Transition Metal Alkylgallyl Complexes: Synthesis, Structure, and Spectroscopic Studies of $(\eta^5\text{-}C_5H_5)(CO)_2FeGa(t\text{-}Bu)_2$, $\{(\eta^5\text{-}C_5H_5)(CO)_2Fe\}_2Ga(t\text{-}Bu)$, and $(\eta^5\text{-}C_5H_5)(CO)_2FeGa(t\text{-}Bu)_2\cdot\{(\eta^5\text{-}C_5H_5)(CO)_2Fe\}_2$

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The preparation and crystallographic and spectroscopic (^1H and ^{13}C NMR and IR) characterization of three new transition metal complexes featuring terminal alkylgallyl groups are described. The compounds $(\eta^5\text{-}C_5H_5)(CO)_2FeGa(t\text{-}Bu)_2$ (**1**), $(\eta^5\text{-}C_5H_5)(CO)_2Fe\}_2Ga(t\text{-}Bu)$ (**2**), and $(\eta^5\text{-}C_5H_5)(CO)_2FeGa(t\text{-}Bu)_2\cdot\{(\eta^5\text{-}C_5H_5)(CO)_2Fe\}_2$ (**3**) were synthesized by a simple salt elimination reaction between $NaFe(\eta^5\text{-}C_5H_5)(CO)_2$ and $(t\text{-}Bu)_2GaCl$ or $t\text{-}BuGaCl_2$ in the appropriate ratio to give **1** or **2** in good yield. The addition of $\{(\eta^2\text{-}C_5H_5)(CO)_2Fe\}_2$ to **1** affords the adduct **3**. In **1** and **2** the average Fe–Ga distances are 2.413(4) and 2.411(5) Å. In the case of **3**, an oxygen from a bridging carbonyl of the dimer $\{(\eta^5\text{-}C_5H_5)(CO)_2Fe\}_2$ serves as a donor atom to the gallium center of $(\eta^2\text{-}C_5H_5)(CO)_2FeGa(t\text{-}Bu)_2$ (i.e. **1**), and the Fe–Ga distance is slightly lengthened to 2.441(1) Å. These distances, in addition to the IR spectra of the carbonyl region, suggest that any π-interaction between the iron and the gallium p-orbital is probably very weak.

Transition metal complexes of the heavier main group 3 elements comprise an area of significant current research interest.[1] In particular, derivatives of organogallium ligands are the subject of attention because of their possible application as single source precursors[2] for binary intermetallic phases. In addition, they are of inherent interest owing to their isolobal relationship to cationic carbene transition metal species. At present, only a few neutral transition metal compounds featuring a terminal transition metal–organogallium fragment have been structurally characterized. Among these are $(\eta^5\text{-}C_5H_5)(CO)_3WGaMe_2$,[3] *cis*-$(Cy_2PCH_2CH_2PCy_2)Pt\{CH_2(t\text{-}Bu)\}\{Ga(CH_2\text{-}t\text{-}Bu)_2\}$[4] (Cy = cyclohexyl), and the base-stabilized species $(\eta^5\text{-}C_5H_5)(CO)_2FeGa(\eta^1\text{-}C_5H_4Me)_2\cdot py$[5] (py = pyridine) and $(CO)_3(PPh_3)Co(Cl)GaCH_2CH_2NMe_2$.[6] The base-free structures of the former two compounds demonstrate a potential for a π-interaction between the coordinatively unsaturated gallium center and the transition metal. In addition both compounds were synthesized by the interaction between a metal hydride and the appropriate gallium trialkyl. Recent work has shown that bulky substituents at gallium centers can often induce stability for unusual coordination numbers and bonding involving the gallium center.[7] In this paper the isolation and characterization of some new organogallium–iron compounds, which were synthesized by a simple salt elimination procedure, are described. Structural and spectroscopic studies were undertaken on these in order to investigate the extent of Fe–Ga π-bonding.

Experimental Section

General Procedures. All work was performed by using Schlenk techniques under N_2 or in a Vacuum Atmospheres HE43-2 drybox under N_2. Solvents were freshly distilled under N_2 from Na/K alloy and degassed twice immediately before use. $\{(\eta^5\text{-}C_5H_5)(CO)_2Fe\}_2$, $GaCl_3$, and t-BuLi were purchased from commercial suppliers and used as received. $(t\text{-}Bu)_2GaCl$[8] and $NaFe(\eta^5\text{-}C_5H_5)(CO)_2$[9] were synthesized by literature procedures. ^1H NMR spectra were obtained with a General Electric QE-300 spectrometer. IR spectra were recorded as a Nujol mull between CsI plates using a Perkin-Elmer PE 1430 spectrometer. The compounds gave satisfactory C and H elemental analyses.

Syntheses of Compounds 1–3. $(\eta^5\text{-}C_5H_5)(CO)_2FeGa(t\text{-}Bu)_2$ (1). $(t\text{-}Bu)_2GaCl$ (3.3 g, 15 mmol) in Et_2O (30 mL) was added dropwise to a rapidly stirred solution of $NaFe(\eta^5\text{-}C_5H_5(CO)_2$ (15 mmol) in THF (50 mL) with cooling in a dry ice/acetone bath. The solution was allowed to come to room temperature overnight whereupon the solvent was removed under reduced pressure. The residue was taken up in toluene (50 mL), and the orange-red solution was filtered. The filtrate was concentrated to *ca.* 10 mL and stored in a −20 °C freezer for 15 h, to afford the product as yellow crystals. Yield: 4.55 g, 84%. Mp: 92–3 °C. ^1H NMR (C_7D_8): δ 4.13 (5H, s, $\eta^5\text{-}C_5H_5$), 1.22 (18 H, s, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_7D_8): δ 216.1 (s, CO), 80.0 (s, $\eta^5\text{-}C_5H_5$), 38.1 (s, $\mathit{C}(CH_3)_3$), 30.4 (s, $C(\mathit{CH}_3)_3$). IR: ν(C–O) 1980 (vs), 1928 cm^{-1}. Anal. Calcd for $C_{15}H_{25}FeGaO_2$: C, 49.92; H, 6.42. Found: C, 50.22; H, 6.38.

$\{(\eta^5\text{-}C_5H_5)(CO)_2Fe\}_2Ga(t\text{-}Bu)$ (2). t-BuLi (8.8 mL of 1.7 M

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Table 1. Summary of Data Collection and Structure Solution and Refinement Parameters for Compounds 1–3

	1	**2**	**3**
formula	$C_{15}H_{23}FeGaO_2$	$C_{18}H_{19}Fe_2GaO_4$	$C_{29}H_{33}Fe_3GaO_6$
fw	360.9	480.8	714.8
cryst descrip	yellow rounded blocks	yellow plates	red plates
cryst size	0.18 × 0.40 × 0.68	0.04 × 0.34 × 0.46	0.04 × 0.18 × 0.24
a, Å	16.011(2)	16.225(5)	8.298(2)
b, Å	9.288(2)	8.743(2)	11.980(2)
c, Å	21.802(3)	12.968(3)	15.291(3)
α, deg			95.17(2)
β, deg	102.87(2)		92.89(2)
γ, deg			107.95(2)
V, Å³	3160.8(8)	1839.7(9)	1435.3(4)
Z	8	4	2
space group	$P2_1/n$	$Pna2_1$	$P\bar{1}$
d_{calc}, g/cm³	1.517	1.736	1.654
lin abs coeff, cm⁻¹	26.18	30.29	133.27
2θ range, deg	0.0–55.0	0.0–55.0	0.0–108.5
no. of obsvd reflns	4850	1920	2967
no. of variables	343	225	210
R, R_w	0.053, 0.062	0.036, 0.036	0.056, 0.062

Table 2. Selected Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters

	x	*y*	*z*	*U*(eq),[b] Å²
		Compound **1**[a]		
Ga(1)	946(1)	1750(1)	996(1)	20(1)
Fe(1)	1210(1)	−766(1)	1250(1)	21(1)
O(1)	509(3)	−1398(5)	−67(2)	37(2)
O(2)	−467(3)	−882(6)	1553(2)	38(2)
C(1)	1547(4)	2664(7)	367(3)	26(2)
C(5)	399(4)	2981(7)	1571(3)	26(2)
C(9)	797(4)	−1127(6)	454(3)	24(2)
C(10)	191(4)	−811(7)	1422(3)	27(2)
C(11)	2344(4)	122(7)	1798(3)	29(2)
C(12)	2549(4)	−815(8)	1330(3)	32(2)
C(13)	2248(4)	−2207(7)	1437(3)	30(2)
C(14)	1847(4)	−2160(7)	1956(3)	30(2)
C(15)	1922(4)	−710(7)	2179(3)	30(2)
		Compound **2**		
Ga(1)	6696(1)	886(1)	441	20(1)
Fe(1)	5408(1)	−366(1)	804(1)	23(1)
Fe(2)	7965(1)	−515(1)	194(1)	22(1)
O(1)	5778(3)	−2482(5)	−851(4)	35(2)
O(2)	4562(3)	1788(6)	−516(4)	39(2)
O(3)	7527(3)	−2681(6)	1787(4)	39(2)
O(4)	8744(4)	1424(7)	1719(5)	50(2)
C(1)	6701(4)	3198(7)	243(5)	28(2)
C(5)	5651(5)	−1626(8)	−187(6)	26(2)
C(6)	4923(5)	935(8)	−2(5)	29(2)
C(7)	5877(5)	−304(8)	2314(5)	31(2)
C(8)	5638(5)	−1801(9)	2043(5)	31(2)
C(9)	4788(5)	−1819(10)	1831(6)	41(3)
C(10)	4490(5)	−317(10)	1954(6)	41(3)
C(11)	5174(5)	618(9)	2246(6)	37(3)
C(12)	7681(4)	−1802(8)	1152(5)	26(2)
C(13)	8427(4)	689(8)	1108(6)	29(2)
C(14)	7737(5)	−1887(9)	−1114(5)	28(2)
C(15)	7568(5)	−330(8)	−1347(5)	30(2)
C(16)	8300(5)	504(8)	−1212(6)	31(2)
C(17)	8933(5)	−517(8)	−898(6)	33(2)
C(18)	8595(5)	−1992(8)	−833(6)	31(2)
		Compound 3		
Ga(1)	2551(1)	981(1)	7542(1)	15(1)
Fe(1)	−416(1)	−94(1)	7712(1)	17(1)
Fe(2)	2664(1)	5263(1)	8319(1)	13(1)
Fe(3)	3014(1)	5057(1)	6690(1)	15(1)
O(1)	−481(6)	1464(5)	9262(3)	30(2)
O(2)	−1197(7)	1485(5)	6552(4)	35(2)
O(3)	2497(6)	2920(4)	7563(3)	20(2)
O(4)	3862(6)	7455(4)	7537(3)	24(2)
O(5)	6132(6)	5623(5)	9011(3)	31(2)
O(6)	6604(6)	5275(5)	6756(3)	29(2)
C(1)	4271(9)	1329(6)	8604(5)	20(2)
C(5)	3432(9)	884(6)	6316(5)	18(2)
C(9)	−656(9)	−1660(6)	6892(5)	24(2)
C(10)	492(10)	−1552(7)	7622(5)	27(2)
C(11)	−369(9)	−1526(7)	8383(5)	26(2)
C(12)	−2098(9)	−1638(6)	8109(5)	25(2)
C(13)	−2250(9)	−1696(6)	7190(5)	26(2)
C(14)	−386(9)	868(7)	8642(5)	23(2)
C(15)	−859(9)	843(7)	7002(5)	23(2)
C(21)	2694(8)	3940(6)	7531(4)	15(2)
C(22)	3450(9)	6445(7)	7535(5)	19(2)
C(23)	4785(9)	5474(6)	8731(5)	18(2)
C(29)	5196(9)	5216(6)	6733(5)	18(2)

[a] One of the molecules in the asymmetric unit only. [b] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

hexane solution, 15 mmol) was added dropwise to a rapidly stirred solution of $GaCl_3$ (2.65 g, 15 mmol) in Et_2O (50 mL) with cooling in a dry ice/acetone bath. The mixture was allowed to come to 0 °C and stirred for a further 1 h. The solution was then added dropwise to 30 mmol of $NaFe(\eta^5\text{-}C_5H_5)(CO)_2$ dissolved in THF (60 mL) with cooling in a dry ice/acetone bath. After the addition, the mixture was allowed to warm to *ca.* 0 °C over 3–4 h, after which stirring was continued for 2 h with cooling in an ice bath. The solvent was then removed under reduced pressure. Extraction with toluene (40 mL) followed by filtration afforded a red solution. Concentration under reduced pressure to *ca.* 10 mL and storage in a −20 °C freezer for 50 h afforded the product **2** as yellow crystals. Yield: 60%. Mp: 141–2 °C. ^1H NMR (C_7D_8): δ 1.4 (9H, s, $C(CH_3)_3$), 4.96 (10H, s, $\eta^5\text{-}C_5H_5$). $^{13}C\{^1H\}$ NMR (C_7D_8): δ 218.8 (s, CO), 82.8 (s, $\eta^5\text{-}C_5H_5$) 43.3 (s, $\mathit{C}(CH_3)_3$), 31.5 (s, $C(\mathit{CH}_3)_3$). IR: ν(C–O) 1978 (vw, sh), 1967 (vs), 1927 (vs), 1915 (vw) cm⁻¹. Anal. Calcd for $C_{18}H_{19}Fe_2GaO_4$: C, 44.96; H, 3.98. Found: C, 44.81, H, 3.86.

$(\eta^5\text{-}C_5H_5)(CO)_2FeGa(\mathit{t}\text{-}Bu)_2\cdot\{(\eta^5\text{-}C_5H_5)(CO)_2Fe\}_2$ (3). $\{(\eta^5\text{-}C_5H_5)(CO)_2Fe\}_2$ (1.77 g, 5 mmol) in CH_2Cl_2 (40 mL) was added to **1** (1.81 g, 5 mmol). After stirring for 1 h, hexane (20 mL) was added. The solution was then concentrated to *ca.* 30 mL and stored for 10 days in a −20 °C freezer to afford the product **3** as red crystals. Yield: 3.25 g, 91%. Mp: 145–8 °C. ^1H NMR (C_7D_8): δ 1.4 (18H, s, $C(CH_3)_3$), 4.20 (10H, s, $\eta^5\text{-}C_5H_5$) 4.42 (5H, s, $\eta^5\text{-}C_5H_5$). IR: ν(C–O) 1982 (ssh), 1963 (vs), 1930 (vs), 1915 (ssh), 1788 (s), 1758 (s) cm⁻¹. Anal. Calcd for $C_{29}H_{33}Fe_3GaO_6$: C, 48.73; H, 4.65. Found: C, 49.11; H, 4.60.

X-ray Crystallographic Studies. The crystals were removed from the Schlenk tube under a stream of N_2 and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber and placed in the low temperature nitrogen stream as described in ref 10.

X-ray data for **1**–**3** were collected at 130 K using Mo Kα (λ = 0.710 73 Å) radiation (**1** and **2**) or Cu Kα (λ = 1.541 78 Å) radiation (**3**) and Siemens R3 m/V or P4 diffractometers equipped with an Enraf-Nonius universal low-temperature device. Calculations were carried out on a Micro Vax 3200 computer using the SHELXTL-Plus program system. Neutral atom scattering factors and the correction for anomalous dispersion were those supplied by SHELXTL-Plus. Some details of the data collections and refinements are provided in Table 1. Further details are available in the supplementary material. All structures were solved by a Patterson synthesis. The compounds were refined by full matrix least-squares procedures. Hydrogen atoms were included by the use of a riding model with C–H distances of 0.96 Å and a fixed isotropic thermal parameter with $U_H = 6.2U_C$. All non-hydrogen atoms in **1** and **2** were refined anisotropically whereas in **3** only the Ga, Fe, and oxygen atoms were so refined. Important atom coordinates and bond distances and angles for **1** and **3** are provided in Tables 2 and 3.

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Table 3. Bond Lengths (Å) and Angles (deg) for Compounds 1–3

Compound **1**^{a}			
Ga(1)–Fe(1)	2.417(1)	Ga(1)–C(1)	2.027(7)
Ga(1)–C(5)	2.033(7)	Fe(1)–C(9)	1.746(6)
Fe(1)–C(10)	1.755(7)	Fe(1)–C(11)	2.107(6)
Fe(10)–C(12)	2.111(6)	Fe(1)–C(13)	2.102(6)
Fe(1)–C(14)	2.109(6)	Fe(1)–C(15)	2.092(6)
O(1)–C(9)	1.156(7)	O(2)–C(10)	1.153(8)
C(11)–C(12)	1.433(10)	C(11)–C(15)	1.413(10)
C(12)–C(13)	1.417(10)	C(13)–C(14)	1.395(10)
C(14)–C(15)	1.427(9)		
Fe(1)–Ga(1)–C(1)	118.3(2)	Fe(1)–Ga(1)–C(5)	118.7(2)
C(1)–Ga(1)–C(5)	121.1(3)	Ga(1)–Fe(1)–C(10)	87.0(2)
Ga(1)–Fe(1)–C(9)	87.1(2)		
C(9)–Fe(1)–C(10)	92.5(3)		
Compound **2**			
Ga(1)–Fe(1)	2.406(1)	Ga(1)–Fe(2)	2.416(1)
Ga(1)–C(1)	2.038(6)	Fe(1)–C(5)	1.737(7)
Fe(1)–C(6)	1.733(7)	Fe(1)–C(7)	2.103(7)
Fe(1)–C(8)	2.072(7)	Fe(1)–C(9)	2.098(8)
Fe(1)–C(10)	2.107(8)	Fe(1)–C(11)	2.093(8)
Fe(2)–C(12)	1.738(7)	Fe(2)–C(13)	1.753(7)
Fe(2)–C(14)	2.110(7)	Fe(2)–C(15)	2.106(7)
Fe(2)–C(16)	2.101(7)	Fe(2)–C(17)	2.114(8)
Fe(2)–C(18)	2.118(7)	O(1)–C(5)	1.160(9)
O(2)–C(6)	1.159(9)	O(3)–C(12)	1.154(9)
O(4)–C(13)	1.143(9)		
C(7)–C(8)	1.410(11)	C(7)–C(11)	1.400(11)
C(8)–C(9)	1.406(12)	C(9)–C(10)	1.408(12)
C(10)–C(11)	1.429(12)	C(14)–C(15)	1.422(10)
C(14)–C(18)	1.441(11)	C(15)–C(16)	1.404(10)
C(16)–C(17)	1.419(11)	C(17)–C(18)	1.404(10)
Fe(1)–Ga(1)–Fe(2)	122.4(1)	Fe(1)–Ga(1)–C(1)	118.7(2)
Fe(2)–Ga(1)–C(1)	118.8(2)	Ga(1)–Fe(1)–C(5)	86.9(2)
Ga(1)–Fe(1)–C(6)	88.7(2)	C(5)–Fe(1)–C(6)	94.2(3)
Ga(1)–Fe(2)–C(13)	88.3(2)	Ga(1)–Fe(2)–C(12)	90.4(2)
		C(12)–Fe(2)–C(13)	91.1(3)
Compound **3**			
Ga(1)–Fe(1)	2.441(1)	Ga(1)–C(1)	2.032(7)
Ga(1)–C(5)	2.052(7)	Ga(1)–O(3)	2.334(9)
Fe(1)–C(9)	2.110(8)	Fe(1)–C(10)	2.101(9)
Fe(1)–C(11)	2.086(8)	Fe(1)–C(12)	2.107(7)
Fe(1)–C(13)	2.107(6)	Fe(1)–C(14)	1.741(8)
Fe(1)–C(15)	1.735(9)	Fe(2)–Fe(3)	2.520(2)
Fe(2)–C(22)	1.920(8)	Fe(2)–C(21)	1.909(7)
Fe(3)–C(21)	1.908(7)	Fe(3)–C(22)	1.939(7)
O(1)–C(14)	1.156(9)	O(2)–C(15)	1.163(11)
O(3)–C(21)	1.187(9)	O(4)–C(22)	1.150(9)
C(9)–C(10)	1.401(12)	C(9)–C(13)	1.410(11)
C(10)–C(11)	1.398(12)	C(11)–C(12)	1.436(11)
C(12)–C(13)	1.399(11)		
Fe(1)–Ga(1)–C(1)	118.7(2)	Fe(1)–Ga(1)–C(5)	118.5(2)
C(1)–Ga(1)–C(5)	117.5(3)	O(3)–Ga(1)–C(1)	94.9(3)
O(3)–Ga(1)–C(5)	96.0(3)	Fe(1)–Ga(1)–O(3)	101.9(3)
Ga(1)–O(3)–C(21)	170.6(5)	Fe(2)–C(21)–Fe(3)	82.6(3)
C(14)–Fe(1)–C(15)	92.7(4)	Fe(3)–C(21)–O(3)	139.9(5)
Fe(2)–C(21)–O(3)	137.3(5)	Fe(2)–C(22)–O(4)	139.9(6)
Fe(2)–C(22)–Fe(3)	81.6(3)	Fe(3)–C(22)–O(4)	138.3(6)
C(32)–Fe(2)–C(22)	97.1(3)	C(21)–Fe(3)–C(22)	96.5(3)

[a] One of the molecules in the asymmetric unit only.

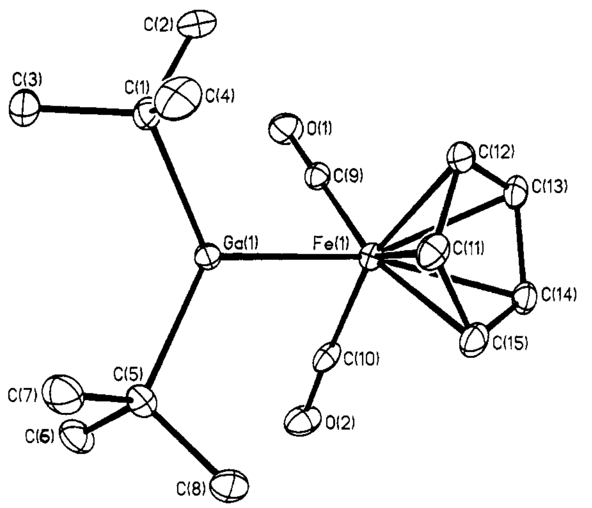

Figure 1. Computer generated drawing of one of the molecules in the asymmetric unit of **1**. H atoms are not shown.

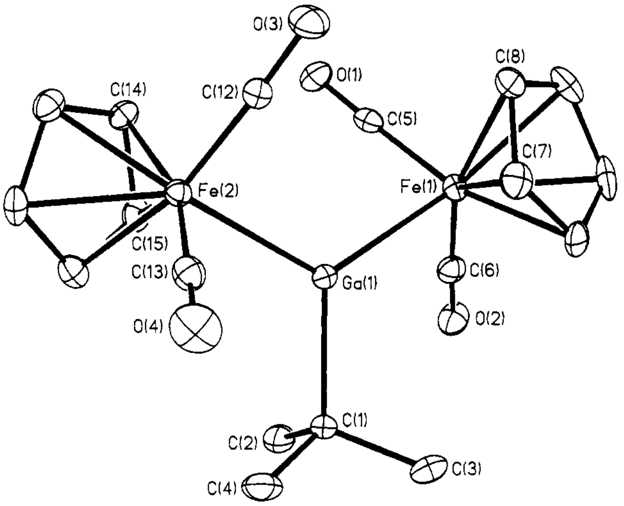

Figure 2. Computer generated drawing of **2**. H atoms are not shown.

Results and Discussion

Synthesis. The novel species **1** and **2** were prepared by the straightforward reaction of the sodium salt of the $[(\eta^5\text{-}C_5H_5)(CO)_2Fe]^-$ anion with either *t*-Bu_2GaCl or *t*-$BuGaCl_2$ (generated in situ). Both **1** and **2** were isolated as base-free species with three-coordination at the gallium centers. Presumably, the ether solvents used in these preparations can, at best, only weakly coordinate to gallium and are easily removed by pumping. However, the acidity of the gallium is shown by the structure of **3** in which one of the bridging carbonyls from the neutral dimer $[(\eta^5\text{-}C_5H_5)(CO)_2Fe]_2$ behaves as an isocarbonyl donor through one of the bridging carbonyl oxygens to gallium. This species was synthesized by the addition of the dimer to **1** in a noncoordinating solvent. The salt elimination route to **1** and **2** is perhaps the simplest route to alkylgallyl complexes. However, unless the gallium center is protected, either sterically or by base stabilization, the complexes are susceptible to disproportionation and decomposition. In the case of **1** and **2** the *t*-Bu groups are of suitable size to effect such stabilization. It is notable, however, that more crowding substituents at gallium, e.g. 2,4,6-*i*-$Pr_3C_6H_2^-$, prevent reaction with the iron centered anion while less bulky substituents, e.g. Me, do not afford stable methylgallyl derivatives—at least under the conditions described here.

Structural Descriptions. $(\eta^5\text{-}C_5H_5)(CO)_2FeGa(t\text{-}Bu)_2$ **(1).** The crystal structure of **1**, which is illustrated in Figure 1 involves two crystallographically independent, chemically identical molecules of **1** per asymmetric unit. There are no close interactions between the molecules. The Fe–Ga distances are 2.409(1) and 2.417(1) Å and the

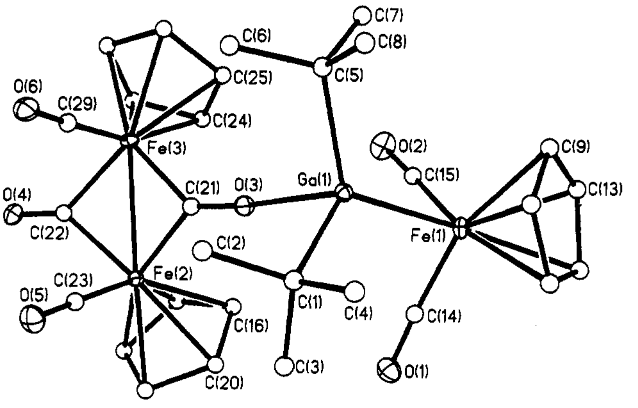

Figure 3. Computer generated drawing of 3. H atoms are not shown.

galliums have an almost trigonal planar coordination. The average Ga–C distances at Ga(1) and Ga(2) are 2.030(7) and 2.037(7) Å. The dihedral angles between the η^5-C_5H_5 (centroid)–Fe–Ga and C–Ga–C planes are 90.2 and 88.2°. The angles surrounding gallium in both molecules are within 3° of 120°, with a somewhat wider C–Ga–C angle being observed at Ga(1), 121.1(3) versus 117.1(3)° at Ga(2). Other distances and angles within the η^5-$C_5H_5(CO)_2$-Fe moieties are unremarkable and are given in Table 3.

$\{(\eta^5\text{-}C_5H_5)(CO)_2Fe\}_2Ga(t\text{-}Bu)$ (2). The structure of 2 which is illustrated in Figure 2 consists of well-separated monomeric units with gallium in a regular trigonal planar coordination by two irons and a carbon. The Ga–Fe distances are 2.406(1) and 2.416(1) Å and the Ga–C bond length is 2.038(6) Å. The dihedral angles between the η^5-C_5H_5 (centroid)–Fe–Ga and the C–Ga–Fe_2 planes are 85.4° for Fe(1) and 80.4° for Fe(2).

$(\eta^5\text{-}C_5H_5)(CO)_2FeGa(t\text{-}Bu)_2\cdot\{(\eta^5\text{-}C_5)(CO)_2Fe\}_2$ (3). The structure of 3 which is illustrated in Figure 3 involves the coordination of the dimer $\{(\eta^5\text{-}C_5H_5(CO)_2Fe\}_2$ (which is in a cis configuration with an Fe–Fe distance of 2.520(3) Å) to a molecule of 1 through the bridging carbonyl C(21)–O(3). The gallium is thus four-coordinate with a Fe–Ga bond length of 2.441(1) Å, Ga–C distances of 2.032(2) and 2.052(7) Å, and a Ga–O(3) distance of 2.334(9) Å. The sum of the interligand angles for the C(1), C(5), and Fe(1) ligands is 354.7°. There is a slight, but significant, difference (>4 standard deviations) between the carbon–oxygen bond lengths in the bridging CO's, 1.187(9) Å for C(21)–O(3) vs 1.150(9) Å for C(22)–O(4). The bridging Fe–C distances are also slightly longer for the coordinating carbonyl group. The coordination at the carbons at both bridging carbonyls is essentially planar but the C–O–Ga angle is 170.6(5)°.

Bonding. The main feature of interest of compounds 1–3 is the nature of the Fe–Ga bond. In 1 and 2 the Fe–Ga bond lengths average 2.413(4) and 2.411(5) Å. These distances are very similar to those observed in the recently reported structure of $\{(\eta^5\text{-}C_5H_5(CO)_2Fe\}_3Ga$,[11] which has an average Fe–Ga distance of 2.444(8) Å. The Fe–Ga distances are slightly shorter than the sum of the covalent radii of Ga (1.25 Å)[7c] and Fe (1.26 Å),[12] which might be indicative of the presence of some π-bonding. Nonetheless, the absence of any major change in the Fe–Ga bond length in the series of compounds above suggests that there is little π-character present. Longer Fe–Ga bonds would have been expected in 2 and $\{(\eta^5\text{-}C_5H_5)(CO)_2Fe\}_3Ga$ where two and three iron centers are required to share overlap with the gallium p-orbital in order to form a π-bond.

The absence of a significant π-interaction in the Fe–Ga bonds in 1 and 2 is also supported by theoretical studies[13] which consider the orbital interactions of the $[(\eta^5\text{-}C_5H_5)(CO)_2Fe]^+$ fragment. Essentially, the most efficient π-overlap with ligands such as carbenes (which are related to dialkylgallyl ligands) involves the a″ orbital at iron. This orbital is oriented parallel to the η^5-C_5H_5 ring plane. Accordingly, the best π-overlap with the carbene (or gallium) p-orbital is observed when the plane of the ligand is perpendicular to the η^5-C_5H_5 ring. This corresponds to a zero dihedral angle between the η^5-C_5H_5 (centroid)–Fe–Ga and C–Ga–C planes. In both 1 and 2, however, the dihedral angles near 90° are observed. The absence of any observed preference for an orientation to give maximum π-bonding suggests that π-interactions between the iron and gallium fragments are quite weak. On the other hand, it could be argued that two large *t*-Bu substituents effectively prevent a $-Ga(t\text{-}Bu)_2$ orientation that would maximize π-bonding. Nonetheless, the structure of $\{(\eta^5\text{-}C_5H_5)(CO)_2Fe\}_3Ga$ shows that the $(\eta^5\text{-}C_5H_5)(CO)_2Fe$ ligand most favorably oriented for π-bonding does not display a shortened Fe–Ga distance.

The structure of 3 also supports the absence of significant π-bonding between Fe and Ga. Coordination of the bridging CO to give the isocarbonyl complexed species 3 results in only a small increase (0.03 Å) in the Fe–Ga bond length to 2.441(1) Å. The coordination of a relatively feeble donor ligand such as isocarbonyl to the gallium centers also suggests that Fe–Ga π-bonding is quite weak. The Ga–O distance, 2.334(9) Å, is well outside the sum of the covalent radii (*ca.* 1.95 Å) for these atoms. The weakness of the Ga–O bond is borne out by the slight pyramidicity produced at gallium in the $FeGa(t\text{-}Bu)_2$ moiety. The Ga–O bond length in 2 may be contrasted with the Al–O distance of 2.002(2) Å observed in the structure of $[(\eta^5\text{-}C_5H_5)(CO)_2Fe]_2\cdot 2AlEt_3$.[14] The difference of over 0.3 Å between the M–O distances for Al and Ga (which have similar sizes) is probably due to the weaker Lewis acidity of Ga and its more hindered environment (two *t*-Bu groups). Further evidence for the weakness of the CO–Ga interaction comes from IR data for 3, which show that the lowest frequency C–O absorption comes at 1750 cm^{-1}. This is only 15 cm^{-1} lower than that observed (1765 cm^{-1}) for the cis isomer of $[(\eta^5\text{-}C_5H_5)(CO)_2Fe]_2$[15] (*cf.* the 125-$cm^{-1}$ shift when $AlEt_3$ coordinates to $[(\eta^5\text{-}C_5H_5)(CO)_2Fe]_2$[14]). Furthermore, the length of the isocarbonyl CO bond itself, 1.187(9) Å, is just slightly longer than that observed (1.150(9) Å) for the non-Ga-coordinating bridging CO. In fact, a comparison of the geometrical features of the *cis*-$\{(\eta^5\text{-}C_5H_5)(CO)_2Fe\}_2$ moiety in 3 shows that they are almost identical to those in the free molecule.[15]

In the IR spectra of 1 and 2, two very strong absorptions were observed at 1980 and 1928 cm^{-1} and 1967 and 1927

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cm^{-1}, respectively. These bands are at somewhat lower frequencies than those observed for $(\eta^5\text{-}C_5H_5)(CO)_2Fe$–alkyl or silyl compounds,[16,17] which show bands near 2010 and 1960 cm^{-1} for alkyls and near 2000 and 1945 cm^{-1} for silyls. The lower frequencies observed for **1** and **2** may be due to increased electron density (and increased back-donation into the π^*-CO orbitals) at the $(\eta^5\text{-}C_5H_5)(CO)_2$-Fe– moiety owing to the more electropositive nature of the Ga(*t*-Bu) substituents. The behavior may be contrasted with the higher CO frequencies observed in the recently reported boryl species $(\eta^5\text{-}C_5H_5)(CO)_2FeBR_2$ (R_2 = Ph_2 or $-OC_6H_4O-$) which are thought to have an Fe–B π-interaction.[18]

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Supplementary Material Available: Full tables of X-ray data collection parameters, atom coordinates, bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters and an ORTEP diagram (27 pages). Ordering information is given on any current masthead page.

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