

## Supplementary Information

### Crystallographic data

Data were collected at 100 K on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo K $\alpha$  radiation (0.71073 Å).

Single crystals of **1** suitable for X-ray analysis have been grown from CHCl<sub>3</sub>/heptane at 0°C. Crystal data for **1**·C<sub>7</sub>H<sub>16</sub>: C<sub>52</sub>H<sub>60</sub>Ga<sub>4</sub>O<sub>12</sub>Rh<sub>6</sub> + C<sub>7</sub>H<sub>16</sub>,  $M = 1873.54$ , tetragonal, space group I-4,  $a = 15.8660(14)$  Å,  $b = 15.866(2)$  Å,  $c = 12.6000(16)$  Å.  $V = 3171.8(6)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.962$  g/cm<sup>-3</sup>,  $\mu = 3.245$  mm<sup>-1</sup>,  $F(000) = 1840$ , 26139 reflections collected, 4606 independent reflections, 4158 reflections with  $I > 2\sigma(I)$ , 192 parameters, GOF = 1.019, R1 = 0.0212 ( $I > 2\sigma(I)$ ), wR2 = 0.0403 (all data), minimum/maximum residual electron density  $-0.640/0.495$  e Å<sup>-3</sup>. Disorder of n-heptane on a four-fold axes. Therefore the solvent was refined isotropically.

Single crystals of **2** suitable for X-ray analysis have been grown from n-hexane solution at  $-30^\circ\text{C}$ .

Crystal data for **2**·0.5C<sub>6</sub>H<sub>14</sub>: C<sub>45</sub>H<sub>45</sub>Ga<sub>3</sub>O<sub>14</sub>Ru<sub>6</sub> + 0.5C<sub>6</sub>H<sub>14</sub>,  $M = 1668.48$ , triclinic, space group  $P-1$ ,  $a = 11.796(7)$  Å,  $b = 11.878(6)$  Å,  $c = 20.135(12)$  Å,  $\alpha = 104.97(4)^\circ$ ,  $\beta = 97.75(5)^\circ$ ,  $\gamma = 91.00(5)^\circ$ .  $V = 2697(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{\text{calcd}} = 2.055$  g/cm<sup>-3</sup>,  $\mu = 3.166$  mm<sup>-1</sup>,  $F(000) = 1618$ , 78183 reflections collected, 12389 independent reflections, 7805 reflections with  $I > 2\sigma(I)$ , 582 parameters, GOF = 1.069, R1 = 0.0579 ( $I > 2\sigma(I)$ ), wR2 = 0.1374 (all data), minimum/maximum residual electron density  $-2.858/2.052$  e Å<sup>-3</sup>. Largest diff. peak near Ru(4) (0.52 Å). Disorder of Cp\* C(36) to C(40) on two positions (50:50). Both were refined as idealized Cp\*. Disorder of hexane on an inversion center, bonds were fixed with 1.54 Å.

**Selected structural parameters of 1 and 2, M = Rh, Ru.**

<b>Bond length and angles</b>	<b>1</b>	<b>2</b>
(Cp* <sub>centroid</sub> – Ga), Å	2.059	2.168 Ga(1); 2.169 Ga(2); 1.976 Ga(3)
(Ga – M <sub>triangle_center</sub> ), Å	1.969	1.972 Ga(1); 1.956 Ga(2)
(Cp* <sub>centroid</sub> – Ga – M <sub>triangle_center</sub> ), deg	172.5	163.0 Ga(1), 163.7 Ga(2)
M – M, Å	Rh(1)–Rh(2)#1 2.8358(4) Rh(1)–Rh(1)#1 2.8424(4) Rh(1)–Rh(1)#2 2.8424(4) Rh(1)–Rh(2) 2.8454(4) Rh(2)–Rh(1)#2 2.8358(3) Rh(2)–Rh(1)#1 2.8358(3) Rh(2)–Rh(1)#3 2.8453(4)	Ru(1)–Ru(2) 2.8823(16) Ru(1)–Ru(3) 2.905(2) Ru(1)–Ru(5) 2.9102(19) Ru(1)–Ru(4) 2.916(2) Ru(2)–Ru(3) 2.8105(19) Ru(2)–Ru(6) 2.896(2) Ru(2)–Ru(5) 2.946(2) Ru(3)–Ru(6) 2.8816(19) Ru(3)–Ru(4) 2.948(2) Ru(4)–Ru(5) 2.883(2) Ru(4)–Ru(6) 2.9066(17) Ru(5)–Ru(6) 2.918(2)
d <sub>av</sub> (M – M) <sup>†</sup> , Å	2.8415(35)	2.900(34)
Ga – C (Cp* <sub>ring</sub> ), Å	2.260(3); 2.305(3); 2.411(3); 2.462(3); 2.516(3)	Ga(1) 2.438(9); 2.103(9); 2.358(8); 2.714; 2.737 Ga(2) 2.141(8); 2.234(8); 2.644; 2.786; 2.551 Ga(3) 2.356(7); 2.382(7); 2.316(7); 2.246(7); 2.266(7)

<sup>†</sup> The value of the standard deviation is given in parentheses.

## Experiment

### General comments

All operations were carried out under dry argon atmosphere using standard Schlenk techniques. All solvents were distilled over appropriate drying agents under an atmosphere of dry argon before use. The ultrasonic treatment of reaction mixtures was performed using a Bioblock Scientific Vibra-Cell (72412) apparatus. GaCp\* was synthesized by literature procedure.<sup>1</sup> The starting clusters Ru<sub>6</sub>(η<sup>6</sup>-C)(CO)<sub>17</sub> was synthesized by refluxing Ru<sub>3</sub>(CO)<sub>12</sub> (Merck) in dry n-octane solution for 12 hours with following chromatographic separation on Silica. The **1** cluster was synthesized as described early.<sup>2</sup>

Infrared spectra were recorded using Bruker Vector 22-FT spectrometer. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded in d<sub>6</sub>-benzene using on a Bruker Avance DRX-500 instrument. Chemical shifts are reported in ppm and are referenced to TMS as an internal standard. Microanalyses were carried out in the Microanalytical Laboratory of the University of Bielefeld.

### Synthesis of **2**

Ru<sub>6</sub>C(CO)<sub>17</sub> (50 mg, 0.046 mmol) was suspended in 30 ml of n-hexane and solution of the GaCp\* (45 mg, 0.219 mmol) in toluene was added under stirring. Monitoring the IR and <sup>1</sup>H NMR spectra showed that formation of the intermediate compound completed in 30 minutes. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 2.10 (15 H, s, Cp\* methyls). IR (ν<sub>max</sub>(CO)/cm<sup>-1</sup>, n-hexane) 2081w, 2073w, 2067m, 2047s, 2028s, 2008s, 1975m, 1939w, 1854vw, br.

Then reaction mixture was sonicated for 10 minutes at ambient temperature and IR and <sup>1</sup>H NMR spectra showed quantitative transformation of the intermediate complex in the **2** cluster. All volatile components were removed then *in vacuo* left brown-red residue which was extracted with n-hexane (3×10 ml). The solution was passed through Cellulose with n-hexane as eluant gave one bloody-red band containing the **2** cluster. Removal of the solvent under vacuum afforded bloody-red crystalline material. Yield: 63 mg, 84%. IR (ν<sub>max</sub>(CO)/cm<sup>-1</sup>, n-hexane) 2081w, 2065s, 2030s, 2016vs, 2007sh, 1994m, 1980vw, 19729w, 1855w, br. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 2.03 (15 H, s, Cp\* methyls). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>) δ 11.19 (5 C, s, Cp\*

methyls), 121.37 (5 C, s, Cp\* ring), 198 (broad signal, CO), 453.90 (1 C, s,  $\eta^6$ -C).  
Found: C, 33.27; H, 3.22. Calc. for C<sub>45</sub>H<sub>45</sub>O<sub>14</sub>Ga<sub>3</sub>Ru<sub>6</sub> : C, 33.25; H, 2.79.

## References

- 1 P. Jutzi, L. O. Schebaum, *Journal of Organometallic Chemistry*, 2002, **654**, 176.
- 2 E. V. Grachova, P. Jutzi, B. Neumann, L. O. Schebaum, H.-G. Stammler, S. P. Tunik, *J. Chem. Soc., Dalton Trans.*, 2002, 302.