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Calixarenes as ligands for transition-metal catalysts: a bis(calix[4]arene-11,23-dicarboxylato) dirhodium complex

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A novel dirhodium tetracarboxylate complex is described in which two calix[4]arene macrocycles, bridged at the upper rim by a Rh–Rh unit, serve as ligands and whose solid-state structure shows an unusual coordination of a toluene molecule in the axial position at each rhodium atom.

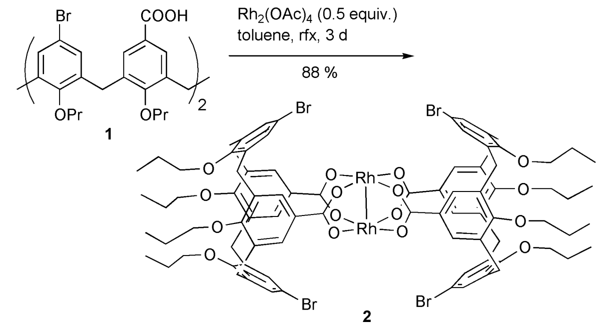
Calixarenes are under active investigation as three-dimensional scaffolds for functional molecular systems.[1,2] The use of calixarenes as ligands for transiton metals is also increasing,[1,3] with an emphasis on complex formation at the lower rim where hydroxy groups and their derivatives offer excellent multiple coordination sites. Examples for metal coordination at the upper rim are still rare: A calix[4]arene with *para*-PPh$_2$ substitution at opposite rings was found to form *trans*-chelate complexes with several transition metals[4] (Ag, Pd, Pt, Ru), and related water-soluble calixarene–phosphanes were investigated as ligands for the Rh-catalysed two-phase hydroformylation of 1-alkenes.[5] Upper-rim mono-functionalised calixarene–diphenylphosphane rhodium complexes have also been prepared.[6]

With a view to the importance of dimeric rhodium(II) acetate [Rh$_2$(OAc)$_4$] and related carboxylate and amidate complexes as catalysts for carbene transfer reactions with diazo compounds,[7] we set out to bridge the upper rim of calix[4]arenes by an Rh–Rh unit and to evaluate the catalytic activity of the resulting complexes. Rh$_2$(OAc)$_4$ reacts with the calix[4]arene-11,23-dicarboxylic acid **1**[8] in boiling toluene under complete exchange of ligands to form the bis(5,17-dibromocalix[4]arene-11,23-dicarboxylato) dirhodium complex **2** (Scheme 1).†

From a toluene solution of **2**, dark-green solvent-containing crystals separate within a few days; when exposed to ambient atmosphere, they rapidly lose toluene and form a green powder. The XRD analysis at −80 °C reveals the composition of **2**·4 toluene.‡ Two solvent molecules are part of the complex, while the remaining two occupy positions between the complex entities. As expected, a Rh–Rh unit bridges a cone-shaped calixarene molecule through coordination of two bidentate carboxylate groups, and it connects two calixarenes in a head-to-head fashion to form an expanded capsula open at two opposite faces[9] (Fig. 1). The complexation of the two carboxylate groups at the upper rim generates a highly distorted pinched-cone conformation of each calixarene macrocycle with two flattened and two nearly parallel opposing aromatic rings.[10] The angles between the least-squares plane defined by the four methylene carbons of the macrocycle and the aromatic ring planes are 146.2, 77.1, 145.5 and 78.5°, and the interplanar angle between the benzene rings bridged by the dirhodium moiety is 24.5°.

Dinuclear quadruply bridged rhodium carboxylate complexes exist typically in the form Rh$_2$[μ-OOCR)$_4$L$_2$ where L is a donor molecule that occupies the available axial position at each octahedrally coordinated metal atom.[11] In the case of **2**, a toluene molecule is found at the axial coordination site, and this represents a rare example of arene coordination at a dirhodium tetracarboxylate complex. The Rh–Rh axis is almost perpendicular to the toluene ring plane (angle Rh1–C$_{p\text{-tolyl}}$–C$_{i\text{-tolyl}}$ 97.3°) and the shortest distances are: Rh1–C$_{para}$ 2.580, Rh1–H$_{para}$ 2.64 (H in calculated position), Rh1–C$_{meta1}$ 2.968, Rh1–C$_{meta2}$ 3.027 Å; the values for the second independent molecule are similar. This geometry is different from the one-dimensional coordination copolymer [Rh$_2$(OOCCF$_3$)$_4$·C$_6$Me$_6$]$_8$,[11f] which features a η^2-coordination of rhodium at the axial hexamethylbenzene ligand with Rh–C distances of 2.770–2.786 Å. The metal–arene coordination in the present case resembles the calculated structures of benzene with Lewis acids MX$_3$ (M = B, Al[12]) where the metal is also positioned over one aromatic ring carbon. However, the geometry of our complex could also be interpreted as a C–H coordination of rhodium, an interesting aspect in the research on aromatic C–H activation by electrophilic transition-metal complexes.[13]

Fig. 2 shows that the complexed toluene molecules also fit quite well in the clefts which are formed by the vicinal *p*-bromophenyl rings of the two calixarene units. Although this arrangement is unsymmetrical, it resembles the perpendicular structures of the benzene dimer[14] and might contribute to the



Scheme 1 Synthesis of the bis(calix[4]arene) dirhodium complex **2**.

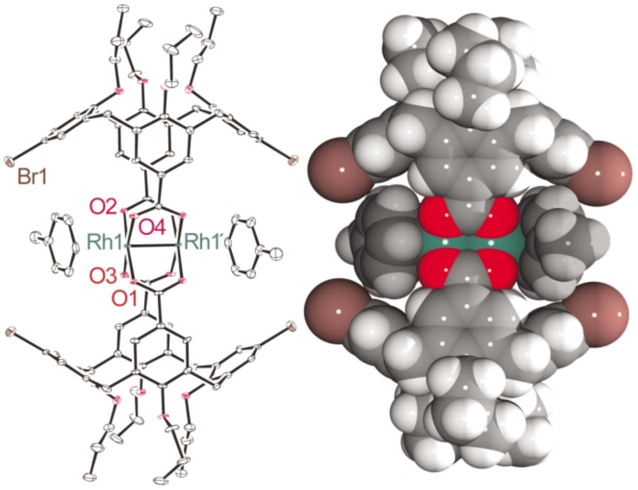


Fig. 1 (Left) ORTEP drawing of complex **2**(toluene)$_2$. Only one of the two independent molecules is shown. The ellipsoids of thermal vibration represent a 20% probability. Selected bond distances (values in square brackets refer to the second molecule): Rh1–Rh1′ (at –*x*, 1 − *y*, 1 − *z*) 2.399(2) [2.395(2)], Rh–O 2.009(6)–2.043(6) [2.026(6)–2.040(6)], Rh–C$_{\text{p-tolyl}}$ 2.580(10) [2.605(10)] Å. Bond angles: O1–Rh1–O3 83.8(2), O1–Rh1-O4 95.7(2), O1–Rh1–Rh1′ 88.8(2), O4–Rh1–Rh1′ 88.3(2)°. (Right) Space filling model of the complex **2**(toluene)$_2$.

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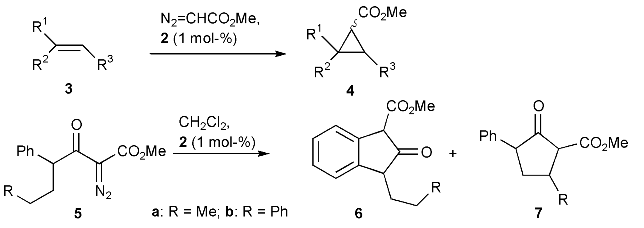

Fig. 2 Reactions catalyzed by **2**.

energetic stabilisation of this host–guest arrangement.[15] For the two independent complex molecules in the unit cell, the shortest distances between H atoms of toluene and C atoms of the calixarene are in the following ranges: H_{meta}–$C_{ipso(\mathrm{Br})}$ 3.01–3.21 Å, H_{meta}–$C_{ortho(\mathrm{Br})}$ 3.30–3.39 Å, H_{ortho}–$C_{ortho(\mathrm{Br})}$ 3.25–3.32 Å.

A preliminary evaluation of the catalytic activity of **2** was carried out for two important carbene transfer reactions, alkene cyclopropanation and intramolecular C–H insertion (Scheme 2). The formation of cyclopropanes **4** from alkenes **3** and methyl diazoacetate (MDA) was readily catalysed by 1 mol% of **2** at 20 °C in CH_2Cl_2 with the following results: styrene, 98% yield, E:Z = 72:28; cyclohexene, 63%, *exo*:*endo* 72:28; 2-methyl-2-butene, 52%, *anti*:*syn* = 45:55. A comparison with the $Rh_2(OAc)_4$-catalysed cyclopropanation of the same alkenes with MDA[16] (93%, 62:38; 90%, 79:21; 97%; 60:40) indicates that steric factors operate in the case of catalyst **2**: the yields decrease for the more highly substituted olefins, and the diastereoselectivity is reversed in the case of the trisubstituted alkene. While a full control over the diastereoselectivity in this type of cyclopropanation reactions is rarely achieved,[7] the steric conditions at the catalytic site are more influential in the case of intramolecular reactions since the latter have more compact transition states. Therefore, we were pleased to find that complex **2** catalyses the intramolecular C–H insertion of α-diazo-β-ketoesters **5a**,**b** with a high preference for carbene insertion into the aromatic C–H bond (R = Me: **6**:**7** = 90:10, 77% total yield; R = Ph: 97:3, 46%). This site selectivity contrasts with the same reaction catalysed by $Rh_2(OAc)_4$ (55:45 ratio for R = Me)[17] but it is close to the selectivity obtained with $Rh_2(OOCCPh_3)_4$ as catalyst[18] for which the steric effect of the bulky triphenylacetate ligands was demonstrated.

In conclusion, we have presented a novel type of upper-rim functionalization of calixarenes with transition-metal units. The coordination motif in **2** that links two calixarene molecules in a head-to-head fashion should also be applicable to other metals. We have shown that the rhodium center in **2** retains its catalytic properties typical for dirhodium carboxylate complexes and that the enhanced steric shielding of the catalytic site may be useful for the control of stereo- and regio-selectivity in catalytic processes.

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Notes and references

† *Physical and spectroscopic data* for **2**: green fine powder from MeOH after drying at 50 °C/0.001 mbar; yield: 1.46 g (88%); decomp. ≥290 °C. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 0.83 (t, 6H), 1.06 (t, 6H), 1.76–1.84 (m, 8H), 3.06 (d, 4H), 3.63 (t, 4H), 3.90 (t, 4H), 4.30 (d, 4H), 6.75 (s, 4H), 7.29 (s, 4H). ^{13}C NMR ($CDCl_3$): δ 9.7, 10.7, 22.8, 23.4, 30.6, 76.5, 77.1, 114.5, 125.3, 129.6, 131.8, 132.0, 138.6, 156.7, 158.6, 185.0. MS (MALDI-TOF, dhb matrix): 1879.5 [M^+], 1900.5 [$(M + Na)^+$]. $C_{84}H_{88}Br_4O_{16}Rh_2$ (1879.0): calc.: C, 53.69; H, 4.72; found: C, 53.79; H 5.12%.

‡ *Crystal data* for **2**$(C_6H_5Me)_4$: $C_{84}H_{88}O_{16}Br_4Rh_2 \cdot 4C_7H_8$: M = 2247.5, triclinic, space group $P\bar{1}$ (no. 2); a = 12.801(2), b = 16.916(3), c = 25.080(5) Å, α = 72.15(2), β = 87.38(2), γ = 85.48(2)°, V = 5151.9(17) Å^3, Z = 2 (two independent molecules, each with a crystallographic centre of symmetry), D_c = 1.449 g cm^{-3}, μ(Mo-Kα) = 1.936 mm^{-1}, T = 193 K; dark-green prism, 0.31×0.42×0.54 mm; Stoe IPDS diffractometer. The structure was solved using SIR 92 and refined by the full-matrix least-squares method on F^2 using SHELX 97. Hydrogen atoms (except for the methyl protons of one toluene molecule) were included at calculated positions and treated as riding on their bond neighbours. Refinement of 1146 variables (8 restraints) gave R = 0.0641 and R_w = 0.1522 for 7340 reflections with $I > 2\sigma(I)$ and R = 0.1038, R_w = 0.1662 for 12010 independent reflections. CCDC reference number 170079. See http://www.rsc.org/suppdata/cc/b1/b110478k/ for crystallographic data in CIF or other electronic format.

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