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Reactions of Transition Metal Carbonyl Dianions with (Organo)gallium Chlorides: Anionic Gallium Complexes of Chromium, Iron, and Manganese. Structure of $[PPN]_2\{[(CO)_4Fe-Ga(CH_3)-Fe(CO)_4]\}$[†]

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Salt elimination reactions between the divalent transition carbonyl metalates $[L(CO)_nM]^{2-}$ (M = Cr, Mn, Fe; L = CO, NO; $n = 3, 4$) and the (organo)gallium halides Cl_aGaR_{3-a} (R = CH_3, CH_2CH_3; $a = 1, 2, 3$) as well as the intramolecularly donor stabilized species $ClGa[(CH_2)_3NMe_2](R)$ (R = Cl, Me, ^{t}Bu) have been studied in some detail. Novel stable anionic (organo)gallium and chlorogallium metal complexes of the types $\{[L(CO)_nM]Ga[(CH_2)_3NMe_2](R)\}^-$ (**1**−**6**), $\{[L(CO)_nM]GaCl_2\}^-$ (**7**, **8**), $\{[L(CO)_nM]Ga(Cl)(R)\}^-$ (**9**, **10**), and $\{[L(CO)_nM]_2Ga(CH_3)\}^{2-}$ (**11**−**13**) have been prepared in high yields and were fully characterized by means of elemental analysis, infrared ν(CO) data, and NMR spectroscopy. The effect of substituents at the Ga center on the Lewis acidity was studied by temperature-dependent NMR (inversion at the N atom of the alkylamine ligand) using the compounds **1**−**6**. The compounds **7**−**10** are supposed to be dimeric. The dianionic complex $[PPN]_2\{[(CO)_4Fe-Ga(CH_3)-Fe(CO)_4]\}$ (**11a**) was also characterized by single-crystal X-ray diffraction: monoclinic, $C2/c$, $a = 2699.1(3)$ pm, $b = 1411.2(2)$ pm, $c = 2392.8(3)$ pm, $\beta = 127.45(1)°$, $V = 7236 \times 10^6$ pm^3, $Z = 4$, and $R = 0.038$ ($R_w = 0.097$). The diminished Lewis acidity of the compounds **1**−**13** is explained by an electrostatic effect, which also stabilizes low-coordinate Ga centers without steric shielding.

Introduction

The chemistry of (organo)gallium halides with transition metal carbonyl *mono*anions has been the subject of a number of recent publications.[1−6] This current interest in transition metal substituted gallanes of the general formula $[L(CO)_nM]_a[GaR_{3-a}(Do)]$ (Do = Lewis donor ligand) is stimulated by the potential application of some representative compounds of this type, e.g. $(CO)_nM-GaEt_2(NMe_3)$ (M = Co, Mn; $n = 4, 5$) or $[\eta^5\text{-}C_5H_5(CO)_2]Fe-Ga\{[(CH_2)_3NMe_2](BH_4)\}$ as single source precursors for OMCVD of the respective intermetallic alloys, such as CoGa,[7,8] MnGa,[9] and FeGa.[10] The chemistry of the halides of the heavier group 13 elements indium and thallium with transition metal carbonyl *di*anions has been studied recently. Examples include the "inidene" complexes $\{(CO)_5Cr-In(Cl)-Cr(CO)_5\}^{2-}$,[11] the linear metallacumulene $\{(CO)_5Cr-Tl-Cr(CO)_5\}^-$,[12] the indium rich complex *cis*-$[(CO)_4Fe]\{(\mu\text{-}Cl)InR\}_2$ (R = $C(SiMe_3)_3$),[13] and the Lewis acid−base adducts $(CO)_nM-In[HB(3,5\text{-}Me_2pz)_3]$ (M = Fe, W; $n = 4, 5$).[14] Older work contains the structure determination of $[(CO)_4FeGa(\eta^1\text{-}CH{=}CH_2)(THF)]_2$.[15] The heterolytic dissociation behavior of *monoanionic* Lewis acid/base adducts $[L(CO)_nM-Ga(C_6H_5)_3]^-$ has also been studied some time ago.[16] These examples summarize the knowledge on the reactivity of (*organo*)gallium compounds with divalent carbonylmetalates yielding anionic or neutral transition metal group 13 metal systems prior to our recent work. We have reported the synthesis of the first *digallylated* transition metal complexes $(CO)_4Fe\{Ga[(CH_2)_3NMe_2](R)\}_2$ (R = ^{t}Bu, Ph), the tetranuclear complex $\{(CO)_4FeGa[(CH_2)_3NMe_2]\}_2$, and some OMCVD applications of these compounds.[10,17] We are challenged by two rather difficult problems: Deriving gallium-rich and volatile transition metal complexes, which might be suitable to deposit gallium-rich thin alloy films, and obtaining rather strong transition metal gallium bonds, which are thought to be advantageous in view of such applications. Therefore we were led to investigate the chemistry of Cl_aGaR_{3-a} with higher valent carbonylmetalates more thoroughly.

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[†] Organo Group 13 Metal Transition Metal Complexes. 15. For part 14, see ref 31. This work is dedicated to Prof. G. Huttner on the occasion of his 60th birthday.

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Table 1. Numbering Scheme of the New Compounds **1**−**13**

no.	M[a]	R	$[R_4E]^+$
	$\{(CO)_nM-Ga[(CH_2)_3NMe_2](R)\}[R_4E]$		
1	Fe	tBu	PPN
2	Fe	Cl	PPN
3	Cr	tBu	PPN
4	Cr	Cl	PPN
5	Cr	Me	PPN
6	Mn	tBu	PPN
	$[(CO)_nM-GaCl_2][R_4E]$		
7	Fe	Cl	PPN
8a	Cr	Cl	Ph_4P
8b	Cr	Cl	K(THF)
9	Fe	Me	PPN
10	Fe	Et	PPN
	$\{[(CO)_nM]_2GaR\}[R_4E]_2$		
11a	Fe	Me	PPN
11b	Fe	Me	Ph_4As
12	Cr	Me	Ph_4As
13	Cr	Et	PPN

[a] $(CO)_nM$: M = Fe, $n = 4$; M = Cr, $n = 5$. M = Mn: $(NO)(CO)_3Mn$.

Experimental Section

All manipulations were undertaken by utilizing standard Schlenk and glovebox techniques under inert-gas atmospheres (purified N_2 or argon). Solvents were dried under N_2 by standard methods and stored over molecular sieves (4 Å, Merck; residual water < 3 ppm, Karl Fischer). Infrared spectra were recorded as solutions between CaF_2 plates with a Perkin-Elmer 1600 FT-IR instrument and are reported in reciprocal centimeters. JEOL JNM-GX400 and JNM-GX270 and Bruker DPX 400 spectrometers were used for NMR spectroscopy (^1H and ^{13}C NMR spectra were referenced to internal solvent and corrected to TMS). All samples for NMR spectra were contained in vacuum-sealed NMR tubes. Melting points were observed in sealed capillares and were not corrected. Starting compounds $Cl_2Ga[(CH_2)_3NMe_2]$,[18] $ClGaMe_2$,[19] $[(CO)_4Fe]K_2$,[20] $[(CO)_5Cr]K_2$,[21] and $[NO(CO)_3Mn]K_2$[22] were prepared as described in the literature. The syntheses of $ClGa[(CH_2)_3NMe_2](R)$ (R = Me, ^tBu) are described below. [PPN]Cl (Fluka), $[Ph_4As]Cl$ (Aldrich), $Tl[PF_6]$ and $[NO][PF_6]$ (Strem), and isoamyl nitrite (Aldrich) were used without further purification as purchased. Abbreviations are as follows: Me = CH_3, Et = CH_2CH_3, ^tBu = *tert*-butyl, Ph = phenyl, PPN = bis(triphenylphosphoranylidene)ammonium. Elemental analyses were provided by the Microanalytic Laboratory of the Technische Universität München. The numbering schemes of the new compounds are given in Table 1.

Synthesis of $ClGa[(CH_2)_3NMe_2](^tBu)$. To a solution of 10.7 g (47.2 mmol) of $Cl_2Ga[(CH_2)_3NMe_2]$ in 250 mL of toluene was slowly added 31.5 mL (47.2 mmol) of ^tBuLi in hexane ($c = 1.5$ mol L^{-1}) at −78 °C. After complete addition the reaction mixture was allowed to warm up to room temperature and was stirred for 16 h. The milky suspension was filtered, and the product was recovered from the white powder ("ate complex") by sublimation. Yield: 11.3 g (96%).

Characterization Data for $ClGa[(CH_2)_3NMe_2](^tBu)$: Colorless waxy solid, subl. 60 °C (10^{-2} Torr); ^1H NMR (399.78 MHz, CD_2Cl_2, 25 °C) δ 0.6 (t, 2 H, $GaCH_2$), 1.05 (s, 9 H, CCH_3), 1.84 (m, 2 H, $GaCH_2CH_2$), 2.40 (t, 2 H, CH_2N), 2.49 (s, 6 H, NCH_3); $^{13}C\{^1H\}$ NMR (67.9 MHz, CD_2Cl_2, 25 °C) δ 13.5 ($GaCH_2$), 24.4 ($GaCH_2CH_2$), 29.4 (GaC), 31.7 (CCH_3), 48.0 (NCH_3), 64.7 (CH_2N). Anal. Calc for $C_9H_{21}ClGaN$ (found): C, 43.5 (43.4); H, 8.5 (8.45); N, 5.6 (5.5); Cl, 14.3 (14.15); Ga, 28.1 (27.8).

Synthesis of $ClGa[(CH_2)_3NMe_2](Me)$. To a solution of 7.8 g (50 mmol) of Cl_2GaMe in 100 mL of diethyl ether a suspension of 4.7 g (50 mmol) of $Li[(CH_2)_3NMe_2]$ was slowly added at dry ice temperature. After complete addition the reaction mixture was allowed to warm up to room temperature and was then stirred for 16 h. The milky suspension was filtered, and the product was isolated from the white powder ("ate complex") by sublimation. Yield: 10 g (97%).

Characterization Data for $ClGa[(CH_2)_3NMe_2](Me)$: White solid, subl. 60 °C (10^{-2} Torr). Anal. Calc for $C_6H_{15}ClGaN$ (found): C, 34.9 (34.9); H, 7.3 (7.3); N, 6.8 (6.8); Cl, 17.2 (17.2).

Syntheses of Bis(triphenylphosphoranylidene)ammonium {[(3-(Dimethylamino)propyl)-*tert*-butylgallio]tetracarbonylferrate, $\{(CO)_4FeGa[(CH_2)_3NMe_2](^tBu)\}[PPN]$ (1), and Bis(triphenylphosphoranylidene)ammonium {[(3-(Dimethylamino)propyl)chlorogallio]tetracarbonylferrate, $\{(CO)_4FeGa[(CH_2)_3NMe_2](Cl)\}[PPN]$ (2). A suspension of 492 mg (2 mmol) of $[(CO)_4Fe]K_2$ in 30 mL of THF was cooled to −78 °C, and 496 mg (2 mmol) of solid $ClGa[(CH_2)_3NMe_2](^tBu)$ was added with vigorous stirring. The reaction mixture was allowed to warm to room temperature, and after 2 h 1.26 g (2.2 mmol) of [PPN]Cl was added. After 1 h the mixture was filtered and the solvent was removed in vacuo followed by extensively washing the brown orange residue with diethyl ether. **1** was obtained in analytically pure form. Yield: 1.8 g (98%). **2** was prepared analogously from 492 mg (2 mmol) of $[(CO)_4Fe]K_2$, 454 mg (2 mmol) of $Cl_2Ga[(CH_2)_3NMe_2]$, and 1.26 g (2.2 mmol) of [PPN]Cl. Yield: 1.7 g (95%).

Characterization Data for 1: Yellow-white powder, mp 116−118 °C; ^1H NMR (399.78 MHz, CD_2Cl_2, 25 °C) δ 0.6 (t, 2 H, $GaCH_2$), 1.05 (s, 9 H, CCH_3), 1.84 (m, 2 H, $GaCH_2CH_2$), 2.40 (t, 2 H, CH_2N), 2.49 (s, 6 H, NCH_3), 7.46−7.51 (m, 30 H, $(Ph_3P)_2N^+$); $^{13}C\{^1H\}$ NMR (67.9 MHz, CD_2Cl_2, 25 °C) δ 13.5 ($GaCH_2$), 24.4 ($GaCH_2CH_2$), 29.4 (GaC), 31.7 (CCH_3), 48.0 (NCH_3), 64.7 (CH_2N), 127.4 (CP, J^1_{CP} = 108 Hz), 129.8 (*m*-Ph), 132.6 (*o*-Ph), 134.1 (*p*-Ph), 223.7 (FeCO); IR (*THF*, cm^{-1}): $\nu(CO)$ = 1955 (s), 1862 (s), 1840 (vs), 1826 (vs). Anal. Calc for $C_{49}H_{51}FeGaN_2O_4P_2$ (found): C, 64.0 (64.0); H, 5.6 (5.6); N, 3.05 (2.9); Fe, 6.1 (5.9); Ga, 7.6 (7.5).

Characterization Data for 2: White powder, mp 147−150 °C; ^1H NMR (270.16 MHz, CD_2Cl_2, 25 °C) δ 0.65 and 0.87 (AA′BB′, 2 H, $GaCH_2$), 1.72 and 1.93 (AA'BB'CC', 2 H, $GaCH_2CH_2$), 2.45 and 2.69 (s, 6 H, NCH_3) 3.41 and 3.69 (AA'BB', 2 H, CH_2N), 7.52−7.67 (m, 30 H, $(Ph_3P)_2N^+$); $^{13}C\{^1H\}$ NMR (67.9 MHz, CD_2Cl_2, 25 °C) δ 18.9 ($GaCH_2$), 23.3 ($GaCH_2CH_2$), 45.0 and 47.8 (NCH_3), 63.1 (CH_2N), 127.4 (CP, J^1_{CP} = 108 Hz), 129.8 (*m*-Ph), 132.6 (*o*-Ph), 134.1 (*p*-Ph), 220.8 (FeCO); IR (THF, cm^{-1}) $\nu(CO)$ = 1981 (m), 1895 (s), 1865 (vs), 1844 (s). Anal. Calc for $C_{45}H_{42}ClFeGaN_2O_4P_2$ (found): C, 60.2 (60.25); H, 4.7 (4.8); N 3.1 (3.1); Cl 3.95 (4.2); Fe, 6.2 (6.5); Ga, 7.8 (8.0).

Syntheses of Bis(triphenylphosphoranylidene)ammonium [(3-(Dimethylamino)propyl)-*tert*-butylgallio]pentacarbonylchromate, $\{(CO)_5CrGa[(CH_2)_3NMe_2](^tBu)\}[PPN]$ (3); Bis(triphenylphosphoranylidene)ammonium [(3-(Dimethylamino)propyl)chlorogallio]pentacarbonylchromate, $\{(CO)_5CrGa[(CH_2)_3NMe_2](Cl)\}[PPN]$ (4); and Bis(triphenylphosphoranylidene)ammonium [(3-(Dimethylamino)propyl)methylgallio]pentacarbonylchromate, $\{(CO)_5CrGa[(CH_2)_3NMe_2](CH_3)\}[PPN]$ (5). A THF suspension (30 mL) of $[(CO)_5Cr]K_2$ (2 mmol), freshly prepared from 440 mg (2 mmol) of $Cr(CO)_6$ and 2.2 equiv of C_8K (600 mg), was cooled to −78 °C, and 496 mg (2 mmol) of solid $ClGa[(CH_2)_3NMe_2](^tBu)$ was added with vigorous stirring. The reaction mixture was allowed to warm to room temperature, and after 2 h 1.26 g (2.2 mmol) of [PPN]Cl was added. After 1 h the mixture was filtered and the graphitic residue was extracted with 30 mL of THF (2 times). The filtrate and the extracts were combined, and the solvent was then removed in vacuo. The remaining yellow-orange residue was extensively washed with diethyl ether. Compound **3** was quantitatively obtained in an analytically pure form. **4** and **5** were prepared in the same manner. Yield: 1.84 g (98%) for **3**, 1.75 g (95%) for **4** (slight yellow powder), and 1.71 g (94,5%) for **5** (yellow powder).

Characterization Data for 3: Pale yellow powder; ^1H NMR (399.78 MHz, CD_2Cl_2, 25 °C) δ 0.62 (t, 2 H, $^3J(H,H)$ = 7.8 Hz, $GaCH_2$), 1.00 (s, 9 H, CCH_3), 1.81 (quint, 2 H, $^3J(H,H)$ = 7.8 Hz, $GaCH_2CH_2$), 2.38 (t, 2 H, $^3J(H,H)$ = 7.8 Hz, CH_2N), 2.51 (s, 6 H, NCH_3), 7.46−7.51 (m, 30 H, $(Ph_3P)_2N^+$). $^{13}C\{^1H\}$ NMR (67.9 MHz, CD_2Cl_2, 25 °C) δ 12.3 ($GaCH_2$), 24.6 ($GaCH_2CH_2$), 28.0 (GaC), 30.6 (CCH_3), 47.7 (NCH_3), 65.2 (CH_2N), 127.4 (CP, J^1_{CP} = 108 Hz), 129.8 (*m*-Ph), 132.6 (*o*-Ph), 134.1 (*p*-Ph), 239.3 (CrCO); ^1H NMR (270.16

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MHz, CD_2Cl_2, −60 °C) δ 0.45 (t, 1 H, $GaCH_2$), 0.60 (t, 1 H, $GaCH_2$), 0.93 (s, 9 H, CCH_3), 1.64 (m, 1 H, $GaCH_2CH_2$), 1.82 (m, 1 H, $GaCH_2CH_2$), 2.19 (t, 1 H, CH_2N), 2.38 (s, 3 H, NCH_3), 2.51 (t, 1 H, CH_2N), 2.56 (s, 3 H, NCH_3), 7.46−7.51 (m, 30 H, $(Ph_3P)_2N^+$); $^{13}C\{^1H\}$ NMR (67.9 MHz, CD_2Cl_2, −60 °C) δ 10.8 ($GaCH_2$), 23.7 ($GaCH_2CH_2$), 27.2 (GaC), 29.8 (CCH_3), 46.2 (NCH_3), 48.1 (NCH_3), 64.3 (CH_2N), 126.0 (CP), 129.2 (*m*-Ph), 131.7 (*o*-Ph), 133.4 (*p*-Ph), 216.1 (CrCO); IR (THF, cm^{-1}) ν(CO) = 1976 (vs), 1872 (s, sh), 1850 (vs, br), 1810 (s, sh). Anal. Calc for $C_{50}H_{51}CrGaN_2O_5P_2$ (found): C, 63.6 (63.5); H, 5.4 (5.4); N, 3.0 (2.9); Cr, 5.5 (5.05); Ga, 7.4 (7.4).

Characterization Data for 4: Yellow powder; ^1H NMR (399.78 MHz, CD_2Cl_2, 25 °C) δ 0.51 and 0.85 (AA'BB', 2 H, $GaCH_2$), 1.63 and 1.90 (AA'BB'CC', 2 H, $GaCH_2CH_2$), 2.29 and 2.91 (AA'BB', 2 H, CH_2N), 2.35 and 2.68 (s, 6 H, NCH_3), 7.49−7.75 (m, 30 H, $(Ph_3P)_2N^+$); $^{13}C\{^1H\}$ NMR (100.54 MHz CD_2Cl_2, 25 °C) δ 12.6 ($GaCH_2$), 22.3 ($GaCH_2CH_2$), 45.6 (NCH_3), 46.8 (NCH_3), 63.7 (CH_2N), 127.5 (CP), 129.9 (*m*-Ph), 132.5 (*o*-Ph), 133.6 (*p*-Ph), 231.4 (CrCO); IR (THF, cm^{-1}) ν(CO) = 2000 (s), 1908 (s, sh), 1872 (vs, br), 1860 (s, sh). Anal. Calc for $C_{46}H_{42}ClCrGaN_2O_5P_2$ (found): C, 59.9 (59.2); H, 4.6 (4.55); N 3.0 (2.9); Cr, 5.6 (5.6); Ga, 7.6 (7.8).

Characterization Data for 5: Yellow powder; ^1H NMR (399.78 MHz, CD_2Cl_2, 25 °C) δ −0.20 (s, 3 H, $GaCH_3$), 0.61 (m, 2 H, $GaCH_2$), 1.82 (m, 2 H, $GaCH_2CH_2$), 2.27 (m, 2 H, CH_2N), 2.44 (s, 6 H, NCH_3), 7.46−7.70 (m, 30 H, $(Ph_3P)_2N^+$); $^{13}C\{^1H\}$ NMR (100.54 MHz CD_2Cl_2, 25 °C) δ 2.2 ($GaCH_3$), 14.4 ($GaCH_2$), 24.6 ($GaCH_2CH_2$), 47.2 (NCH_3), 64.3 (CH_2N), 127.4 (CP, J^1_{CP} = 108 Hz), 129.8 (*m*-Ph), 132.6 (*o*-Ph), 134.1 (*p*-Ph), 228.3 (CrCO); ^1H NMR (399.78 MHz, CD_2Cl_2, −60 °C) δ −0.21 (s, 3 H, $GaCH_3$), 0.18 (t, 1 H, $GaCH_2$), 1.04 (t, 1 H, $GaCH_2$), 1.79 (m, 1 H, $GaCH_2CH_2$), 1.85 (m, 1 H, $GaCH_2CH_2$), 2.22 (t, 1 H, CH_2N), 2.32 (t, 1 H, CH_2N), 2.38 (s, 3 H, NCH_3), 2.50 (s, 3 H, NCH_3), 7.46−7.70 (m, 30 H, $(Ph_3P)_2N^+$); $^{13}C\{^1H\}$ NMR (100.54 MHz, CD_2Cl_2, −60 °C) δ 2.0 ($GaCH_3$), 15.0 ($GaCH_2$), 24.6 ($GaCH_2CH_2$), 46.6 (NCH_3), 47.8 (NCH_3), 64.5 (CH_2N), 127.5 (CP), 129.9 (*m*-Ph), 132.5 (*o*-Ph), 133.6 (*p*-Ph), 217.0 (CrCO), 228.3 (CrCO); IR (THF, cm^{-1}) ν(CO) = 1978 (vs), 1854 (vs, br), 1806 (s, sh). Anal. Calc for $C_{48}H_{45}CrGaN_2O_5P_2$ (found): C, 63.1 (63.4); H, 5.0 (5.15); N, 3.1 (3.05); Cr, 5.7 (5.65); Ga, 7.6 (7.4).

Synthesis of Bis(triphenylphosphoranylidene)ammonium [(3-(Dimethylaminopropyl)-*tert*-butylgallio]tricarbonylnitrosylmanganate, $\{(CO)_3(NO)MnGa[(CH_2)_3NMe_2](^tBu)\}[PPN]$ (6). A suspension of 2 mmol $[NO(CO)_3Mn]K_2$ in 30 mL of THF was cooled to −78 °C, and 496 mg (2 mmol) of solid $ClGa[(CH_2)_3NMe_2](^tBu)$ was added with vigorous stirring. The reaction mixture was allowed to warm to room temperature, and after 2 h 1.26 g (2.2 mmol) of [PPN]Cl was added. After 1 h the mixture was filtered and the solvent removed in vacuo. The brown residue was thoroughly washed with diethyl ether, and 1.62 g (88%) of compound **6** was obtained.

Characterization Data for 6: ^1H NMR (399.78 MHz, CD_2Cl_2, 25 °C) δ 0.66 and 0.90 (t, 2 H, $GaCH_2$), 1.05 (s, 9 H, CCH_3), 1.78 and 1.96 (m, 2 H, $GaCH_2CH_2$), 2.51 and 2.66 (s, 6 H, NCH_3), 3.05 and 3.28 (t, 2 H, CH_2N), 7.46−7.51 (m, 30 H, $(Ph_3P)_2N^+$); $^{13}C\{^1H\}$ NMR (67.9 MHz, CD_2Cl_2, 25 °C) δ 15.7 ($GaCH_2$), 22.4 ($GaCH_2CH_2$), 28.3 (GaC), 31.1 (CCH_3), 46.4 and 48.1 (NCH_3), 64.2 (CH_2N), 127.4 (CP), 129.8 (*m*-Ph), 132.6 (*o*-Ph), 134.1 (*p*-Ph), CO not observed; IR (THF, cm^{-1}) ν(CO, NO) = 1931 (s), 1847 (s), 1812 (vs), 1598 (s, NO). Anal. Calc for $C_{48}H_{51}MnGaN_3O_4P_2$ (found): C, 62.6 (61.2); H, 5.6 (5.2); N 4.6 (4.3); Mn, 6.0 (5.9); Ga, 7.6 (7.2).

Synthesis of Bis[bis(triphenylphosphoranylidene)ammonium] Bis[(dichlorogallio)tetracarbonylferrate], $\{[(CO)_4FeGaCl_2][PPN]\}_2$ (7). A suspension of 492 mg (2 mmol) of $[(CO)_4Fe]K_2$ in 30 mL of THF was cooled to −78 °C, and 352 mg (2 mmol) of $GaCl_3$ was added with vigorous stirring. The reaction mixture was allowed to warm to room temperature, and after 3 h 1.26 g (2.2 mmol) of [PPN]Cl was added. After 1 h the mixture was filtered and the solvent was removed in vacuo. The yellow-white residue was extensivly washed with diethyl ether. Compound **7** was obtained in an analytically pure form in a yield of 1.6 g (94.5%).

Characterization Data for 7: Yellow-white powder; ^1H NMR (399.78 MHz, CD_2Cl_2, 25 °C) δ 7.46−7.51 (m, 30 H, $(Ph_3P)_2N^+$); $^{13}C\{^1H\}$ NMR (67.9 MHz, CD_2Cl_2, 25 °C) δ 127.4 (CP, J^1_{CP} = 108 Hz), 129.8 (*m*-Ph), 132.6 (*o*-Ph), 134.1 (*p*-Ph), 223.7 (FeCO); IR (THF, cm^{-1}) ν(CO) = 1996 (s), 1906 (s, sh), 1886 (vs). Anal. Calc for $C_{40}H_{30}Cl_2FeGaNO_4P_2$ (found): C, 56.7 (56.3); H, 3.6 (3.8); N, 1.65 (1.85); Fe, 6.6 (6.35); Ga, 8.2 (8.5) %.

Syntheses of Bis(tetraphenylphosphonium) Bis[(dichlorogallio)-pentacarbonylchromate], $\{[(CO)_5CrGaCl_2](Ph_4P)\}_2$ (8a), and Its [(Tetrahydrofuran)potassium] Salt, $[(CO)_5CrGaCl_2][K(THF)]$ (8b). A suspension of 4 mmol of $[(CO)_5Cr]K_2$, freshly prepared from $Cr(CO)_6$ (880 mg, 4 mmol) and C_8K (1.2 g, 2.2 equiv), in 60 mL of THF was cooled to −78 °C, and 705 mg (4 mmol) of $GaCl_3$ was added with vigorous stirring. The reaction mixture was allowed to warm to room temperature, and after 3.5 h 1.5 g (4 mmol) of $[Ph_4P]Cl$ was added. After 1 h the mixture was filtered and the graphitic residue was extracted 2 times with 20 mL of THF. In the case of **8b** the reaction mixture was filtered without addition of any salt. The THF solutions were combined, the solvent was removed in vacuo, and the residue was dried. The remaining yellow-orange residue was extensively washed with diethyl ether. Compound **8a** was obtained analytically pure and quantitatively (1.33 g). Compound **8b** was obtained as microcrystalline white needles after washing with a mixture of cold diethyl ether/pentane. Yield: 820 mg (92%).

Characterization Data for 8a: Yellow powder; ^1H NMR (399.78 MHz, CD_2Cl_2, 25 °C) δ 7.60−7.93 (m, 20 H, $(Ph_4P)^+$); $^{13}C\{^1H\}$ NMR (67.9 MHz, CD_2Cl_2, 25 °C) δ 117.9 (CP, J^1_{CP} = 89 Hz), 131 (*o*-Ph, J^2_{CP} = 13), 134.8 (*m*-Ph, J^3_{CP} = 10), 136.1 (*p*-Ph, J^4_{CP} = 3), 225.3 (CrCO); IR (THF, cm^{-1}) ν(CO) = 1995 (s), 1938 (s, sh), 1915 (vs), 1883 (m, sh). Anal. Calc for $C_{29}H_{20}Cl_2CrGaO_5P$ (found): C, 51.8 (51.7); H, 3.0 (3.1); Cl, 10.55 (10.3); Cr, 7.7 (7.6); Ga, 10.4 (9.9).

Characterization Data for 8b: White needles; IR (Et_2O, cm^{-1}) ν(CO) = 1998 (s), 1941 (s, sh), 1916 (vs), 1877 (m, sh). Anal. Calc for $C_9H_8Cl_2CrGaKO_6$ (found): C, 24.35 (25.1); H, 1.8 (2.05); Cl, 16.0 (15.4); Cr, 11.7 (11.5); Ga, 15.7 (15.9).

Syntheses of Bis[bis(triphenylphosphoranylidene)ammonium] Bis[(methylchlorogallio)tetracarbonylferrate], $\{[(CO)_4FeGa(Cl)(CH_3)][PPN]\}_2$ (9) and Bis[bis(triphenylphosphoranylidene)ammonium] Bis[(ethylchlorogallio)tetracarbonylferrate], $\{[(CO)_4FeGa(Cl)(CH_2CH_3)][PPN]\}_2$ (10). Synthesis was according to the procedure described for compound **7**, using 311 mg of Cl_2GaMe and 339 mg of Cl_2GaEt, respectively. After salt metatheses white or slightly pink microcrystalline powders were obtained in 91% (1.55 g) and 93% (1.61 g) yield.

Characterization Data for 9: White powder; ^1H NMR (399.78 MHz, CD_2Cl_2, 25 °C) δ 0.13 (s, 3 H, CH_3), 7.46−7.51 (m, 30 H, $(Ph_3P)_2N^+$); $^{13}C\{^1H\}$ NMR (67.9 MHz, CD_2Cl_2, 25 °C) δ 2.3 (CH_3), 127.4 (CP, J^1_{CP} = 108 Hz), 129.8 (*m*-Ph), 132.6 (*o*-Ph), 134.1 (*p*-Ph), 223.7 (FeCO); IR (THF, cm^{-1}) ν(CO) = 1997 (m), 1906 (s), 1877 (vs). Anal. Calc for $C_{41}H_{33}ClFeGaNO_4P_2$ (found): C, 57.7 (57.3); H, 3.9 (3.75); N, 1.6 (1.6); Fe, 6.5 (6.4); Ga, 8.2 (7.95).

Characterization Data for 10: White powder; ^1H NMR (399.78 MHz, CD_2Cl_2, 25 °C) δ 0.66 (q, 2 H, CH_2), 1.08 (t, 3 H, CH_3), 7.45−7.56 (m, 30 H, $(Ph_3P)_2N^+$); $^{13}C\{^1H\}$ NMR (67.9 MHz, CD_2Cl_2, 25 °C) δ 4.1 (CH_2), 9.9 (CH_3), 127.4 (CP, J^1_{CP} = 108 Hz), 129.8 (*m*-Ph), 132.6 (*o*-Ph), 134.1 (*p*-Ph), 223.7 (FeCO); IR (THF, cm^{-1}) ν(CO) = 1996 (m), 1981 (m), 1907 (s), 1876 (vs). Anal. Calc for $C_{42}H_{35}ClFeGaNO_4P_2$ (found): C, 59.1 (57.9); H, 4.1 (4.0); N 1.6 (1.55) %.

Syntheses of Bis[bis(triphenylphosphoranylidene)ammonium] {(Methylgallio)bis[tetracarbonylferrate], $\{[(CO)_4Fe]_2Ga(CH_3)\}[PPN]_2$ (11a), and Bis(tetraphenylarsonium) Salt $\{[(CO)_4Fe]_2Ga(CH_3)\}(Ph_4As)_2$ (11b). A suspension of $[(CO)_4Fe]K_2$ (492 mg, 2 mmol) in 30 mL of THF was cooled to −78 °C, and 271 mg (2 mmol) of $ClGaMe_2$ was added. Upon being warmed to room temperature within 2 h the reaction mixture became more homogeneous and developed a yellow-orange color. Then, a slight excess of [PPN]Cl (1.26 g, 2.2 mmol) or $[Ph_4As]Cl$ (0.9 g, 2.2 mmol) was added (intense odor of gallium alkyls). The color of the mixture turned yellow, and a white precipitate formed. After 30 min the solution was filtered and the solvent removed by vacuum distillation. The orange-brown residue was washed thoroughly with 50 mL of Et_2O with vigorous stirring, by which treatment the residue transformed into a flaky precipitate. The solvent was filtered off, and the powder was washed another 2 times with 50 mL of ether and dried overnight at $<10^{-4}$ Torr. Yields: **11a**, 1.3 g (87% based upon iron); **11b**, 1.09 g (92% based upon iron). Crystallization of **11a** from THF/heptane gave yellow, well-shaped crystals.

Table 2. Crystallographic and Data Collection Parameters for $\{[(CO)_4Fe]_2Ga(CH_3)\}[PPN]_2$ (**11a**)

formula	$C_{81}H_{63}Fe_2GaN_2O_8P_4$
fw	1497.71
cryst system	monoclinic
space group	*C*2/*c* (No. 15)
λ, pm	71.073
a, pm	2699.1(3)
b, pm	1411.2(2)
c, pm	2392.8(3)
β, deg	127.45(1)
V, 10^6 pm^3	7236
Z	4
ρ_{calc}, g cm^{-3}	1.375
μ(Mo Kα), cm^{-1}	9.1
no. of reflcns	6171
no. of obsd reflcns	4343
cutoff	$I > 4.0\sigma(I)$
R^a	0.038
$R_w{}^b$	0.097

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. $R_w = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2]^{1/2}$.

Table 3. Selected Interatomic Distances (pm) and Angles (deg) for the Anionic Part of **11a**

Distances			
Ga−Fe	241.58(6)	Fe−C(2)	173.5(4)
Fe−C(1)	174.2(6)	Fe−C(3)	176.1(3)
Ga−C	202.1(4)	Fe−C(4)	174.3(4)
Angles			
Fe−Ga−C	112.32(2)	Ga−Fe−C(1)	75.85(13)
Fe−Ga−Fe(a)	135.36(3)	Ga−Fe−C(2)	71.02(16)
Fe(a)−Ga−C	112.32(2)	Ga−Fe−C(3)	90.19(13)
Ga−Fe−C(4)	81.13(14)		

Characterization Data for 11a: ^{1}H NMR (399.78 MHz, CD_2Cl_2, 25 °C) δ −0.27 (s, 3 H, $GaCH_3$), 7.26−7.88 (m, 30 H, $(Ph_3P)_2N^+$); $^{13}C\{^1H\}$ NMR (100.54 MHz, CD_2Cl_2, 25 °C) δ −0.5 ($GaCH_3$), 127.4 (CP, $J^1{}_{CP}$ = 108 Hz), 129.8 (*m*-Ph), 132.6 (*o-Ph*), 134.1 (*p*-Ph), 223.8 (FeCO); ^{31}P NMR (161.85 MHz, CD_2Cl_2, 25 °C) δ 21.4; IR (THF, cm^{-1}) ν(CO) = 1952 (vs), 1874 (vs, sh), 1851 (vs), 1827 (vs, sh). Anal. Calc for $C_{81}H_{63}Fe_2GaN_2O_8P_4$ (found): C, 65.0 (64.6); H, 4.3 (4.6); N, 1.9 (1.8); Fe, 7.45 (7.1); Ga, 4.65 (5.05).

Characterization Data for 11b: IR (THF, cm^{-1}) ν(CO) = 1956 (s), 1876 (vs, sh), 1865 (vs), 1840 (vs). Anal. Calc for $C_{57}H_{43}As_2Fe_2GaO_8$ (found): C, 57.7 (56.4); H, 3.65 (3.8); Fe, 9.4 (9.4); Ga, 5.9 (5.5).

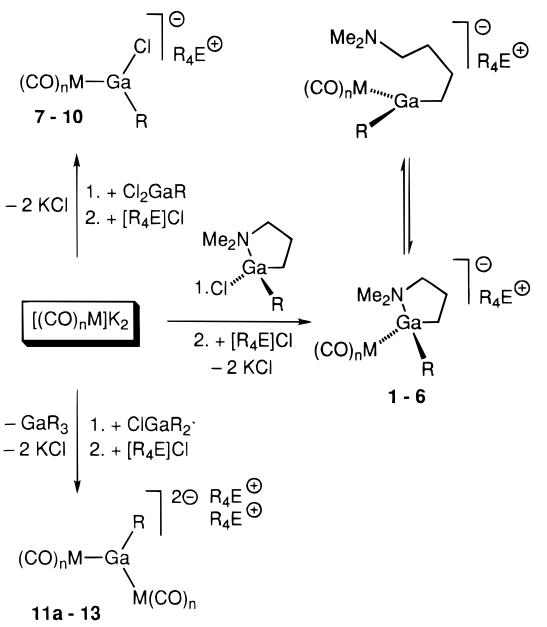
Synthesis of Bis(tetraphenylarsonium) {(Methylgallio)bis[pentacarbonylchromate], $\{[(CO)_5Cr]_2Ga(CH_3)\}(Ph_4As)_2$ (12). To a suspension of C_8K (600 mg, 4.4 mmol) in THF (30 mL) was added a sample of $Cr(CO)_6$ (440 mg, 2 mmol) at dry ice temperature. After 3 h 271 mg (2 mmol) of $ClGaMe_2$ was added to the greenish-gray suspension. The reaction mixture was allowed to warm to room temperature whereupon the solution developed a muddy green color. Finally, after addition of $[Ph_4As]Cl$ (1 g, 2.1 mmol) the color turned to deep red. Workup as described for compound **5** gave 1.05 g of a yellow microcrystalline powder. Yield: 85% (based upon chromium). Orange crystalline needles were obtained from THF/heptane.

Characterization Data for 12: ^{1}H NMR (399.78 MHz, CD_2Cl_2, 25 °C) δ −0.28 (s, 3 H, $GaCH_3$), 7.61−7.79 [m, 20 H, (Ph_4As^+)]; $^{13}C\{^1H\}$ NMR (100.54 MHz, CD_2Cl_2, 25 °C) δ −0.1 ($GaCH_3$), 120.7 (CAs), 131.7 (*m*-Ph), 133.3 (*o*-Ph), 135.3 (*p*-Ph), 211 and 217 (CrCO); IR (THF, cm^{-1}) ν(CO) = 1994 (m), 1982 (m), 1958 (m), 1912 (m, sh), 1880 (vs, sh), 1856 (vs). Anal. Calc for $C_{59}H_{43}As_2Cr_2GaO_{10}$ (found): C, 57.35 (56.5); H, 3.5 (3.5); Cr, 8.4 (8.2); Ga, 5.6 (5.9).

Synthesis of Bis[bis(triphenylphosphoranylidene)ammonium] {(Ethylgallio)bis[pentacarbonylchromate], $\{[(CO)_5Cr]_2Ga(CH_2CH_3)\}[PPN]_2$. Synthesis and workup followed the same procedure as described for compound **12**, with the only difference of using 170 mg (1 mmol) of Cl_2GaEt. Yield: 1.42 g (91% based on chromium).

Characterization Data for 13: ^{1}H NMR (270.16 MHz, CD_2Cl_2, 25 °C) δ −0.41 (q, 2 H, $GaCH_2$), 0.83 (t, 3 H, CH_2CH_3), 7.24−7.63 (m, 30 H, $(Ph_3P)_2N^+$); $^{13}C\{^1H\}$ NMR (67.9 MHz, CD_2Cl_2, 25 °C) δ −0.8 ($GaCH_2$), 14.0 (CH_2CH_3), 127.4 (CP), 129.8 (*m*-Ph), 132.6 (*o*-Ph), 134.1 (*p*-Ph), 216.3 and 224.3 (CrCO); IR (THF, cm^{-1}) ν(CO) = 1994 (m), 1957 (vs), 1882 (vs), 1851 (vs). Anal. Calc for $C_{84}H_{65}Cr_2GaN_2O_{10}P_4$ (found): C, 64.7 (63.85); H, 4.2 (4.6); N, 1.8 (1.8); Cr, 6.7 (6.4); Ga, 4.5 (4.3).

Scheme 1. Synthetic Pathways to Anionic Transition Metal Gallanes and Dianionic Gallium “Inidene” Complexes



Single-Crystal X-ray Diffraction Analysis of 11a. Crystals of compound **11a** were grown by standard cooling techniques at low temperature from a mixture of THF/heptane. Preliminary examination and data collection were carried out on a IPDS Image Plate Systeme (Stoe & Cie) diffractometer with a rotating anode. Final cell constants were obtained by least-squares refinement of 1720 reflections. For the crystallographic and selected bonding parameters see Tables 2 and 3. Further details can be obtained from the Supporting Information or directly from the authors (R.A.F. and E.H.).

Results and Discussion

A. Syntheses and Properties. The combination of equimolar quantities of the *intramolecularly* base stabilized alkylgallium chlorides $Cl_aGa[(CH_2)_3NMe_2](R)_{2-a}$ (*a* = 1, 2) and the carbonylmetalate dianions $[L(CO)_nM]^{2-}$ (M = Cr, Mn, Fe; L = CO, NO; *n* = 3, 4) in THF as reaction medium leads to the new monoanionic complexes **1**−**6** (Scheme 1). To isolate these complex salts as analytically pure microcrystalline, solvent-free powders, it is necessary to exchange the remaining potassium cation by noncoordinating counterions, e.g. PPN^+, Ph_4P^+, or Ph_4As^+. The solvent and the type of counterion of the carbonylmetalate is of crucial importance for the course of these reactions. $K_2[Fe(CO)_4]$ and $Cl_2Ga[(CH_2)_3NMe_2]$ react to give the intermediate species $K\{(CO)_4Fe{-}Ga[(CH_2)_3NMe_2](Cl)\}$ (**2-K**), which is clearly identified by the ν(CO) IR spectrum that shows similar absorptions as the corresponding PPN salt **2**. Without the exchange of the potassium cation but rather on replacing the polar coordinating solvent THF by toluene, the second equivalent of KCl is eliminated from the intermediate **2-K** and the neutral tetranuclear complex $\{(CO)_4FeGa[(CH_2)_3NMe_2]\}_2$ is obtained.[16] This compound can be viewed as the dimerization product of the presumably unstable and still unknown “gallylene” complex $(CO)_4Fe{=}Ga[(CH_2)_3NMe_2]$. This formal dimerization can be blocked by introduction of the sterically very demanding 1,1-bis(trimethylsilyl)-3-(dimethylamino)propyl ligand[16,23] at the gallium center. The pres-

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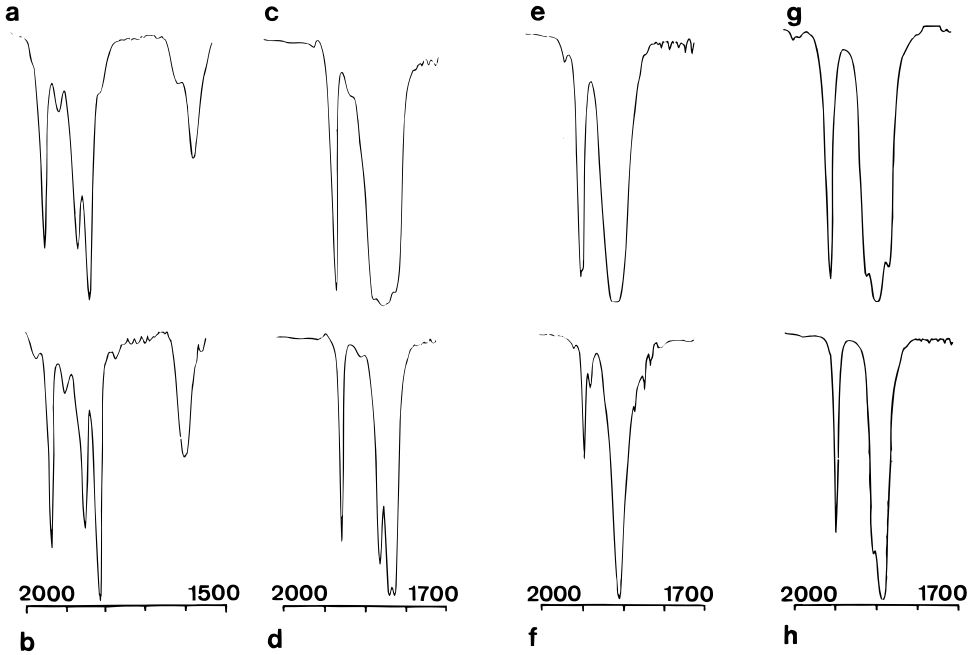

Figure 1. (a, b) IR spectra in the region 2000−1500 cm^{-1}. (c−h) IR spectra in the region 2100−1700 cm^{-1}. Markers indicate 100 cm^{-1} separation. Key: (a) **6-K**; (b) **6**; (c) **1-K**; (d) **1**; (e) **8a-K**; (f) **8a**; (g) **7-K**; (h) **7** . All spectra were recorded as thin films of THF solutions between CaF_2 plates, except spectrum f, which was run in CH_2Cl_2. (The supposed primary products, the potassium salts of the complex anions, are denoted as No-K.)

ence of the anionic species $\{[(CO)_4Fe-Ga[C(TMS)_2(CH_2)_2NMe_2](Cl)\}K$ in THF solution was suggested by the IR spectrum, but the compound did not eliminate KCl upon solvent exchange as it is observed for **2-K**. Also, the steric requirements of the transition metal fragment do play a decisive role. The reaction of $K_2[Cr(CO)_5]$ with $Cl_2Ga[(CH_2)_3NMe_2]$ stops at the stage of monosubstitution (**4**). The different steric requirements of a $Cr(CO)_5$ compared to a $Fe(CO)_4$ moiety in transition metal group 13 chemistry are also nicely shown by the molecular structures of $\{(CO)_5Cr-Tl-Cr(CO)_5\}^{-}$ [12] and $\{(CO)_4Fe-Tl-Fe(CO)_4\}^{-}$.[24] The iron system is associated in the solid state via Tl−Tl interactions, while the chromium complex is monomeric. With the nitrosyl derivative $[(NO)(CO)_3Mn]^{2-}$ however, which is formally isoelectronic to $[(CO)_4Fe]^{2-}$, only the monosubstituted gallium complex $\{(NO)(CO)_3Mn-Ga[(CH_2)_3NMe_2](^tBu)\}^{-}$ (**6**) is obtained (Figure 1). This latter result is a consequence of the diminished nucleophilicity at the metal center caused by the strong π-accepting nitrosyl substituent.[25] The remaining halide functionality of $\{(CO)_5Cr-Ga[(CH_2)_3NMe_2](Cl)\}^{-}$ (**4**) can be removed with $Tl[PF_6]$ as TlCl. The resulting red oily product consists of neutral species which were identified on the basis of their IR ν(CO) patterns. NMR data (toluene-d_8) for the product reveal only a single signal pattern for the alkylamine ligand. Thus the gallium center seems to have no chiral ligand sphere any more. But an unambiguous clear identification of the product could not be achieved. Single electron oxidation occurs in the case of $\{(CO)_5Cr-Ga[(CH_2)_3NMe_2](^tBu)\}^{-}$ (**3**) when treated with Tl^+, Ag^+, and Fc^+ to give deep red THF solutions containing paramagnetic compounds which we are currently investigating.

(Organo)gallium halides *without* intramolecular adduct stabilization behave differently when treated with divalent carbonylmetalates. The methyl and ethyl analogs of **2** and **4**, $[(CO)_nM]Ga(R)_2(THF)]^{-}$, which we could not isolate from the reaction mixtures, split off GaR_3 quite rapidly, which species were recovered as their THF adducts, to yield the dianionic gallium complexes **11a**,**b**, **12**, and **13**. The course of this reaction is in accordance with the general instability of L_nM-GaR_2 compounds,[1] exhibiting three coordinated gallium centers and sterically less demanding alkyl groups. To date, the only base-free dialkylgallium transition metal compounds which have been isolated in a pure form and were thoroughly characterized by single-crystal X-ray diffraction studies are $(\eta^5-C_5H_5)(CO)_3WGaMe_2$,[26] $(\eta^5-C_5H_5)(CO)_2FeGa^tBu_2$,[27] *cis*-$[(Cy_2PCH_2CH_2PCy_2)(^tBuCH_2)]PtGa(CH_2{}^tBu)_2$ (Cy = cyclohexyl),[28] and $[(CO)_4Co]_2Ga(2,4,6-{}^tBu_3C_6H_2)$.[6] Alternatively, but less selectively, the reaction of Cl_2GaR (R = Me, Et) with 2 equiv of divalent carbonylmetalates results in the formation of **11a**−**13**, too. Interestingly, with $GaCl_3$ and 2 equiv of the respective carbonylmetalate, the corresponding chloro complexes $\{[(CO)_nM]_2(\mu-GaCl)\}^{2-}$ have not been obtained so far.

We also tried to isolate compounds of the type $\{[(CO)_nM]_mGaCl_{3-m}\}^{|2m-3|-}$ (m = 1, 2, 3), but up to now we were only successful for $m = 1$. In the latter case we isolated compounds for which analytical data are consistant with the base-free (e.g. THF free) formulas $[(CO)_4FeGaCl_2](PPN)$ (**7**) and $[(CO)_5CrGaCl_2](Ph_4P)$ (**8a**). With coordinating counterions, e.g. potassium, $[(CO)_5CrGaCl_2][K(THF)]$ (**8b**) was obtained (exactly one molecule of THF by elemental analysis). In a similar manner the mixed alkyl chloro compounds $[(CO)_4FeGa(Cl)(R)](PPN)$ (R = Me, Et) (**9**, **10**) could also be isolated. These compounds do not split off GaR_3. This behavior can be explained with the formation of tetranuclear dianionic intermediates (Scheme 2), analogous to the known neutral congeners, from which only those species with twice alkylated gallium centers could split off trialkylgallium leading to formation of "inidene" complexes.

The structure of the solvent-free compounds **7**−**10** would be interesting, but so far we were not lucky to obtain suitable single crystals. In the solid state, the anionic parts of the complex salts are likely to be associated via the Ga atom (for the iron

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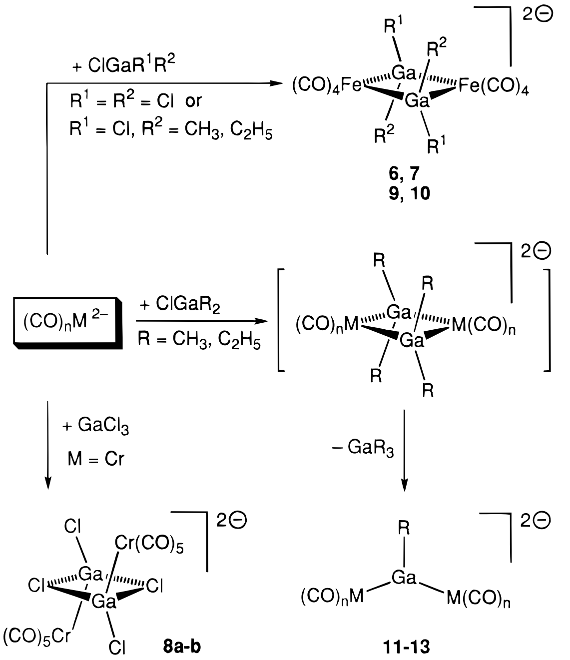
Scheme 2. Proposed Dianionic Dimeric Structures[a]



[a] For $R^1 = R^2 = Cl$ and $R^1 = Cl$ and $R^2 =$ alkyl these structures are stable; with $R^1 = R^2 =$ alkyl they are not and split off trialkylgallium.

compounds) or Cl bridges (for the chromium compounds) because of the favored tetracoordination of gallium. The situation in solution is discussed later on. So these compounds should be better formulated as dianionic dimers $\{[(CO)_nM-Ga(R^1)(R^2)]_2\}^{2-}$ ($R^1 = R^2 = Cl$ or $R^1 = Cl$, $R^2 =$ alkyl).

Reaction of $[(CO)_5Cr]^{2-}$ with 2 equiv of donor-stabilized dialkylgallium chlorides $ClGa[(CH_2)_3NMe_2](R)$ (R = Me, ${}^tBu$) results in the formation of the monoanionic compounds **3** and **5**. The digallylated neutral species like $(CO)_4Fe\{Ga[(CH_2)_3NMe_2](R)\}_2$ (R = ${}^tBu$, Ph)[17] were not formed. We attribute this result to the diminished nucleophilicity of the monoanionic intermediates (**3-K** to **5-K**). Therefore, a second substitution reaction is unlikely, similar to the system $[NO(CO)_3Mn]^{2-}$. A digallylation of the divalent chromium anion would give a heptacoordinated chromium center, which however is not at all an unlikely species. For example the "super"-reduced $[(CO)_4Cr]^{4-}$ reacts with 3 equiv of Ph_3SnCl to form the anionic product $[(CO)_4Cr(SnPh_3)_3]^-$,[29] which reveals a seven coordinated chromium center. Also octacoordinated carbonylmetalate species are known, e.g. $(CO)_5V(AuPPh_3)_3$, which is formed in the reaction of $[(CO)_5V]^{3-}$ with the very strong electrophile $ClAu(PPh_3)$. This structure is supported by the formation of Au−Au bonds resulting in a VAu_3 tetrahedron.[30] From these comparisons, it is evident that the important fact is the number of π-acidic ligands (CO, NO) at the d-metal vs its total charge, which controls the nucleophilicity at the metal center and thus the general reactivity toward organogallium chlorides. It has to be pointed out that a diminished nucleophilicity at the transition metal results in an increased tendency to form isocarbonyl structures M−CO−Ga.[25] In the course of the syntheses of the neutral Ga(I) transition metal complexes $(CO)_nM-E(R)(tmeda)$ (R = Cl, alkyl)[31,32] the analogues monoanionic molybdenum and tungsten compounds $[(CO)_nM-Ga(R^1)(R^2)]^-$ ($R^1 = R^2 = Cl$; $R^1 = Cl$, $R^2 =$ Me, Et) could also prepared (identification on the basis of IR data) but were not isolated.

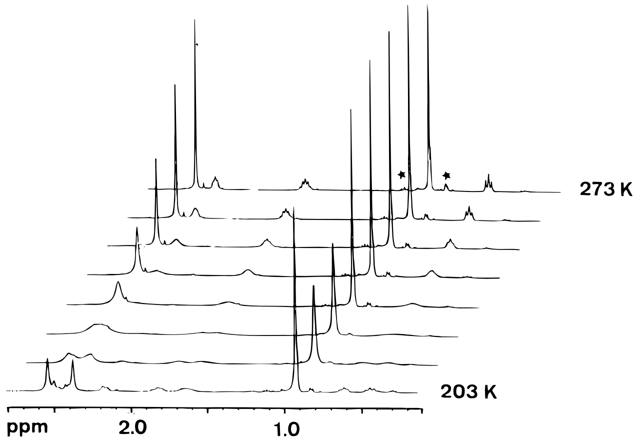


Figure 2. ${}^1H$ NMR spectra of **3** (CD_2Cl_2) in the alkyl region at variable temperatures. The weak signals at 0.3, 0.83, 1.0, 1.1, and 2.42 ppm are caused by the slow decomposition of the compound in the solvent.

The potassium salt **8b** is the key compound to a new class of gallium(I) transition metal complexes. Treatment of this salt with dichloromethane leads to the elimination of the remaining equivalent of KCl yielding the neutral species $(CO)_5CrGaCl(THF)_2$, formally described as a Cr^0 complex of Ga^ICl,[31,32] similar to the polymeric $[(CO)_5CrInCl(THF)]_\infty$.[33] In solution the compounds are very air and moisture sensitive; in CH_2Cl_2 they decompose slowly. For this reason it is very difficult or even impossible to obtain perfectly clean NMR spectra of these compounds (Figure 2). Samples dissolved in CD_2Cl_2 should be frozen until starting the NMR measurements. The solid compounds can be handled in air for a few minutes. In general, the iron compounds were more sensitive than the chromium systems.

B. Spectroscopic Characterization. IR(ν(CO)) Spectra: (Figure 1). For the manganese compound **6** significant ion-pairing effects were observed upon the exchange of the cation. The iron and chromium compounds may exhibit such effects, but the changes of the ν(CO)-absorption frequencies and/or signal patterns in the course of the salt metathesis are much weaker. The ion-pairing effects for compound **6** were however considerable.[25] IR data for the reaction solution exhibit for ν(NO) one absorption at 1565 cm^{-1} and three ν(CO) absorptions at 1939, 1865, and 1826 cm^{-1} for the $2A' + A''$ bands for local C_s symmetry and a *cis* configuration of the NO and gallium ligand (Figure 1a). After the exchange of the potassium cation with the noncoordinating cations PPN^+ the ν(NO) band shifted to 1598 cm^{-1} whereas the ν(CO) bands were observed at somewhat lower wavenumbers (1932, 1847, and 1812 cm^{-1}; Figure 1b). This may indicate that the potassium cation was weakly bonded to the nitrosyl group. The IR ν(CO) of the iron compounds **1** and **2** and of the chromium compounds **3**−**5** reveal the typical $2A_1 + E$ pattern for $LM(CO)_4$ and $LM(CO)_5$ complexes with local C_s symmetry (Figure 1c,d). The E bands are split. The IR spectra of the chloride-substituted compounds **2** and **4** show a change in position of the A_1(a) and the E bands in comparison to the alkylated systems **1**, **3**, and **5**. This documents the higher Lewis acidity of the GaCl(R) moiety and corresponds well with the IR data of the related neutral compounds (which exhibit higher wavenumbers). For the

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dichloro derivatives **7** and **8a,b** this trend is rather drastic, with a significant shift of ν(CO) to higher wavenumbers (for the chromium compound **8a,b** the A_1(e) bands remain nearly in the same positions; only the shift for the E bands is remarkable, Figure 1e,f).

The situation for the FeGa species **7**, **9**, and **10** is very similar, and the IR spectra (THF) of the reaction mixtures show the expected four ν(CO) absorptions for a *cis*-$(CO)_4FeL_2$ fragment, whereas the IR spectrum (CH_2Cl_2) of the isolated compounds (after salt metatheses) reveals only three ν(CO) absorptions (Figure 1g,h). This change of the signal patterns could be explained either by ion-pairing effects of the potassium cation with the carbonyls or with solvent effects (THF vs CH_2Cl_2) combined with an accidentally close position of the absorption signals. Regarding the above mentioned neutral tetranuclear FeGa compounds we assume a tetranuclear structure with μ-[Ga(Cl)(R)]-bridged $Fe(CO)_4$ moieties as the most probable. Compared with $[(CO)_4FeGa(C_2H_3)(THF)]_2$, the corresponding dianionic dimeric structures could also be viewed as Lewis adducts of two chloride ions (replacing the THF molecule) to the neutral species $[(CO)_4FeGa(R)]_2$.

In the case of the related chromium compounds **8a**,**b** such structural features would lead to heptacoordinated chromium centers. Due to the mentioned decrease in nucleophilicity of a $M(CO)_5$ moiety compared with a $M(CO)_4$ we rather tend to formulate Cl-bridged dimeric structures with a still hexacoordinated chromium. Additionally, on the basis of the IR data a force constant analysis for the octahedral $(CO)_5ML$ complexes using the classical "Cotton−Kraihanzel" approximation was made.[34−37] In general the Ga fragments seem to behave as strong σ-donors revealing also some π-acceptor capability.[31,32] To explain the π-acceptor properties, the electron back-donation into empty σ*(Ga−X) orbitals has to be taken into account.

Dynamic NMR Studies. The NMR data for the hydrocarbon-free compounds **7** and **8a** ensure that no traces of any remaining solvent, e.g. THF, are included in the crystals. As mentioned above, **8b** eliminates KCl when treated with CD_2Cl_2 to give soluble $(CO)_5CrGa(Cl)(THF)_2$ and, besides KCl, some insoluble CrGa species (elemental analysis). Those species become soluble on adding stoichiometric amounts of THF and were identified as $(CO)_5CrGa(Cl)(THF)_2$ (for details see ref 31).

Compounds **1**−**6**, which contain a $Ga[(CH_2)_3NMe_2]$ fragment, provide the opportunity to study the dynamics of the Lewis acid/base adduct in solution by variation of the remaining substituents at the gallium center. For the chloride complexes **2** and **4** the (dimethylamino)propyl ligand is N-coordinated to the gallium atom, even at room temperature, which results in a five-membered heterocycle exhibiting a chiral gallium center. This is clearly indicated by the doubling of the signal pattern. All ring protons are now diastereotopic as well as the methyl carbon atoms. The N−CH_3 groups are also diasterotopic, exhibiting two singlets in the ^1H NMR spectra. The chirality of the gallium center also implies that a fourth substituent different from chloride is bonded at the gallium, which has to be the transition metal.

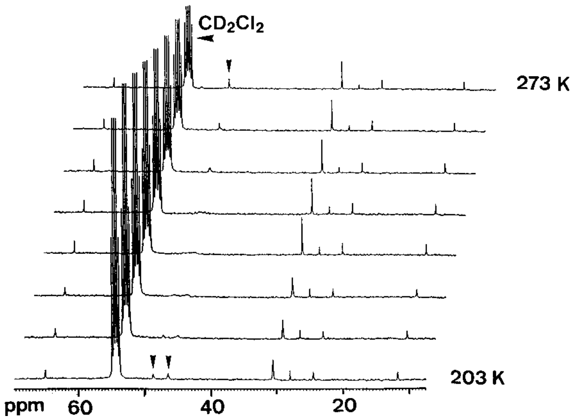

Figure 3. ^{13}C NMR spectra of **3** (CD_2Cl_2) in the alkyl region at variable temperatures.

The situation is more complex for the twice alkylated systems **1**, **3**, **5**, and **6**. ^1H and ^{13}C NMR spectra were measured at various temperatures (Figures 2 and 3). At room temperature the proton NMR exhibits only a simple signal pattern. On cooling of the sample to −60 °C, the signals split and the typical pattern for the diastereotopic protons develops. The temperature dependency of the adduct ring fuxionality was studied in detail for compounds $\{(CO)_5Cr-Ga[(CH_2)_3NMe_2](R)\}^-$ (**3**, R = ^tBu; **4**, R = Cl; **5**, R = Me). The enthalpy of activation for the inversion at the nitrogen center upon ring opening is a sensitive indicator for the steric and electronic situation at the gallium center. The free enthalpies of activation ΔG^*_T were calculated using the formula $k_{coal} = \pi(1/\sqrt{2})\Delta\nu$ and the Eyring equation.[38] Because the signals for the diastereotopic methyl groups in the ^{13}C NMR spectra were sharper and the separation of the peaks was better, compared to the ^1H NMR data, the activation parameters were calculated from the ^{13}C NMR data. For the sterically most crowded compound **3**, the temperature of coalescence was 251 K and $\Delta G^*_{251} = 48.1$ (±0.2) kJ mol^{-1}. Within the accessible temperature range (from −80 to +40 °C, CD_2Cl_2) the characteristic signal pattern for diastereotopic protons was observed for compound **4**. This shows, that T_{coal} of **4** is at least greater than +40 °C, the boiling point of the solvent. With the approximation $T_{koal} \geq 313$ K and a signal separation about 100 Hz for the *N*-methyl carbon signals, as observed for **3** and **5**, $\Delta G^*_{T(koal)}$ of compound **4** is estimated to be above 60 kJ mol^{-1}. This finding agrees nicely with the increased Lewis-acidity of the Ga center of **4** compared to the alkyl derivatives **3** and **5**. The value of $\Delta G^*_{281} = 55.6$ (±0.2) kJ mol^{-1} obtained for **5**, which is sterically less crowded than **3**, fits well into this picture.

Within the series GaCl > GaMe > Ga^tBu the Ga−N bond weakens significantly. The coalescence phenomena did not depend on the concentration of the gallium species (0.01−0.1 mol L^{-1}). This rules out intermolecular exchange processes. Most interestingly, the neutral congeners of **3**−**5**, $(CO)_5Mn-Ga[(CH_2)_3NMe_2](R)$,[2] show the very same behavior but at somewhat higher temperatures (>+50 °C). From this it can be concluded that the negative charge at the transition metal fragment has some important electrostatic effect, since the fragments $[(CO)_5Cr]^-$ and $(CO)_5Mn$ are isolobal.

C. Structure and Bonding of 11a. The molecular structure of the organometallic dianionic part of $\{[(CO)_4Fe]_2Ga(CH_3)\}[PPN]_2$ (**11a**) in the solid state is shown in Figure 4 (the counterions have been omitted for clarity). Selected bond lengths and angles are compiled in Table 2. Two slightly distorted trigonal pyramidally configurated $(CO)_4Fe$ units are bridged by a $Ga(CH_3)$ moiety. For the structure solution and refinement a crystallographic C_2 symmetry of **11a** was assumed, with the $Ga(CH_3)$ unit on the C_2 axis. This is, from a puristic

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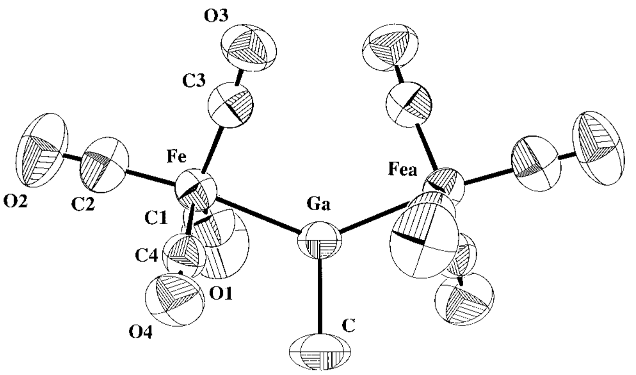

Figure 4. Structure of the complex anion of compound **11a**, in the crystal. The countercations (PPN) and the hydrogen atoms are omitted for clarity (ORTEP plot, 50% probability).

point of view, however not correct, because of the positions of the hydrogen substituents at the carbon atom, which are incompatible with the assumed crystallographic C_2 symmetry. Attempts to resolve the disorder of the hydrogen positions of the CH_3 group did not improve the quality of the refined data. Some shortening of the calculated Ga−C bond could however be expected by this disorder, but the Ga−C bond distance of 202.1(5) pm is quite normal.[3,4,9]

The coordination geometry of the $(CO)_4Fe$ fragments are similar to other compounds of the type $(CO)_4M{-}X$, i.e. $[(CO)_4Co]_2Ga[(CH_2)_3NEt_2]$.[4] The equatorial carbonyl substituents show the so-called umbrella effect. For example, the angle C1−Fe−Ga of 75.85(13)° is rather small and similar to other small angles found for related compounds, e.g. $(CO)_4Co{-}Ga(CH_2{}^tBu)_2(THF)$ with 76.4(1)°.[1] Compound **11a** adds to the rare examples of transition metal gallium complexes which exhibit a tricoordinate (organo)gallium center $RGaM_2$ (R = alkyl, aryl) mentioned earlier. Generally complexes of the type $(L_nM)_aGaR_{3-a}$ (a = 1, 2) must be stabilized either by bulky alkyl or aryl substituents or by Lewis base adduct formation at the gallium center $(L_nM)_aGaR_{3-a}(Do)$ (Do = Lewis donor ligand). The complex $[(CO)_4Co]_2Ga(Ar)$ (Ar = 2,4,6-^{t}BuC$_6$H$_2$), which is isoelectronic to **11a**, represents a prominent example.[6] Otherwise fast symmetrization into $(L_nM)_3Ga$ and GaR_3 occurs.[1] The interesting fact is that **11a** does not add a base ligand, such as tetrahydrofuran or amine donors like $N(CH_3)_3$ and NC_7H_{13} (quinuclidine), although exhibiting a sterically less demanding small CH_3 group at the gallium atom. In this respect **11a** (and also the Cr-congener **12**) differs from closely related gallium transition metal carbonyl complexes exhibiting a tetra- or pentacoordinated Ga center: $[(CO)_nM]_2Ga[(CH_2)_3N(CH_3)_2]$ (M = Mn, Co; n = 5,4)[4,9] and $[(THF)(C_2H_3)GaFe(CO)_4]_2$.[15]

As a consequence of the crystallographic C_2 symmetry, the atoms Fe1, Fe′, Ga, and C are coplanar. However, the angle Fe1−Ga−Fe1′ of 135.36(3)° is considerably different from the ideal value of 120° for an trigonal planar arrangement (other $[L_nM]_2GaR$ complexes, see examples above, exhibit angles M−Ga−M close to 120°). But this angle is rather similar to the typical values around 140° for so-called transition metal "inidene" complexes $[L_nM{-}E(X){-}ML_n]^m$ (M = transition metal, e.g. Cr, Mn, etc.; E = main group element, e.g. In, Tl, Ge, Sn, etc.; X = halide or alkyl; $m = -2, -1, 0, +1$).[11,39−42] Besides this angle, a comparably short M−E distance and a somewhat elongated E−X bond are accepted structural indications for "inidene" complexes exhibiting a three-center−four-electron bonded M−E−M core. In addition to this, intense absorption bands in the electron spectra are characteristic features for such bonding situations. But like other known *anionic* "inidene" complexes, **11a** shows no intense absorptions in the visible region of the electronic spectra. The Fe−Ga distance of 241.58(6) pm is not significantly shortened compared to σ(Fe−Ga) bonds which range around 245(±10) pm. A rather short Fe−Ga bond of 236.18(3) pm was found for $Cp(CO)_2Fe{-}GaCl_2[N(CH_3)_3]$.[2] Transition metal gallium single bonds generally vary over a long range depending on the substituents at both metal centers. Compare, for example, $(CO)_4Co{-}Ga(CH_2{}^tBu)_2(THF)$[1] of 257.83(4) pm with $(Me_3P)(CO)_3Co{-}GaCl_2(NMe_3)$ of 234.2(1) pm.[43] On the other hand, a $L_nFe{=}GaR_2$ double-bonded system has not been reported to date, which one could use to compare with the Fe−Ga bond of **11a**. The Fe−Ga bond length of $[(THF)(C_2H_3)GaFe(CO)_4]_2$,[15] which represents the structurally closest congener of **11a**, amounts to 251(1) pm, which is in fact 10 pm longer than the value of **11a**. But this compound contains a tetracoordinated gallium center, which explains the longer bond. In conclusion, the structural features of **11a** do not allow us to assign a significant Fe−Ga multiple-bonding contribution.

It still remains that **11a** shows no Lewis acidity at the gallium center, which fact cannot be explained by steric arguments as was clearly shown by comparison with other closely related systems exhibiting tetracoordinate gallium centers and isolobal transition metal fragments. Typical "inidene" complexes with some M−E multibonding characteristics, however, exhibit a Lewis acidic bridging main group element. Apparently **11a** represents a special case. The $(CO)_4Fe$ fragments of **11a** are somewhat negatively polarized, as it is evident from the ν(CO) IR data and by comparison with the complexes **1** and **2** for example. The overall charge of **11a** is comparably high. This may give rise to an electrostatic repulsion with the dipolar moment of an incoming Lewis base, thus giving rise to some activation barrier for the Lewis adduct formation. The negative charging may be regarded as a kind of protection technique to achieve low-coordinated Ga centers without sterically very demanding shielding substituents, as it is necessary for neutral complexes.

Conclusions

Anionic transition metal gallium complexes of chromium, iron and manganese were obtained from the interaction of transition metal carbonyl dianions with (organo)gallium chlorides. The diminished Lewis acidity of gallium center in **1**−**13** is mainly explained by electrostatic protection. This latter effect opens up new ways of studying the M−Ga bond in such compounds without the necessity of steric shielding. For example, the replacement of the CH_3 substituents of **11a,b** or **12** with π-accepting or π-donating groups without losing the three-coordinate structure should give rise to interesting intramolecular charge transfer phenomena, which clearly warrant further investigations.

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Supporting Information Available: An X-ray crystallographic file in CIF format for compound **11a** is available. Access information is given on any current masthead page.

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