Articles

Terminal Coordination of a Gallium(I) Species to a Transition Metal. Syntheses and Crystal Structures of $Ru\{GaCl(THF)_2\}\{GaCl_2(THF)\}_2(CO)_3\cdot 0.5THF$ and $Ru_2\{GaCl_2(THF)\}_2(CO)_8$

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The reaction of $Ru_3(CO)_{12}$ with Ga_2Cl_4 in the presence of gallium metal in refluxing toluene, followed by crystallization from tetrahydrofuran, produces $Ru\{GaCl(THF)_2\}\{GaCl_2(THF)\}_2(CO)_3\cdot 0.5$ THF (**1**) and $Ru_2\{GaCl_2(THF)\}_2(CO)_8$ (**2**) (THF = tetrahydrofuran). The ruthenium atom in **1** has an approximately octahedral coordination environment, with meridinal arrangements of carbonyl ligands and gallium atoms. The $GaCl(THF)_2$ group is in a position trans to one of the $GaCl_2(THF)$ groups. The crystal structure of **2** consists of a linear arrangement of metal atoms in which two $GaCl_2(THF)$ groups are in axial positions with respect to the metal−metal bond of an $Ru_2(CO)_8$ unit. Crystal data for **1**: monoclinic space group $P2_1/c$ (No. 14), $a = 17.367(3)$ Å, $b = 12.054(2)$ Å, $c = 16.049(3)$ Å, $\beta = 95.18(1)°$, $Z = 4$, $R = 0.0527$, $R_w = 0.0718$. Crystal data for **2**: monoclinic space group $P2_1/c$ (No. 14), $a = 11.980(1)$ Å, $b = 6.944(1)$ Å, $c = 16.097(3)$ Å, $\beta = 96.81(1)°$, $Z = 2$, $R = 0.0300$, $R_w = 0.0510$. The title complexes are the first compounds to contain ruthenium−gallium bonds, and compound **1** is the second structurally-characterized example of a complex in which a gallium(I) species is terminally coordinated to a transition metal.

Introduction

The study of low-valent transition metal compounds in which the metal is bound to one of the heavier group 13 elements (Al, Ga, In, Tl) has been a growing field of interest in recent years.[1] Although the great majority of these compounds have been prepared via salt elimination reactions between alkali metal salts of transition metal complex anions and a group 13 trihalide, a variety of transition metal−indium complexes have been obtained by the reaction of a reduced indium(I) halide with a low-valent organometallic compound containing a metal−metal bond to give products that appear to result from the insertion of the indium(I) halide into the metal−metal bond.[2] The greater instability of gallium(I) halides relative to their indium(I) cogeners renders their use in similar reactions somewhat more problematic, but there are a few instances in which gallium(I) or gallium(II) halide species have been used to prepare mixed-metal complexes.[3−6] The pioneering work in this field was initiated by Graham, Patmore, and Hoyano, who carried out reactions of gallium(II) halides with $Co_2(CO)_8$ and $Mn_2(CO)_{10}$ to give $Co\{GaX_2(THF)\}(CO)_4$ (X = Cl, Br, I)[3] and $Mn(GaBr_2)(CO)_5$,[4] respectively. Haupt, Flörke, and Preut have reported the structure of $Re_2(CO)_8\{\mu\text{-}GaRe(CO)_5\}_2$, which was obtained from the reaction of $Re_2(CO)_{10}$ with a mixture of GaI_3 and gallium metal in refluxing xylene.[5]

Transition metal complexes of low-valent main group element species have a long and extensive history of investigation.[7] The paradigm for these molecules is the metal−carbene complex, in which a formally divalent carbon can be considered to donate an electron pair to the metal.[8] Although complexes in which the carbene is terminally bound to a single transition metal are common, this mode of coordination is quite rare for analogous species of other main group elements, which overwhelmingly prefer to bridge two or more metal centers.[9] Examples of compounds containing terminal coordination of group 13 element species analagous to these are exceedingly rare, even in the case of thallium, for which the 1+ oxidation state is most

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(1) (a) Boocock, S. K.; Shore, S. B. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 6, Chapter 41.2, pp 947−981. (b) Carmalt, C. J.; Norman, N. C.; Clarkson, L. M. *Comprehensive Organometallic Chemistry II*; Abel, E. W.; Stone, F. G. A.; Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 1, Chapter 12, pp 545−571. (b) Whitmire, K. H. *J. Coord. Chem. Sect. B* **1988**, *17,* 95. (c) Compton, N. A.; Errington, R. J.; Norman, N. C. *Adv. Organomet. Chem.* **1990**, *31,* 91.

(2) (a) Patmore, D. J.; Graham, W. A. G. *Chem. Commun.* **1965**, 591. (b) Patmore, D. J.; Graham, W. A. G. *Inorg. Chem.* **1966**, *5,* 1586. (c) Hsieh, A. T. T.; Mays, M. J. *Inorg. Nucl. Chem. Lett.* **1971**, *7,* 223. (d) Haupt. H.-J.; Wolfes, W.; Preut, H. *Inorg. Chem.* **1976**, *15,* 2920. (e) Haupt. H.-J.; Preut, H.; Wolfes, W. *Z. Anorg. Allg. Chem.* **1979**, *448,* 93. (f) Clarkson, L. M.; Clegg, W.; Hockless, D. C. R.; Norman, N. C.; Farrugia, L. J.; Bott, S. G.; Atwood, J. L. *J. Chem. Soc., Dalton Trans.* **1991**, 2241. (g) Clarkson, L. M.; Norman, N. C.; Farrugia, L. J. *J. Organomet. Chem* **1990**, *390,* C10. (h) Clarkson, L. M.; Norman, N. C.; Farrugia, L. J. *Organometallics* **1991**, *10,* 1286. (i) Clarkson, L. M.; McCrudden, K.; Norman, N. C.; Farrugia, L. J. *Polyhedron* **1990**, *9,* 2533. (j) Lin, C.-C.; Kong, G.; Cho, C.; Whittlesey, B. R. *Inorg. Chem.* **1993**, *32,* 2705.

(3) Patmore, D. J.; Graham, W. A. G. *Inorg. Chem.* **1966**, *5,* 1586.

(4) Hoyano, J.; Patmore, D. J.; Graham, W. A. G. *Inorg. Nucl. Chem. Lett.* **1968**, *4,* 201.

(5) Haupt, H.-J.; Flörke, U.; Preut, H. *Acta Crystallogr.* **1986**, *C42,* 665.

(6) Green, M. L. H.; Mountford, P.; Smout, G. J.; Speel, S. R. *Polyhedron* **1990**, *9,* 2763.

(7) Fehlner, T. P. *Inorganometallic Chemistry*; Plenum Press: New York, 1992; Chapter 2, pp 22−33.

(8) Dötz, K. H. *Transition Metal Carbene Complexes,* Verlag Chemie: Weinheim, Germany, 1983.

(9) (a) Zybill, C.; Müller, G. *Organometallics,* **1988**, *7,* 1368. (b) Petz, W. *Chem. Rev.* **1986**, *86,* 1019. (c) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31,* 123. (d) Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P. *J. Chem. Soc., Chem. Commun.* **1987**, 1282.

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stable.[10] In the case of indium, Behrens, Moll, Sixtus, and Thiele[11] have described the preparation of the complexes $M\{InX(THF)\}(CO)_5$ (M = Cr, Mo, W; X = Cl, Br, I) by the reaction of $Na_2M_2(CO)_{10}$ with InX_3 and have reported the crystal structure of $Cr\{InBr(THF)\}(CO)_5$. Several related compounds containing indium(I) species coordinated to chromium, molybdenum, tungsten, and iron carbonyl complexes are also known.[12] Of particular relevence to the present work is a recent report by Schulte, Herdtweck, Raudaschl-Sieber, and Fischer[13] of a series of compounds of general formula $(OC)_5CrER(TMEDA)$ (E = Ga, Al; R = Cl or alkyl; TMEDA = tetramethylethylenediamine) that are the first examples of the coordination of terminal Ga^I and Al^I species to a transition metal.

The following sections describe the synthesis and structural characterization of two new transition metal−gallium complexes that were prepared by the reaction of a reduced gallium halide with triruthenium dodecacarbonyl. These are the first compounds to contain ruthenium−gallium bonds, and compound **1** is only the second structurally-characterized example of a complex in which a gallium(I) species is terminally coordinated to a transition metal.

Experimental Section

General Methods. All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques or under argon in a drybox. Ruthenium trichloride hydrate was purchased from the Pressure Chemical Company, and $Ru_3(CO)_{12}$ was prepared according to the literature method.[14] Gallium trichloride and gallium metal were obtained from Johnson Matthey, and the gallium trichloride was resublimed prior to use. Ga_2Cl_4 (identity confirmed by melting point) was prepared in situ by a slight modification of the literature method[15] and was used immediately. Solvents were freshly distilled under an atmosphere of dry nitrogen from sodium (hexane, toluene), sodium−potassium alloy (tetrahydrofuran, diethyl ether), or calcium hydride (dichloromethane, acetonitrile) before use. Infrared spectra were routinely obtained on a Perkin-Elmer 1600 Series Fourier-transform spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded on an IBM AF-200 (200 MHz) or AF-300 (300 MHz) Fourier-transform spectrometer and were calibrated relative to deuteriochloroform resonances. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

Preparation of $Ru\{GaCl(THF)_2\}\{GaCl_2(THF)\}_2(CO)_3 \cdot 0.5THF$ (1). A solution of $GaCl_3$ (0.83 g, 4.7 mmol) in toluene (60 mL) and gallium metal (0.5868 g, 8.417 mmol) were heated at reflux for 15 h. The mixture was allowed to cool to 23 °C, and $Ru_3(CO)_{12}$ (0.1561 g, 0.2442 mmol) was added. This mixture was then heated at reflux for 8 h. The formation of a yellow-orange precipitate was noted immediately after heating was initiated, and the solution quickly became colorless. The yellow-orange precipitate gradually disappeared and was replaced by an off-white precipitate after 8 h. This mixture was allowed to cool to 23 °C, and the solution was transferred via cannula away from the solid to another flask. The white precipitate was washed with hot toluene (2 × 25 mL), and the resulting solutions were removed via cannula. Tetrahydrofuran (60 mL) was then added to the white solid to produce a light yellow-green solution that was filtered away from the remaining solid. Colorless crystals of **1** were obtained by layering hexanes over the tetrahydrofuran solution. Yield: 0.15 g, 0.17 mmol (23% based on ruthenium). Anal. Calcd for $C_{21}H_{36}Cl_5Ga_3O_{7.5}Ru$: C, 28.15; H, 4.05. Calcd for $C_{19}H_{32}Cl_5Ga_3O_7Ru$ (loss of 0.5 THF): C, 26.54; H, 3.75. Found: C, 26.52; H, 3.55. Infrared spectrum (KBr disk): 2963 (w), 2896 (w), 2053 (m), 1978 (vs), 1262 (m), 1179 (w), 1095 (m), 1042 (m), 1012 (m), 917 (w), 837 (m), 805 (sh), 668 (w), 595 (s), 572 (m), 530 (m) cm^{-1}. Infrared spectrum (ν_{CO}, THF solution): 2052 (m), 1982 (vs), 1924 (w) cm^{-1}. ^1H NMR spectrum in $CDCl_3$: 2.08(m, 16H, $O(CH_2C\mathit{H}_2C\mathit{H}_2CH_2)$), 4.29(m, 16H, $O(C\mathit{H}_2CH_2CH_2C\mathit{H}_2)$) ppm. Mp: The compound turns red at 70 °C and melts at 120−122 °C. $Ru\{GaCl(THF)_2\}\{GaCl_2(THF)\}_2(CO)_3$ is soluble in tetrahydrofuran and chloroform and is insoluble in hexane and toluene.

Preparation of $Ru_2\{GaCl_2(THF)\}_2(CO)_8$ (2). A solution of $GaCl_3$ (1.03 g, 5.85 mmol) in toluene (30 mL) and gallium metal (1.10 g, 15.8 mmol) were heated at reflux for 3 h and then allowed to cool to 23 °C. $Ru_3(CO)_{12}$ (0.40 g, 0.63 mmol) was added, and the mixture was again heated to reflux for a total of 2 min. At this time the orange color of the solution disappeared and an insoluble yellow solid formed. The mixture was allowed to cool to 23 °C, and the solution was filtered via cannula into another flask. The remaining yellow solid was washed with hot toluene (50 mL), and the resulting solution was removed via cannula. All volatile materials were removed under vacuum from the yellow solid, which was then dissolved in tetrahydrofuran (20 mL). This solution was filtered via cannula into another flask and hexanes (20 mL) were carefully layered on top. Yellow crystals of **2** formed after the mixture was allowed to stand undisturbed at 23 °C for 12 h. Yield: 0.6197 g, 0.7276 mmol (77% based on Ru). Anal. Calcd for $C_{16}H_{16}Cl_4Ga_2O_{10}Ru_2$: C, 22.56; H, 1.89. Found: C, 22.58; H, 1.63. Infrared spectrum (KBr disk): 2966 (w), 2883 (w), 2120 (w), 2095 (w), 2008 (s), 1979 (m), 1970 (m), 1097 (w), 1001 (w), 839 (w), 625 (m), 587 (m) cm^{-1}. Infrared spectrum (ν_{CO}, THF solution): 2114 (w), 2083 (w), 2029 (s), 1982 (m) cm^{-1}. ^1H NMR spectrum in $CDCl_3$: 2.13 (m, 8H, $O(CH_2C\mathit{H}_2C\mathit{H}_2CH_2)$), 4.31 (m, 8H, $O(C\mathit{H}_2CH_2CH_2C\mathit{H}_2)$) ppm. Mp: The compound melts at 95 °C with a color change from yellow to dark red. $Ru_2\{GaCl_2(THF)\}_2(CO)_8$ is soluble in tetrahydrofuran, acetonitrile, chloroform, and diethyl ether. It is insoluble in toluene and hexanes.

Crystal Structure Determination. Suitable crystals were coated with a high-boiling paraffin oil and then cooled to 173 K in an atmosphere of dry nitrogen. Data collection was performed on a Siemens Model P4 automated diffractometer, equipped with a graphite monochromator, using Mo Kα radiation. The unit cell parameters were determined and refined by a least squares fit of 24 high-angle reflections. Data were corrected for Lorentz and polarization effects, and semiempirical absorption corrections based upon Ψ-scans were applied. There was no correction for extinction. The space group determinations were based upon a check of the Laue symmetry and systematic absences present and were confirmed by structure solution. The structures were determined by direct methods followed by successive cycles of full-matrix least squares refinement and difference Fourier analysis using the SHELXTL-IRIS software package provided by Siemens Analytical X-Ray Instruments, Inc. The parameters refined included the atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions but were not refined. ORTEP[16] drawings are shown with 30% probability ellipsoids. Full details for the structure determinations are available in the Supporting Information. The crystal lattice of **1** contains two molecules of tetrahydrofuran per unit cell that reside on centers of symmetry. These molecules therefore exhibit a 50/50 disorder with respect to the oxygen atom positions. There is half a molecule of tetrahydrofuran in the asymmetric unit, and this was refined as two carbon atoms with full occupancy and an oxygen atom with 50% site occupancy.

Results and Discussion

Crystal Structure of $Ru\{GaCl(THF)_2\}\{GaCl_2(THF)\}_2(CO)_3$ (1). The ruthenium atom in **1** has an approximately

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[10] (a) Nagle, J. K.; Balch, A. L.; Olmstead, M. M. *J. Am. Chem. Soc.* **1988**, *110*, 319. (b) Balch, A. L.; Rowley, S. P. *J. Am. Chem. Soc.* **1990**, *112*, 6139. (c) Balch, A. L.; Neve, F.; Olmstead, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 2995. (d) Balch, A. L.; Davis, B. J.; Fung, E. Y.; Olmstead, M. M. *Inorg. Chim. Acta* **1993**, *212*, 149.

[11] Behrens, H.; Moll, M.; Sixtus, E.; Thiele, G. *Z. Naturforsch. B* **1977**, *32*, 1109.

[12] (a) Veith, M.; Kunze, K. *Angew. Chem.* **1991**, *103*, 92; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 95. (b) Reger, D. L.; Mason, S. S.; Rheingold, A. L.; Haggerty, B. S.; Arnold, F. P. *Organometallics*, **1994**, *13*, 5049.

[13] Schulte, M. M.; Herdtweck, E.; Raudaschl-Sieber, G.; Fischer, R. A. *Angew. Chem.* **1996**, *108*, 489; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 424.

[14] Bruce, M. I.; Jensen, C. M.; Jones, N. L. *Inorg. Synth.* **1989**, *26*, 259.

[15] Beamish, J. C.; Wilkinson, M.; Worrall, I. J. *Inorg. Chem.* **1978**, *17*, 2026.

[16] Johnson, C. K. *ORTEPII. Report ORNL-5138*; Oak Ridge National Laboratory: Oak Ridge, TN.

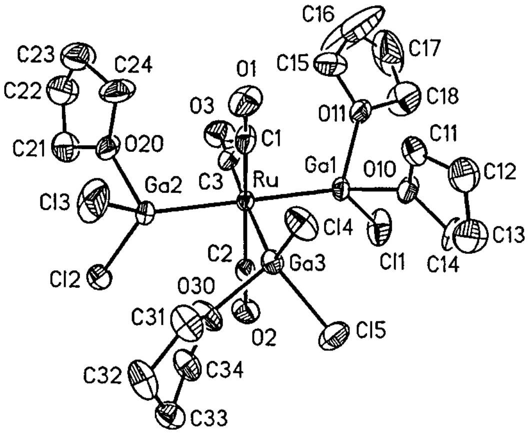

Figure 1. ORTEP drawing of Ru{GaCl(THF)$_2$}{GaCl$_2$(THF)}$_2$(CO)$_3$ (**1**).

Table 1. Crystallographic Data for Ru{GaCl(THF)$_2$}{GaCl$_2$(THF)}$_2$(CO)$_3$·0.5THF (**1**) and Ru$_2${GaCl$_2$(THF)}$_2$(CO)$_8$ (**2**)

	1	**2**
chem formula	$C_{21}H_{36}Cl_5Ga_3O_{7.5}Ru$	$C_{16}H_{16}Cl_4Ga_2O_{10}Ru_2$
fw	895.98	851.7
space group	monoclinic, $P2_1/c$ (No. 14)	monoclinic, $P2_1/c$ (No. 14)
a, Å	17.367(3)	11.980(1)
b, Å	12.054(2)	6.944(1)
c, Å	16.049(3)	16.097(3)
β, deg	95.18(3)	96.81(1)
V, Å^3	3346(1)	1329.7(3)
Z	4	2
temp, °C	−100	−100
λ, Å (Mo K$_{\alpha)}$	0.710 73	0.710 73
ρ(calc), g cm^{-3}	1.779	2.127
μ(Mo Kα), cm^{-1}	32.70	35.66
R^a	0.0527	0.0300
$R_w{}^b$	0.0718	0.0510

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

octahedral coordination geometry, with meridinal arrangements of carbonyl ligands and gallium atoms (Figure 1). The GaCl(THF)$_2$ group is in a position trans to one of the GaCl$_2$(THF) groups, and the coordination environments about the two types of gallium atoms are remarkably similar.

The Ru−Ga(1) distance of 2.432(1) Å for the coordinated gallium(I) species is only slightly less than the other two Ru−Ga distances in the complex (2.459(1) and 2.478(1) Å) as well as the Ru−Ga distance in **2** (2.453(1) Å). The substituents on the gallium atoms adopt sterically-favorable staggered configurations with respect to the substituents on the ruthenium, such that when the molecule is viewed down a ruthenium−gallium bond one of the substituents on the gallium makes an X−Ga−Ru−Y torsion angle of approximately 45° with a ruthenium substituent while the other two gallium substituents have minimum torsion angles of 10−30° with other ruthenium substituents. The Ru−Ga−X angles (X = Cl, O) are greater than the ideal tetrahedral angle of 109.5°, and the X−Ga−X angles are substantially less. The GaCl(THF)$_2$ group can be considered to be a solvent-stabilized coordinated gallium(I) species, and as such, it donates two electrons to the ruthenium center. If each of the GaCl$_2$(THF) groups donates one electron, the ruthenium achieves an 18-electron count and therefore satisfies the effective atomic number rule. The structural data are not indicative of any substantial multiple bonding between the ruthenium and the gallium(I) center.

Crystal Structure of Ru$_2${GaCl$_2$(THF)}$_2$(CO)$_8$ (2). The solid-state structure of this complex (Figure 2) bears many similarities to that reported for {Ru(SnMe$_3$)(CO)$_4$}$_2$.[17] Both molecules reside on crystallographic centers of symmetry and have mutually eclipsed configurations for the carbonyl ligands on the adjacent ruthenium atoms. The four independent

Table 2. Selected Bond Distances (Å) and Angles (deg) for Ru{GaCl(THF)$_2$}{GaCl$_2$(THF)}$_2$(CO)$_3$·0.5THF (**1**)

Ru−Ga(1)	2.432 (1)	Ru−Ga(2)	2.459 (1)
Ru−Ga(3)	2.478 (1)	Ru−C(1)	1.922 (11)
Ru−C(2)	1.919 (10)	Ru−C(3)	1.918 (10)
Ga(1)−Cl(1)	2.213 (3)	Ga(1)−O(10)	2.014 (7)
Ga(1)−O(11)	2.034 (6)	Ga(2)−Cl(2)	2.232 (4)
Ga(2)−Cl(3)	2.224 (4)	Ga(2)−O(20)	2.062 (7)
Ga(3)−Cl(4)	2.218 (3)	Ga(3)−Cl(5)	2.241 (3)
Ga(3)−O(30)	2.031 (7)		

Ga(1)−Ru−Ga(2)	177.5(1)	Ga(1)−Ru−Ga(3)	89.4(1)
Ga(2)−Ru−Ga(3)	92.7(1)	Ga(1)−Ru−C(1)	92.8(3)
Ga(2)−Ru−C(1)	88.7(3)	Ga(3)−Ru−C(1)	84.2(3)
Ga(1)−Ru−C(2)	90.9(3)	Ga(2)−Ru−C(2)	88.2(3)
Ga(3)−Ru−C(2)	82.1(3)	C(1)−Ru−C(2)	165.8(4)
Ga(1)−Ru−C(3)	88.5(3)	Ga(2)−Ru−C(3)	89.3(3)
Ga(3)−Ru−C(3)	177.6(3)	C(1)−Ru−C(3)	97.1(4)
C(2)−Ru−C(3)	96.8(4)	Ru−Ga(1)−Cl(1)	126.0(1)
Ru−Ga(1)−O(10)	127.2(2)	Cl(1)−Ga(1)−O(10)	95.7(2)
Ru−Ga(1)−O(11)	113.7(2)	Cl(1)−Ga(1)−O(11)	97.5(2)
O(10)−Ga(1)−O(11)	87.3(3)	Ru−Ga(2)−Cl(2)	121.6(1)
Ru−Ga(2)−Cl(3)	125.9(1)	Cl(2)−Ga(2)−Cl(3)	104.8(1)
Ru−Ga(2)−O(20)	106.9(2)	Cl(2)−Ga(2)−O(20)	95.9(2)
Cl(3)−Ga(2)−O(20)	93.5(2)	Ru−Ga(3)−Cl(4)	121.4(1)
Ru−Ga(3)−Cl(5)	120.1(1)	Cl(4)−Ga(3)−Cl(5)	103.2(1)
Ru−Ga(3)−O(30)	115.6(2)	Cl(4)−Ga(3)−O(30)	96.4(2)
Cl(5)−Ga(3)−O(30)	94.8(2)	Ga(1)−O(10)−C(11)	121.7(5)
Ga(1)−O(10)−C(14)	126.8(7)	C(11)−O(10)−C(14)	109.8(8)
Ga(1)−O(11)−C(15)	127.3(7)	Ga(1)−O(11)−C(18)	123.8(7)
C(15)−O(11)−C(18)	108.1(9)	Ga(2)−O(20)−C(21)	130.4(6)
Ga(2)−O(20)−C(24)	118.4(7)	C(21)−O(20)−C(24)	109.6(8)
Ga(3)−O(30)−C(31)	125.9(6)	Ga(3)−O(30)−C(34)	120.5(6)
C(31)−O(30)−C(34)	111.0(7)	Ru−C(1)−O(1)	178.6(9)
Ru−C(2)−O(2)	177.1(9)	Ru−C(3)−O(3)	178.3(9)

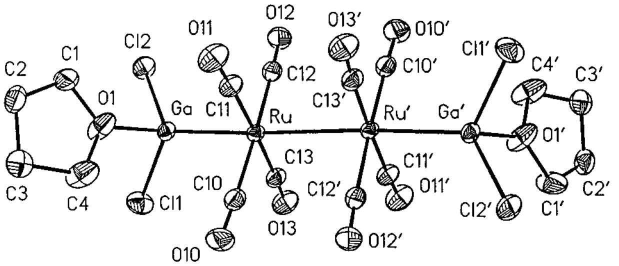

Figure 2. ORTEP drawing of Ru$_2${GaCl$_2$(THF)}$_2$(CO)$_8$ (**2**).

Table 3. Selected Bond Distances (Å) and Angles (deg) for Ru$_2${GaCl$_2$(THF)}$_2$(CO)$_8$ (**2**)

Ru−Ga	2.453 (1)l	Ru−C(10)	1.940 (4)
Ru−C(11)	1.946 (5)	Ru−C(12)	1.947 (4)
Ru−C(13)	1.945 (5)	Ru−Ru′	2.950 (1)
Ga−Cl(1)	2.211 (1)	Ga−Cl(2)	2.206 (1)
Ga−O(1)	2.007 (4)		

Ga−Ru−C(10)	89.8(1)	Ga−Ru−C(11)	91.0(1)
C(10)−Ru−C(11)	89.0(2)	Ga−Ru−C(12)	87.5(1)
C(10)−Ru−C(12)	177.2(2)	C(11)−Ru−C(12)	91.7(2)
Ga−Ru−C(13)	87.3(1)	C(10)−Ru−C(13)	89.7(2)
C(11)−Ru−C(13)	177.9(2)	C(12)−Ru−C(13)	89.5(2)
Ga−Ru−Ru′	176.9(1)	C(10)−Ru−Ru′	93.2(1)
C(11)−Ru−Ru′	88.8(1)	C(12)−Ru−Ru′	89.5(1)
C(13)−Ru−Ru′	92.9(1)	Ru−Ga−Cl(1)	117.4(1)
Ru−Ga−Cl(2)	121.9(1)	Cl(1)−Ga−Cl(2)	106.0(1)
Ru−Ga−O(1)	113.6(1)	Cl(1)−Ga−O(1)	95.2(1)
Cl(2)−Ga−O(1)	97.9(1)	Ga−O(1)−C(1)	122.7(3)
Ga−O(1)−C(4)	128.3(3)	C(1)−O(1)−C(4)	109.0(4)

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(17) Howard, J. A. K.; Kellett, S. C.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1975**, 2332.

carbonyl ligands in **2** show very little deviation from a square planar arrangement about the ruthenium atom, with a maximum deviation of 0.0285 Å from the least-squares plane through the ruthenium and the four carbonyl carbons. The orientation of the $GaCl_2(THF)$ moiety is somewhat unusual in that the Ga−Cl(2) bond nearly eclipses the Ru−C(12) bond, with a Cl(2)−Ga−Ru−C(12) torsion angle of 7.3°. The coordination geometry about the gallium atom is considerably distorted from an ideal tetrahedron. The Cl−Ga−O angles of 95.2(1) and 97.9(1)° are substantially less than the ideal tetrahedral angle of 109.5°, whereas the Ru−Ga−Cl angles of 117.4(1) and 121.9(1)° are significantly greater. The oxygen atom of the tetrahydrofuran ligand is virtually planar in that the sum of the C−O−C and the two Ga−O−C angles is 360.0°. The Ru−Ru distance of 2.950(1) Å is virtually identical to the analogous distance of 2.943(1) Å in $\{Ru(SnMe_3)(CO)_4\}_2$,[17] and the Ru−Ga distance of 2.453(1) Å is very close to the analogous distances observed in compound **1**.

Preparation of the Complexes. The mode of formation of the title complexes is far from clear. The identities and structures of low-valent gallium halides have been the subject of research and speculation for some time and may well depend upon the solvent used. A number of studies have focused on materials that analyze for the empirical formula $GaCl_2$. A crystal structure determination for "gallium dichloride" prepared from $GaCl_3$ and gallium metal at 180 °C, followed by fusion under a layer of paraffin, led to the formulation of this compound as separate Ga^+ and $GaCl_4^-$ ions.[18] Preparation of "gallium dichloride" from Hg_2Cl_2 and gallium metal, followed by dissolution in benzene, gave $[\{(C_6H_6)_2Ga\}^+\{GaCl_4\}^-]_2$, which was also characterized by X-ray crystallography.[19] Other studies in which "gallium dichloride" adducts were formed with various donor ligands lent support to a $Ga[GaCl_4]$ formulation.[20] However a literature preparation[15] for "Ga_2Cl_4" in which gallium(III) chloride was heated with excess gallium metal in benzene gave a material that dissolved in 1,4-dioxane to give the crystallographically-characterized complex $(diox)Cl_2Ga$-$GaCl_2(diox)$, which contains a Ga−Ga bond.[21] We have employed a similar procedure, using toluene in place of benzene, which produces material that has the same melting point as that reported for the "Ga_2Cl_4" prepared in benzene.[15]

Addition of $Ru_3(CO)_{12}$ to a crude mixture of the "Ga_2Cl_4" and gallium metal in toluene does not result in any observable change at ambient temperature; however, there is rapid reaction after the mixture is heated at reflux for a few minutes. If the reaction is halted at this point and the toluene-insoluble portion is dissolved in tetrahydrofuran, a high yield of $Ru_2\{GaCl_2(THF)\}_2(CO)_8$ can be obtained. If heating is continued for 8 h, a similar workup procedure produces $Ru\{GaCl(THF)_2\}\{GaCl_2(THF)\}_2(CO)_3 \cdot 0.5THF$, with no $Ru_2\{GaCl_2(THF)\}_2(CO)_8$ observed. It is obvious that cleavage of the Ru−Ru bonds of the starting material is a prominent feature of this reaction; however, at this time we cannot make any firm conclusions concerning the detailed process by which the products are formed. Despite the apparent fact that the reduced gallium chloride can exist in a variety of states depending upon conditions, it is interesting to note that the reactions of $Co_2(CO)_8$,[3] $Mn_2(CO)_{10}$,[4] and $Ru_3(CO)_{12}$ with "gallium dihalides" all give products that contain GaX_2 substituents on the transition metal.

The use of low-valent gallium compounds as reagents for preparing transition metal−gallium complexes has not been extensively investigated to date but shows promise as a way to obtain species that may not be accessible via traditional salt-elimination routes. We are currently examining reactions of these compounds with other transition metal substrates as possible sources of new mixed-metal complexes.

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Supporting Information Available: Tables of crystallographic data, positional and anisotropic thermal parameters for the non-hydrogen atoms, and calculated bond distances and angles (9 pages). Ordering information is given on any current masthead page.

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(18) Garton, G.; Powell, H. M. *J. Inorg. Nucl. Chem.* **1957**, *4*, 84.

(19) Schmidbaur, H.; Thewalt, U.; Zafiropoulos, T. *Organometallics*, **1983**, *2*, 1550.

(20) Brewer, F. M.; Chadwick, J. R.; Garton, G. *J. Inorg. Nucl. Chem.* **1961**, *23*, 45.

(21) Beamish, J. C.; Small, R. W. H.; Worrall, I. J. *Inorg. Chem.* **1979**, *18*, 220.