound **8**: monoclinic space group $C2/c$, $Z = 16$. $a = 30.717(7)$, $b = 8.746(2)$, $c = 28.677(6)$ Å, $\alpha = 90$, $\beta = 94.99(5)$, $\gamma = 90°$, $V = 7675(3)$ Å^3, and $R = 0.0526$ ($R_w = 0.1591$). Compound **9**: monoclinic space group $P2_1/c$, $Z = 4$. $a = 14.157(1)$, $b = 24.395(2)$, $c = 13.547(1)$ Å, $\alpha = 90$, $\beta = 97.86(2)$, $\gamma = 90°$, $V = 4633.9(8)$ Å^3, and $R = 0.0522$ ($R_w = 0.1334$). © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Aluminium; Gallium; Indium; Group III transition metal bonds; X-ray single crystal structure

1. Introduction

The renewed interest in the chemistry of transition metal (M) to Group III metal (E) bonded systems has been stimulated by the use of such compounds in materials science, as well as by the recent accessibility of low valent Group III metal compounds RE (R = Cp*, C(TMS)$_3$) as versatile starting materials for synthesis [1–5]. Examples include the compound [(CO)$_4$Co–GaEt$_2$(NMe$_3$)] which has been used as precursor for OMCVD (organic metal chemical vapor deposition) of β-CoGa [6] or [Cp*Al–Fe(CO)$_4$], the first example of a Cp*Al unit bonded to a transition metal center in a terminal fashion [7]. Contributing to the recent discussion of polar effects versus π-backbonding in heterobimetallic metal bonds [8,9], especially emphasizing bonds between transition metals and more electropositive (early) main group metals, we have been

---

* Corresponding author. Tel.: +49-234-3224174; fax: +49-234-3214174.

E-mail address: rfischer@aci.ruhr-uni-bochum.de (R.A. Fischer).

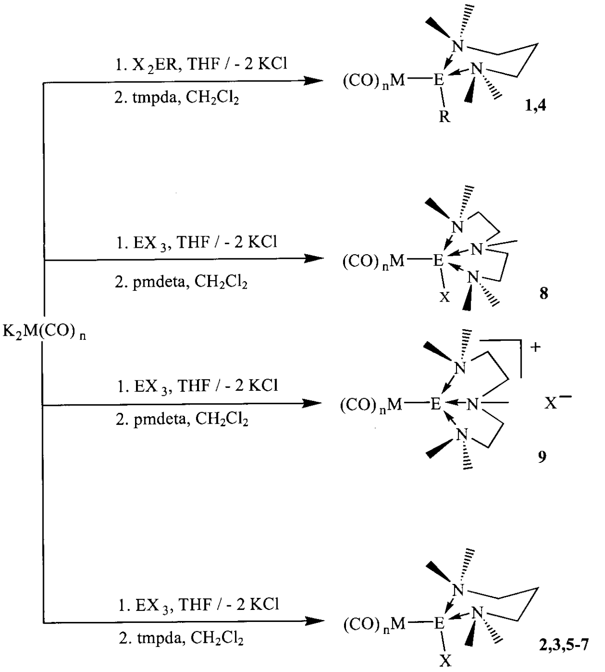
PII: S0022-328X(00)00279-5

particularly interested to study related complexes exhibiting adduct stabilized Group III metal centers of the general formula $[(CO)_nM–E(X)L_2]$ (M = Cr, W, Fe; E = Al, Ga, In; $n = 5, 4$; X = Cl, Br, I; as well as alkyl groups; L_2 = chelating amine donor) [10]. In addition, complexes of this type with mono alkyl moieties RE rather than dialkyl groups R_2E bonded to the transition metal center, e.g. $[(CO)_5Cr–Ga(Et)(tmeda)]$, have been shown to allow a perfect molecular control of the thin film stoichiometry during OMCVD [11]. This was attributed to a stronger M–E interaction and suppressed redistribution of alkyl groups which in turn would otherwise lead to the formation of relatively stable Group III metal alkyls R_3E [12–14], the species of which are then lost during the decomposition of the precursor ultimately resulting in Group III metal deficient alloy films [6,11,15–17]. We were thus motivated to investigate in more detail the synthesis and structure of the title complexes and in particular the coordination chemistry at the Group III metal center.

2. Results and discussion

2.1. Synthesis

The reduction of the transition metal–carbonyl $Cr(CO)_6$ and $W(CO)_6$ with two equivalents of potassium graphite KC_8 in THF and $Fe(CO)_5$ with K-Selectride™ [18] yields the corresponding dianionic species $K_2[M(CO)_n]$ (M = Cr, W, $n = 5$; M = Fe, $n = 4$) which is subsequently treated with Group 13 metal halogenides EX_3 (E = Al, Ga, In; X = Cl, Br, I), X_2ER (E = Al, Ga; X = Cl, R = Me, ᵗBu) and the chelating Lewis base tmpda and pmdeta. Double salt-elimination leads to the final neutral products. Depending on the metal combination and the *N*-ligand (pmdeta) cationic products such as **9** were obtained. The two compounds **3** and **7** had previously been claimed on the basis of IR and NMR data but no structural information was given. We obtained the bimetallic compounds via this route outlined in Scheme 1 following studies reported in earlier publications [10].



Scheme 1. Synthesis of compounds **1**–**9** (M = Cr, W, $n = 5$; M = Fe, $n = 4$; E = Al, Ga, In; X = Cl, Br, I; R = Me, ᵗBu). For the numbering scheme of the compounds see Table 1.

2.2. Spectroscopic characterization

2.2.1. NMR spectra

The ^1H-NMR spectra of the complexes **1**–**7** with the tmpda ligand exhibit diastereotopic *N*-methyl protons and typically reveal two signals. Depending on the degree of conformational flexibility of the chelate ring at the Group 13 metal center, more or less complex coupling patterns for the methylene units are observed expectedly [19]. The ^{13}C-NMR spectra are as expected without unusual features. The ^1H- and ^{13}C-NMR spectra of the complexes **8** and **9** with the pmdeta ligand are similar to the complexes above.

2.2.2. Vibrational (ν(CO)) spectra

The IR absorptions in the ν(CO) range between 1866 and 2031 cm^{-1} of the neutral or cationic product complexes (Table 1) are shifted to significant higher energies than those of the anionic intermediates of 1830–2000 cm^{-1} [20]. In general, the ν(CO) absorptions for the chloro derivatives are shifted hypsochromic about 15 cm^{-1} compared to the corresponding alkyl compounds which agrees with the qualitative expectation that the overall donor capacity of the halide-substituted EX fragment towards the transition metal fragment should be lower. A comparison of the ν(CO) frequencies of some of the neutral iron–gallium products with those of the cationic intermediate is interesting. For the isolated neutral $[(CO)_4Fe–Ga[(I)(tmpda)]$ (**2**) the ν(CO) bands are observed at 2013, 1932 and 1893 cm^{-1} which are shifted to somewhat higher wavenumbers than those of the new cationic compound $[(CO)_4Fe–Ga[(pmdeta)]^+I^-$ (**9**) (1998, 1920 and 1887 cm^{-1}). This is against the general trend that the ν(CO) absorptions of neutral or cationic carbonyl complexes are observed at higher wavenumbers than those of closely related anionic species. This effect may be explained by a localization of electron density at the iodo ligand of **2** leading to a stronger σ-acceptor property of the gallium fragment. In other words, the iodide group is already preformed in the neutral intermediate and easily splits off. On the other

Table 1
Infrared ν(CO) data for complexes **1**–**9** [a]

Compound	No.	ν(CO)
$[(CO)_4Fe–Ga(CH_3)(tmpda)]$	**1**	1994 (vs), 1907 (vs, sh), 1870 (vs)
$[(CO)_4Fe–Ga(Cl)(tmeda)]$	[b]	2011 (vs), 1928 (vs), 1881 (vs)
$[(CO)_4Fe–Al(Cl)(tmpda)]$	**3**	1999 (vs), 1914 (m, sh), 1871 (vs)
$[(CO)_5W–Al(^tBu)(tmpda)]$	**4**	2018 (vs), 1934 (vs), 1875 (vs, sh)
$[(CO)_5W–Al(Cl)(tmpda)]$	[b]	2030 (vs), 1934 (s, sh), 1888 (vs, br)
$[(CO)_5Cr–Al(CH_2CH_3)(tmeda)]$	[b]	2001 (vs), 1936 (vs), 1870 (vs, br)
$[(CO)_5Cr–Al(Cl)(tmpda)]$	**6**	2014 (m), 1924 (vs), 1874 (vs)
$[(CO)_5Cr–Ga(CH_3)(tmeda)]$	[b]	1992 (vs), 1905 (s), 1863 (vs)
$[(CO)_5Cr–Ga(Cl)(tmpda)]$	**7**	2031 (m), 1945 (vs), 1898 (vs)
$[(CO)_4Fe–In(Br)(tmpda)]$	**5**	2013 (vs), 1959 (w, sh), 1932 (m, sh), 1895 (vs)
$[(CO)_4Fe–In(Br)(pmdeta)]$	**8**	2004 (vs), 1925 (m), 1890 (vs), 1866 (vs)
$[(CO)_4Fe–Ga(I)(tmpda)]$	**2**	2013 (vs), 1932 (m, sh), 1893 (vs)
$[(CO)_4Fe–Ga(pmdeta)]^+I^-$	**9**	1998 (vs), 1920 (vs, sh), 1887 (vs)

[a] All ν(CO) IR data were obtained in CH_2Cl_2 solution between NaCl plates.

[b] Data taken from R.A. Fischer, M.M. Schulte, J. Weiß, L. Zsolnai, A. Jacobi, G. Huttner, G. Frenking, C. Boehme, S.F. Vyboishchikov, J. Am Chem. Soc. 120 (1998) 1237.

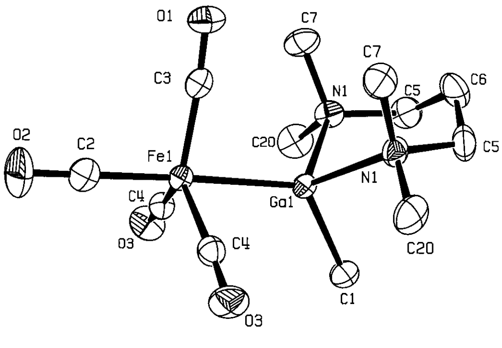


Fig. 1. Molecular structure of $[(CO)_4Fe–Ga(Me)(tmpda)]$ (**1**).

hand we have three amino functions (pmdeta) in the cationic complex **9**. As expected, an amine is a better donor to the gallium center than an iodo ligand.

2.2.3. Electronic spectroscopy

Luminescence from transition metal stabilized AlX complexes $[(CO)_5W–Al(X)(tmpda)]$ (X = Cl, ^{t}Bu) [10] is observed in the visible spectral region. The lowest-energy electronic transition in these compounds is assigned as a d–d band on the basis of the long luminescence lifetime observed in low-temperature glasses and the weak absorption band. The characteristics of the electronic spectra are discussed elsewhere in detail. The similarity to reference compounds of the type $[(CO)_5W–L]$ (L = pyridine, etc.) was clearly established [21].

2.3. Structure and bonding

The molecular structures of **1**–**9** (except **3** and **7**) were established by X-ray single crystal structure analysis. The structures with the atomic numbering scheme

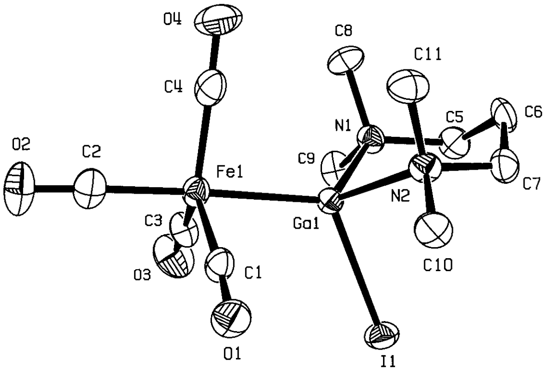


Fig. 2. Molecular structure of $[(CO)_4Fe–Ga(I)(tmpda)]$ (**2**).

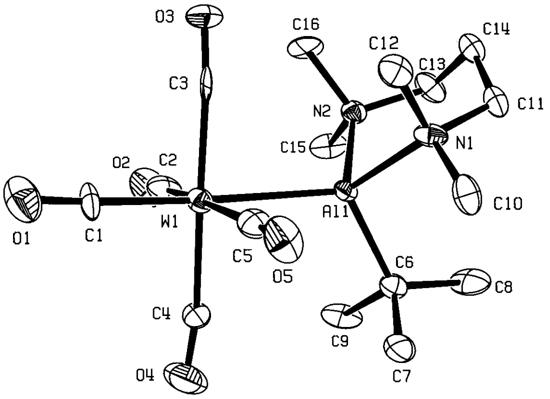


Fig. 3. Molecular structure of $[(CO)_5W–Al(^tBu)(tmpda)]$ (**4**).

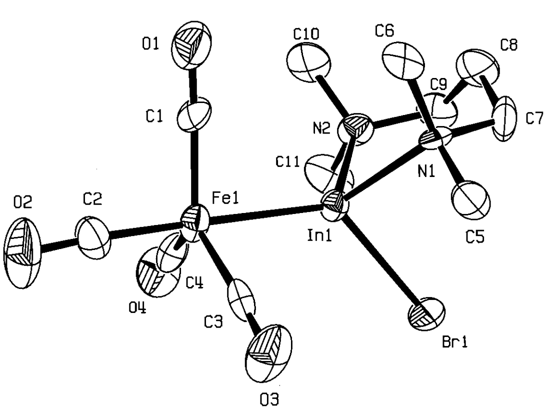


Fig. 4. Molecular structure of $[(CO)_4Fe–In(Br)(tmpda)]$ (**5**).

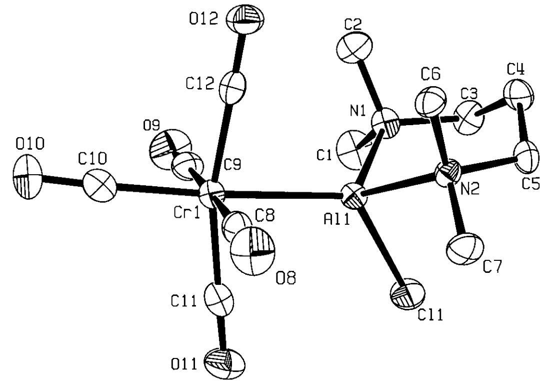


Fig. 5. Molecular structure of $[(CO)_5Cr–Al(Cl)(tmpda)]$ (**6**).

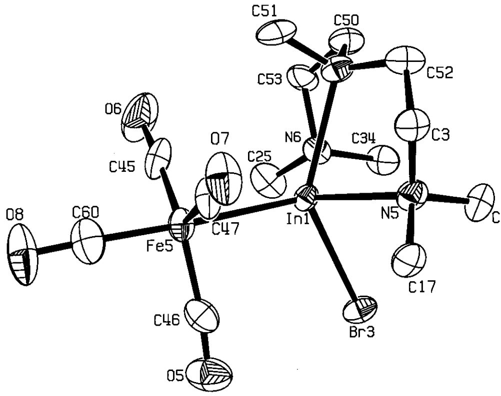


Fig. 6. Molecular structure of $[(CO)_4Fe–In(Br)(pmdeta)]$ (**8**).

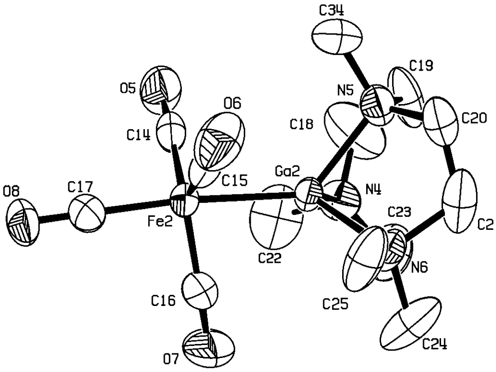


Fig. 7. Molecular structure of $[(CO)_4Fe–Ga(pmdeta)]^+I^-$ (**9**).

are shown in Figs. 1–7. The crystallographic data are summarized in Table 2, and selected bond lengths and angles are listed in Tables 3 and 4, respectively. All compounds are monomeric in the solid state without noticeably short intermolecular contacts (Figs. 1–7). The Fe–Al/Ga/In bonds of **1** (as well **2**, **3**, **5** and **8**) and the W–Al (Cr–Al) [22] bonds of **4**, **6** and **7** lie in a usual range for related molecular compounds [10,23–26]. The metal–metal distances range around the sum of the covalent radii. The W–Al distance of 2.741(4) Å in compound **4** compares well with those of hydride-bridged W–Al bonds ranging from 2.62 to 2.75 Å [23,24]. One noticeable feature of the series of structures presented here and other related ones is the shortening of the M–E bond when alkyl substituents at the Group 13 element are replaced by halide residues. A good example is the series $[(PPh_3)(CO)_3]Co–Ga\{[(CH_2)_3NEt_2](CH_3)\}$ [12] with 2.496(1) Å, $[(PPh_3)(CO)_3]Co–Ga\{[(CH_2)_3NEt_2](Cl)\}$ [12] with 2.372(1) Å, and $[(Me_3P)(CO)_3]Co–GaCl_2(NMe_3)$ with 2.342(1) Å [25,26]. Also other M–E bond distances are known to cover a broad range depending on the particular ligand surrounding the metal centers as shown by the comparison of $[(\eta^5\text{-}C_5H_5)Al–Fe(CO)_4]$ (2.231(3) Å) with $[(\eta^5\text{-}C_5Me_5)(CO)_2]Fe–Al\{[(CH_2)_3NMe_2](^tBu)\}$ (2.456(1) Å) [13] and $[(CO)_4Fe–Ga(Me)(tmpda)]$ (2.416(3) Å) with $[(\eta^5\text{-}C_5H_5)(CO)_2]Fe–Ga[Cl_2]$ (2.362(3) Å) [12] and with $[(\eta^5\text{-}C_5H_5)(CO)_2]Fe–Ga\{[(CH_2)_3NMe_2](Et)\}$ (2.457(1) Å) [26]. The shortest Fe–Ga bond to date of 2.248(7) Å was observed for $[(CO)_4Fe–Ga(C_6H_3Mes^*_2)]$ ($Mes^*_2 = 2,4,6\text{-}^iPr_3C_3H_2$), which contains a linear dicoordinated Ga center, while all other cited Fe–Ga distances refer to tetracoordinated Ga centers [27]. The Fe–In bond lengths of **5** and **8** (2.497(2) Å and 2.543(1) Å) are within the usual range and are consistent with the higher coordination number of **8** [28]. Given that the sum of the covalent radii of the two metals is 2.71 Å, the bond distance observed in complex **5** and **8** is very short. The new compounds thus correspond nicely to the previously known systems.

Against this background the cationic complex **9** is very interesting and warrants a more detailed description. The gallium atom of **9** has a pseudotetrahedral geometry. The N–Ga–N angles are restrained to 85.8(2)–107.5(3)° by the chelate rings (pmdeta). The Ga–N bond distances are normally around 2.09 Å [10,29]. The structure of the iron fragment is a trigonal bipyramid with the gallium located at an axial position. The C–Fe–C bond angles from the axial carbonyl group range from 94.1(4) to 95.0(3)°, and those in the equatorial plane range from 114.0(4) to 122.5(4)°. The Ga–Fe–C angles to these equatorial carbonyl groups range from 80.5(3) to 89.1(2)°. While this arrangement is very close to a regular trigonal bipyramid, the equatorial CO ligands are tilted towards the bulky [(pmdeta)Ga] group to a greater extent than usually observed in other axially substituted $[Fe(CO)_4L]$ ($L = PPh_3$, PPh_2H, C_5H_5N, C_3Ph_2S) complexes [30]. This arrangement (umbrella effect) is very similar to that observed in $[\{HB(3,5\text{-}Me_2pz)_3\}GaFe(CO)_4]$ [31], $[\{HB(3,5\text{-}Me_2pz)_3\}InFe(CO)_4]$ [28k]; as well as in $[(\eta^5\text{-}C_5Me_5)GaFe(CO)_4]$ [32]: a significant bending of the equatorial CO towards the M–E bond vector can be regarded as a structural indication of a rather polar M–E bond [8,9].

Table 2
Crystallographic data for the new compounds **1**, **2**, **4**–**6**, **8** and **9**

	1	**2**	**4**	**5**	**6**	**8**	**9**
Empirical formula	$C_{12}H_{21}FeGaN_2O_4$	$C_{11}H_{18}FeGaIN_2O_4$	$C_{16}H_{27}AlN_2O_5W$	$C_{11}H_{18}BrFeInN_2O_4$	$C_7H_{18}AlClCrN_2O_5$	$C_{13}H_{23}BrFeInN_3O_4$	$C_{28}H_{50}Cl_4Fe_2GaI_2N_6O_8$
Formula weight	382.88	494.74	538.23	492.85	324.35	535.92	1245.48
Crystal class	Orthorhombic	Triclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	*Pnma*	$P\bar{1}$	$P2_1/n$	$P2_12_12_1$	$C2/c$	$C2/c$	$P2_1/c$
Lattice parameters							
a (Å)	13.240(16)	8.2059(13)	8.780(5)	7.534(3)	26.458(5)	30.717(7)	14.155(1)
b (Å)	11.623(14)	8.2783(13)	14.284(4)	14.978(9)	8.998(5)	8.746(2)	24.395(2)
c (Å)	10.316(13)	14.348(2)	16.339(5)	15.192(9)	15.567(3)	28.677(6)	13.547(1)
α (°)	90	75.155(3)	90	90	90	90	90
β (°)	90	83.953(3)	96.91(2)	90	115.83(5)	94.99(5)	97.87(2)
γ (°)	90	62.117(3)	90	90	90	90	90
V (Å^3)	1588(3)	832.7(2)	2034.2(14)	1714.4(16)	3336(2)	7675(3)	4633.9(8)
Z	4	2	4	4	10	16	4
D_{calc} (g cm^{-3})	1.602	1.973	1.757	1.909	1.546	1.855	1.785
F(000)	784	480	1056	960	1540	4224	2448
Crystal size (mm)	$0.20 \times 0.20 \times 0.30$	$0.20 \times 0.20 \times 0.30$	$0.1 \times 0.1 \times 0.2$	$0.3 \times 0.3 \times 0.2$	$0.30 \times 0.28 \times 0.14$	$0.2 \times 0.2 \times 0.3$	$0.2 \times 0.2 \times 0.3$
Absorption coefficient	2.623	4.354	5.748	4.533	5.232	4.943	5.413
Radiation (Mo–K$_\alpha$) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Temperature (K)	203(2)	293(2)	293(2)	293(2)	193(2)	293(2)	293(2)
θ Range for data collection (°)	2.50–24.97	2.81–25.07	2.51–25.05	1.91–25.28	2.42–25.00	2.03–24.98	1.67–25.10
Index ranges (°)	$-11 \leq h \leq 15$, $-13 \leq k \leq 13$, $-12 \leq l \leq 4$	$-8 \leq h \leq 9$, $-9 \leq k \leq 9$, $-16 \leq l \leq 17$	$0 \leq h \leq 10$, $0 \leq k \leq 16$, $-19 \leq l \leq 19$	$-6 \leq h \leq 5$, $-5 \leq k \leq 17$, $-18 \leq l \leq 2$	$-8 \leq h \leq 31$, $-10 \leq k \leq 10$, $-18 \leq l \leq 16$	$-23 \leq h \leq 35$, $-10 \leq k \leq 9$, $-24 \leq l \leq 33$	$-14 \leq h \leq 16$, $-29 \leq k \leq 29$, $-16 \leq l \leq 16$
Reflections collected	3512	4369	3733	2720	3016	8778	23953
Independent reflections	1417 [$R_{int} = 0.0520$]	2904 [$R_{int} = 0.0494$]	3485 [$R_{int} = 0.0625$]	2199 [$R_{int} = 0.0379$]	2948 [$R_{int} = 0.0586$]	6215 [$R_{int} = 0.0419$]	8199 [$R_{int} = 0.0421$]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1417/0/104	2904/0/181	3481/0/227	2199/0/182	2945/0/199	6215/0/416	8199/0/469
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0364$, $wR_2 = 0.1037$	$R_1 = 0.046$, $wR_2 = 0.0828$	$R_1 = 0.0577$, $wR_2 = 0.1303$	$R_1 = 0.0409$, $wR_2 = 0.1363$	$R_1 = 0.0343$, $wR_2 = 0.0650$	$R_1 = 0.0526$, $wR_2 = 0.1591$	$R_1 = 0.0522$, $wR_2 = 0.1334$
R indices (all data)	$R_1 = 0.0404$, $wR_2 = 0.1074$	$R_1 = 0.0432$, $wR_2 = 0.0859$	$R_1 = 0.1023$, $wR_2 = 0.1467$	$R_1 = 0.0436$, $wR_2 = 0.1451$	$R_1 = 0.0691$, $wR_2 = 0.0722$	$R_1 = 0.0648$, $wR_2 = 0.1882$	$R_1 = 0.0644$, $wR_2 = 0.1433$
Goodness-of-fit on F^2	0.874	0.998	0.866	1.076	0.738	1.102	1.032
Extinction coefficient	0.0033(9)	0.006(1)	0.0002(3)	0.0011(10)	0.0013(2)	0.0009(2)	0.0013(5)
Largest difference peak and hole (e Å^{-3})	$+0.646$ and -0.777	$+0.758$ and -0.0859	$+2.935$ and -2.536	$+0.731$ and -0.980	$+0.267$ and -0.285	$+1.653$ and -1.620	$+2.404$ and -1.160

Table 3
Selected bond lengths (Å) and angles (°) for the new compounds **1**, **2**, **4**–**6** and **8**

[(CO)$_4$Fe–Ga(Me)(tmpda)] (**1**)			
Ga(1)–Fe(1)	2.416(3)	Fe(1)–C(2)	1.785(6)
Ga(1)–N(1)	2.132(3)	C(2)–O(2)	1.167(7)
Ga(1)–N(1) #1	2.132(3)	N(1)–C(7)	1.498(4)
Ga(1)–C(1)	1.997(5)	N(1)–C(5)	1.520(4)
Fe(1)–C(4)	1.765(4)	C(5)–C(6)	1.505(5)
C(2)–Fe(1)–Ga(1)	178.07(17)	N(1)–Ga(1)–Fe(1)	116.37(8)
C(3)–Fe(1)–Ga(1)	87.46(13)	C(1)–Ga(1)–N(1)	100.96(13)
C(4)–Fe(1)–Ga(1)	82.58(10)	N(1)–Ga(1)–N(1) #1 [a]	93.61(17)
O(2)–C(2)–Fe(1)	179.7(5)	C(7)–N(1)–C(20)	106.7(3)
C(1)–Ga(1)–Fe(1)	123.42(15)	C(5)–C(6)–C(5) #1 [a]	116.1(5)
[(CO)$_4$Fe–Ga(I)(tmpda)] (**2**)			
Ga(1)–Fe(1)	2.3371(8)	Fe(1)–C(2)	1.771(5)
Ga(1)–N(1)	2.094(4)	C(2)–O(2)	1.150(6)
Ga(1)–N(2)	2.109(4)	N(1)–C(8)	1.489(6)
Ga(1)–I(1)	2.6421(6)	N(1)–C(5)	1.493(6)
Fe(1)–C(1)	1.768(5)	C(5)–C(6)	1.513(7)
C(2)–Fe(1)–Ga(1)	177.17(18)	N(1)–Ga(1)–Fe(1)	120.50(11)
C(3)–Fe(1)–Ga(1)	84.06(16)	I(1)–Ga(1)–N(1)	99.18(10)
C(4)–Fe(1)–Ga(1)	88.30(16)	N(1)–Ga(1)–N(2)	95.59(15)
O(2)–C(2)–Fe(1)	178.0(5)	C(11)–N(2)–C(10)	106.6(4)
I(1)–Ga(1)–Fe(1)	117.18(3)	C(5)–C(6)–C(7)	115.9(4)
[(CO)$_5$W–Al(^{t}Bu)(tmpda)] (**4**)			
W(1)–Al(1)	2.741(4)	W(1)–C(2)	2.012(14)
Al(1)–N(1)	2.110(11)	W(1)–C(3)	2.016(14)
Al(1)–N(2)	2.136(11)	W(1)–C(4)	2.030(12)
Al(1)–C(6)	2.056(14)	W(1)–C(5)	2.030(14)
W(1)–C(1)	1.975(13)	C(2)–O(2)	1.161(5)
C(1)–W(1)–Al(1)	176.0(4)	C(6)–Al(1)–W(1)	117.8(4)
C(2)–W(1)–Al(1)	88.2(5)	N(1)–Al(1)–W(1)	114.1(3)
C(3)–W(1)–Al(1)	86.8(3)	N(1)–Al(1)–N(2)	93.3(4)
C(4)–W(1)–Al(1)	91.8(4)	N(2)–Al(1)–C(6)	108.0(5)
C(5)–W(1)–Al(1)	84.7(4)	N(2)–Al(1)–W(1)	118.8(2)
[(CO)$_4$Fe–In(Br)(tmpda)] (**5**)			
In(1)–Fe(1)	2.4968(18)	Fe(1)–C(2)	1.759(12)
In(1)–N(1)	2.303(11)	C(2)–O(2)	1.179(16)
In(1)–N(2)	2.307(8)	N(1)–C(6)	1.491(14)
In(1)–Br(1)	2.5835(17)	N(1)–C(7)	1.502(14)
Fe(1)–C(1)	1.791(15)	C(7)–C(8)	1.542(17)
C(2)–Fe(1)–In(1)	176.6(4)	N(1)–In(1)–Fe(1)	119.7(2)
C(3)–Fe(1)–In(1)	83.6(3)	Br(1)–In(1)–N(1)	94.5(2)
C(4)–Fe(1)–In(1)	86.0(4)	N(1)–In(1)–N(2)	91.4(3)
O(2)–C(2)–Fe(1)	176.10(15)	C(11)–N(2)–C(10)	108.1(4)
Br(1)–In(1)–Fe(1)	126.50(7)	C(7)–C(8)–C(9)	115.20(13)
[(CO)$_5$Cr–Al(Cl)(tmpda)] (**6**)			
Cr(1)–Al(1)	2.482(1)	Cr(1)–C(9)	1.882(4)
Al(1)–N(1)	2.070(3)	Cr(1)–C(10)	1.845(3)
Al(1)–N(2)	2.041(3)	Cr(1)–C(11)	1.871(3)
Al(1)–Cl(1)	2.198(1)	Cr(1)–C(12)	1.862(3)
Cr(1)–C(8)	1.891(4)	C(8)–O(8)	1.151(4)
C(8)–Cr(1)–Al(1)	91.64(10)	Cl(1)–Al(1)–Cr(1)	123.63(5)
C(9)–Cr(1)–Al(1)	89.52(11)	N(1)–Al(1)–Cr(1)	119.16(9)
C(10)–Cr(1)–Al(1)	174.62(12)	N(1)–Al(1)–N(2)	118.57(9)
C(11)–Cr(1)–Al(1)	81.93(10)	N(2)–Al(1)–Cl(1)	96.08(8)
C(12)–Cr(1)–Al(1)	84.23(10)	N(2)–Al(1)–Cr(1)	118.57(9)
[(CO)$_4$Fe–In(Br)(pmdeta)] (**8**)			
In(1)–Fe(5)	2.543(1)	Fe(5)–C(46)	1.793(9)
In(1)–N(5)	2.361(6)	C(45)–O(6)	1.161(12)
In(1)–N(6)	2.375(6)	N(1)–C(6)	1.491(14)
In(1)–Br(3)	2.672(1)	N(1)–C(7)	1.502(14)
Fe(5)–C(45)	1.773(10)	C(7)–C(8)	1.542(17)
C(2)–Fe(1)–In(1)	176.6(4)	N(1)–In(1)–Fe(1)	119.7(2)
C(3)–Fe(1)–In(1)	83.6(3)	Br(1)–In(1)–N(1)	94.5(2)
C(4)–Fe(1)–In(1)	86.0(4)	N(1)–In(1)–N(2)	91.4(3)
O(2)–C(2)–Fe(1)	176.10(15)	C(11)–N(2)–C(10)	108.1(4)
Br(1)–In(1)–Fe(1)	126.50(7)	C(7)–C(8)–C(9)	115.20(13)

[a] Symmetry transformations used to generate equivalent atoms: #1 x, $-y+1/2$, z.

The most interesting feature of the structure is the observation of a quite short Ga–Fe bond distance of 2.310(1) Å. For comparison, the single-bond Ga–Fe distances in a number of compounds with tetracoordinated gallium average at 2.43 Å [12,33]. Three neutral complexes with comparable short Ga–Fe bond distances with tetracoordinated Ga have recently been reported. A shorter bond distance of 2.2731(4) Å is observed in [(η^5-C_5Me_5)GaFe(CO)$_4$] [32], and two only marginal longer bond distances of 2.315(3) Å in [{HB(3,5-Me$_2$pz)$_3$}GaFe(CO)$_4$] and 2.338(2) Å in [(CO)$_4$Fe–Ga(Cl)(tmpda)] are known.

3. Conclusions

Taken together the above comparison and discussions and realizing that the Fe–Ga distance in **9** of 2.310(1) Å is very close to the Fe–Ga distance of 2.315(3) Å in [{HB(3,5-Me$_2$pz)$_3$}GaFe(CO)$_4$] it follows that the bonding in the two compounds appears to be very similar. However, the [{HB(3,5-Me$_2$pz)$_3$}GaFe(CO)$_4$] system was described as a Ga(I) compound while **9** should be taken clearly as a Ga(III) compound (extreme view as a contact ion pair {[(CO)$_4$Fe^{2-}][Ga(pmdeta)$^{3+}$]}. Our results show, that a description of Ga(I) rather the Ga(III) is irrelevant in these cases and does not correlate with structural or other spectroscopic (IR) data. This agrees with the general quantum chemical analysis of the nature of the chemical bond between a transition metal and a Group 13 element [10,34].

4. Experimental

4.1. General methods

All manipulations were undertaken utilizing standard Schlenk and glovebox techniques under inert gas atmospheres (purified N_2 or argon). Solvents were dried

Table 4
Selected bond lengths (Å) and angles (°) for $[(CO)_4Fe–Ga(pmdeta)]^+ I^-$ (**9**)

Ga(2)–Fe(2)	2.310(1)	N(6)–C(34)	1.515(11)
Ga(2)–N(4)	2.095(6)	C(16)–O(2)	1.152(10)
Ga(2)–N(5)	2.064(6)	N(4)–C(36)	1.439(13)
Ga(2)–N(6)	2.079(6)	N(4)–C(39)	1.548(13)
Fe(2)–C(16)	1.759(9)	C(31)–C(44)	1.548(14)
C(25)–Fe(2)–Ga(2)	80.5(3)	N(5)–Ga(2)–Fe(2)	127.49(18)
C(16)–Fe(2)–Ga(2)	89.1(2)	N(6)–Ga(2)–Fe(2)	120.41(17)
C(40)–Fe(2)–Ga(2)	174.9(2)	N(5)–Ga(2)–N(6)	85.8(2)
C(35)–Fe(2)–Ga(2)	87.0(2)	N(5)–Ga(2)–N(4)	107.5(3)
N(4)–Ga(2)–Fe(2)	120.7(2)	N(6)–Ga(2)–N(4)	86.2(3)

under Ar by standard methods and stored over molecular sieves (4 Å, Merck; residual water < 3 ppm, Karl Fischer) [35]. Infrared spectra were recorded as solutions between NaCl plates with a Perkin–Elmer 1720X Fourier transform spectrometer and are reported in reciprocal centimeters. ^{1}H- and ^{13}C-NMR spectra were recorded on Bruker DPX 250, DPX200 and DRX400 spectrometers (^{1}H- and ^{13}C-NMR were referenced to internal solvent and corrected to TMS). All samples for NMR spectra were contained in vacuum-sealed NMR tubes. Starting compounds Cl_2GaMe, Cl_2Al^tBu, GaI_3, $K_2[Fe(CO)_4]$, $K_2[Cr(CO)_5]$ and $K_2[W(CO)_5]$ were prepared as described in the literature [36–39]. $AlCl_3$, $GaCl_3$ and $InBr_3$ were purchased from Aldrich, dried, and purified by sublimation. Abbreviations are as follows: Me = CH_3, ^{t}Bu = *tert*-butyl, tmpda = *N*,*N*,*N*′,*N*′-tetramethylpropylenediamine, pmdeta = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine. Elemental analyses were provided by the Microanalytik Laboratory of the Ruhr University of Bochum. Selected spectroscopic and analytical data of the new compounds are compiled in Tables 1–9.

4.1.1. Synthesis of methyl(tetracarbonyliron)-(tetramethylpropylenediamin)gallium $[(CO)_4Fe–Ga(Me)(tmpda)]$ (*1*)

A suspension of the dianion $K_2[Fe(CO)_4]$ (492 mg, 2 mmol) in 40 ml THF was prepared and cooled to −78°C. Then a solution of a stoichiometric quantity (2 mmol) of the respective gallium compound (Cl_2GaMe) in 20 ml of THF, also cooled to −78°C, was added. The mixture was allowed to warm to room temperature (r.t.) and stirred for 3 h. Then the Lewis base ligand (262 mg, 2 mmol) was added. After 1 h of stirring at 25°C, the solvent was removed in vacuo and the residue was extracted twice with 40 ml of CH_2Cl_2. After the sedimentation of the KCl, the reddish solution was slowly filtered using the cannula technique. The obtained clear solution was concentrated to a volume of 15 ml and stored at −30°C. From the resulting solution the compound separated as well-shaped colorless crystals. After the mother liquor was decanted and further concentration of a second crop was collected giving a total yield of typically 90–95%. The crystals could be handled in air and were stable against moisture for a short time. Anal. Calc. for $C_{12}H_{21}FeGaN_2O_4$: C, 37.64; H, 5.90; N, 7.32. Found: C, 37.44; H, 5.73; N, 7.12%. IR (CH_2Cl_2, cm^{-1}): ν(CO) = 1994 (vs), 1907 (vs, sh), 1870 (vs). ^{1}H-NMR (250 MHz, CD_2Cl_2, 298 K, δ ppm): 3.16 (t, $^3J = 13.6$ Hz, 4H, NCH_2), 2.76 (s, 6H, $N(CH_3)_2$), 2.58 (s, 6H, $N(CH_3)_2$), 2.21 (quint, $^3J = 14.7$ Hz, 2H, $CH_2CH_2CH_2$), 0.13 (s, 3H, $GaCH_3$). ^{13}C-NMR (100 MHz, CD_2Cl_2, 298 K, δ ppm): 25.5 ($CH_2CH_2CH_2$), 51.9 (NMe_2), 52.9 (NMe_2), 64.4 (NCH_2), 224.8 (Fe–CO).

4.1.2. Synthesis of iodo(tetracarbonyliron)-(tetramethylpropylenediamin)gallium $[(CO)_4Fe–Ga(I)(tmpda)]$ (*2*)

The complex was synthesized similar to **1** and well-shaped colorless crystals were obtained with a yield of 92%. Anal. Calc. for $C_{11}H_{18}FeGaIN_2O_4$: C, 26.70; H, 3.90; N, 5.66. Found: C, 26.41; H, 3.87; N, 5.64%. IR (CH_2Cl_2, cm^{-1}): ν(CO) = 2013 (vs), 1932 (m, sh), 1893 (vs). ^{1}H-NMR (250 MHz, CD_2Cl_2, 298 K, δ ppm): 3.80 (t, $^3J = 26.1$ Hz, 4H, NCH_2), 2.87 (s, 6H, $N(CH_3)_2$), 2.82 (s, 6H, $N(CH_3)_2$), 2.21 (quint, $^3J = 26.7$ Hz, 2H, $CH_2CH_2CH_2$). ^{13}C-NMR (100 MHz, CD_2Cl_2, 298 K, δ ppm): 25.4 ($CH_2CH_2CH_2$), 49.9 (NMe_2), 54.2 (NMe_2), 63.7 (NCH_2), 221.7 (Fe–CO).

4.1.3. Synthesis of chloro(tetracarbonyliron)-(tetramethylpropylenediamin)aluminum $[(CO)_4Fe–Al(Cl)(tmpda)]$ (*3*)

The complex was synthesized similar to **1** and well-shaped colorless crystals were obtained with a yield of 88%. Anal. Calc. for $C_{11}H_{18}AlClFeN_2O_4$: C, 36.64; H, 4.99; N, 7.77. Found: C, 36.44; H, 4.77; N, 7.54%. IR (CH_2Cl_2, cm^{-1}): ν(CO) = 1999 (vs), 1914 (m, sh), 1871 (vs). ^{1}H-NMR (250 MHz, CD_2Cl_2, 298 K, δ ppm): 3.24 (t, $^3J = 23.7$ Hz, 4H, NCH_2), 2.88 (s, 6H, $N(CH_3)_2$), 2.78 (s, 6H, $N(CH_3)_2$), 2.44 (quint, $^3J = 22.7$ Hz, 2H, $CH_2CH_2CH_2$). ^{13}C-NMR (100 MHz, CD_2Cl_2, 298 K, δ ppm): 25.2 ($CH_2CH_2CH_2$), 52.2 (NMe_2), 54.7 (NMe_2), 64.8 (NCH_2), 224.2 (Fe–CO).

4.1.4. Synthesis of tert-butyl(pentacarbonyltungsten)-(tetramethylpropylenediamin)aluminum $[(CO)_5W–Al(^tBu)(tmpda)]$ (*4*)

A suspension of the dianion $K_2[W(CO)_5]$ (2 mmol) in 40 ml THF was prepared and cooled to −78°C. Then a solution of Cl_2Al^tBu (362 mg, 2 mmol) in 20 ml of THF, also cooled to −78°C, was added. The mixture was allowed to warm to r.t. and stirred for 3 h. To this the Lewis base ligand (262 mg, 2 mmol) was added. After 1 h of stirring at 25°C, the THF reaction mixture was filtered from the graphite and the solvent was removed in vacuo. The residue was extracted twice with

40 ml of CH_2Cl_2. This was necessary to achieve quantitative separation from the byproduct KCl, which has a significant solubility in THF. The light-yellow extracts were combined and the solution was concentrated to a volume of 10 ml, stored at −30°C. From this solution the compound separated as well-shaped light-yellow crystals with a yield of 93%. Anal. Calc. for $C_{16}H_{27}AlN_2O_5W$: C, 35.70; H, 5.06; N, 5.20. Found: C, 35.42; H, 5.09; N, 5.18%. IR (CH_2Cl_2, cm^{-1}): $\nu(CO) =$ 2018 (m), 1934 (vs), 1875 (vs, sh). ^1H-NMR (300 MHz, d_8-THF, 298 K, δ ppm): 2.19 (t, $^3J = 7.1$ Hz, 4H, NCH_2), 2.10 (s, 12H, $N(CH_3)_2$), 1.52 (quint, $^3J = 7.1$ Hz, 2H, $CH_2CH_2CH_2$), 0.98 (s, 9H, $(CH_3)_3$). ^{13}C-NMR (75 MHz, d_8-THF, 298 K, δ ppm): 27.0 ($C(CH_3)_3$), 29.9 ($CH_2CH_2CH_2$), 32.8 ($C(CH_3)_3$), 45.7 (NMe_2), 58.4 (NCH_2), 210.7, 211.5 (W–CO).

4.1.5. *Synthesis of bromo(tetracarbonyliron)-(tetramethylpropylenediamin)indium [(CO)$_4$Fe–In(Br)(tmpda)] (**5**)*

The complex was synthesized similar to **1** and well-shaped yellow crystals were obtained with a yield of 89%. Anal. Calc. for $C_{11}H_{18}BrFeInN_2O_4$: C, 26.80; H, 3.72; N, 5.75. Found: C, 27.02; H, 3.85; N, 5.83%. IR (CH_2Cl_2, cm^{-1}): $\nu(CO) = 2013$ (vs), 1959 (w, sh), 1932 (m, sh), 1895 (vs). ^1H-NMR (250 MHz, CD_2Cl_2, 298 K, δ ppm): 3.58 (t, $^3J = 24.9$ Hz, 4H, NCH_2), 2.69 (s, 6H, $N(CH_3)_2$), 2.62 (s, 6H, $N(CH_3)_2$), 2.20 (quint, $^3J = 25.7$ Hz, 2H, $CH_2CH_2CH_2$). ^{13}C-NMR (63 MHz, CD_2Cl_2, 298 K, δ ppm): 22.4 ($CH_2CH_2CH_2$), 45.9 (NMe_2), 49.2 (NMe_2), 60.1 (NCH_2), 217.1 (Fe–CO).

4.1.6. *Synthesis of chloro(pentacarbonylchrom)-(tetramethylpropylenediamin)aluminum [(CO)$_5$Cr–Al(Cl)(tmpda)] (**6**)*

The complex was synthesized similar to **4** and well-shaped light-yellow crystals were obtained with a yield of 90%. Anal. Calc. for $C_7H_{18}AlClCrN_2O_5$: C, 25.90; H, 5.54; N, 8.63. Found: C, 26.12; H, 5.29; N, 8.48%. IR (CH_2Cl_2, cm^{-1}): $\nu(CO) = 2014$ (m), 1924 (vs), 1874 (vs). ^1H-NMR (250 MHz, CD_2Cl_2, 298 K, δ ppm): 3.52 (t, $^3J = 24.9$ Hz, 4H, NCH_2), 2.72 (s, 6H, $N(CH_3)_2$), 2.69 (s, 6H, $N(CH_3)_2$), 2.19 (quint, $^3J = 25.7$ Hz, 2H, $CH_2CH_2CH_2$). ^{13}C-NMR (63 MHz, CD_2Cl_2, 298 K, δ ppm): 21.5 ($CH_2CH_2CH_2$), 46.2 (NMe_2), 49.2 (NMe_2), 58.8 (NCH_2), 208.1 (Cr–CO).

4.1.7. *Synthesis of chloro(pentacarbonylchrom)-(tetramethylpropylenediamin)gallium [(CO)$_5$Cr–Ga(Cl)(tmpda)] (7)*

The complex was synthesized similar to **4** and well-shaped colorless crystals were obtained with a yield of 91%. Anal. Calc. for $C_7H_{18}ClCrGaN_2O_5$: C, 22.88; H, 4.90; N, 7.62. Found: C, 22.78; H, 5.09; N, 7.54%. IR (CH_2Cl_2, cm^{-1}): $\nu(CO) = 2031$ (m), 1945 (vs), 1898 (vs). ^1H-NMR (300 MHz, CD_2Cl_2, 298 K, δ ppm): 3.32 (t, $^3J = 7.1$ Hz, 4H, NCH_2), 2.71 (s, 12H, $N(CH_3)_2$), 2.13 (quint, $^3J = 7.1$ Hz, 2H, $CH_2CH_2CH_2$). ^{13}C-NMR (75 MHz, CD_2Cl_2, 298 K, δ ppm): 23.9 ($CH_2CH_2CH_2$), 45.7 (NMe_2), 49.6 (NMe_2), 58.4 (NCH_2), 206.7 (Cr–CO).

4.1.8. *Synthesis of bromo(tetracarbonyliron)-(pentamethyldiethylenetriamin)indium [(CO)$_4$Fe–In(Br)(pmdeta)] (**8**)*

A suspension of 492 mg (2 mmol) of $K_2[Fe(CO)_4]$ in 40 ml of THF was cooled to −78°C, and 710 mg (2 mmol) of solid $InBr_3$ was added with vigorous stirring. The reaction mixture was allowed to warm up to r.t., and after 3 h, about 347 mg (2 mmol) of pmdeta was added. After 1 h, the mixture was filtered and the solvent was removed in vacuo followed by extensive washing of the yellow residue with CH_2Cl_2. The compound was separated from the solution as yellow crystals with a yield of 93%. Anal. Calc. for $C_{13}H_{23}BrFeInN_3O_4$: C, 29.10; H, 4.29; N, 7.83. Found: C, 29.28; H, 4.15; N, 7.93%. IR (CH_2Cl_2, cm^{-1}): $\nu(CO) = 2004$ (vs), 1925 (m), 1890 (vs), 1866 (vs). ^1H-NMR (250 MHz, CD_2Cl_2, 298 K, δ ppm): 3.18 (m, 8H, CH_2CH_2), 2.89 (m, 3H, NCH_3), 2.71 (s, 6H, $N(CH_3)_2$), 2.63 (s, 6H, $N(CH_3)_2$). ^{13}C-NMR (63 MHz, CD_2Cl_2, 298 K, δ ppm): 60.3 (NCH_2), 54.7 (NMe_2), 53.6 (NMe_2), 49.2 (NMe), 217.1 (Fe–CO).

4.1.9. *Synthesis of (tetracarbonyliron)-(pentamethyldiethylenetriamin)gallium-iodid [(CO)$_4$Fe–Ga(pmdeta)]$^+$I$^-$ (**9**)*

A suspension of $K_2[Fe(CO)_4]$ (492 mg, 2 mmol) in THF was cooled to −78°C. Then a solution of GaI_3 (900 mg, 2 mmol) in 20 ml of THF, also cooled to −78°C, was added. The reaction mixture was allowed to warm up to r.t. and stirred for 3 h. This was followed by the addition of pmdeta (347 mg, 2 mmol). After 1 h of stirring at 25°C, the solvent was removed in vacuo and the residue was extracted twice with 40 ml of CH_2Cl_2. After filtration, the obtained light-orange solution was concentrated to a volume of 10 ml and stored at −30°C. After solvent extraction in vacuo, the complex was obtained as well-shaped light-orange crystals with an 90% yield. Anal. Calc. for $C_{28}H_{50}Cl_4Fe_2In_2N_6O_8$: C, 26.97; H, 4.01; N, 6.74. Found: C, 27.01; H, 4.15; N, 6.58%. IR (CH_2Cl_2, cm^{-1}): $\nu(CO) = 1998$ (vs), 1920 (vs, sh), 1887 (vs). ^1H-NMR (250 MHz, CD_2Cl_2, 298 K, δ ppm): 2.94 (m, 8H, CH_2CH_2), 2.83 (m, 3H, NCH_3), 2.68 (s, 6H, $N(CH_3)_2$), 2.62 (s, 6H, $N(CH_3)_2$). ^{13}C-NMR (63 MHz, CD_2Cl_2, 298 K, δ ppm): 55.8 (NCH_2), 54.1 (NMe_2), 53.9 (NMe_2), 48.6 (NMe), 217.9 (Fe–CO).

5. Supplementary data

Intensity data for **1**, **2**, **4**, **5**, **6**, **8** and **9** were collected with a Siemens P4 diffractometer (Mo–K_α radiation,

$\lambda = 0.71073$ Å, graphite monochromator, ω-scan). Empirical absorption correction was applied. The structures were solved by direct methods [40] and refined by least-squares methods based on F^2 with all observed reflections [41]. The thermal reliability index wR_2 is defined as $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. All non-hydrogen atoms were refined anisotropically.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, quoting the reference numbers CCDC-139127 (**1**), CCDC-139128 (**2**), CCDC-139129 (**4**), CCDC-139130 (**5**), CCDC-139131 (**6**), CCDC-139132 (**8**) and CCDC-139133 (**9**). Copies of the data can be obtained free of charge on application to: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for their financial support. Excellent service was provided by the computer centers HRZ Heidelberg and HRZ Bochum.

References

[1] R.A. Fischer, J. Weiß, Angew. Chem. Int. Ed. Engl. 38 (1999) 2830.
[2] C. Dohmeier, D. Loos, H. Schnöckel, Angew. Chem. Int. Ed. Engl. 35 (1996) 129.
[3] C. Dohmeier, C. Robl, M. Tacke, H. Schnöckel, Angew. Chem. Int. Ed. Engl. 30 (1991) 564.
[4] W. Uhl, Angew. Chem. Int. Ed. Engl. 32 (1993) 1386.
[5] R.J. Wehmschulte, K. Ruhland-Senge, M.M. Olmstead, H. Hope, B.E. Sturgeon, P.P. Power, Inorg. Chem. 32 (1993) 2983.
[6] R.A. Fischer, A. Miehr, Chem. Mater. 8 (1996) 497.
[7] J. Weiss, D. Stetzkamp, B. Nuber, R.A. Fischer, C. Boehme, G. Frenking, Angew. Chem. Int. Ed. Engl. 36 (1997) 70.
[8] M. Stürmann, W. Saak, H. Marsmann, M. Weidenbruch, Angew. Chem. Int. Ed. 115 (1999) 187.
[9] (a) B.E. Bursten, K.J. Novo-Gradac, J. Am. Chem. Soc. 109 (1987) 904. (b) B.E. Bursten, R.J. Strittmatter, Angew. Chem. Int. Ed. Engl. 30 (1991) 1069. (c) G.S. Ferguson, P.T. Wolczanski, L. Parkanyi, M. Zonnevyelle, Organometallics 7 (1988) 1967. (d) D. Selent, M. Ramm, C. Janiak, J. Organomet. Chem. 501 (1995) 235. (e) G. Jansen, M. Schubart, B. Findeis, L.H. Gade, I.J. Scowen, M. McPartlin, J. Am. Chem. Soc. 120 (1998) 7239. (f) J.E. Bender IV, A.J. Shusterman, M.M. Banaszak Holl, J.W. Kempf, Organometallics 18 (1999) 1547.
[10] R.A. Fischer, M.M. Schulte, J. Weiss, L. Zsolnai, A. Jacobi, G. Huttner, G. Frenking, C. Boehme, S.F. Vyboishchikov, J. Am. Chem. Soc. 120 (1998) 1237.
[11] M.M. Schulte, E. Herdtweck, G. Raudaschl-Sieber, R.A. Fischer, Angew. Chem. Int. Ed. Engl. 35 (1996) 424.
[12] R.A. Fischer, A. Miehr, T. Priermeier, Chem. Ber. 128 (1995) 831.
[13] (a) R.A. Fischer, T. Priermeier, Organometallics 13 (1994) 4306. (b) H. Braunschweig, J. Müller, B. Gaufer, Inorg. Chem. 35 (1996) 7443. (c) B.N. Anand, I. Krossing, H. Nöth, Inorg. Chem. 36 (1997) 1979.
[14] R.A. Fischer, E. Herdtweck, T. Priermeier, Inorg. Chem. 33 (1994) 934.
[15] R.A. Fischer, A. Miehr, M.M. Schulte, Adv. Mater. 7 (1995) 58.
[16] R.A. Fischer, A. Miehr, E. Herdtweck, J. Chem. Soc. Chem. Commun. (1995) 337.
[17] R.A. Fischer, W. Scherer, M. Kleine, Angew. Chem. Int. Ed. Engl. 32 (1993) 748.
[18] $K(s\text{-}C_4H_9)_3BH$ is sold by the Aldrich Chemical Co. as a 0.5 M THF solution under the trade name K-Selectride.
[19] O. Segnitz, Diploma Thesis, University of Heidelberg, Germany, 1998.
[20] R.A. Fischer, M.M. Schulte, E. Herdtweck, M.R. Mattner, Inorg. Chem. 36 (1997) 2010.
[21] J. Weiss, R.A. Fischer, Y. Pelletier, C. Reber, Inorg. Chem. 37 (1998) 3316.
[22] Q. Yu, A. Purath, A. Donchev, H. Schnöckel, J. Organomet. Chem. 584 (1999) 94.
[23] A.R. Barron, D. Lyons, G. Wilkinson, M. Motevalli, A.J. Howes, M.B. Hursthouse, J. Chem. Soc. Dalton Trans. (1986) 279.
[24] A.R. Barron, G. Wilkinson, M. Motevalli, M.B. Hursthouse, J. Chem. Soc. Dalton Trans. (1987) 837.
[25] A. Miehr, R.A. Fischer, E. Herdtweck, unpublished results.
[26] R.A. Fischer, W.J. Scherer, J. Organomet. Chem. 459 (1993) 65.
[27] J. Su, X.-W. Li, R.C. Crittendon, F.C. Campara, G.H. Robinson, Organometallics 16 (1997) 4511.
[28] (a) H. Preut, H.-J. Haupt, Acta Crystallogr. Sect. B 35 (1979) 2191. (b) J.L. Atwood, S.G. Bott, P.B. Hitchcock, C. Eaborn, R.S. Shariffundin, J.D. Smith, C. Sullivan, J. Chem. Soc. Dalton Trans. (1987) 747. (c) J.M. Cassidy, K. Whitmire, Acta Crystallogr. Sect. C 46 (1990) 1781. (d) V.G. Albano, M. Cane, M.C. Iapalucci, G. Longoni, M. Monari, J. Organomet. Chem. 407 (1991) C9. (e) L.M. Clarkson, N.C. Norman, L.J. Farrugia, Organometallics 10 (1991) 1286. (f) K. Merzweiler, F. Rudolph, L. Brands, Z. Naturforsch. Teil B 47 (1992) 470. (g) R.A. Fischer, J. Behm, T. Priermeier, W. Scherer, Angew. Chem. Int. Ed. Engl. 32 (1993) 746. (h) C.-C. Lin, G. Kong, H. Cho, B.R. Whittlesey, Inorg. Chem. 32 (1993) 2705. (i) R.A. Fischer, E. Herdtweck, T. Priermeier, Inorg. Chem. 33 (1994) 934. (j) P. Braunstein, M. Knorr, M. Strampfer, A. DeCian, J. Fischer, J. Chem. Soc. Dalton Trans. (1994) 117. (k) D.L. Reger, S.S. Mason, A.L. Rheingold, B.S. Haggerty, F.P. Arnold, Organometallics 13 (1994) 5049. (l) C.J. Carmalt, N.C. Norman, R.F. Pember, L.J. Farrugia, Polyhedron 14 (1995) 417.
[29] D.L. Reger, Y. Ding, Organometallics 12 (1993) 4485.
[30] (a) P.E. Riley, R.E. Davis, Inorg. Chem. 19 (1980) 159. (b) B.T. Kilbourn, U. Reaburn, D.T. Thompson, J. Chem. Soc. A (1969) 1906. (c) F.A. Cotton, B.M. Troup, J. Am. Chem. Soc. 96 (1974) 3438. (d) G. Dettlaf, U. Behrens, E. Weiss, J. Organomet. Chem. 152 (1978) 95.
[31] D.L. Reger, D.G. Garza, Organometallics 17 (1998) 3624.
[32] P. Jutzi, B. Neumann, G. Reumann, H.-G. Stammler, Organometallics 17 (1998) 1305.
[33] (a) X. He, R.A. Bartlett, P.P. Power, Organometallics 13 (1994) 548. (b) R.M. Campell, L.M. Clarkson, W. Clegg, D.C.R. Hockless, N.L. Pickett, N.C. Norman, Chem. Ber. 124 (1992) 55.
[34] J. Uddin, C. Boehme, G. Frenking, Organometallics 19 (2000) 571.
[35] D.D. Perrin, W.L.F. Amarego, D.R. Perrin, Purification of Laboratory Chemicals, Pergamon, New York, 1980.
[36] J.A. Gladysz, W. Tam, J. Org. Chem. 43 (1978) 2279.
[37] M.M. Schulte, Ph.D. Thesis, TU München, München, 1996.
[38] M.A. Schwindt, T. Lejon, L.S. Hegedus, Organometallics 9 (1990) 2814.
[39] H. Lehmkuhl, O. Olbrysch, H. Nehl, Liebigs Ann. Chem. (1973) 708.
[40] G.M. Sheldrick, SHELX-86, University of Göttingen, Germany, 1986.
[41] G.M. Sheldrick, SHELXL-97, University of Göttingen, Germany, 1997.