IUCrData

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Dicarbonyl-1$\kappa^2 C$-μ-chlorido-2:3$\kappa^2 Cl$:Cl-pentachlorido-2$\kappa^2 Cl$,3$\kappa^3 Cl$-[1(η^6)-toluene]-digallium(III)ruthenium(I)(*Ru—Ga*)

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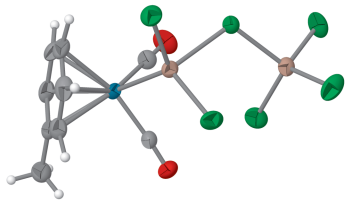
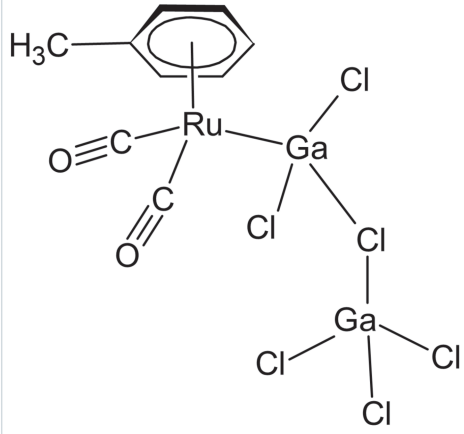
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $[RuGa_2Cl_6(C_7H_8)(CO)_2]$ or $[(CO)_2(GaCl_2)(\eta^6\text{-toluene})\text{-}Ru]^+[GaCl_4]^-$, was isolated from the reaction of Ga_2Cl_4 with diphenylsilanediol in toluene, followed by the addition of $Ru_3(CO)_{12}$. The compound contains a ruthenium–gallium metal–metal bond with a length of 2.4575 (2) Å.

3D view



Chemical scheme



Structure description

The reaction of Ga_2Cl_4 with $Ru_3(CO)_{12}$ in toluene was demonstrated to produce two ruthenium–gallium metal clusters (Harakas & Whittlesey, 1997). The title compound (Fig. 1) was isolated during an attempt to synthesize the ruthenium–gallium diphenylsiloxane analogue of the previously reported iron–gallium dimethylsiloxane cluster (Demmin *et al.*, 2024).

The title compound can be described as $[(CO)_2(GaCl_2)(\eta^6\text{-toluene})\ Ru]^+\ [GaCl_4]^-$. A single positive charge on the ruthenium complex provides a total of 18 electrons for the metal center with $[GaCl_4]^-$ for charge balance. This bonding model is supported by the Ga1—Cl3 bond length of 2.4619 (5) Å, which is significantly longer than the other Ga—Cl bond lengths (Table 1) observed in the title compound. In contrast, $[\{CpFe(CO)_2\}Ga(Cl{*}GaCl_3)(\mu\text{-}Cl)]_2$ is described as a Lewis acid–base complex *i.e.* $[\{CpFe(CO)_2\}GaCl_2]_2{\cdot}2GaCl_3$ (Borovik *et al.*, 1999). The bond angles for the terminal $GaCl_3$ are 112.87, 114.74, and 114.09°, which are all significantly greater than the 109.5° of tetrahedral geometry. For the title compound, the corresponding angles around Ga2 (Table 1) are much closer to the ideal tetrahedral geometry, which is consistent with $[GaCl_4]^-$. In tetraethyl ammonium tetrachloridogallium (Bolte *et al.*, 2023), the Cl—Ga—Cl bond angles range from 108.1 to 110.1°. An analogous Lewis acid–base bonding model for the title complex would require a 19 electron ruthenium metal center or that Ga1 carries one formal negative charge, both of which are unlikely.

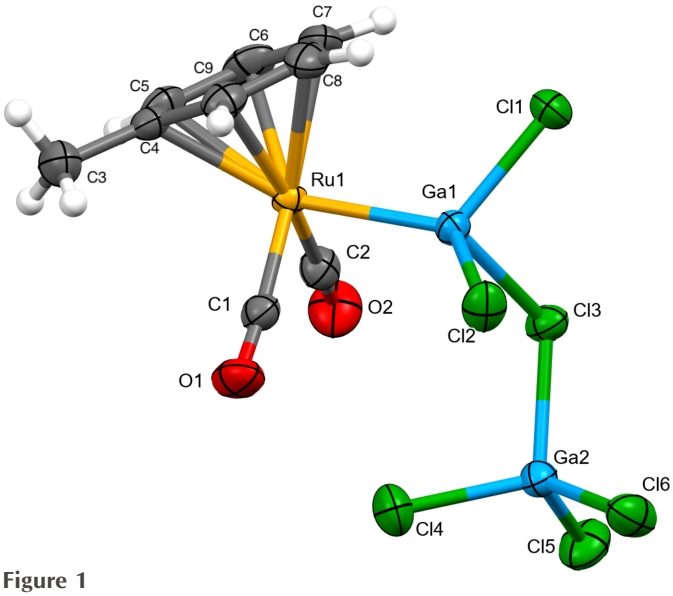


Figure 1
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

The Ru1—Ga1 bond length of 2.4575 (2) Å for the title compound is very similar to the value of 2.453 (1) Å observed for $Ru_2\{GaCl_2(THF)\}_2(CO)_8$ (Harakas & Whittlesey, 1997). The packing is shown in Fig. 2

During the work-up of the reaction, the title compound was isolated directly from the toluene solution. It is unknown at this time the role of diphenylsilanediol, if any, in the formation of the title compound. A solid that was insoluble in toluene in the reaction flask was extracted with THF forming an orange solution. This reaction product, which may contain the desired diphenylsiloxane metal cluster, has not yet been fully characterized.

Synthesis and crystallization

All manipulations were carried out under argon using standard Schlenk line techniques. Our previous work (Demmin *et al.*, 2024) demonstrated that silicone-based vacuum grease can contaminate gallium halide reactions. Therefore, PTFE sleeves and non-silicone based vacuum grease were used on all glassware in this experiment. In a 250 ml Schlenk flask, gallium (5.60 g, 80.3 mmole) and $GaCl_3$ 5.00 g (28.4, mmole) were combined followed by toluene (175 ml). The mixture was heated to reflux for 24 h to produce a solution containing gallium(II) chloride (Ga_2Cl_4), excess gallium was present.

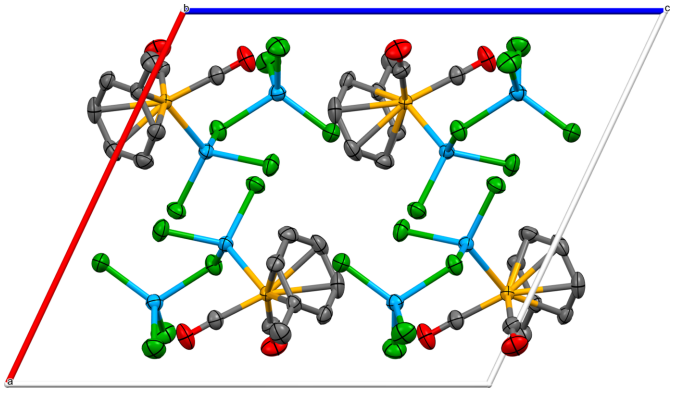


Figure 2
Crystal packing diagram viewed along the *b* axis. Hydrogen atoms have been omitted for clarity.

Table 1
Selected geometric parameters (Å, °).

Ru1—Ga1	2.4575 (2)	Ga2—Cl6	2.1413 (6)
Ga1—Cl2	2.1665 (5)	Ga2—Cl4	2.1456 (6)
Ga1—Cl1	2.1888 (5)	Ga2—Cl5	2.1521 (6)
Ga1—Cl3	2.4619 (5)	Ga2—Cl3	2.2583 (5)
Cl6—Ga2—Cl4	114.95 (3)	Cl6—Ga2—Cl3	110.96 (2)
Cl6—Ga2—Cl5	110.36 (3)	Cl4—Ga2—Cl3	106.43 (2)
Cl4—Ga2—Cl5	109.67 (3)	Cl5—Ga2—Cl3	103.82 (2)

Table 2
Experimental details.

Crystal data	
Chemical formula	$[RuGa_2Cl_6(C_7H_8)(CO)_2]$
M_r	601.36
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	248
a, b, c (Å)	13.1598 (6), 9.7142 (4), 15.3369 (7)
β (°)	115.257 (1)
V (Å^3)	1773.19 (14)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	4.76
Crystal size (mm)	0.36 × 0.34 × 0.31
Data collection	
Diffractometer	Bruker D8 Quest Eco, Photon II 7
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.21, 0.32
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	66270, 4424, 4133
R_{int}	0.031
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.668
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.016, 0.041, 1.09
No. of reflections	4424
No. of parameters	182
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.65, −0.43

Computer programs: *APEX3* and *SAINT* (Bruker, 2019), *SHELXT2018/2* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*) and *ShelXle* (Hübschle *et al.*, 2011).

A solution containing gallium(II) chloride (Ga_2Cl_4), excess gallium was present.

Diphenylsilanediol (0.306 g, 1.41 mmol) was added to a 150 ml Schlenk flask followed by toluene (50 ml). To this flask, 10 ml of the Ga_2Cl_4 stock solution was added *via* cannula. The dark-gray mixture was refluxed under argon for 72 h resulting in a light-gray mixture. The reaction flask was cooled to 25°C and $Ru_3(CO)_{12}$ (0.225 g, 0.352 mmol) was then added. The mixture was heated to reflux for an additional 72 h. This resulted in a mixture with a suspended gray solid/gel and colorless solution. The colorless solution was decanted into a 150 ml Schlenk flask *via* cannula. After standing at 25°C for 10 days, colorless crystals were observed.

A single crystal was coated with NVH oil and mounted on a MiTeGen loop under a stream of argon gas then cooled to −25°C for data collection.

Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 2.

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full crystallographic data

IUCrData (2024). **9**, x240657 [https://doi.org/10.1107/S2414314624006576]

Dicarbonyl-1κ^2*C*-μ-chlorido-2:3κ^2*Cl*:*Cl*-pentachlorido-2κ^2*Cl*,3κ^3*Cl*-[1(η^6)-toluene]digallium(III)ruthenium(I) (*Ru—Ga*)

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Crystal data

$[RuGa_2Cl_6(C_7H_8)(CO)_2]$
M_r = 601.36
Monoclinic, $P2_1/c$
a = 13.1598 (6) Å
b = 9.7142 (4) Å
c = 15.3369 (7) Å
β = 115.257 (1)°
V = 1773.19 (14) Å^3
Z = 4
$F(000)$ = 1144
D_x = 2.253 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9595 reflections
θ = 2.7–28.3°
μ = 4.76 mm^{-1}
T = 248 K
Block, clear colourless
0.36 × 0.34 × 0.31 mm

Data collection

Bruker D8 Quest Eco, Photon II 7 diffractometer
Detector resolution: 7.3910 pixels mm^{-1}
phi and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.21, T_{max} = 0.32
66270 measured reflections
4424 independent reflections
4133 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 28.3°, θ_{min} = 2.7°
h = −17→17
k = −12→12
l = −20→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.016
$wR(F^2)$ = 0.041
S = 1.09
4424 reflections
182 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0179P)^2 + 1.0566P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.65 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ru1	0.24301 (2)	0.66776 (2)	0.55005 (2)	0.02484 (4)
Ga1	0.37587 (2)	0.52947 (2)	0.68455 (2)	0.02795 (5)
Ga2	0.21861 (2)	0.26035 (2)	0.77462 (2)	0.03228 (5)
Cl1	0.53434 (4)	0.47105 (6)	0.68030 (4)	0.04053 (11)
Cl2	0.41255 (5)	0.58077 (6)	0.83247 (3)	0.04424 (12)
Cl3	0.31993 (4)	0.28855 (5)	0.68851 (4)	0.03697 (10)
Cl4	0.09559 (5)	0.42180 (6)	0.73078 (5)	0.05227 (13)
Cl5	0.13673 (5)	0.06499 (6)	0.72620 (5)	0.05478 (14)
Cl6	0.32572 (4)	0.25357 (7)	0.92593 (4)	0.05277 (15)
O1	0.12790 (15)	0.73771 (17)	0.67684 (13)	0.0519 (4)
O2	0.10336 (14)	0.40984 (18)	0.48352 (13)	0.0573 (4)
C1	0.17226 (16)	0.7071 (2)	0.63130 (14)	0.0338 (4)
C2	0.15713 (16)	0.5047 (2)	0.51002 (14)	0.0367 (4)
C3	0.1370 (2)	1.0026 (3)	0.48306 (18)	0.0502 (5)
H3A	0.151190	1.085031	0.454310	0.075000*
H3B	0.148544	1.022284	0.548647	0.075000*
H3C	0.060080	0.972800	0.445748	0.075000*
C4	0.21607 (15)	0.8907 (2)	0.48377 (13)	0.0324 (4)
C5	0.18667 (17)	0.7958 (2)	0.40924 (13)	0.0389 (4)
H5	0.107892	0.790389	0.359964	0.047000*
C6	0.2656 (2)	0.6935 (3)	0.41157 (15)	0.0478 (5)
H6	0.241232	0.618942	0.362932	0.057000*
C7	0.37233 (19)	0.6881 (2)	0.48817 (17)	0.0458 (5)
H7	0.423488	0.610611	0.493398	0.055000*
C8	0.40090 (17)	0.7834 (2)	0.56321 (16)	0.0432 (5)
H8	0.471964	0.772111	0.622005	0.052000*
C9	0.32405 (16)	0.8811 (2)	0.56150 (14)	0.0371 (4)
H9	0.340902	0.937264	0.619916	0.044000*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ru1	0.02522 (6)	0.02903 (7)	0.02071 (6)	−0.00104 (5)	0.01024 (5)	0.00055 (5)
Ga1	0.02861 (9)	0.03056 (10)	0.02508 (9)	0.00314 (7)	0.01183 (7)	0.00206 (7)
Ga2	0.03015 (10)	0.03326 (11)	0.03336 (10)	−0.00027 (8)	0.01347 (8)	0.00417 (8)
Cl1	0.0333 (2)	0.0472 (3)	0.0458 (3)	0.00639 (19)	0.0213 (2)	0.0039 (2)
Cl2	0.0559 (3)	0.0468 (3)	0.0281 (2)	0.0091 (2)	0.0161 (2)	−0.00377 (19)
Cl3	0.0476 (2)	0.0293 (2)	0.0424 (2)	−0.00163 (19)	0.0273 (2)	0.00116 (18)
Cl4	0.0467 (3)	0.0490 (3)	0.0610 (3)	0.0157 (2)	0.0228 (3)	0.0080 (3)
Cl5	0.0554 (3)	0.0405 (3)	0.0623 (3)	−0.0155 (2)	0.0192 (3)	0.0040 (3)
Cl6	0.0389 (2)	0.0864 (4)	0.0323 (2)	0.0041 (3)	0.0145 (2)	0.0060 (3)
O1	0.0721 (11)	0.0459 (9)	0.0607 (10)	0.0051 (8)	0.0503 (9)	0.0003 (8)
O2	0.0500 (9)	0.0449 (9)	0.0626 (10)	−0.0152 (8)	0.0103 (8)	−0.0092 (8)
C1	0.0408 (9)	0.0295 (9)	0.0349 (9)	0.0002 (7)	0.0198 (8)	0.0036 (7)
C2	0.0334 (9)	0.0387 (10)	0.0334 (9)	−0.0019 (8)	0.0099 (7)	−0.0010 (8)

C3	0.0545 (13)	0.0464 (12)	0.0567 (14)	0.0116 (10)	0.0304 (11)	0.0103 (10)
C4	0.0365 (9)	0.0339 (9)	0.0302 (8)	−0.0027 (7)	0.0175 (7)	0.0051 (7)
C5	0.0422 (10)	0.0474 (11)	0.0233 (8)	−0.0055 (9)	0.0101 (7)	0.0060 (8)
C6	0.0754 (15)	0.0475 (12)	0.0321 (10)	−0.0045 (11)	0.0342 (11)	−0.0027 (9)
C7	0.0519 (12)	0.0497 (12)	0.0532 (12)	0.0122 (10)	0.0392 (11)	0.0147 (10)
C8	0.0308 (9)	0.0520 (12)	0.0473 (11)	−0.0053 (9)	0.0172 (8)	0.0101 (10)
C9	0.0371 (9)	0.0378 (10)	0.0343 (9)	−0.0111 (8)	0.0133 (8)	0.0000 (8)

Geometric parameters (Å, º)

Ru1—C1	1.8856 (19)	Ga2—Cl4	2.1456 (6)
Ru1—C2	1.890 (2)	Ga2—Cl5	2.1521 (6)
Ru1—C6	2.2803 (19)	Ga2—Cl3	2.2583 (5)
Ru1—C7	2.2834 (19)	O1—C1	1.125 (2)
Ru1—C8	2.294 (2)	O2—C2	1.127 (3)
Ru1—C9	2.3027 (19)	C3—C4	1.502 (3)
Ru1—C5	2.3223 (19)	C4—C5	1.389 (3)
Ru1—C4	2.3536 (19)	C4—C9	1.415 (3)
Ru1—Ga1	2.4575 (2)	C5—C6	1.426 (3)
Ga1—Cl2	2.1665 (5)	C6—C7	1.396 (3)
Ga1—Cl1	2.1888 (5)	C7—C8	1.398 (3)
Ga1—Cl3	2.4619 (5)	C8—C9	1.379 (3)
Ga2—Cl6	2.1413 (6)		
C1—Ru1—C2	89.37 (9)	Cl2—Ga1—Cl1	107.54 (2)
C1—Ru1—C6	152.94 (9)	Cl2—Ga1—Ru1	120.934 (17)
C2—Ru1—C6	94.99 (9)	Cl1—Ga1—Ru1	117.546 (16)
C1—Ru1—C7	157.35 (9)	Cl2—Ga1—Cl3	97.36 (2)
C2—Ru1—C7	112.70 (9)	Cl1—Ga1—Cl3	93.035 (19)
C6—Ru1—C7	35.62 (9)	Ru1—Ga1—Cl3	115.292 (15)
C1—Ru1—C8	121.78 (9)	Cl6—Ga2—Cl4	114.95 (3)
C2—Ru1—C8	146.39 (9)	Cl6—Ga2—Cl5	110.36 (3)
C6—Ru1—C8	63.59 (9)	Cl4—Ga2—Cl5	109.67 (3)
C7—Ru1—C8	35.56 (9)	Cl6—Ga2—Cl3	110.96 (2)
C1—Ru1—C9	96.35 (8)	Cl4—Ga2—Cl3	106.43 (2)
C2—Ru1—C9	166.51 (8)	Cl5—Ga2—Cl3	103.82 (2)
C6—Ru1—C9	74.46 (8)	Ga2—Cl3—Ga1	112.77 (2)
C7—Ru1—C9	63.31 (8)	O1—C1—Ru1	175.86 (18)
C8—Ru1—C9	34.91 (8)	O2—C2—Ru1	177.7 (2)
C1—Ru1—C5	117.03 (8)	C5—C4—C9	118.47 (18)
C2—Ru1—C5	103.73 (8)	C5—C4—C3	121.72 (19)
C6—Ru1—C5	36.09 (8)	C9—C4—C3	119.81 (19)
C7—Ru1—C5	64.28 (8)	C5—C4—Ru1	71.49 (11)
C8—Ru1—C5	74.78 (7)	C9—C4—Ru1	70.35 (11)
C9—Ru1—C5	62.79 (7)	C3—C4—Ru1	130.19 (13)
C1—Ru1—C4	94.20 (7)	C4—C5—C6	119.83 (19)
C2—Ru1—C4	132.21 (8)	C4—C5—Ru1	73.96 (11)
C6—Ru1—C4	63.40 (8)	C6—C5—Ru1	70.35 (11)

C7—Ru1—C4	75.08 (7)	C7—C6—C5	120.5 (2)
C8—Ru1—C4	63.34 (7)	C7—C6—Ru1	72.31 (11)
C9—Ru1—C4	35.37 (7)	C5—C6—Ru1	73.56 (11)
C5—Ru1—C4	34.55 (7)	C6—C7—C8	119.2 (2)
C1—Ru1—Ga1	86.05 (6)	C6—C7—Ru1	72.07 (12)
C2—Ru1—Ga1	85.82 (6)	C8—C7—Ru1	72.63 (11)
C6—Ru1—Ga1	120.86 (7)	C9—C8—C7	120.2 (2)
C7—Ru1—Ga1	90.38 (6)	C9—C8—Ru1	72.89 (11)
C8—Ru1—Ga1	84.29 (6)	C7—C8—Ru1	71.81 (12)
C9—Ru1—Ga1	106.70 (5)	C8—C9—C4	121.73 (19)
C5—Ru1—Ga1	154.66 (5)	C8—C9—Ru1	72.20 (12)
C4—Ru1—Ga1	141.95 (5)	C4—C9—Ru1	74.28 (11)