Syntheses and structures of mono-, di- and tetranuclear rhodium or iridium complexes of thiacalix[4]arene derivatives†

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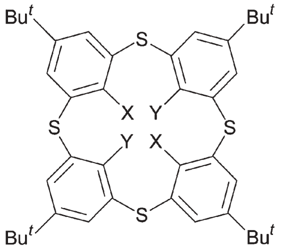
The reactions of [Cp*MCl$_2$]$_2$ (Cp* = η^5-C$_5$Me$_5$, M = Rh, Ir) with thiacalix[4]arene (TC4A(OH)$_4$) and tetramercaptothiacalix[4]arene (TC4A(SH)$_4$) gave the mononuclear complexes [(Cp*M){η^3-TC4A(OH)$_2$(O)$_2$}] and the dinuclear complexes [(Cp*M)$_2${η^3:η^3-TC4A(S)$_4$}] respectively, while the analogous reactions with dimercaptothiacalix[4]arene (TC4A(OH)$_2$(SH)$_2$) produced the tetranuclear complexes [(Cp*M)$_2$(Cp*MCl$_2$)$_2$-{η^3:η^3:η^1:η^1-TC4A(O)$_2$(S)$_2$}].

Sulfur donor ligands have attracted much attention in recent years because of their flexible coordination ability, leading to the formation of a variety of mono- and polynuclear metal–sulfur complexes.[1] Recent studies in our laboratory have focused on the pursuit of rational synthetic pathways towards metal–sulfur clusters of a desired framework.[2,3] During the course of these studies, novel catalytic reactions have been developed by using a cubane-type Mo$_3$PdS$_4$ cluster[4] or thiolate-bridged diruthenium complexes.[5–7] On the other hand, the chemistry of metallocalixarenes have long received interest due to their unique structural features and chemical properties.[8] Recently, sulfur-containing calix[4]arenes, such as thiacalix[4]arene **1**[9,10] and tetramercaptothiacalix[4]arene **2**,[11] have been prepared and were found to form various polynuclear metal complexes. We previously obtained the dihydrido complexes [{MH$_2$(PMe$_2$Ph)$_3$}{η^3-TC4A(OH)$_2$(O)$_2$}] from the reaction of **1** with *cis*-[M(N$_2$)$_2$(PMe$_2$Ph)$_4$] (M = Mo, W).[12] Recently, we have reported the reaction of **1** with [(η^5-C$_5$H$_5$)TiCl$_3$] in the presence of NEt$_3$, followed by the addition of *cis*-[Mo(N$_2$)$_2$(PMe$_2$Ph)$_4$] to afford the Ti–Mo hetero-bimetallic complex [Ti(μ_2-C$_5$H$_5$)MoH(PMe$_2$Ph)$_2$-{TC4A(O)$_4$}], the X-ray analysis of which shows an unusual α-agostic μ_2-η^5:η^2-coordination of the cyclopentadienyl ligand to the two metals.[13] This demonstrates the usefulness of thiacalixarene and its derivatives as ligands for the synthesis of multimetallic complexes. We have now succeeded in the synthesis of a new thiacalix[4]arene, dimercaptothiacalix[4]arene **3**. Here we report on the synthesis and structures of mono-, di- and tetranuclear rhodium or iridium complexes of thiacalix[4]arene derivatives **1**, **2** and **3** (Fig. 1).



TC4A(X)$_2$(Y)$_2$
1 X = Y = OH
2 X = Y = SH
3 X = OH, Y = SH
4 X = OMe, Y = OH
5 X = OMe, Y = OC(=S)NMe$_2$
6 X = OMe, Y = SC(=O)NMe$_2$
7 X = OMe, Y = SH

Fig. 1 Thiacalix[4]arene derivatives.

Dimercaptothiacalix[4]arene **3** was synthesized from **1**. Firstly, the two hydroxy groups in **1** were protected by the reaction of **1** with methyl iodide in the presence of potassium carbonate, in acetone, under reflux to give bis(methyl ether) **4** in 89% yield.[14] Compound **4** was then transformed into **5** in 83% yield by reaction with *N,N*-dimethylthiocarbamoyl chloride (K$_2$CO$_3$, acetone, reflux). The thermal rearrangement of **5** to **6** was achieved in 96% yield by heating the solid at 260 °C *in vacuo*. The subsequent reduction of **6** by LiAlH$_4$ in dry THF gave rise to **7** in 45% yield. Finally, treatment of **7** with BBr$_3$ in CH$_2$Cl$_2$ resulted in the formation of **3** in 89% yield.

The reaction of [Cp*MCl$_2$]$_2$ (M = Rh, Ir; Cp* = η^5-C$_5$Me$_5$) with **1** in the presence of K$_2$CO$_3$ in THF at room temperature gave the mononuclear complexes [Cp*M{η^3-TC4A(OH)$_2$(O)$_2$}] (M = Rh (**8a**, 98%), Ir (**8b**, 97%)). The structures of **8a** and **8b** were characterized by ^{1}H NMR spectroscopy and the structure of **8b** confirmed by X-ray diffraction.§ Complex **8b**, obtained by recrystallization from CH$_2$Cl$_2$–hexane, contains two CH$_2$Cl$_2$ molecules, one each on the inside and outside of the thiacalix[4]arene moieties in cone conformations. Interestingly, the reaction of an excess of [Cp*MCl$_2$]$_2$ with **1** did not produce bimetallic complexes—probably due to the intramolecular hydrogen bonds observed in the structures of complexes **8**. Actually, in the ^{1}H NMR spectra, a signal assigned to the two phenolic hydrogens in complexes **8** appeared at lower fields (**8a**: δ 10.98, **8b**: δ 10.57) to the equivalent hydrogens in **1** (δ 9.60). In contrast, treatment of TC4A(SH)$_4$, **2**, even with one equiv. of [Cp*MCl$_2$]$_2$ gave the bimetallic complexes [(Cp*M)$_2${η^3:η^3-TC4A(S)$_4$}] (M = Rh (**9a**, 61%), Ir (**9b**, 68%)) (Scheme 1), the structures of which were determined by X-ray diffraction.§ Complexes of type **9** have an approximately C_{2h} symmetry, the TC4A(S)$_4$ ligand adopting a 1,2-alternate conformation, coordinating to the two metals as a bis(dithiolate–thioether tridentate) ligand.

Surprisingly, TC4A(OH)$_2$(SH)$_2$, **3**, reacted with 2 equiv. of [Cp*MCl$_2$]$_2$ in the presence of NEt$_3$ to give the tetranuclear

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† Electronic Supplementary Information (ESI) available: Experimental details, ^{1}H NMR spectroscopic data and elemental analyses for all the complexes. See http://dx.doi.org/10.1039/b502999f

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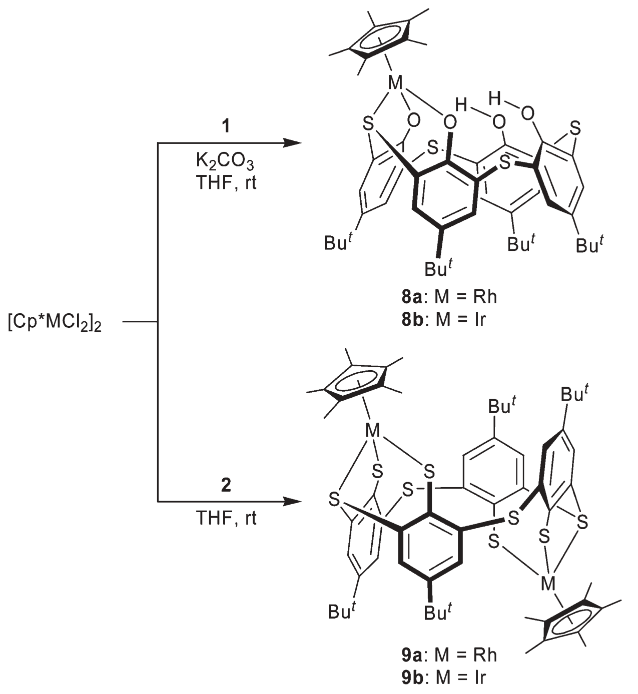


Scheme 1 Syntheses of $[\mathrm{Cp^*M}\{\eta^3\text{-TC4A(OH)}_2(\mathrm{O})_2\}]$ (M = Rh (**8a**), Ir (**8b**)) and $[(\mathrm{Cp^*M})_2\{\eta^3{:}\eta^3\text{-TC4A(S)}_4\}]$ (M = Rh (**9a**), Ir (**9b**)).

complexes $[(\mathrm{Cp^*M})_2(\mathrm{Cp^*MCl_2})_2\{\eta^3{:}\eta^3{:}\eta^1{:}\eta^1\text{-TC4A(O)}_2(\mathrm{S})_2\}]$ (M = Rh (**10a**, 70%), Ir (**10b**, 63%)). The structures of **10a** and **10b** were characterized by ^{1}H NMR spectroscopy and the structure of **10b** was revealed by X-ray analysis.[15] The ORTEP drawing of **10b** is shown in Fig. 2.§ Complex **10b**, recrystallized from $\mathrm{CH_2Cl_2}$–hexane, consists of two Cp*Ir fragments, two $\mathrm{Cp^*IrCl_2}$ fragments and four solvating $\mathrm{CH_2Cl_2}$ molecules with the tetradeprotonated $\mathrm{TC4A(O)_2(S)_2}$ ligand. This ligand adopts a cone conformation, containing no $\mathrm{CH_2Cl_2}$ molecules. The two Cp*Ir fragments occupy *syn* positions with respect to the mean plane defined by the macrocycle, the $\mathrm{TC4A(O)_2(S)_2}$ ligand coordinates to them as a bis(phenolate–thioether–thiolate tridentate) ligand and the two $\mathrm{Cp^*IrCl_2}$ moieties are bonded to the remaining two thioether sulfurs. Thus a molecule of **3** is incorporated into complexes **10** as a tetraanionic ligand.

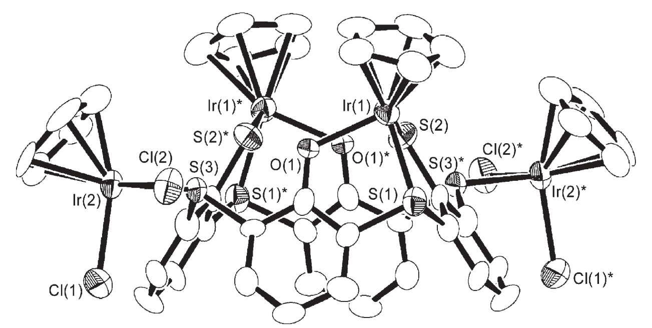
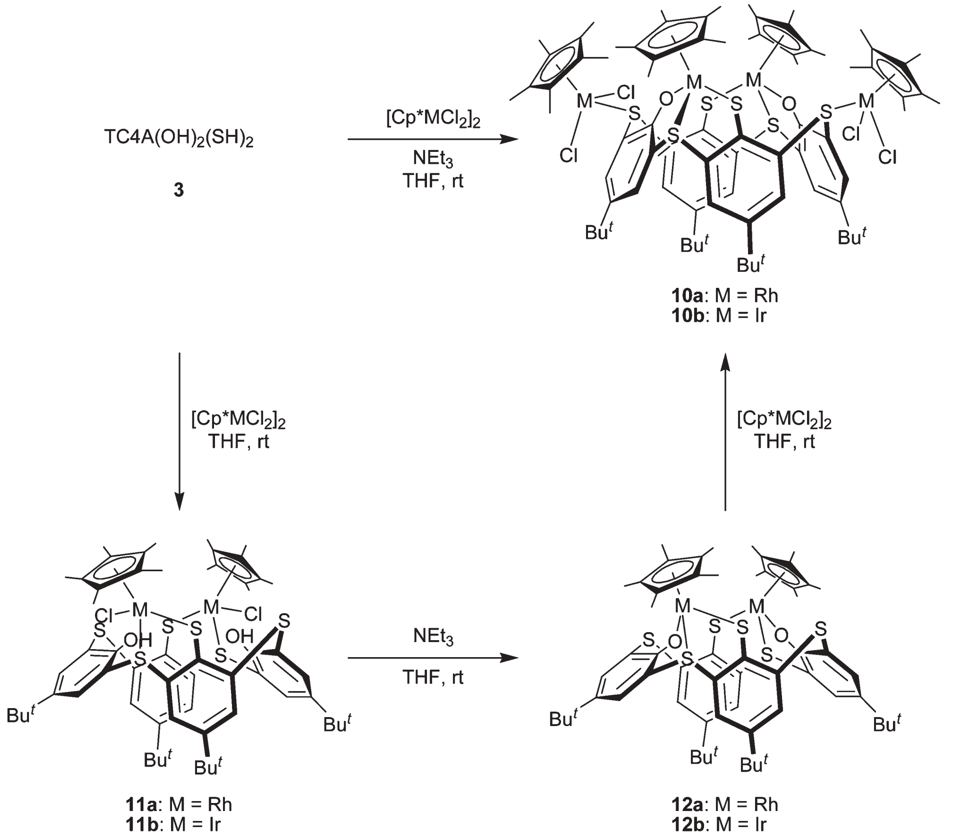


Fig. 2 ORTEP drawing of **10b** with the hydrogen atoms, methyl groups of the cyclopentadienyl ligands, *tert*-butyl groups and solvent molecules omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): Ir(1)–S(1) = 2.321(5), Ir(1)–S(2) = 2.328(6), Ir(1)–O(1) = 2.10(1), Ir(2)–S(3) = 2.385(5).



Scheme 2 Syntheses of $(\mathrm{Cp^*M})_2(\mathrm{Cp^*MCl_2})_2\{\eta^3{:}\eta^3{:}\eta^1{:}\eta^1\text{-TC4A(O)}_2(\mathrm{S})_2\}$ (M = Rh (**10a**), Ir (**10b**)).

On the other hand, the reaction of **3** with $[Cp^*MCl_2]_2$ without base gave the dinuclear complexes $[(Cp^*MCl)_2\{\eta^2:\eta^2\text{-}TC4A(OH)_2(S)_2\}]$ (M = Rh (**11a**, 77%), Ir (**11b**, 73%)). X-ray analyses showed that the double-deprotonated dimercaptothiacalixarene ligand, $TC4A(OH)_2(S)_2$, adopts a cone conformation and coordinates to the two metals as a bis(thiolate–thioether bidentate) ligand. The ^1H NMR spectra displayed a signal assigned to the two phenolic protons at δ 7.33 for **11a** and 6.67 for **11b**. Treatment of complexes **11** with 2 equiv. of NEt_3 followed by recrystallization from hexane gave $[(Cp^*M)_2\{\eta^3:\eta^3\text{-}TC4A(O)_2(S)_2\}]$ (M = Rh (**12a**, 98%), Ir (**12b**, 93%)). In the ^1H NMR spectra, the signal assigned to the two protons of the OH groups disappeared and the formation of NH_4Cl was observed. When complexes **12** were allowed to react further with one equiv. of $[Cp^*MCl_2]_2$, complexes **10a** and **10b** were formed in 70% and 62% yield respectively (Scheme 2). These results indicate that complexes **12** have approximately C_{2v} symmetry and that the $TC4A(O)_2(S)_2$ ligand adopts a cone conformation, coordinating to the two metals as a bis(thiolate–thioether–phenolate tridentate) ligand.

In conclusion, a new thiacalix[4]arene **3** has now been synthesized which can bind four molecules of $[Cp^*MCl_2]$ (M = Rh, Ir) to form tetranuclear complexes **10**, while similar reactions with thiacalix[4]arenes **1** and **2** give mononuclear and dinuclear complexes **8** and **9** respectively. Detailed studies on the differences in reactivities of thiacalix[4]arenes **1**, **2** and **3** towards various metal complexes are now in progress.

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Notes and references

§ Crystal data for **8b**·$2CH_2Cl_2$: $C_{52}H_{65}Cl_4IrO_4S_4$, M = 1216.36, orthorhombic, space group *Pnma* (# 62), a = 12.2677(8), b = 23.102(2), c = 19.400(1) Å, V = 5498.1(6) Å^3, D_{calcd} = 1.469 g cm^{-3}, T = 293 K, Z = 4, μ(Mo-Kα) = 28.22 cm^{-1}, structure solution by direct methods, refinement on F^2, 12518 unique reflections (R_{int} = 0.044), $R1$ = 0.073, $wR2$ = 0.179, GOF = 1.14, CCDC 270131. Crystal data for **9a**: $C_{60}H_{74}Rh_2S_8$, M = 1257.54, monoclinic, space group *C*2/m (# 12), a = 20.71(1), b = 12.942(6), c = 13.568(6) Å, β = 99.764(6)°, V = 3585(3) Å^3, D_{calcd} = 1.165 g cm^{-3}, T = 293 K, Z = 1, μ(Mo-Kα) = 7.23 cm^{-1}, structure solution by direct methods, refinement on F^2, 6581 unique reflections (R_{int} = 0.043), $R1$ = 0.072, $wR2$ = 0.237, GOF = 1.23, CCDC 270132. Crystal data for **9b**: $C_{60}H_{74}Ir_2S_8$, M = 1436.16, monoclinic, space group *P*-1 (# 2), a = 11.019(4), b = 12.333(5), c = 13.359(4) Å, α = 67.49(1), β = 65.78(1), γ = 81.55(2)°, V = 1529.4(9) Å^3, D_{calcd} = 1.559 g cm^{-3}, T = 293 K, Z = 1, μ(Mo-Kα) = 46.67 cm^{-1}, structure solution by direct methods, refinement on F^2, 6581 unique reflections (R_{int} = 0.043), $R1$ = 0.049, $wR2$ = 0.129, GOF = 1.10, CCDC 270129. Crystal data for **10b**·$4CH_2Cl_2$: $C_{84}H_{112}Cl_{12}Ir_4O_2S_6$, M = 2540.48, monoclinic, space group *C*2/c (# 15), a = 34.408(5), b = 12.624(2), c = 25.155(4) Å, β = 110.396(6)°, V = 10241(3) Å^3, D_{calcd} = 1.648 g cm^{-3}, T = 293 K, Z = 4, μ(Mo-Kα) = 56.71 cm^{-1}, structure solution by direct methods, refinement on F^2, 4664 unique reflections (R_{int} = 0.076), $R1$ = 0.072, $wR2$ = 0.162, GOF = 1.12, CCDC 265752. See http://dx.doi.org/10.1039/b502999f for crystallographic data in CIF or other electronic format.

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