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# Site-selective and stepwise complexation of two M(cod)$^+$ (M = Rh, Ir) fragments with calix[4]arene†

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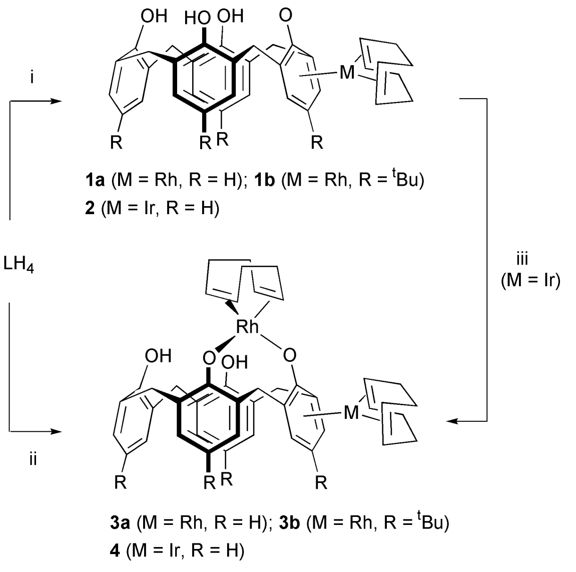
**The reaction of [(cod)M(μ-OMe)]$_2$ (M = Rh, Ir; cod = cycloocta-1,5-diene) with calix[4]arenes (LH$_4$) in the molar ratio of 0.5–0.6 : 1 gave the rhodium and iridium π-arene complexes [(cod)M(η$^6$-LH$_3$)], while that in the molar ratio of 1.1–1.5 : 1 (M = Rh) led to the selective formation of the dinuclear complexes [{(cod)Rh}$_2$(η$^6$:η$^2$-LH$_2$)] in which one of the Rh(cod)$^+$ fragments is coordinated by an η$^6$-aryl group and the other by two phenolic oxygen atoms; the stepwise synthesis of the Rh–Ir heterobimetallic analogue of the latter complex was further achieved.**

Metal complexes of calixarenes have recently been attracting intense interest because of their unique structural features and chemical properties. They serve as molecular models of metal species bound on oxo surfaces[1] and behave as metalloreceptors which recognize various guest molecules and ions.[2,3] However, the chemistry of late transition metal derivatives of calixarenes has so far been studied mainly with chemically modified calixarenes such as the phosphine derivatives,[2,4,5] and late transition metal complexes of the parent calixarenes have not been explored extensively.[6,7] Here we describe the synthesis and structures of mono- and di-nuclear rhodium and iridium complexes of calix[4]arenes, where site-selective and stepwise incorporation of M(cod)$^+$ (M = Rh, Ir; cod = cycloocta-1,5-diene) fragments was observed.

When [(cod)Rh(μ-OMe)]$_2$ was allowed to react with calix[4]arene (L$^1$H$_4$) or *p-tert*-butylcalix[4]arene (L$^2$H$_4$) in the molar ratio of 0.5–0.6 : 1 at room temperature, the rhodium complex [(cod)Rh(η$^6$-L$^1$H$_3$)] (**1a**) or [(cod)Rh(η$^6$-L$^2$H$_3$)] (**1b**), respectively, was obtained as the sole product in high yield (Scheme 1). The $^1$H NMR spectrum of **1a** displayed characteristic high-field shifted aromatic signals at $\delta$ 5.01 (t, 1H, $J$ = 6.0 Hz) and 6.34 (d, 2H, $J$ = 6.0 Hz), indicating that the calix[4]arene ligand is bound to the Rh(cod)$^+$ fragment at the aromatic ring with the η$^6$-coordination mode. It should be mentioned that the reaction of [(cod)Rh(μ-OMe)]$_2$ with $p$-CH$_3$C$_6$H$_4$OH was reported to yield the dinuclear complex [(cod)Rh(μ-OC$_6$H$_4$CH$_3$)]$_2$, in which the OC$_6$H$_4$CH$_3$ ligands are coordinated to the rhodium atoms at the phenolic oxygens.[8] An analogous iridium complex [(cod)Ir(η$^6$-L$^1$H$_3$)] (**2**) was also synthesized from L$^1$H$_4$ and [(cod)Ir(μ-OMe)]$_2$.



**1a** (M = Rh, R = H); **1b** (M = Rh, R = $^t$Bu)
**2** (M = Ir, R = H)

**3a** (M = Rh, R = H); **3b** (M = Rh, R = $^t$Bu)
**4** (M = Ir, R = H)

**Scheme 1** *Reagents*: i, [(cod)M(μ-OMe)]$_2$ (M = Rh, Ir; 0.5–0.6 mol); ii, [(cod)Rh(μ-OMe)]$_2$ (1.1–1.5 mol); iii [(cod)Rh(μ-OMe)]$_2$ (0.7 mol).

The molecular structure of **1a**·2CH$_2$Cl$_2$ was confirmed by X-ray crystallographic study.‡ An ORTEP drawing is depicted in Fig. 1. The rhodium atom is bound to one of the aromatic rings with the Rh(1)–C distances at 2.246(6)–2.409(5) Å, and the phenolic OH on the η$^6$-aryl group is deprotonated to make the calix[4]arene ligand monoanionic. The calix[4]arene ligand adopts the cone conformation, and one of the solvating CH$_2$Cl$_2$ molecules was found to be located in the cavity surrounded by the aryl rings. Similar η$^6$-coordination of calixarenes has been observed for some Rh(III), Ir(III), Ru(II),[6] and Cr(0)[9] complexes.

On the other hand, the reaction of [(cod)Rh(μ-OMe)]$_2$ with L$^1$H$_4$ or L$^2$H$_4$ in the molar ratio of 1.1–1.5 : 1 at 50 °C afforded the dinuclear complex [{(cod)Rh}$_2$(η$^6$:η$^2$-L$^1$H$_2$)] (**3a**) or [{(cod)Rh}$_2$(η$^6$:η$^2$-L$^2$H$_2$)] (**3b**), respectively (Scheme 1). In each case, no other product except for a small amount of complex **1** was detected by the $^1$H NMR analysis of the crude reaction mixture. The molecular structure of **3a**·CH$_2$Cl$_2$ was unambiguously determined by X-ray diffraction study.‡ As shown in Fig. 2, complex **3a** consists of two Rh(cod)$^+$ fragments and one calix[4]arene ligand, where one rhodium atom is coordinated by an η$^6$-aryl group as observed in **1a**, while the other Rh(cod)$^+$ fragment is bonded to the calix[4]arene ligand through two deprotonated phenolic oxygen atoms including that of the π-coordinated C$_6$H$_3$O group. Thus, the calix[4]arene molecule is incorporated in complex **3a** as a dianionic ligand. The cone structure of the calix[4]arene is similar to that found for **1a**, and the uncoordinated hydroxy groups form intramolecular hydrogen bonds within the lower rim. It should also be noted that one of the CH$_2$ protons of the calix[4]arene ligand

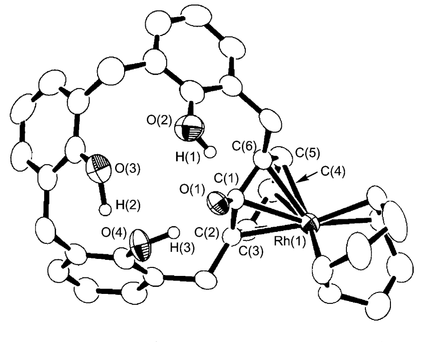


**Fig. 1** Molecular structure of **1a**: Rh(1)–C(1) = 2.409(5), Rh(1)–C(2) = 2.258(5), Rh(1)–C(3) = 2.295(6), Rh(1)–C(4) = 2.292(6), Rh(1)–C(5) = 2.246(6), Rh(1)–C(6) = 2.355(6), C(1)–O(1) = 1.284(6) Å.

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† Electronic supplementary information (ESI) available: experimental section. Fig. S1: structure of one of the independent molecules of **4**. See http://www.rsc.org/suppdata/cc/b2/b201992m/

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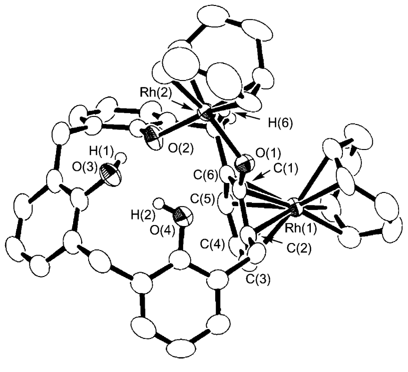


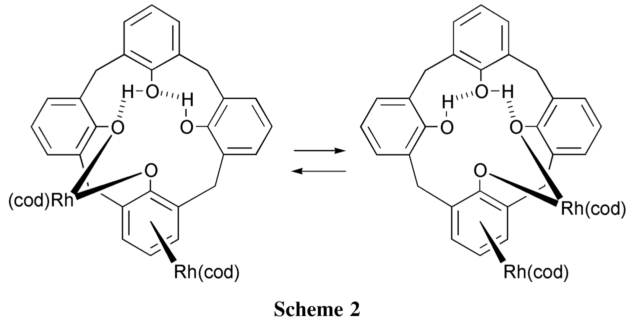
**Fig. 2** Molecular structure of **3a**: Rh(1)–C(1) = 2.373(4), Rh(1)–C(2) = 2.409(5), Rh(1)–C(3) = 2.322(5), Rh(1)–C(4) = 2.210(5), Rh(1)–C(5) = 2.280(5), Rh(1)–C(6) = 2.328(4), Rh(2)–O(1) = 2.063(3), Rh(2)–O(2) = 2.095(3), C(1)–O(1) = 1.287(5), C(8)–O(2) = 1.342(5), O(2)···O(3) = 2.476(5), O(3)···O(4) = 2.625(5), Rh(2)···H(6) = 2.44 Å.

[H(6)] is located close to the O-bound rhodium center [Rh(2)] with the estimated Rh(2)···H(6) distance at 2.44 Å. The short interatomic distance suggests that this $CH_2$ group has a weak interaction with the Rh(2) atom.[10]

The site-selective complexation of the two Rh(cod)$^+$ fragments is worth mentioning. The introduction of the first rhodium center onto an aromatic ring of the calixarene ligand is considered to control the second complexation to occur at the oxygen atoms in the lower rim but not at other aromatic rings. This result makes a sharp contrast to the reactions of calixarenes with $[Cp^*M(acetone)_3]^{2+}$ (M = Rh, Ir) or $[(p\text{-cymene})Ru(acetone)_3]^{2+}$ which have been reported to give rise to the multiple $\eta^6$-coordination at the aromatic rings.

In spite of the unsymmetric molecular structure of **3a** shown above, its $^1H$ NMR spectrum at room temperature exhibited three triplets [$\delta$ 4.57 (1H), 6.52 (2H), 6.56 (1H)] and four doublets [$\delta$ 6.20, 6.95, 7.00, 7.02 (2H each)] due to the aromatic protons, suggesting an apparent $C_s$ symmetry of the molecule. This behavior indicates that the structure of **3a** is fluxional in the solution state, and can be accounted for by considering the migration of the O-bound rhodium center as depicted in Scheme 2. In fact, on cooling at −70 °C the $^1H$ NMR spectrum of **3a** changed to a pattern which is consistent with the solid state structure. It is also interesting to note that an extraordinary low-field shift was observed at this temperature for one methylene proton of the calix[4]arene ligand [$\delta$ 7.10 (d, $J$ = 12.2 Hz)] while the other methylene protons resonate in the expected region ($\delta$ 3.02–4.48). In some square-planar $d^8$ metal complexes, the $^1H$ NMR signal for the CH group located at the pseudo axial position of the metal center has been known to exhibit a downfield shift,[5,10] and the signal at $\delta$ 7.10 for **3a** is obviously assigned to the H(6) atom.

The stepwise and site-selective complexation process was further applied to the synthesis of a mixed metal species. Thus, treatment of complex **2** with $[(cod)Rh(\mu\text{-OMe})]_2$ cleanly afforded the Rh–Ir heterobimetallic complex $[\{(cod)Rh\}\{(cod)Ir\}(\eta^6{:}\eta^2\text{-}L^1H_2)]$ (**4**) as the sole product, and the crystallographic as well as $^1H$ NMR analyses of this complex (structure not shown) confirmed that no scrambling of the metal fragments takes place during the reaction. The present study demonstrates that unmodified calixarenes can provide two distinct types of coordination sites, $\eta^6$-arene and phenolic oxygens, to accumulate late transition metal fragments, where the first complexation at the $\eta^6$-arene site enhances the second complexation at the oxygen site. Further investigation into the chemical properties of complexes **1–4** is now in progress.



**Scheme 2**

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## Notes and references

‡ *Crystal data*: for **1a**·$2CH_2Cl_2$: $C_{38}H_{39}Cl_4O_4Rh$, $M$ = 804.44, monoclinic, space group $P2_1/n$, $a$ = 10.705(4), $b$ = 20.317(2), $c$ = 16.187(2) Å, $\beta$ = 93.46(2)°, $V$ = 3514(1) Å$^3$, $T$ = 294 K, $Z$ = 4, $\mu$(MoK$\alpha$) = 8.29 cm$^{-1}$, 8471 reflections measured, 8052 unique ($R_{int}$ = 0.015) and 4548 observed [$I > 3\sigma(I)$], $R$ = 0.051, $R_w$ = 0.051 [$F$, for unique reflections with $I > 3\sigma(I)$ and 425 parameters].

For **3a**·$CH_2Cl_2$: $C_{45}H_{48}Cl_2O_4Rh_2$, $M$ = 929.59, monoclinic, space group $P2_1/c$, $a$ = 8.800(3), $b$ = 19.972(3), $c$ = 22.563(3) Å, $\beta$ = 100.86(2)°, $V$ = 3894(1) Å$^3$, $T$ = 294 K, $Z$ = 4, $\mu$(MoK$\alpha$) = 10.26 cm$^{-1}$, 9507 reflections measured, 8941 unique ($R_{int}$ = 0.017) and 5537 observed [$I > 3\sigma(I)$], $R$ = 0.041, $R_w$ = 0.042 [$F$, for unique reflections with $I > 3\sigma(I)$ and 488 parameters].

For **4**: $C_{44}H_{46}IrO_4Rh$, $M$ = 933.97, triclinic, space group $P\bar{1}$, $a$ = 13.593(2), $b$ = 13.720(1), $c$ = 19.038(2) Å, $\alpha$ = 93.940(9)°, $\beta$ = 98.81(1)°, $\gamma$ = 90.40(1)°, $V$ = 3499.7(7) Å$^3$, $T$ = 294 K, $Z$ = 4, $\mu$(MoK$\alpha$) = 43.25 cm$^{-1}$, 16 732 reflections measured, 16 058 unique ($R_{int}$ = 0.019) and 9419 observed [$I > 3\sigma(I)$], $R$ = 0.037, $R_w$ = 0.038 [$F$, for unique reflections with $I > 3\sigma(I)$ and 902 parameters].

CCDC reference numbers 180835, 182158 and 182159. See http://www.rsc.org/suppdata/cc/b2/b201992m/ for crystallographic data in CIF or other electronic format.

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