Unusual selective substitution of triply bridging carbonyl ligands for GaCp* in $Rh_6(CO)_{16}$. Synthesis and structural characterization of the $Rh_6(\mu_3\text{-CO})_{4-x}(\mu_3\text{-GaCp*})_x(CO)_{12}$ clusters, $x = 1\text{–}4$†

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Reactions of hexanuclear rhodium clusters with GaCp* ($Cp^* = C_5Me_5$) result in unusual substitution of face bridging CO ligands to give a series of the $Rh_6(\mu_3\text{-CO})_{4-x}(\mu_3\text{-GaCp*})_x(CO)_{12}$ substituted derivatives.

For many years interest in the chemistry of rhodium carbonyl complexes has been inspired by their well known catalytic properties in various transformations of organic substrates,[1,2] in particular, the $Rh_6(CO)_{16}$ cluster displays high catalytic activity in carbonylation, hydroformylation, oxidation and other more specific organic reactions.[1] It is also well known that reactivity of binary carbonyls can be substantially modified by substitution of CO for various heteroligands, such as halides and phosphines,[3,4] which makes the study of the $Rh_6(CO)_{16}$ substituted derivatives of particular interest. On the other hand, the GaCp* organometallic fragment has attracted much attention as a novel ligand in transition metal complexes.[5] This "metallonucleophii" demonstrates high flexibility in Cp* bonding to the gallium atom[5] and in the modes of Ga to multinuclear metal center coordination.[6,7] These properties may evidently give rise to unusual structural patterns formed in GaCp* reactions with transition metal clusters. In the present communication we report the reactions of $Rh_6(CO)_{16}$ and its acetonitrile derivative with GaCp*, which gave the first example of selective substitution of the face bridging carbonyl groups in $Rh_6(CO)_{16}$ to afford a series of $Rh_6(\mu_3\text{-CO})_{4-x}(\mu_3\text{-GaCp*})_x\text{-}(CO)_{12}$ clusters.

Reaction of the labile $Rh_6(CO)_{15}(NCMe)$ cluster with one equivalent of GaCp* in THF affords mono- $Rh_6(\mu_3\text{-CO})_3(\mu_3\text{-GaCp*})(CO)_{12}$ (**1**) and di-substituted $Rh_6(\mu_3\text{-CO})_2(\mu_3\text{-GaCp*})_2\text{-}(CO)_{12}$ (**2**) complexes, whereas treatment of the parent $Rh_6(CO)_{16}$ with a large excess of GaCp* gives closely analogous tris- $Rh_6(\mu_3\text{-CO})(\mu_3\text{-GaCp*})_3(CO)_{12}$ (**3**) and tetra-substituted $Rh_6(CO)_{12}(\mu_3\text{-GaCp*})_4$ (**4**) derivatives as stable crystalline complexes which may be separated by column chromatography on silica.† Single crystals of **1**, **2** and **3** have been obtained and their structures were established by single-crystal X-ray analysis.‡ The ORTEP[8] views of the molecules are shown in Figs. 1–3 and selected structural parameters are given in Table 1.

The stoichiometry of **1–4**, provided that GaCp* acts as a two electron donor, gives the usual 86 electron count that fits completely to a stable hexanuclear octahedral cluster framework[9] as in the parent $Rh_6(CO)_{16}$. In fact, six rhodium atoms in **1–3** form a closed octahedron, surrounded by four face bridging ligands and, with twelve terminal ligands, this is very similar to the molecular structure of the other $Rh_6(CO)_{16}$ derivatives.[10] However, typical CO substitution reactions studied earlier resulted in insertion of two electron nucleophiles into terminal sites
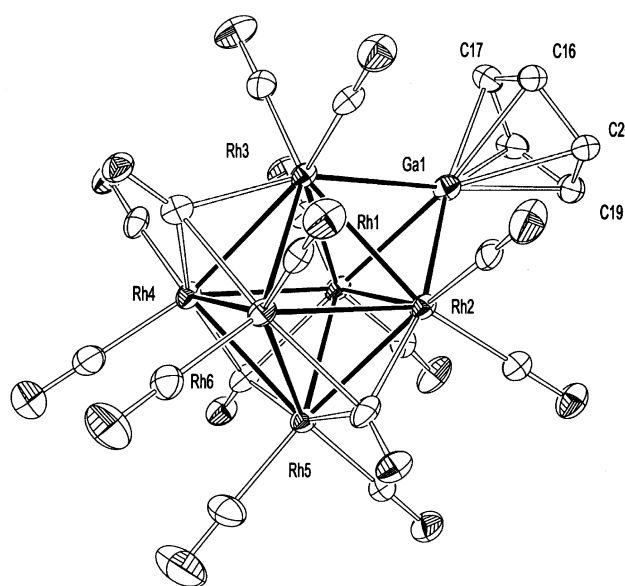

Fig. 1 Molecular structure of $Rh_6(\mu_3\text{-CO})_3(\mu_3\text{-GaCp*})(CO)_{12}$, **1**.
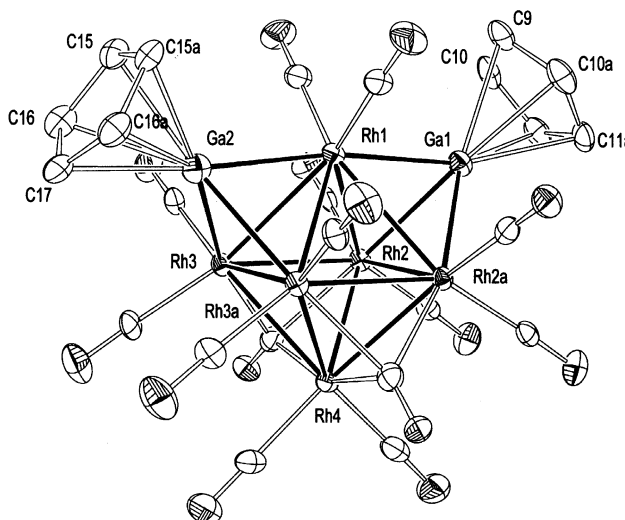

Fig. 2 Molecular structure of $Rh_6(\mu_3\text{-CO})_2(\mu_3\text{-GaCp*})_2(CO)_{12}$, **2**.

only, leaving the "$Rh_6(\mu_3\text{-CO})_4$" fragment intact even in the case of potentially bridging halide anions.[11,12] The clusters **1–3** instead display face bridging CO substitution for GaCp*, to leave the fairly labile terminal CO environment of the starting clusters unchanged.

Table 1 Selected structural parameters for **1–3**

Bond length and angles	1	2	3
(Cp*$_{centroid}$–Ga)/Å	1.976(6)	1.971(6), Ga(1); 1.974(6), Ga(2)	1.996(5), Ga(1); 2.100(5), Ga(2); 1.998(5), Ga(3)
(Ga–Rh$_{triangle\ center}$)/Å	2.008(1)	2.002(1), Ga(1); 1.999(1), Ga(2)	1.977(1), Ga(1); 1.949(1), Ga(2); 1.980(1), Ga(3)
(Cp*$_{centroid}$–Ga–Rh$_{triangle\ center}$)/°	176.1(2)	174.7(2), Ga(1); 176.1(2), Ga(2)	178.4(2), Ga(1); 168.5(2), Ga(2); 173.8(2), Ga(3)
d_{av}(Rh–Rh),[a] Ga bonded triangles/Å	2.835(0.016)	2.825(0.010)	2.824(0.010)
d_{av}(Rh–Rh),[a] remote (to Ga) bonds/Å	2.758(0.012)	2.759(0.001)	2.759(0.007)

[a] Values of variance are given in parentheses.
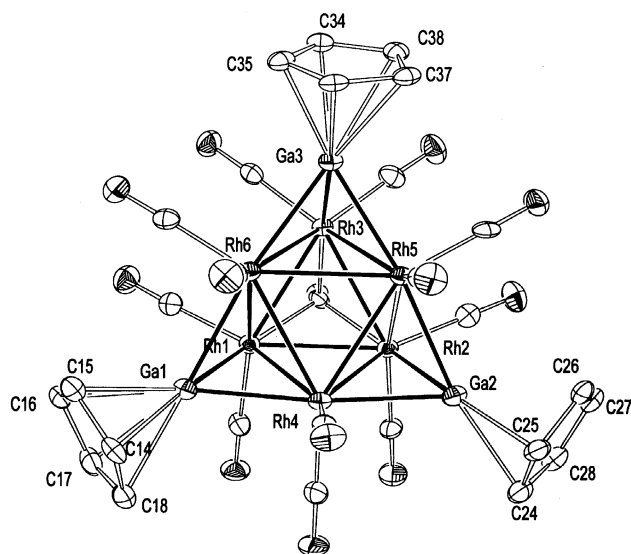
Fig. 3 Molecular structure of Rh$_6$(μ_3-CO)$_2$(μ_3-GaCp*)$_3$(CO)$_{12}$, **3**.

The GaCp* ligand in **1** occupies a nearly symmetrical position over the Rh(1)Rh(2)Rh(3) triangle. The Ga–Rh distances range from 2.5680(7) to 2.6309(7) Å and the Cp*$_{centroid}$–Ga–Rh$_{triangle\ center}$ vector does not deviate significantly from linearity. The presence of such a strong σ-donor as GaCp* results in substantial distortions of the parent Rh$_6$ octahedron, the distortions being located in the vicinity of the substitution site. Elongation of the Rh–Rh bonds inside the gallium bound rhodium triangle looks very similar to the structural effect of weak π-acceptors, which has been mentioned earlier,[10] for the terminally substituted Rh$_6$(CO)$_{16}$ derivatives. The structure of **1** revealed in the solid state is evidently maintained in solution. The ^{1}H and ^{13}C{^{1}H} spectra of **1** displays a set of signals: 2.23 ppm (CH$_3$), 10.94 ppm (CH$_3$) and 118.3 ppm (C$_5$), which is typical for symmetrical coordination of the Cp* moiety. All these resonances are slightly low field shifted as compared with the corresponding signals of terminally bonded GaCp* fragments.[6,13,14] This deshielding is typical for the bridging GaCp* coordination.[6,7]

Molecular structures of **2** and **3** represent further substitution of bridging CO ligands in the parent cluster. In **2** both GaCp* ligands occupy symmetrical face bridging positions over the rhodium triangle with only slight deviations from idealized η^5-Cp* coordination to gallium. Similar to **1** the Rh–Rh bonds adjacent to coordinated gallium atoms, see Table 1, are also substantially elongated. The room temperature NMR spectra of **2** (^{1}H, 2.21 ppm (CH$_3$); ^{13}C{^{1}H}, 11.04 ppm (CH$_3$), 118.7 ppm (C$_5$)) correspond to equivalent Cp* fragments coordinated to the Ga atoms in an idealized η^5 mode and fit well to the solid state structure.

Substitution of the third bridging CO in Rh$_6$(CO)$_{16}$ to form cluster **3** resulted in almost no changes in the coordination of the two bridging GaCp*, whereas the third one proved to be coordinated in a highly distorted manner. The structural parameters of the Ga(1) and Ga(3) environment in **3** are very similar to those found in **2**. In contrast, the Ga(2)Cp* ligand

displays substantial deviations from the symmetrical coordination mode with two long Ga–C$_{Cp*}$ contacts, 2.517(5) and 2.665(5) Å. The Cp*$_{centroid}$–Ga(2)–Rh$_{triangle}$ vector also deviates from linearity to give the value of 168.5°. The η^5 → η^3 haptotropic shift of the Ga(2)Cp* fragment is also accompanied by a stronger Ga–Rh bonding that shows up in a shorter Ga–Rh$_{triangle\ center}$ distance, 1.949(1) Å, cf. 1.977(1) and 1.980(1) Å for Ga(1) and Ga(3), respectively. The effects observed most likely stem from the transfer of electronic density of the other GaCp* units onto the Rh$_6$ core. This is in accord with the resonance scheme suggested earlier,[6] where the lower acceptor ability of the coordination center results in lower polarity of the bond between gallium and transition metal atoms and consequently to an increase of the bond order. Room temperature NMR spectra: 2.14 ppm (^{1}H); 118.3 ppm and 10.7 ppm (^{13}C{^{1}H}), indicate highly fluxional behaviour of **3** under these conditions, which leads to effective three fold symmetry of the molecule.

We have not yet obtained crystals of **4** suitable for X-ray analysis and its structure has been characterised on the basis of spectroscopic data. The ESI mass spectrum of **4** displays a pattern containing the signals of the Rh$_6$(CO)$_{12}$(GaCp*)$_4$ molecular ion and two fragments from CO dissociation. The IR spectrum of **4** shows two bands in the terminal CO region, 2028s and 1988vw cm^{-1}, and no absorption in the area typical for bridging carbonyl ligands. Room temperature NMR spectra of **4** point to stereochemical nonrigidity of the molecule ligand sphere showing in the ^{1}H spectrum one singlet of methyl groups at 2.11 ppm and two signals corresponding to aromatic (119.4 ppm) and methyl carbons (10.83 ppm) of Cp* in the ^{13}C{^{1}H} spectrum. These spectroscopic data clearly point to exhaustive substitution of four bridging COs in Rh$_6$(CO)$_{16}$ to give in **4** the structure containing a Rh$_6$ octahedron surrounded by four triply bridging GaCp* ligands and twelve terminal CO ligands.

Acknowledgements

Notes and references

‡ Crystallographic data for **1**: C$_{25}$H$_{15}$GaO$_{15}$Rh$_6$, M = 1242.55, monoclinic, a = 12.5540(3), b = 15.5970(4), c = 17.1100(5) Å, β = 98.2290(11)°, U = 3315.72(15) Å^3, T = 100(2) K, space group $P2_1/n$, Z = 4, μ(Mo-K) = 3.779 mm^{-1}, 68198 reflections measured, of which 9563 (R_{int} = 0.090) were used in all calculations. The final $wR(F^2)$ was 0.0827 (all data).

For **2**: C$_{34}$H$_{30}$Ga$_2$O$_{14}$Rh$_6$, M = 1419.48, monoclinic, a = 11.3400(3), b = 15.2260(5), c = 12.6640(5) Å, β = 114.1911(13)°, U = 1994.58(12) Å^3, T = 100(2) K, space group $P2_1/m$, Z = 2, μ(Mo-K) = 3.779 mm^{-1}, 36192 reflections measured, of which 3646 (R_{int} = 0.080) were used in all calculations. The final $wR(F^2)$ was 0.0653 (all data).

For **3**: C$_{43}$H$_{45}$Ga$_3$O$_{13}$Rh$_6$·2CH$_2$Cl$_2$, M = 1766.26, orthorhombic, a = 12.43400(10), b = 17.4920(2), c = 24.9780(3) Å, U = 5432.60(10) Å^3, T = 100(2) K, space group $P2_12_12_1$, Z = 4, μ(Mo-K) = 3.492 mm^{-1}, 72288 reflections measured, of which 12394 (R_{int} = 0.058) were used

in all calculations. The final $wR(F^2)$ was 0.0576 (all data). CCDC reference numbers 172643–172645. See http://www.rsc.org/suppdata/dt/b1/b109327d/ for crystallographic data in CIF or other electronic format.

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