Anion Binding within the Cavity of π-Metalated Calixarenes

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Abstract: The synthesis of a range of bi- and tetrametalated macrocyclic complexes based upon calix[4]arene, *p-tert*-butylcalix[4]arene and related tetraalkoxy derivatives, of type [{M(L)}$_2$(calixarene-*n*H)]X$_{4-n}$ and [{M(L)}$_4$(calixarene-2H)]X$_6$ (M = Rh, Ir, Ru; L = Cp*, *p*-MeC$_6$H$_4$CHMe$_2$; *n* = 0, 1, 2; X = BF$_4$, CF$_3$SO$_3$, HSO$_4$, I, ReO$_4$, H$_2$PO$_4$, *etc*., not all combinations) is reported. A related trimetallic calix[5]arene derivative [{Ir(η^5-C$_5$Me$_5$)}$_3$(*p-tert*-butylcalix-[5]arene-H)][BF$_4$]$_5$ has also been synthesized. In all cases, the presence of the transition metal centers results in a significant enhancement in the acidity of the hydroxyl functionalities at the calixarene lower rim. For the tri- and tetrametalated derivatives, the host−guest behavior of the calixarene is drastically altered such that anionic guest species are included within the molecular cavity. The function of the new tetrametallic hosts [{Ru(η^6-*p*-MeC$_6$H$_4$-CHMe$_2$)}$_4$(η^6:η^6:η^6:η^6-C$_{28}$H$_{22}$O$_4$)]$^{6+}$ (**15**) and [{Ir(η^5-C$_5$Me$_5$)}$_4$(η^6:η^6:η^6:η^6-C$_{28}$H$_{22}$O$_4$)]$^{6+}$ (**16**) as anion receptors has been confirmed by X-ray crystal structure investigations upon BF$_4^-$ (**15a, 16a**), HSO$_4^-$ (**16c**), SO$_4^{2-}$ (**15c**), and I$^-$ (**15d**) derivatives, which clearly demonstrate a cooperative effect arising from the arrangement of four metal centers about a common, rigid binding pocket, resulting in anion−host contacts as low as 2.85 Å (BF$_4$···C$_{calix}$). The anion binding properties of host **15** in aqueous solution have also been investigated by ^{1}H NMR titration, giving binding constants in the range 100−550 M^{-1} for nitrate and halide anions, with the binding constant decreasing in the order Cl$^-$ > Br$^-$ > I$^-$. Significantly increased binding is observed in nonaqueous media. This novel form of anion complexation contrasts to the formation of weakly bound, van der Waals inclusion complexes commonly observed in calixarene chemistry.

Introduction

The noncovalent binding of anionic guest species is a relatively unexplored, although increasingly topical field.[1] Importantly, anions such as phosphates and nitrates have been implicated in environmental contamination, resulting in eutrophication,[2] while biological polyphosphates form a vital part of the metabolic processes of all living organisms. Indeed anionic materials in general comprise the substrates for the majority of enzymatic reactions.[3] Also of interest are anionic species such as ^{99}TcO$_4^-$ containing the long-lived β-emitter ^{99}Tc ($t_{1/2} = 2.13 \times 10^5y$), present in the environment as a consequence of releases from the nuclear fuel cycle, atomic weapons testing, and the

use of ^{99}Mo/^{99}Tc pertechnetate generators in medical applications.[4] The design of host systems which can *selectively* complex such anionic species in order to assess or ameliorate their environmental impact is of clear importance, and yet, in comparison to the analogous supramolecular chemistry of cations,[5] this has not yet been achieved with any significant degree of success.[1]

In natural systems, recognition and transport of anions such as inorganic phosphate and sulfate is carried out by binding proteins which rely upon a complex array of hydrogen bonding interactions in order to selectively recognize their individual substrates.[6] This strategy has recently been adopted by Reinhoudt *et al.* in order to produce synthetic anion receptors.[7] Other approaches to the design of artificial anion complexation agents include the incorporation of Lewis acidic centers such as boron, silicon, mercury, and tin;[8] the synthesis of cationic polyammonium and polyguanidinium hosts;[9] and the incorporation of transition metal species with vacant coordination sites.[10] In this report, we describe a new, very simple approach to selective anion recognition based upon size and shape compatibility

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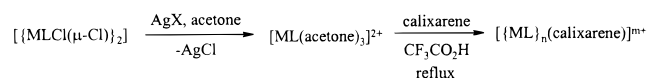(3) Lange, L. G., III; Riordan, J. F.; Vallèe, B. L. *Biochemistry* **1974**, *13*, 4361.

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Scheme 1. Synthesis of New Organometallic Host Cations

$$[\{MLCl(\mu\text{-}Cl)\}_2] \xrightarrow[\text{-AgCl}]{\text{AgX, acetone}} [ML(\text{acetone})_3]^{2+} \xrightarrow[\substack{\text{CF}_3\text{CO}_2\text{H} \\ \text{reflux}}]{\text{calixarene}} [\{ML\}_n(\text{calixarene})]^{m+}$$

between anion and organometallic host molecules based upon the calixarenes (**1**).[11] Parts of this work have already appeared in preliminary form.[12]

Results and Discussion

Bimetallic Hosts. The bowl-shaped calix[4]arene (**1a**) forms solid state inclusion compounds incorporating neutral guests such as acetone[13] or toluene[14] within the molecular cavity. We
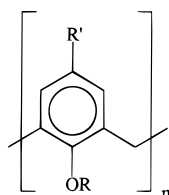
R = R' = H, n = 4 **1a**
R = H, R' = *t*-Bu, n = 4 **1b**
R = Me, R' = *t*-Bu, n = 4 **1c**
R = Et, R' = H, n = 4 **1d**
R = n-Pr, R' = H, n = 4 **1e**
R = H, R' = *t*-Bu, n = 5 **1f**

have shown recently, however, that for the related trimeric macrocycle cyclotriveratrylene (CTV)[15] addition of two or three cationic transition metal centers to the outer faces of the aromatic rings results in the inclusion of anionic guest species such as BF_4^-, $CF_3SO_3^-$, ReO_4^-, $^{99}TcO_4^-$, *etc*. Accordingly, a similar strategy was adopted with the calixarenes involving the reaction of calix[4]arene (**1a**) with $[\{Ru(\eta^6\text{-}p\text{-}MeC_6H_6CHMe_2)Cl(\mu\text{-}Cl)\}_2]$ (**2a**)[16] and $[\{M(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ (M = Rh, **2b**; Ir, **2c**),[17] either in acetone or acetone/CF_3CO_2H mixture, according to the method outlined in Scheme 1.[18] Treatment of complex

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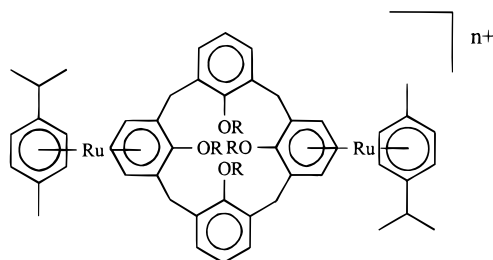
2b with Ag[BF$_4$], followed by refluxing with an equimolar quantity of **1a** in CF_3CO_2H resulted in the isolation of the bimetallic calixarene complex $[\{Rh(\eta^5\text{-}C_5Me_5)\}_2(\eta^6:\eta^6\text{-}calix\text{-}[4]arene)][BF_4]_4$ (**3**) in 83% yield. Treatment of calixarene **1a**
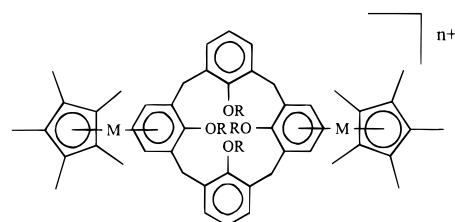
n=4, 4R=H, M=Rh **3**
n=3, 3R=H, M=Rh **8a**; M=Ir **8b**
n=2, 2R=H, M=Rh **7**
n=4, R=n-Pr, M=Ir **12**
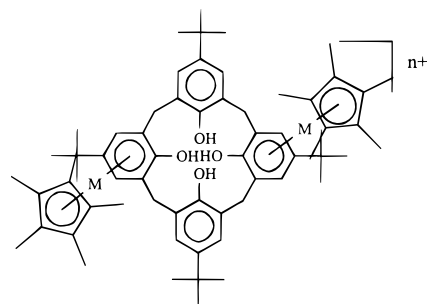
n=4, M=Rh **5a**; M=Ir **5b**
n=3, M=Rh **9a**; M=Ir **9b**

R=3H, n=3 **4a, 4b**
R=Et, n=4 **13**

with **2a** gave a mixture of the deprotonated diruthenium species $[\{Ru(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)\}_2(\eta^6:\eta^6\text{-}calix[4]arene\text{-}H)][BF_4]_3$ (**4a**) as well as a significant quantity of a further tetranuclear product $[\{Ru(\eta^6\text{-}arene)\}_4(\eta^6:\eta^6:\eta^6:\eta^6\text{-}calix[4]arene\text{-}2H)][BF_4]_6$ (*vide infra*) even over a very short reaction time in the presence of excess **1a**. However, direct reaction of **2a** with **1a** in CF_3CO_2H according to the method of Rybinskaya *et al.*[18c] cleanly gave the analogous hydrogen bis(trifluoroacetate) salt $[\{Ru(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)\}_2(\eta^6:\eta^6\text{-}calix[4]arene\text{-}H)][H(CF_3CO_2)_2]_3$ (**4b**)- as the sole product. Similarly, clean dimetallic products were obtained in the presence of $H_2PO_4^-$, WO_4^{2-}, and $CH_3CO_2^-$, suggesting an anion-mediated inhibition of the formation of tri- and tetrametalated products. Analogous reactions of **2b** and **2c** with *p-tert*-butylcalix[4]arene (**1b**) resulted in the isolation of the bimetallic species $[\{M(\eta^5\text{-}C_5Me_5)\}_2(\eta^6:\eta^6\text{-}p\text{-}tert\text{-}butylcalix\text{-}[4]arene)][BF_4]_4$ (M = Rh, **5a**; Ir, **5b**) again in high yield. Complexes of type **3**−**5** were characterized on the basis of their ^{1}H NMR spectra (Table 1) which displayed a single AB quartet

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assigned to the protons of the bridging methylene functionalities as well as two sets of resonances assigned to the protons of the calixarene aromatic rings (*e.g.* for **3**: δ 7.17 (d), 6.77 (t), and 7.02 (d), 6.61 (t)), indicating that the two metal centers are situated on opposite faces of the macrocycle in each case, and that the cone conformation is retained. In addition, the ^{1}H NMR spectrum of **5b** displayed a broad peak at δ 7.34 ppm assigned to the hydroxyl functionalities of the metalated macrocycle. The formulations of complexes **3** and **5** were also confirmed by mass spectrometry, which displayed clear molecular ion peaks for each compound at *m/z* 898 (**3**), 1123 (**5a**), and 1301 (**5b**) along with higher mass signals corresponding to the cationic host molecules in association with one tetrafluoroborate anion. Complexes **3** and **5** may be regarded as analogues of the unstable π-phenol species [Ir(η^5-Cp*)(η^6-PhOH)][PF$_6$]$_2$ (**6**).[18d] Complex **6** has been observed to deprotonate readily to form the hydrogen bonded dimer [Ir(η^5-Cp*)$_2${(η^6-PhO)$_2$H}][PF$_6$]$_3$, while treatment with Na$_2$CO$_3$ results in the formation of the oxocyclohexadienyl cation [Ir(η^5-Cp*)(η^5-PhO)][PF$_6$]. Similarly, the acidity of the calixarene phenolic protons in complexes **3**−**5** is significantly enhanced with respect to the free calixarene, as evidenced by the extreme broadness of the signals for the hydroxyl protons in the ^{1}H NMR spectra of these materials. Reaction of **3** with excess Na$_2$CO$_3$ in acetone resulted in the loss of two of the phenolic protons to give the dication [{Rh(η^5-C$_5$Me$_5$)}$_2$(η^6:η^6-calix[4]arene-2H)][BF$_4$]$_2$ (**7**). The ^{1}H NMR spectrum of this complex (Table 1) proved similar to that of **3** except for a significant shift in the position of the AB quartet assigned to the methylene bridges, and the appearance of a relatively sharp signal at δ 10.28 ppm close to the chemical shift of the hydroxyl resonance in free calix[4]arene, integrating for two protons. Interestingly, reaction of **2b,c** with calixarene **1a** (after pretreatment with Ag[BF$_4$]) in acetone in the presence of only a small amount of CF$_3$CO$_2$H results in the precipitation of further species [{M(η^5-C$_5$Me$_5$)}$_2$(η^6:η^6-calix[4]arene-H)][BF$_4$]$_3$ (M = Rh, **8a**; Ir, **8b**), analogous to complexes **4a,b**, in which only one of the phenolic protons has been removed from the base of the calixarene. The ^{1}H NMR spectrum of **8a** demonstrates a chemical shift for the high-field portion of the signals assigned to the methylenic bridges that is intermediate between those of **3** and **7** (3.20 ppm *vs* 3.42 (**3**) and 3.01 ppm (**7**)). Also many of the resonances are split into pairs, suggesting an asymmetric complex in which there is a slight difference between the two coordinated rings. The identity of **8a** was confirmed by addition of HBF$_4$ to an NMR sample, resulting in its immediate conversion into **3**. The identity of the iridium complex **8b** was also confirmed by FAB-MS *m/z* 1078 (M$^+$) and associated fragmentation peaks.

Behavior similar to that of **3**, **7**, and **8a** was observed for the complexes based upon *p-tert*-butylcalix[4]arene. Recrystallization of the tetracations **5a,b** by slow diffusion of diethyl ether into a nitromethane solution of the complexes resulted in the formation of the solvates [{M(η^5-C$_5$Me$_5$)}$_2$(η^6:η^6-*p-tert*-butylcalix-[4]arene-H)][BF$_4$]$_3$·nNO$_2$CH$_3$·Et$_2$O (M = Rh, n = $^2/_3$, **9a**; M = Ir, n = 1, **9b**), while if **5b** is allowed to stand in the more basic solvent dimethylformamide (DMF) over a period of several weeks, large colorless crystals of composition [{Ir(η^5-C$_5$Me$_5$)}$_2$(η^6:η^6-*p-tert*-butylcalix[4]arene-2H)][BF$_4$]$_2$·DMF (**10**) are obtained. As with **3**, **7**, and **8**, the ^{1}H NMR spectra of **5b**, **9**, and **10** show a consistent trend in the chemical shift of the high-field wing of the signal assigned to the methylenic bridges (Table 1) with shielding increasing with degree of deprotonation. The X-ray crystal structure of complex **9b** has already been reported[12c] and clearly demonstrates the inclusion of a molecule of diethyl ether within the *p-tert*-butylcalix[4]arene cavity, while the nitromethane solvent molecule and tetrafluoroborate anions

are situated externally to the calixarene bowl. The analogous rhodium complex **9a** has also been characterized by X-ray crystallography and is isostructural to **9b** (Figure 1). Notably, as for **9b**, the Rh−C(1) distances for the metalated rings A and C (2.364(6) and 2.327(6) Å) are significantly longer than for the remaining Rh−C$_{calix}$ bond lengths of 2.262(6) and 2.272(6) Å (av), consistent with an η^5-oxocyclohexadienyl description for deprotonated phenolate ligands.[18d] This trend is also reflected in the shortening of the C(1)−O bond: C(1A)−O(1A), 1.291-(7); C(1C)−O(1C), 1.335(7) Å [*cf.* C(1B,D)−O(1B,D), 1.381-(7) Å (av)], suggesting that it may be O(1A) that is deprotonated. Examination of the hydrogen bonding network at the base of the calixarene reveals, however, that there are *two* long, non-hydrogen-bonded contacts O(1A)−O(1D) (2.73(1) Å) and O(1C)−O(1D) (2.80(1) Å), indicating some disorder between the deprotonation of O(1A) and O(1C), as observed for **9b**.

In spite of the presence of the two transition metal centers, the calixarene cavity in **9a** is occupied by a diethyl ether guest molecule (not one of the tetrafluoroborate anions). The guest is threaded between the *tert*-butyl groups, forming a short contact of 3.24(2) Å from the ether oxygen O(1S) to the calixarene methyl carbon atom C(11C). The most deeply penetrating carbon atom, C(1S), is situated at distances of 3.62-(2), 3.63(2), 3.63(2), and 3.82(2) Å from the centroids of rings A, C, D, and B respectively, suggesting the possibility of weak −CH$_3$···π-hydrogen bonding interactions.[19]

The X-ray crystal structure of the deprotonation product **10** is closely related to that of **9a,b** except for the pattern of intramolecular hydrogen bonding at the calixarene lower rim. Strong hydrogen bonded contacts are observed between O(1A)···O(1B) and O(1C)···O(1D), 2.57(1) and 2.65(1) Å, respectively, while much longer distances are found between O(1A)···O(1D) and O(1B)···O(1C) of 2.99(1) and 2.96(1) Å (*cf.* distances of 2.52(1)−2.76(1) Å for **9b**).[12c] These values may be compared to the dilithium salt of **1b** in which the hydrogen bonded O···O contacts are as short as 2.40 Å (av), while the nonbonded distances are much longer at 3.14 Å (av).[20] The shorter nonbonded contacts in **10** are a consequence of the out of plane deformation of the phenolic oxygen atoms, arising from the partial η^5-oxocyclohexadienyl nature of the coordinated calixarene rings. Atoms O(1A) and O(1C) deviate by 0.20(1) and 0.29(1) Å from the planes containing C(2A−6A) and C(2C−6C), respectively. The corresponding deviations for C(1A,C) are 0.14(1) and 0.19(1) Å. The maximum deviation of atoms within the plane is 0.03 Å, and no such deviation is noted for O(1B) and O(1D). The conformation of the calixarene ring itself is slightly distorted form the ideal 4-fold symmetry with the two metalated rings (A and C) approaching one another more closely than rings B and D, presumably as a consequence of the reduced π···π repulsions between the two nonmetalated rings (intercentroid separations: A···C, 6.40(1) Å; B···D, 6.70-(1) Å; *cf.* 6.57(1) and 6.73(1) Å for **9a**).

Also interestingly, in the case of **10**, the calixarene molecular cavity is *not* occupied by the DMF solvent molecule, which is situated in pairs, along with two tetrafluorobroate anions, in a region of void space in the lattice, Figure 2. Indeed, the calixarene cavity is apparently empty, with the *tert*-butyl group of a neighboring molecule situated to one side of the cavity rim. This contrasts to the self-inclusion, with a substituent of one calixarene acting as the guest for another, which has been noted in the case of *p-tert*-butylcalix[5]arene,[21] which forms an infinite inclusion chain in the solid state. For complex **10** it

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Table 1. ^{1}H NMR Data for New Complexes^a

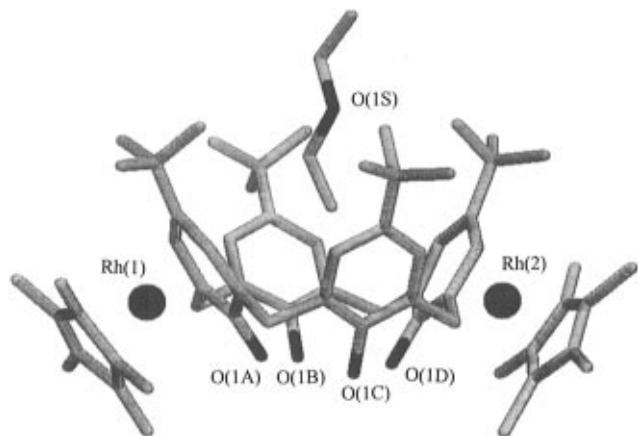| compound | arene/Cp* | calixarene | | |
		arom. C−H	−CH$_2$−	other
[{Rh(C$_5$Me$_5$)}$_2$(C$_{28}$H$_{24}$O$_4$)][BF$_4$]$_4$ (**3**)	2.23 (s, 30H)	7.17 (d, 4H, ^3J 7.6) 7.02 (d, 4H, ^3J 6.0) 6.77 (t, 2H, ^3J 7.6) 6.61 (t, 2H, ^3J 6.0)	4.27, 3.42 (AB, 8H, ^2J 12.8)	
[{Ru(p-MeC$_6$H$_4$CHMe$_2$)}$_2$(C$_{28}$H$_{24}$O$_4$)]-[H{CF$_3$CO$_2$}$_2$]$_3$ (**4b**)	6.60, 6.52 (AB, 8H, ^3J 6.5) 2.96 (sp, 2H, ^3J 6.9) 2.47 (s, 6H) 1.37 (d, 12H, ^3J 6.9)	7.09 (d, 4H, ^3J 7.6) 6.71 (t, 2H, ^3J 7.6) 6.58 (d, 4H, ^3J 5.6) 6.05 (t, 2H, ^3J 5.6)	4.40, 3.21 (AB, 8H, ^2J 12.7)	
[{Rh(C$_5$Me$_5$)}$_2$(C$_{44}$H$_{56}$O$_4$)][BF$_4$]$_4$ (**5a**)	2.21 (s, 30H)	7.26 (s, 4H) 7.24 (s, 4H)	4.17, 3.41 (AB, 8H, ^2J 12.9)	1.39 (s, 18H, *t*Bu) 1.15 (s, 18H, *t*Bu)
[{Ir(C$_5$Me$_5$)}$_2$(C$_{44}$H$_{56}$O$_4$)]-[BF$_4$]$_4$ (**5b**)2.27 (s, 30H)	7.27 (s, 4H)	4.11, 3.23 (AB, 8H, ^2J 12.6) 7.17 (s, 4H)	7.34 (bs, 4H, O*H*)	1.41 (s, 18H, *t*Bu) 1.16 (s, 18H, *t*Bu)
[{Rh(C$_5$Me$_5$)}$_2$(C$_{28}$H$_{22}$O$_4$)]-[BF$_4$]$_2$ (**7**)2.15 (s, 30H)	7.04 (d, 4H, ^3J 7.6)	4.28, 3.01 (AB, 8H, ^2J 12.0) 6.72 (d, 4H, ^3J 5.9) 6.66 (t, 2H, ^3J 7.6) 6.28 (t, 2H, ^3J 5.9)	10.28 (s, 2H, O*H*)	
[{Rh(C$_5$Me$_5$)}$_2$(C$_{28}$H$_{23}$O$_4$)][BF$_4$]$_3$ (**8a**)	2.16 (s, 15H) 2.15 (s, 15H)	7.07 (d, 4H, ^3J 7.7) 6.85 (d, 2H, ^3J 5.9) 6.84 (d, 2H, ^3J 5.9) 6.68 (t, 2H, ^3J 7.7) 6.43 (t, 2H, ^3J 5.9)	4.24, 3.22 (AB, 8H, ^2J 12.7)	
[{Ir(C$_5$Me$_5$)}$_2$(C$_{28}$H$_{23}$O$_4$)][BF$_4$]$_3$ (**8b**)	2.34 (s, 30H)	7.22 (d, 4H, ^3J 7.6) 7.02 (d, 4H, ^3J 5.8) 6.77 (t, 2H, ^3J 7.6) 6.61 (t, 2H, ^3J 5.8)	4.21, 3.38 (AB, 8H, ^2J 12.9)	
[{Rh(C$_5$Me$_5$)}$_2$(C$_{44}$H$_{55}$O$_4$)]-[BF$_4$]$_3$·0.7NO$_2$Me·Et$_2$O (**9a**)	2.18 (s, 30H)	7.22 (s, 4H) 7.14 (s, 4H)	4.20, 3.26 (AB, 8H, ^2J 12.4)	1.40 (s, 18H, *t*Bu) 1.12 (s, 18H, *t*Bu)
[{Ir(C$_5$Me$_5$)}$_2$(C$_{44}$H$_{55}$O$_4$)]-[BF$_4$]$_3$·NO$_2$Me·Et$_2$O (**9b**)	2.25 (s, 30H)	7.21 (s, 4H) 7.07 (s, 4H)	4.12, 3.12 (AB, 8H, ^2J 12.2)	1.39 (s, 18H, *t*Bu) 1.08 (s, 18H, *t*Bu)
[{Ir(C$_5$Me$_5$)}$_2$(C$_{40}$H$_{48}$O$_4$)][BF$_4$]$_4$ (**12**)	2.38 (s, 30H)	7.55 (d, 4H, ^3J 7.6) 7.31 (t, 2H, ^3J 7.6) 6.59 (t, 2H, ^3J 6.0) 6.37 (d, 4H, ^3J 6.0)	4.67, 3.48 (AB, 8H, ^2J 15.4)	4.30 (m, 4H, OPr) 4.10 (m, 4H, OPr) 2.22 (m, 4H, OPr) 1.85 (m, 4H, OPr) 1.22 (t, 6H, ^3J 7.4, OPr) 0.89 (t, 6H, ^3J 7.5, OPr)
[{Ru(p-MeC$_6$H$_4$CHMe$_2$)}$_2$(C$_{36}$H$_{40}$O$_4$)]-[BF$_4$]$_4$ (**13**)	6.96, 6.88 (AB, 8H, ^3J 6.6) 3.03 (sp, 2H, ^3J 6.8) 2.58 (s, 6H) 1.38 (d, 12H, ^3J 6.8)	7.49 (d, 4H, ^3J 7.6) 7.26 (t, 2H, ^3J 7.6) 6.28 (t, 2H, ^3J 5.9) 6.03 (d, 4H, ^3J 5.9)	4.53, 3.45 (AB, 8H, ^2J 15.2)	4.42 (m, 4H, OEt) 4.33 (m, 4H, OEt) 1.79 (t, 6H, ^3J 6.8, OEt) 1.35 (t, 6H, ^3J 6.8, OEt)
[{Ir(C$_5$Me$_5$)}$_3$(C$_{55}$H$_{69}$O$_5$)]-[BF$_4$]$_5$·0.5NO$_2$Me·2Et$_2$O (**14**)	2.30 (s, 30H) 2.26 (s, 15H)	7.47 (s, 1H) 7.46 (s, 1H) 7.38 (s, 1H) 7.37 (s, 1H) 7.35 (s, 1H) 7.34 (s, 1H) 7.30 (s, 1H) 7.29 (s, 1H) 7.28 (s, 1H) 7.11 (s, 1H)	4.52, 2.98 (AB, 4H, ^2J 12.4) 3.86, 3.06 (AB, 4H, ^2J 12.4) 3.29 (s, 2H)	1.47 (s, 9H, *t*Bu) 1.46 (s, 18H, *t*Bu) 1.20 (s, 18H, *t*Bu)
[{Ru(p-MeC$_6$H$_4$CHMe$_2$)}$_4$(C$_{28}$H$_{22}$O$_4$)]-[BF$_4$]$_6$ (**15a**)	6.81, 6.77 (AB, 16H, ^3J 6.7) 3.02 (sp, 4H, ^3J 6.9) 2.47 (s, 12H) 1.39 (d, 24H, ^3J 6.9)	6.75 (d, 8H, ^3J 5.9) 6.27 (t, 4H, ^3J 5.9)	4.37, 3.50 (AB, 8H, ^2J 12.4)	
[{Ru(p-MeC$_6$H$_4$CHMe$_2$)}$_4$(C$_{28}$H$_{22}$O$_4$)]-[CF$_3$SO$_3$]$_6$ (**15b**)	6.81, 6.77 (AB, 16H, ^3J 6.7) 3.01 (sp, 4H, ^3J 6.9) 2.47 (s, 12H) 1.39 (d, 24H, ^3J 6.9)	6.82 (d, 8H, ^3J 5.9) 6.27 (t, 4H, ^3J 5.9)	4.37, 3.74 (AB, 8H, ^2J 11.6)	
[{Ru(p-MeC$_6$H$_4$CHMe$_2$)}$_4$(C$_{28}$H$_{22}$O$_4$)]-[SO$_4$][HSO$_4$]$_4$ (**15c**)^b	6.57, 6.52 (AB, 16H, ^3J 6.7) 2.80 (sp, 4H, ^3J 6.8) 2.34 (s, 12H) 1.25 (d, 24H, ^3J 6.8)	6.45 (d, 8H, ^3J 5.8) 6.08 (t, 4H, ^3J 5.8)	4.09, 3.01 (AB, 8H, ^2J 13.5)	
[{Ir(C$_5$Me$_5$)$_4$(C$_{28}$H$_{22}$O$_4$)][BF$_4$]$_6$ (**16a**)	2.29 (s, 60H)	7.10 (d, 8H, ^3J 6.0) 6.74 (t, 4H, ^3J 6.0)	4.04, 3.04 (AB, 8H, ^2J 12.0)	
[{Ir(C$_5$Me$_5$)$_4$(C$_{28}$H$_{22}$O$_4$)][CF$_3$SO$_3$]$_6$ (**16b**)	2.33 (s, 60H)	7.33 (d, 8H, ^3J 6.0) 6.78 (t, 4H, ^3J 6.0)	4.03, 3.31 (AB, 8H, ^2J 12.0)	
[{Ir(C$_5$Me$_5$)$_4$(C$_{28}$H$_{22}$O$_4$)][HSO$_4$]$_7$ (**16c**)^b	2.19 (s, 60H)	6.79 (d, 8H, ^3J 5.8) 6.47 (t, 4H, ^3J 5.8)	3.65, 2.72 (AB, 8H, ^2J 13.3)	

^{a} 200 or 250 MHz, NO$_2$CD$_3$, 20 °C, J_{H-H} (Hz), s = singlet, d = doublet, AB = AB pattern, sp = septet, m = multiplet. ^{b} Solvent D$_2$O.

is clear that the cavity is too sterically constricted for the inclusion of either DMF, BF$_4^-$, or a *tert*-butyl substituent.

Because of the complications encountered with the loss of calixarene protons in complexes **3**−**10** attempts were made to

(21) (a) Atwood, J. L.; Juneja, R. K.; Junk, P. C.; Robinson, K. D. *J. Chem. Crystallogr.* **1994**, *24*, 573. (b) Gallagher, J. F.; Ferguson, G.; Bohmer, V.; Kraft, D. *Acta Crystallogr., Sect. C* **1994**, *50*, 73.

metalate the analogous *p-tert*-butylcalix[4]arene methyl ether (**1c**)^{11} using both **2a,c**. Unfortunately in the case of **2a**, as a consequence of the conformational mobility of the calixarene, metalated products were isolated as a mixture of a number of isomers which could not be separated. Reaction of **2c** with the tetramethoxy-*p-tert*-butylcalix[4]arene (**1c**) proceeded somewhat more smoothly to give the bimetallic complex [{Ir(η^5-C$_5$Me$_5$)}$_2$-

Figure 1. X-ray crystal structure of the dirhodium *p-tert*-butylcalix-[4]arene complex **9a** showing the included molecule of diethyl ether (hydrogen atoms omitted for clarity).

$(\eta^6:\eta^6$-tetramethoxycalix[4]arene)][BF$_4$]$_4$ (**11**). The mass spectrum of **11** clearly demonstrates the incorporation of two metal centers with a molecular ion peak at m/z 1359 along with fragmentation peaks associated with the loss of 1−4 methyl substituents and one Cp*Ir moiety, as well as peaks corresponding to the cation in **11** in association with one tetrafluoroborate anion. The ^{1}H NMR spectrum of **11** suggested the presence of a number of different isomers of which one, exhibiting three signals in the low-field region in the ratio 1:1:2 (δ 7.78, 7.59, and 7.48 ppm), was the most prominent (*ca.* 70%). It is tentatively suggested that these signals might be assigned to a partial cone conformer with one nonmetalated ring inverted.

Similar problems involving the formation of isomeric mixtures of this type, were encountered by Shinkai *et al.* in the metalation of **1c** with Cr(CO)$_3$ moieties.[22] These workers have shown, however, that cleaner metalated products may be obtained by using conformationally immobile calixarenes. Consistent with these results, reaction of **2c** with the cone conformer of the propyl ether derivative **1e**[22,23] proceeded much more cleanly and, under similar conditions, gave rise to the bimetallic species [{Ir(η^5-C$_5$Me$_5$)}$_2$($\eta^6:\eta^6$-tetra-*n*-propoxycalix-[4]arene)][BF$_4$]$_4$ (**12**) in 84% yield. Similarly, reaction of **2a** with the analogous tetraethoxycalix[4]arene (**1d**) gave [{Ru-(η^6-*p*-MeC$_6$H$_4$CHMe$_2$)}$_2$($\eta^6:\eta^6$-tetraethoxycalix[4]arene)]-[BF$_4$]$_4$ (**13**) as a single isomer. The ^{1}H NMR spectra of **12** and **13** (Table 1) were consistent with metalation of opposite sides of the calixarene and the retention of the cone conformation as expected. In the case of **12**, the formulation was also confirmed by a FAB mass spectrum (m/z 1248 (M$^+$), 1334 (M$^+$ + BF$_4$)).

**Hosts Based on Calix[5]arene**. Reaction of *p-tert*-butylcalix-[5]arene (**1f**) with excess **2c** under similar conditions to those employed in the synthesis of **5a,b** was also attempted. The ^{1}H NMR spectrum of the resulting product (Table 1) exhibits two resonances in the ratio 2:1 assigned to the Cp* protons and three signals arising form the *tert*-butyl protons, strongly suggesting a trimetallic complex exhibiting either a 1, 2, 3 or 1, 3, 4 metalation pattern for the five calixarene aromatic rings. This interpretation is supported by the observation of ostensibly five signals in the low-field region of the spectrum arising from the calixarene ring protons, although the fact that these signals are slightly split to give a total of 10 lines as well as being somewhat broad, suggests that, even if the calixarene retains a cone conformation, there is not a plane of mirror symmetry in the

(22) (a) Iki, H.; Kikuchi, T.; Shinkai, S. *J. Chem. Soc., Perkin Trans. 1* **1992**, 669. (b) Iki, H.; Kikuchi, T.; Shinkai, S. *J. Chem. Soc., Perkin Trans. 1* **1993**, 205. (c) Kikuchi, T.; Iki, H.; Tsuzuki, H.; Shinkai, S. *Supramol. Chem.* **1993**, *1*, 103.
(23) Iwanoto, K.; Araki, K.; Shinkai, S. *J. Org. Chem.* **1991**, *56*, 4955.

molecule, perhaps because of conformational differences or the loss of one or more of the hydroxyl protons, as observed for complexes **3** and **5**. The FAB mass spectrum of this material clearly showed it to be a trimetallic species with a peak at m/z 1964 (M$^+$ + 2BF$_4$) as well as fragmentation peaks associated with the loss of one tetrafluoroborate anion and one Cp*Ir moiety. The formulation of this material was confirmed by a single-crystal X-ray structure determination (reported previously[12d]) which showed it to consist of [{Ir(η^5-C$_5$Me$_5$)}$_3$-(*p-tert*-butylcalix[5]arene-H)][BF$_4$]$_5$·0.5NO$_2$Me·*n*Et$_2$O (**14**) (*n*

14
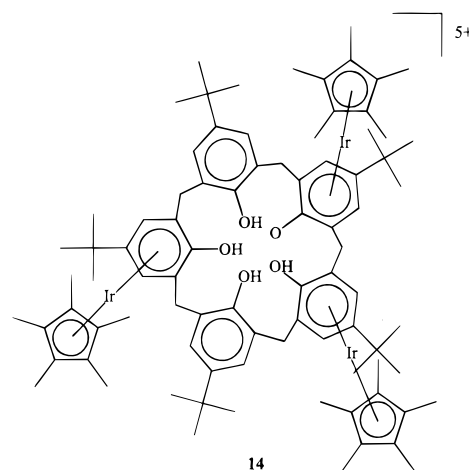
= *ca.* 2), Figure 3. Importantly, the incorporation of two metal centers on adjacent calixarene rings results in a dramatic change in the host−guest behavior of the system. One of the tetrafluoroborate anions found to be deeply included within the large calix[5]arene cavity, as opposed to diethyl ether in the cases of **9a,b**. The closest approach of the fluorine atoms of the included BF$_4^-$ anion to the calixarene is F(2A)···C(3C) (2.93(3) Å), significantly shorter than that observed for BF$_4^-$···Cp* or BF$_4^-$···arene distances for the anions outside the calixarene cavity (typically in excess of 3.10 Å[12a,15b]), suggesting a significant degree of cooperativity between the two metal centers. The loss of one of the phenolic protons to give a 5+ species is consistent with the high acidity observed for complexes **5** and related species.[18d]

Tetrametallic Hosts. Reaction of calix[4]arene (**1a**) with 2 equiv of the ruthenium chloro complex **2a** (after pretreatment with AgX in acetone) under relatively forcing conditions (24−48 h, refluxing CF$_3$CO$_2$H) results in the clean formation of the tetrametallic hosts [{Ru(η^6-*p*-cymene)}$_4$(calix[4]arene-2H)]X$_6$ (X = BF$_4^-$, **15a**; CF$_3$SO$_3^-$, **15b**; 4HSO$_4^-$ + SO$_4^{2-}$, **15c**; PF$_6^-$, **15d**). The analogous reactions with the more sterically crowded

15
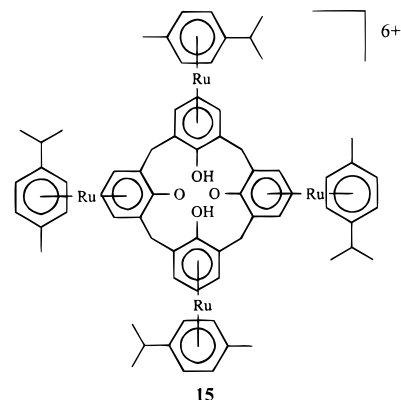
1b did not form tetrametallic products, possibly due to kinetic effects arising from the restricted approach of the solvated metal−arene fragment to the dimetalated precursor. Complexes
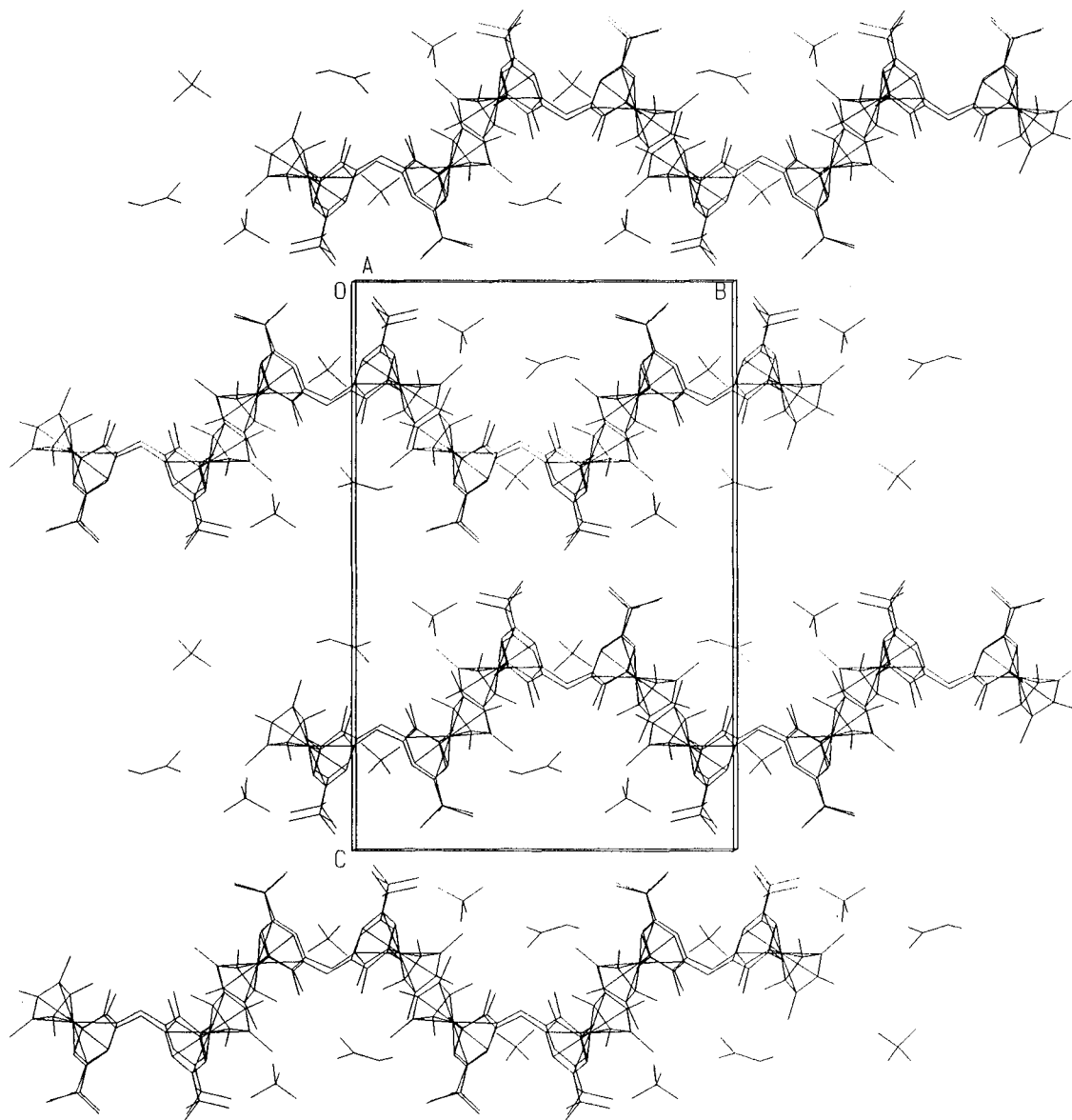
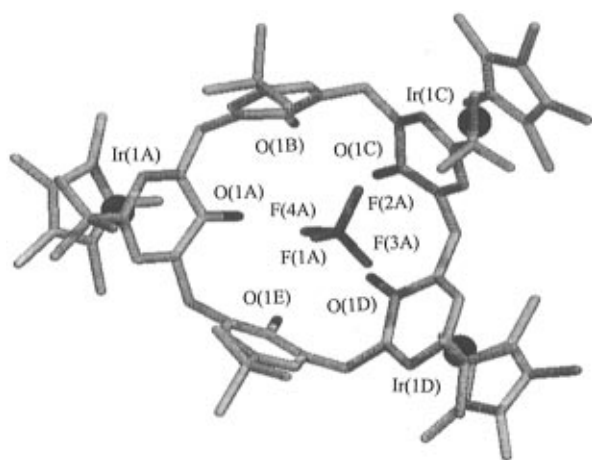**Figure 2.** Crystal packing in complex **10**.

Figure 3. X-ray crystal structure of the trimetallic *p-tert*-butylcalix-[5]arene complex **14** showing the included tetrafluoroborate anion (hydrogen atoms omitted for clarity).[12d]

15 were characterized on the basis of their ^{1}H NMR spectra (Table 1) which exhibited the expected highly symmetrical pattern indicating that all four calixarene rings are equivalent on the NMR time scale. The organometallic hosts may readily be distinguished from free **1a** by the upfield chemical shift of

the calixarene ring protons [*e.g.*, **15b** δ 6.82 (d), 6.27 (t), *cf.* **1a** 7.22 (d), 6.78(t) in the same solvent] and the low value of $^3J_{\text{H-H}}$ of only 5.9 Hz, compared to around 7.0 Hz observed for all nonmetalated rings in derivatives of **1a** (Table 1). The $\{^1\text{H}\}-$ ^{13}C NMR spectrum of **15b** is also consistent with the proposed formulation with the expected total of 12 signals[24] including a low-field resonance (δ 144.3 ppm) assigned to the carbon atom attached to the phenolic oxygen atom, consistent with an oxocyclohexadienyl description for the coordinated calixarene rings. The enhanced acidity[18d] of the tetrametalated species results in the spontaneous loss of two phenolic protons to yield a 6+ species, even in the presence of CF_3CO_2H. Interestingly, complexes of type **15** were only formed in the presence of noncoordinating anions such as BF_4^-, $CF_3SO_3^-$, *etc.* Compound **2a** was treated with a wide range of silver salts, but in the case of more coordinating anions (Cl$^-$, $CF_3CO_2^-$, $CH_3CO_2^-$, $H_2PO_4^-$, WO_4^{2-}), only bimetallic species of type **4** were obtained as the sole products. This behavior might be explained by consideration of the leaving ability of the various anions from the metal center. The initial metalation steps may require less anion dissociation from the organometallic precursor than the third and fourth stages on the basis of steric considerations. There

(24) ^{13}C NMR spectrum of **15b** (δ/ppm, 298 K, 63.3 MHz): δ 144.3, 121.7, 111.7, 102.0, 95.9, 95.0, 91.5, 88.0, 33.1, 29.4, 22.9, 18.1.
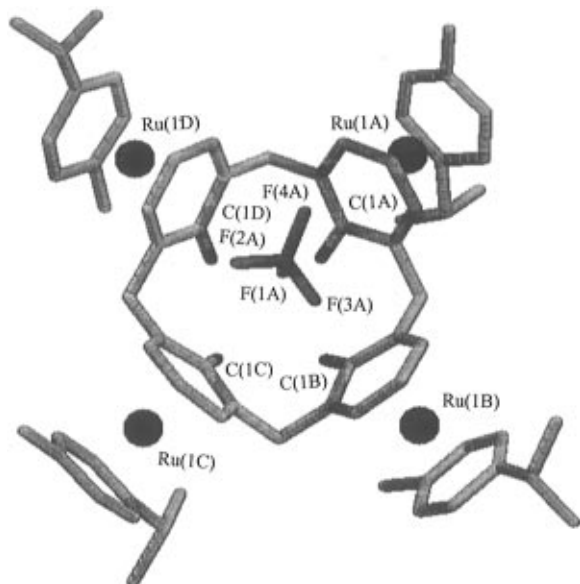
Figure 4. X-ray crystal structure of the tetrametallic complex **15a** showing the included BF_4^- anion. Shortest anion−host contacts F(1A)···C(1A), C(1D), C(1B), and C(1C) are 2.85, 2.87, 3.06, and 3.11 Å, respectively.

Figure 5. X-ray crystal structure of the tetrametallic complex **15d** showing the included I^- anion. Anion−calixarene ring centroid contacts I(1)···Cn(D), Cn(A), Cn(C), and Cn(B) are 3.60, 3.72, 3.73, and 3.78 Å, respectively.

is certainly ample evidence for the coordination of carboxylate and halide anions to (arene)ruthenium(II) species,[25] while BF_4^-, $CF_3SO_3^-$, and even SO_4^{2-} are generally found to be noncoordinating or only weakly coordinating.[18,26] This hypothesis may also explain our inability to form tetrametallic complexes based upon the more sterically hindered *p-tert*-butylcalix[4]arene (**1b**). These observations contrast to significant difficulties encountered in isolating the bimetallic species **4a** itself because of its marked tendency to form **15a** and free **1a**, possibly as a consequence of the low solubility of **1a**.

The nature of the host−anion interactions in complexes of type **15** were investigated by an X-ray crystal structure determination upon the tetrafluoroborate salt **15a** (Figure 4).[12a,b] This structure convincingly demonstrates the excellent size complimentarity of the small calix[4]arene cavity for the small, tetrahedral BF_4^- anion, one of which is deeply included within the calixarene bowl. The shortest anion−host contacts are from the most deeply included fluorine atom, F(1A), to the lower-rim carbon atoms C(1A), C(1D), C(1B), and C(1C) at 2.85(2), 2.87(2), 3.06(2), and 3.11(2) Å, respectively, showing the anion to be slightly inclined toward rings A and D. This may be contrasted to distances of upwards of 2.95(3) Å in **14** and related complexes of CTV which possesses a much shallower bowl.[15] For comparison, the shortest anion−C contacts for anions external to the calixarene cavity are in excess of 3.10 Å. The strength of the anion binding in **15a** is also highlighted by the relatively small crystallographic thermal parameters for the included anion, demonstrating the high degree of size complimentarity between anion and cavity. The distance of F(1A) from the plane containing the four calixarene oxygen atoms is 2.70 Å, as opposed to *ca.* 4 Å for van der Waals inclusion species such as *p-tert*-butylcalix[4]arene·toluene[14] or even the methyl sulfate anion in $[NH_4]_6[p$-sulfonatocalix[4]arene][MeOSO_3]·2H_2O.[27] This extremely deep anion penetration highlights the cooperative
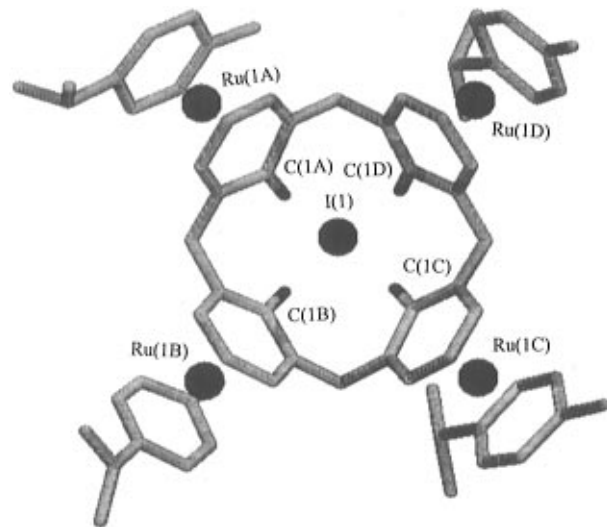
effect arising from the presence of four metal centers and suggests tight anion binding as well as offering a basis for size- and shape-selective discrimination between anionic guests.

The presence of four metal centers has the effect of restoring the pseudo-4-fold symmetry of the calixarene with intercentroid separations of 6.52(1) Å for both rings A···C and B···D. This may be compared to the 0.16(1) and 0.30(1) Å differences in these two distances observed for **5a** and **10**, respectively. Also, as for complexes **5a** and **10**, there is a significant amount of evidence to support a partial oxocyclohexadienyl description for the deprotonated calixarene ligands, with short C(1)−O(1) distances [1.29(1) Å (av)] and a significant out of plane deviation for C(1) and O(1) of all four calixarene rings.

Addition of a small excess of [NBu_4]I to a nitromethane solution of **15a** results in the isolation of the iodide salt [{Ru-(η^6-*p*-cymene)}_4(calix[4]arene-2H)]I_6·2H_2O·2NO_2Me (**15d**). Surprisingly, this metathesis is accompanied by a marked color change from pale yellow to orange, possibly as a result of second sphere charge transfer effects. Similar metathesis reactions gave the analogous perrhenate salt [{Ru(η^6-*p*-cymene)}_4(calix[4]-arene-2H)][ReO_4]_6 (**15e**) and the dihydrogen phosphate salt [{Ru(η^6-*p*-cymene)}_4(calix[4]arene-2H)][H_2PO_4]_6·6H_2O (**15f**). The X-ray crystal structure of the iodide complex **15d** was determined (Figure 5). The structure clearly establishes the replacement of all six BF_4^- anions with I^-, with one iodide anion deeply included within the calixarene cavity at a distance of 4.00(1) Å from the plane of the phenolic oxygen atoms. This may be compared to a distance of 4.11(2) Å for the boron atom in **15a** but clearly represents a significantly shallower penetration than F(1A) in **15a** (2.70 Å), as expected from the large ionic radius of the iodide anion. The included anion is situated centrally in the calixarene cavity with I···centroid distances ranging from 3.60−3.78 Å, while the shortest I···C_calix contact is I(1)···C4(B) (3.76(2) Å). As for **15a**, the included anion also displays significantly smaller thermal parameters than the remaining counterions, suggesting a tight fit within the calixarene cavity. The iodide ion I(1) also forms a hydrogen bonding interaction to one of the water molecules outside the calixarene cavity, I(1)···O_w(1) (3.49(3) Å). As for **15a**, the hydrogen bonding network at the calixarene lower rim is consistent with the loss of two of the phenolic protons with two short hydrogen bonded contacts and two longer non-bonded distances: O(1A)···O(1B) and O(1D) of 2.40(3) and 2.90(3) Å; O(1C)···O(1B) and O(1D) of 2.80(3) and 2.44(3) Å.

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(27) Bott, S. G.; Coleman, A. W.; Atwood, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 610.

Anion Binding within π-Metalated Calixarene Cavity

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Reaction of **1a** with **2c** after pretreatment with Ag_2SO_4 results in the formation of the mixed sulfate/hydrogen sulfate salt **15c**. The composition of **15c** is an interesting one in that it consists of a mixture of one SO_4^{2-} and four HSO_4^- anions as determined by analytical data (see Experimental Section). Attempts were made to crystallographically characterize this material. Extremely small, pale yellow crystals were obtained by diffusion of acetone into an aqueous solution of this compound, and some limited data were obtained using a CCD diffractometer system. The structure determination is not of high precision as a consequence of the paucity of observed data and significant crystal disorder and is not reported in detail, but is sufficient to confirm the composition of the material. As anticipated from the results obtained for **15a,d**, the cavity of the host in **15c** is occupied by a sulfate anion, included in a similar way to the tetrahedral BF_4^- in **15a**. The host cation and guest anion are situated upon a crystallographic mirror plane (space group *Pnnm*), resulting in serious disorder problems of all the anions as well as a significant quantity of solvent water. This crystallographic symmetry results in only one unique anion (that inside the cavity) and two symmetry related pairs, suggesting that it is the SO_4^{2-} ion that occupies the cavity while the HSO_4^- counterions are external to the tetrametallic host.

Reaction of the iridium complex **2d** with **1a** in a similar way to the ruthenium analogues also resulted in the isolation of a tetrametallic host $[\{Ir(\eta^5\text{-}C_5Me_5)\}_4(\eta^6{:}\eta^6{:}\eta^6{:}\eta^6\text{-calix[4]arene-}nH)]X_{8-n}$ ($n = 2$, X = BF$_4$, **16a**; X = CF$_3$SO$_3$, **16b**; $n = 1$, X = HSO$_4$, **16c**). Complexes **16a,c** were both characterized by

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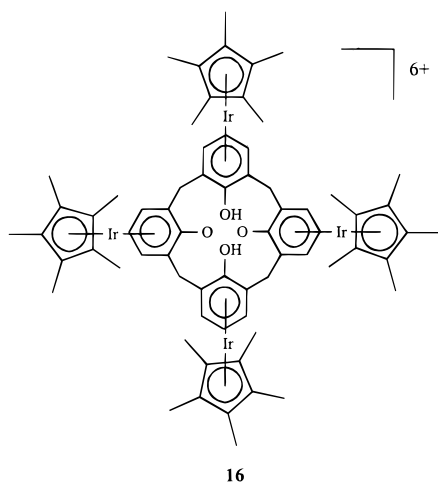
X-ray crystallography. In the case of the BF_4^- salt **16a**, the BF_4^- anion penetrates the host cavity in the same way as **15a** with close $F(1A)\cdots C(1C,B,A,D)$ contacts of 2.91(3)−2.99(3) Å, although the paucity in observed data did not result in a smooth refinement. At the calixarene lower rim, the hydrogen bonding pattern confirms the loss of two phenolic protons to give an overall charge of 6+, with two short $O\cdots O$ contacts of 2.57(3) Å (av) and two longer ones of 2.69(3) Å (av), consistent with the results observed for **10** and complexes **15**.

The hydrogen sulfate salt **16c** was crystallized under relatively acidic conditions by diffusion of acetone into an aqueous solution of the complex, resulting in the isolation of a hepta-cationic species. One of the HSO_4^- anions is deeply included within the calixarene cavity with four symmetry-equivalent $O(1A)\cdots C$ contacts of 2.96(3) Å (Figure 6). Unfortunately the high symmetry of the crystal system results in a 3-fold rotational disorder of the included anion about the $S{-}O(1A)$ axis, as well as other associated problems. The location of a total of seven anions confirms the charge on the complex, which exhibits the usual deformations associated with the metalated calixarene rings.
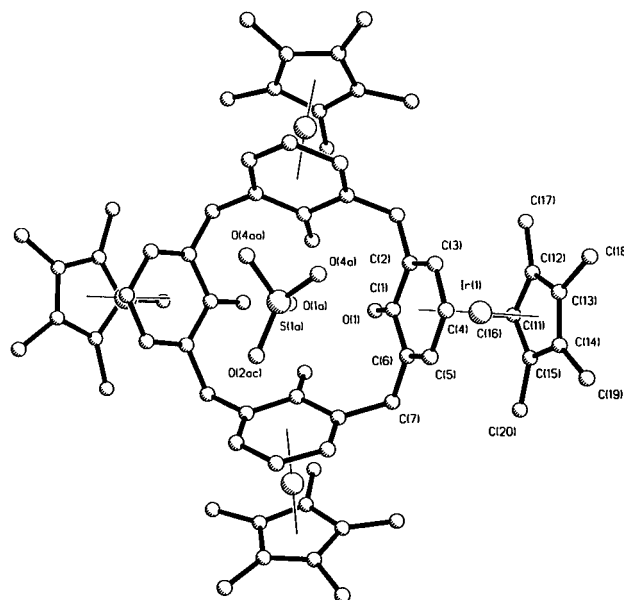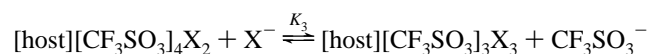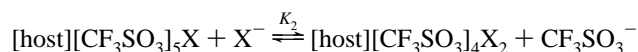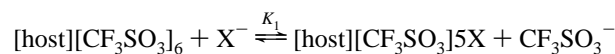

Figure 6. X-ray crystal structure of the tetrairidium complex **17c** showing the included HSO_4^- anion. Closest anion−calixarene contact $O(1A)\cdots C(1)$ is 2.96 Å.
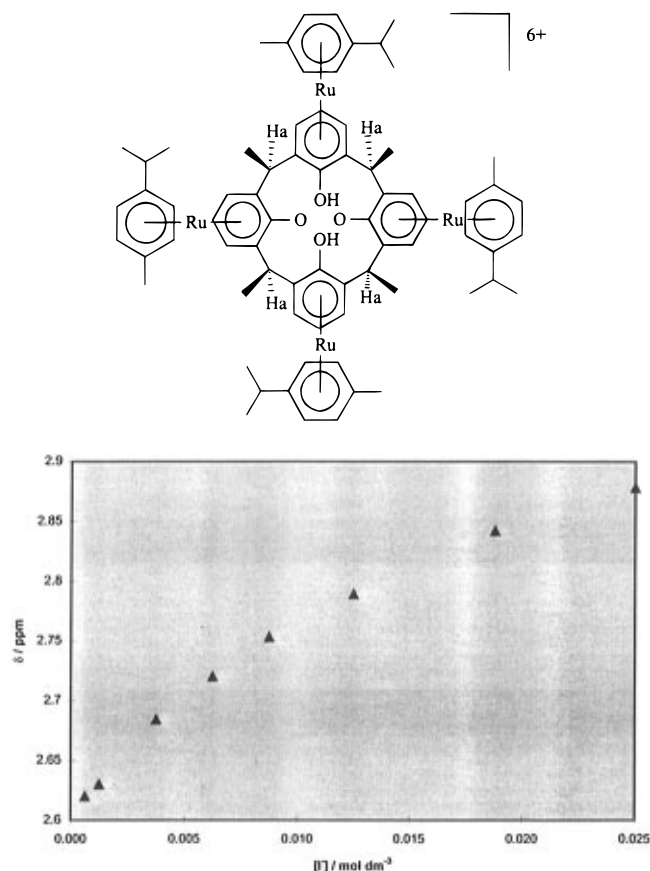
Solution Studies

Given the convincing evidence for solid state anion binding by complexes of type **15** and **16**, a series of ^{1}H NMR titration studies were carried out to assess the degree of anion affinity in solution. Because of the environmental interest in new anion hosts,[2] water was chosen as a solvent even though this strongly solvating medium is expected to compete significantly with the host.

The ^{1}H NMR spectra of solutions of the tetrametallic trifluoromethane sulfonate complex **15b** were monitored as a function of increasing concentrations of the sodium salt of various anions. As a control, $NaCF_3SO_3$ was used to assess the effects of ionic strength on the chemical shifts of the resonances. No change was noted in the range 0.025−1.75 M, indicating the spectrum to be independent of ionic strength. Addition of NaI, however, resulted in significant changes, which were most pronounced for the doublet H_a assigned to the methylene protons of the calixarene (Figure 7). Data were obtained up to an anion:host mole ratio of 20:1 at which point precipitation occurred. Analysis of the resulting titration curve using the EQNMR software[28] gave a binding constant, K_1, of 51 M^{-1}. Analogous titrations were carried out with NaBr and NaCl. No precipitation occurred with these anions and titrations were continued to large anion concentrations (up to 1000:1 anion:host ratio). In both cases, an initially rapid change in the chemical shift of H_a was noted, followed by a plateau and a subsequent slower chemical shift increase, suggesting the operation of several binding processes. Chemical shifts changes of up to 0.76 ppm were observed with the maximum chemical shift of 3.41 ppm for Br^- (compared to 2.65 ppm in the free host). The titration curves for Cl^- and Br^- were modeled in terms of three equilibria, shown below (X = Cl, Br, NO$_3$):

$$[\text{host}][CF_3SO_3]_6 + X^- \overset{K_1}{\rightleftharpoons} [\text{host}][CF_3SO_3]5X + CF_3SO_3^-$$

$$[\text{host}][CF_3SO_3]_5X + X^- \overset{K_2}{\rightleftharpoons} [\text{host}][CF_3SO_3]_4X_2 + CF_3SO_3^-$$

$$[\text{host}][CF_3SO_3]_4X_2 + X^- \overset{K_3}{\rightleftharpoons} [\text{host}][CF_3SO_3]_3X_3 + CF_3SO_3^-$$

(28) Hynes, M. J. *J. Chem. Soc., Dalton Trans.* **1993**, 311.

Figure 7. Effect of adding I⁻ on the chemical shift of doublet assigned to H_a at 1.25×10^{-3} M **15b**.

EQNMR analysis in terms of these equilibria, along with data for NaNO₃ yielded the binding constants shown in Table 3. In contrast, virtually no changes in the ¹H NMR spectrum of **15b** were noted upon titration with Na₂SO₄, NaH₂PO₄, or NaCH₃-CO₂.

While **15b** does not display a great deal of selectivity between the anions, it is noteworthy that there is a significant decreasing trend in K_1 as ionic radius increases going from Cl⁻ to Br⁻ to I⁻, strongly suggesting that the binding of the first anion occurs within the calixarene cavity and that the degree of binding is influenced by the fit of the anion to the cavity. This is especially striking since the anion hydration energy *decreases* in the order Cl⁻, Br⁻, I⁻.[29] This result is consistent with the X-ray crystal structure of the iodide complex **15d** which shows that the I⁻ anion is somewhat too large to fit inside the cavity effectively. The notion of K_1 representing intracavity binding is also supported by the much lower values of K_2 and K_3 (which represent binding of an anion between pairs of metal centers external to the cavity) and, by implication, equilibrium constants for binding a fourth anion and so on. The results suggest that halides can only compete effectively with CF₃SO₃⁻ (present as host counterion) in cases where there is restricted access to the binding site where their smaller size enables them to fit the cavity better. The very much larger K_2 value obtained in the case of nitrate is interesting and may represent that fact that the planar geometry of the nitrate anion enables it to insert effectively between two metal centers on the outside of the cavity, while it is unable to penetrate very deeply within the calixarene bowl.

The lack of binding of SO₄²⁻ and H₂PO₄⁻ is unsurprising given the relatively high hydration energies of these anions, suggesting that the host is simply unable to compete with the solvent in D₂O solution, even though sulfate complexes have

been isolated in the solid state for both hosts **15** and **16**. The lack of any change in the chemical shift of H_a for acetate is more difficult to explain, although it may arise from the higher pK_a of acetic acid, resulting in partial protonation of the acetate, or a lower charge density. Some chemical shift changes were noted for the acetate methyl group from 2.10 ppm at 1:1 acetate:host ratio to 1.91 ppm at 10:1 and above, perhaps indicating a different, hydrophobic type of binding.

Interestingly, for both **15a,b**, in nitromethane-d_3 solution, the signal for H_a in particular is shifted relative to its position in D₂O, occurring at 3.71 ppm (Table 1), suggesting increased anion binding in organic media where anion solvation energies are lower. Similar chemical shifts are noted in acetone-d_6 and acetic acid-d_4.

Binding constants of between 100 and 10 000 M⁻¹ have been obtained by Beer *et al.* for anions such as Cl⁻ and H₂PO₄⁻ with a large variety of organometallic receptors containing the amide functionality.[1f] Importantly, however, all of these measurement have been carried out in less polar solvents such as acetone, acetonitrile, and dimethyl sulfoxide, in which there will be significantly reduced anion−solvent interactions compared to the present work in which water is used as a solvent. For comparison, the binding constant of 18-crown-6 for K⁺ in aqueous solution is *ca.* 100 M⁻¹.[30] Also, anions binding to the cation in **15b** must compete with 6 mol equiv of CF₃SO₃⁻/mol of host. To assess the effects of trifluoromethane sulfonate competition with the binding, an NMR titration was carried out with a varying mixture of CF₃SO₃⁻ and Br⁻ such as to give a constant ionic strength. In this case, bromide binding was significantly suppressed in regions of high trifluoromethane sulfonate concentration, highlighting the competition between the two anions.

To assess the effects of solvent, iodide binding (as the NBu₄⁺ salt) by **15b** was also examined in acetic acid-d_4. Unfortunately, precipitation occurred at iodide:host ratios of greater than 2:1 even at 1.25×10^{-3} M host concentration; however, even at this small host:guest ratio, a change of 0.52 ppm in the chemical shift of H_a had been observed. Calculations on this limited data indicate a value for K_1 of *ca.* 1500 M⁻¹ though a precise figure could not be obtained due to lack of data. Clearly, however, binding is significantly enhanced in less strongly solvating media.

Interestingly, a large dependence of the chemical shift of H_a on host concentration in aqueous solution was also noted. Since addition of excess NaCF₃SO₃ has no effect on the NMR spectrum, this concentration dependence was modeled in terms of the association of two host cations of type **15** to give a dimer in solution. EQNMR analysis gave the equilibrium constant for this process, $K_{self} = 42$ M⁻¹. The precise nature of this association is unclear, though the lack of any change in any resonances other than H_a might rule out mechanisms such as hydrophobic inclusion of one isopropyl group in the cavity of a second host. Whatever the nature of this self association, it may also have an inhibitory effect on the degree anion binding.

Conclusion

The ability to bind anions in a size- and shape-selective fashion is of extreme importance in the detection and removal of unwanted environmental contaminants and is also of interest in the development of synthetic enzyme mimics. This study has conclusively demonstrated that the host−guest properties of the calixarenes may be significantly modified in such a way as to include anionic guest species, by capping of the calixarene faces with transition metal centers. The results obtained herein

(29) Goldman, S.; Bates, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 1476.

(30) de Jong, F.; Reinhoudt, D. N. *Stability and Reactivity of Crown Ether Complexes*; Academic Press: London, 1981.

Table 2. Crystal Data for New Compounds[a]

	9a	10	15d	16a	16c
formula	$C_{68.7}H_{94}B_3F_{12}N_{0.7}O_{6.3}Rh_2$	$C_{67}H_{91}O_5B_2F_8Ir_2N$	$C_{70}H_{88}O_{10}I_6N_2Ru_4$	$C_{72.5}H_{82}B_6F_{24}Ir_4O_4$	$C_{68}H_{124}Ir_4O_{49}S_7$
fw (g mol^{-1})	1496.37	1548.43	2283.18	2307.04	2710.88
space group	$P2_1/a$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	P4/n
a (Å)	19.667(9)	14.808(3)	14.512(2)	14.316(8)	21.913(4)
b (Å)	14.245(1)	18.979(3)	15.531(4)	21.220(2)	21.913(4)
c (Å)	27.676(12)	29.325(3)	19.893(5)	31.636(5)	9.6687(14)
α (deg)	90	90	68.39(2)	90	90
β (deg)	108.71(2)	103.79(1)	84.84(2)	102.95(1)	90
γ (deg)	90	90	67.97(2)	90	90
U (Å^3)	7344(5)	8004(2)	3858(1)	9366(6)	4643(1)
Z	4	4	2	4	2
D_c (g cm^{-3})	1.35	1.29	1.97	1.64	1.94
μ (Mo Kα, cm^{-1})	5.28	3.38	31.87	57.52	131.53[f]
$F(000)$	3097	3104	2018	4412	2680
crystal size (mm)	0.4 × 0.2 × 0.1	0.6 × 0.4 × 0.2	0.4 × 0.3 × 0.1	0.3 × 0.2 × 0.05	0.2 × 0.1 × 0.06
max 2θ (deg)	50	50	46	40	120[f]
no. of reflns coll	11831	15101	11189	8707	3613
no. of independent reflns	11473	14058	8558	5780	3411
obsd reflns $I > 2\sigma(I)$	6254	9493	5534[c]	2803	1846
crystal decay			−23% corr.		
refinement method[b]	F^2	F^2	F	F^2	F^2
parameters	873	763	777	420	319
R, R_w, or wR_2 (obsd data)	0.068, 0.181	0.072, 0.198	0.088, 0.119	0.090, 0.223	0.080, 0.201
R, wR_2 (all data)[d]	0.138, 0.205	0.119, 0.239		0.315, 0.287	0.142, 0.238
largest residual peak (e Å^{-3})	1.45[e]	3.1[e]	1.7[e]	1.3[e]	2.6[e]

[a] Mo Kα radiation, λ = 0.710 69 Å; temperature 20 °C. [b] Full-matrix least squares on either F or F^2. [c] $I > 3\sigma(I)$. [d] Structures refined using SHELXL-93.[32] [e] Close to one of the metal atoms. [f] Cu Kα radiation, λ = 1.5406 Å.

Table 3. Binding Constants[a] (M^{-1}) in Aqueous Solution for Host **15b** with Various Anions Analyzed by EQNMR[28]

anion	K_1	K_2	K_3
Cl$^-$	551	8.1	0.05
Br$^-$	133	13.6	0.35
I$^-$	51		
NO$_3^-$	49	109	0.06
CH$_3$CO$_2^-$	0		
H$_2$PO$_4^-$	0		
SO$_4^{2-}$	0		

[a] Errors generally *ca.* 10%.

may be generalized into three criteria for anion selective organometallic anion-binding hosts:

(i) Two or more metal centers must be situated upon adjacent macrocycle aromatic residues.

(ii) The host cavity must be sufficiently free of steric hindrance at the upper rim to incorporate the anion.

(iii) Tight binding occurs when there is a close complimentarity between anion and cavity size allowing the anion to interact equally with all metal centers.

The effect played by anion solvation, especially in highly polar solvents such as water, is also a highly important factor.

Experimental Section

Instruments. NMR spectra were recorded either on a Bruker ARX-250 spectrometer operating at 250.1 MHz (^{1}H) and 63.3 MHz (^{13}C) or a Nicolet NT-200 instrument (200 MHz, ^{1}H). Infrared spectra were recorded as Nujol mulls on NaCl plates using a PE710B spectrophotometer, while mass spectra were run in fast atom bombardment mode in *m*-nitrobenzyl alcohol matrix. Microanalyses were performed by Atlantic Microlabs, Norcross, GA. In many cases, attempts to obtain meaningful analytical data were complicated by the presence of varying amounts of solvent molecules strongly retained by these compounds even after drying *in vacuo* and calculated analytical data are corrected for this where indicated. All manipulations except for the synthesis of starting materials were carried out in air and the products showed no oxygen sensitivity or chemical instability toward moisture, although many new complexes lost enclathrated solvent molecules when exposed to the atmosphere.

Materials. The chloro complexes [{Ru(η^6-*p*-MeC$_6$H$_4$CHMe$_2$)Cl-(μ-Cl)}$_2$][16] and [{Ir(Cp*)Cl(μ-Cl)}$_2$][17] and calix[*n*]arenes were prepared

according to published literature procedures.[22,23,31,32] Ruthenium and iridium trichloride hydrates were obtained from Johnson Matthey plc, and RuCl$_3$·xH$_2$O (x = *ca.* 2) was purified before use by repeated dissolution in water and boiling to dryness. All other reagents and materials were obtained from the usual commercial sources.

Preparations. [{Rh(η^5-C$_5$Me$_5$)}$_2$(η^6:η^6-C$_{28}$H$_{24}$O$_4$)][BF$_4$]$_4$ (3). The compound [{Rh(η^5-C$_5$Me$_5$)Cl(μ-Cl)}$_2$] (**2b**) (0.14 g, 0.23 mmol) was treated with Ag[BF$_4$] (0.19 g, 0.98 mmol) in acetone (10 cm^3) and the mixture stirred for 15 min. The precipitated AgCl was removed by filtration through Celite and the filtrate evaporated to an orange oil. To this oil was added calix[4]arene (**1a**) (0.05 g, 0.12 mmol), and the mixture was refluxed in CF$_3$CO$_2$H (10 cm^3) for 5 h to give a yellow solution. When cool the mixture was filtered and evaporated to *ca.* 1 cm^3. Gradual addition of diethyl ether to the solution gave the product as a bright yellow precipitate which was washed with acetone/diethyl ether mixture (1:4) and dried. Yield: 0.12 g, 0.10 mmol, 83%. Anal. Calcd for C$_{48}$H$_{54}$O$_4$B$_4$F$_{16}$Rh$_2$·2C$_4$H$_{10}$O·4CF$_3$CO$_2$H: C, 49.26; H, 5.04. Found: C, 49.45; H, 5.15%.

[{Ru(*p*-MeC$_6$H$_4$CHMe$_2$)}$_2$(C$_{28}$H$_{23}$O$_4$)][H{CF$_3$CO$_2$}$_2$]$_3$ (4b). The complex [{Ru(η^6-*p*-MeC$_6$H$_4$CHMe$_2$)Cl(μ-Cl)}$_2$] (**2a**) (0.12 g, 0.20 mmol) was refluxed with calix[4]arene (**1a**) (0.04 g, 0.094 mmol) in CF$_3$CO$_2$H (10 cm^3) for 12 h. When cool the resulting solution was filtered and diluted with diethyl ether (30 cm^3), resulting in the precipitation of the product as a pale yellow, hygroscopic solid which was isolated by filtration, washed with a further aliquot of diethyl ether, and dried. Yield: 0.10 g, 0.063 mmol, 67%. Anal. Calcd for C$_{60}$H$_{55}$O$_{16}$F$_{18}$Ru$_2$: C, 45.72; H, 3.52. Found: C, 46.10; H, 3.65%.

[{Rh(η^5-C$_5$Me$_5$)}$_2$(η^6:η^6-C$_{44}$H$_{56}$O$_4$)][BF$_4$]$_4$ (5a). The compound [{Rh(η^5-C$_5$Me$_5$)Cl(μ-Cl)}$_2$] (**2b**) (0.12 g, 0.19 mmol) was treated with Ag[BF$_4$] (0.16 g, 0.82 mmol) in acetone (10 cm^3), followed by refluxing with *p-tert*-butylcalix[4]arene (**1b**) (0.12 g, 0.18 mmol) in CF$_3$CO$_2$H (10 cm^3) for 12 h as for **3**, to give a yellow-brown solution. When cool the mixture was filtered and evaporated to *ca.* 1 cm^3. Gradual addition of diethyl ether to the solution gave the product as a bright yellow precipitate which was washed with diethyl ether and dried. Yield: 0.18 g, 0.12 mmol, 67%. Anal. Calcd for C$_{64}$H$_{86}$O$_4$B$_4$F$_{16}$Rh$_2$·2CF$_3$CO$_2$H: C, 49.95; H, 5.50. Found: C, 50.55; H, 5.65%.

[{Ir(η^5-C$_5$Me$_5$)}$_2$(η^6:η^6-C$_{44}$H$_{56}$O$_4$)][BF$_4$]$_4$ (5b). The compound [{Ir(η^5-C$_5$Me$_5$)Cl(μ-Cl)}$_2$] (**2c**) (0.22 g, 0.34 mmol) was treated with Ag[BF$_4$] (0.22 g, 1.13 mmol) in acetone (10 cm^3), followed by refluxing with *p-tert*-butylcalix[4]arene (**1b**) (0.08 g, 0.12 mmol) in CF$_3$CO$_2$H

(31) Gutsche, C. D.; Levine, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 2652.
(32) Stewart, D. R.; Gutsche, C. D. *Org. Prep. Proceed. Intl.* **1993**, *25*, 137.

(10 cm^3) for 6 h as for **3**, to give a pale yellow solution. When cool the mixture was filtered and evaporated to *ca.* 1 cm^3. Gradual addition of diethyl ether to the solution gave the product as a bright yellow precipitate which was washed with diethyl ether and dried. Yield: 0.14 g, 0.085 mmol, 71%. Anal. Calcd for C$_{64}$H$_{86}$O$_4$B$_4$F$_{16}$Ir$_2$·CF$_3$CO$_2$H: C, 44.90; H, 4.95. Found: C, 45.45; H, 5.20%.

[{Rh(η^5-C$_5$Me$_5$)}$_2$(η^6:η^6-C$_{28}$H$_{22}$O$_4$)][BF$_4$]$_2$ (7). Complex **3** (0.04 g, 0.032 mmol) was treated with Na$_2$CO$_3$ (0.2 g, excess) in acetone suspension for 2 h resulting in a yellow suspension. Water (5 cm^3) and CH$_2$Cl$_2$ (5 cm^3) were added, and the mixture was filtered to give the product as an orange solid. Yield: 0.03 g, 0.028 mmol, 88%. Anal. Calcd for C$_{48}$H$_{52}$O$_4$B$_2$F$_8$Rh$_2$·2H$_2$O: C, 52.00; H, 5.10. Found: C, 52.20; H, 4.95%.

[{Rh(η^5-C$_5$Me$_5$)}$_2$(η^6:η^6-C$_{28}$H$_{23}$O$_4$)][BF$_4$]$_3$ (8a). The compound [{Rh(η^5-C$_5$Me$_5$)Cl(μ-Cl)}$_2$] (**2b**) (0.12 g, 0.19 mmol) was treated with Ag[BF$_4$] (0.15 g, 0.77 mmol) in acetone (10 cm^3) and the mixture stirred for 15 min. The precipitated AgCl was removed by filtration through Celite. Calixarene **1a** (0.15 g, 0.35 mmol) and CF$_3$CO$_2$H (1 cm^3) were added, and the mixture was refluxed for 2 h, resulting in the precipitation of the product as a bright yellow powder which was isolated by filtration, washed with diethyl ether, and dried. Yield: 0.08 g, 0.069 mmol, 36%. Anal. Calcd for C$_{48}$H$_{53}$O$_4$B$_3$F$_{12}$Rh$_2$·4C$_3$H$_6$O: C, 51.75; H, 5.55. Found: C, 52.18; H, 5.05%.

[{Ir(η^5-C$_5$Me$_5$)}$_2$(η^6:η^6-C$_{28}$H$_{23}$O$_4$)][BF$_4$]$_3$ (8b). The compound [{Ir(η^5-C$_5$Me$_5$)Cl(μ-Cl)}$_2$] (**2c**) (0.12 g, 0.15 mmol) was treated with Ag[BF$_4$] (0.13 g, 0.67 mmol) in acetone (10 cm^3) and the mixture stirred for 15 min. The precipitated AgCl was removed by filtration through Celite. Calixarene **1a** (0.07 g, 0.16 mmol) and CF$_3$CO$_2$H (1 cm^3) were added, and the mixture was refluxed for 2 h, resulting in the precipitation of the product as a white powder which was isolated by filtration, washed with diethyl ether, and dried. Yield: 0.12 g, 0.084 mmol, 56%. Anal. Calcd for C$_{48}$H$_{53}$O$_4$B$_3$F$_{12}$Ir$_2$: C, 43.05; H, 4.05. Found: C, 43.20; H, 4.10%.

[{M(η^5-C$_5$Me$_5$)}$_2$(η^6:η^6-C$_{44}$H$_{55}$O$_4$)][BF$_4$]$_3$·nNO$_2$CH$_3$· Et$_2$O (M = Rh, 9a; Ir, 9b). Recrystallization of complexes **5a** (0.05 g, 0.034 mmol) and **5b** (0.05 g, 0.030 mmol) by diffusion of diethyl ether vapor into a nitromethane (1 cm^3) solution of the complexes gave the deprotonation products **9a,b** which were analyzed by ^{1}H NMR spectroscopy (Table 1) and X-ray crystallography (Table 2).

[{Ir(η^5-C$_5$Me$_5$)}$_2$(η^6:η^6-C$_{44}$H$_{54}$O$_4$)][BF$_4$]$_2$·DMF (10). A solution of complex **5b** (0.05 g, 0.030 mmol) in DMF (5 cm^3) was allowed to stand in air for a period of *ca.* 2 weeks, resulting in the deposition of large colorless prisms of the inclusion complex **10** which were analyzed by ^{1}H NMR spectroscopy (Table 1) and X-ray crystallography (Table 2). Removal of DMF was effected by heating at 80 °C *in vacuo* for 6 h to give the guest-free product. Anal. Calcd for C$_{64}$H$_{84}$O$_4$B$_2$F$_8$Ir$_2$: C, 52.10; H, 5.75. Found: C, 51.90; H, 5.70%.

[{Ir(η^5-C$_5$Me$_5$)}$_2$(η^6:η^6-C$_{32}$H$_{32}$O$_4$)][BF$_4$]$_4$ (11). The compound [{Ir(η^5-C$_5$Me$_5$)Cl(μ-Cl)}$_2$] (**2c**) (0.11 g, 0.14 mmol) was treated with Ag[BF$_4$] (0.11 g, 0.57 mmol) in acetone (10 cm^3), followed by refluxing with *p-tert*-butyltetramethoxycalix[4]arene (**1c**) (0.09 g, 0.13 mmol) in CF$_3$CO$_2$H (10 cm^3) for 12 h as for **3**, to give the product as a white precipitate on addition of diethyl ether. Yield: 0.20 g, 0.12 mmol, 92%. Anal. Calcd for C$_{68}$H$_{94}$O$_4$B$_4$F$_{16}$Ir$_2$·CF$_3$CO$_2$H: C, 46.15; H, 5.25. Found: C, 45.65; H, 5.00%.

[{Ir(η^5-C$_5$Me$_5$)}$_2$(η^6:η-C$_{40}$H$_{48}$O$_4$)][BF$_4$]$_4$ (12). The compound [{Ir(η^5-C$_5$Me$_5$)Cl(μ-Cl)}$_2$] (**2c**) (0.13 g, 0.16 mmol) was treated with Ag[BF$_4$] (0.13 g, 0.67 mmol) in acetone (10 cm^3), followed by refluxing with tetra-*n*-propoxycalix[4]arene (**1e**) (0.04 g, 0.067 mmol) in CF$_3$CO$_2$H (10 cm^3) for 12 h as for **3**, to give the product as a white precipitate on addition of diethyl ether. Yield: 0.09 g, 0.056 mmol, 84%. Anal. Calcd for C$_{60}$H$_{78}$O$_4$B$_4$F$_{16}$Ir$_2$·2CF$_3$CO$_2$H: C, 42.15; H, 4.40. Found: C, 41.75; H, 4.50%.

[{Ru(η^6-p-MeC$_6$H$_4$CHMe$_2$)}$_2$(η^6:η^6-C$_{36}$H$_{40}$O$_4$)][BF$_4$]$_4$ (13). The compound [{Ru(η^6-p-MeC$_6$H$_4$CHMe$_2$)Cl(μ-Cl)}$_2$] (**2a**) (0.25 g, 0.41 mmol) was treated with Ag[BF$_4$] (0.35 g, 1.80 mmol) in acetone (10 cm^3), followed by refluxing with tetraethoxycalix[4]arene (**1d**) (0.10 g, 0.19 mmol) in CF$_3$CO$_2$H (10 cm^3) for 48 h as for **3**, to give the product as a yellow precipitate on addition of diethyl ether. Yield: 0.21 g, 0.13 mmol, 68%. Anal. Calcd for C$_{56}$H$_{68}$O$_4$B$_4$F$_{16}$Ru$_2$·2CF$_3$CO$_2$H: C, 42.45; H, 4.00. Found: C, 42.70; H, 4.45%.

[{Ir(η^5-C$_5$Me$_5$)}$_3$(η^6:η^6:η^6-C$_{55}$H$_{69}$O$_5$)][BF$_4$]$_5$ (14). The compound [{Ir(η^5-C$_5$Me$_5$)Cl(μ-Cl)}$_2$] (**2c**) (0.11 g, 0.14 mmol) was treated with

Ag[BF$_4$] (0.12 g, 0.62 mmol) in acetone (10 cm^3), followed by refluxing with *p-tert*-butylcalix[5]arene (**1f**) (0.05 g, 0.062 mmol) in CF$_3$CO$_2$H (10 cm^3) for 12 h as for **3**, to give the product as a white precipitate on addition of diethyl ether. Yield: 0.09 g, 0.056 mmol, 84%. Anal. Calcd for C$_{85}$H$_{114}$O$_5$B$_5$F$_{20}$Ir$_3$: C, 45.85; H, 5.15. Found: C, 46.00; H, 5.10%. Recrysallization by diffusion of diethyl ether vapour into a nitromethane solution of the complex gave the solvate [{Ir(η^5-C$_5$Me$_5$)}$_3$-(η^6:η^6:η^6-C$_{55}$H$_{69}$O$_5$)][BF$_4$]$_5$·0.5NO$_2$Me·2Et$_2$O, which was characterized by X-ray crystallography.

[{Ru(η^6-p-MeC$_6$H$_4$CHMe$_2$)}$_4$(η^6:η^6:η^6:η^6-C$_{28}$H$_{22}$O$_4$)][BF$_4$]$_6$ (15a). The compound [{Ru(η^6-p-MeC$_6$H$_4$CHMe$_2$)Cl(μ-Cl)}$_2$] (**2a**) (0.12 g, 0.20 mmol) was treated with Ag[BF$_4$] (0.16 g, 0.82 mmol) in acetone (10 cm^3), followed by refluxing with calix[4]arene (**1a**) (0.04 g, 0.094 mmol) in CF$_3$CO$_2$H (10 cm^3) for 24 h, as for **3**, to give the product as a pale yellow precipitate on addition of diethyl ether. Yield: 0.11 g, 0.058 mmol, 62%. Anal. Calcd for C$_{68}$H$_{78}$O$_4$B$_6$F$_{24}$Ru$_4$·CF$_3$CO$_2$H: C, 42.05; H, 4.00. Found: C, 42.15; H, 4.05%. The analogous triflate salt (**15b**) and hexafluorophosphate salt were prepared in 98% overall yield in an identical fashion, substituting Ag[CF$_3$SO$_3$] or Ag[PF$_6$] for Ag[BF$_4$]. Anal. Calcd for C$_{74}$H$_{78}$O$_{22}$S$_6$F$_{18}$Ru$_4$·6H$_2$O (**15b**): C, 37.57; H, 3.83. Found: C, 37.45; H, 3.70%.

[{Ru(η^6-p-MeC$_6$H$_4$CHMe$_2$)}$_4$(η^6:η^6:η^6:η^6-C$_{28}$H$_{22}$O$_4$)][HSO$_4$]$_4$-[SO$_4$]·4H$_2$O (15c). The compound [{Ru(η^6-p-MeC$_6$H$_4$CHMe$_2$)Cl(μ-Cl)}$_2$] (**2a**) (0.15 g, 0.24 mmol) was treated with Ag$_2$[SO$_4$] (0.32 g, 1.03 mmol) in a mixture of acetone (10 cm^3), water (10 cm^3), and CF$_3$-CO$_2$H (1 cm^3) for *ca.* 30 min. The mixture was filtered through Celite to remove AgCl and evaporated to a yellow oil. This oil was dissolved in CF$_3$CO$_2$H (10 cm^3) and refluxed with calix[4]arene (**1a**) (0.04 g, 0.094 mmol) for 48 h. When cool the mixture was filtered and evaporated to *ca.* 2 cm^3. Addition of acetone (10 cm^3) to this mixture gave the product as a pale yellow precipitate which was isolated by filtration, washed with acetone, and dried. Yield: 0.11 g, 0.059 mmol, 63%. Anal. Calcd for C$_{68}$H$_{82}$O$_{24}$S$_5$Ru$_4$·4H$_2$O: C, 42.54; H, 4.69; S, 8.35. Found: C, 42.05; H, 4.45; S, 8.65%.

[{Ru(η^6-p-MeC$_6$H$_4$CHMe$_2$)}$_4$(η^6:η^6:η^6:η^6-C$_{28}$H$_{22}$O$_4$)]X$_6$ (X = ReO$_4$, 15e; H$_2$PO$_4$, 15f). The triflate complex [{Ru(η^6-p-MeC$_6$H$_4$CHMe$_2$)}$_4$-(η^6:η^6:η^6:η^6-C$_{28}$H$_{22}$O$_4$)][CF$_3$SO$_3$]$_6$ (**15b**) (0.10 g, 0.044 mmol) was treated with [n-Bu$_4$N][ReO$_4$] or [n-Bu$_4$N][H$_2$PO$_4$] (0.2 g, excess) in water (2 cm^3), resulting in the precipitation of the products as white solids. Anal. Calcd for C$_{68}$H$_{78}$O$_{28}$Re$_6$Ru$_4$ (**15e**): C, 29.07; H, 2.80. Found: C, 29.15; H, 2.90%. Anal. Calcd for for C$_{68}$H$_{90}$O$_{28}$P$_6$Ru$_4$·6H$_2$O (**15f**): C, 39.77; H, 5.01. Found: C, 39.11; H, 4.45%.

[{Ir(η^5-C$_5$Me$_5$)}$_4$(η^6:η^6:η^6:η^6-C$_{28}$H$_{22}$O$_4$)][BF$_4$]$_6$ (16a). The compound [{Ir(η^5-C$_5$Me$_5$)Cl(μ-Cl)}$_2$] (**2c**) (0.21 g, 0.26 mmol) was treated with Ag[BF$_4$] (0.21 g, 1.08 mmol) in acetone (10 cm^3), followed by refluxing with calix[4]arene (**1a**) (0.06 g, 0.14 mmol) in CF$_3$CO$_2$H (10 cm^3) for 24 h as for **3**. The mixture was filtered and the resulting solution evaporated to *ca.* 1 cm^3. Addition of diethyl ether (10 cm^3) gave the product as a white precipitate. Yield: 0.25 g, 0.11 mmol, 85%. Anal. Calcd for C$_{68}$H$_{82}$O$_4$B$_6$F$_{24}$Ir$_4$: C, 36.25; H, 3.65. Found: C, 36.00; H, 3.75%. The analogous triflate salt (**16b**) was prepared in an identical fashion in 94% yield by substituting Ag[CF$_3$SO$_3$] for Ag-[BF$_4$].

[{Ir(η^5-C$_5$Me$_5$)}$_4$(η^6:η^6:η^6:η^6-C$_{28}$H$_{22}$O$_4$)][HSO$_4$]$_7$·12H$_2$O (16c). The compound [{Ir(η^5-C$_5$Me$_5$)Cl(μ-Cl)}$_2$] (**2c**) (0.14 g, 0.17 mmol) was treated with Ag$_2$[SO$_4$] (0.20 g, 0.65 mmol) in a mixture of acetone (10 cm^3), water (10 cm^3), and CF$_3$CO$_2$H (1 cm^3) for *ca.* 30 min, as for **15c**. Treatment with calix[4]arene (**1a**) (0.03 g, 0.075 mmol) in CF$_3$-CO$_2$H (10 cm^3) for 60 h, followed by workup as for **15c**, gave the product as a white powder. Yield: 0.11 g, 0.046 mmol, 61%. Anal. Calcd for C$_{68}$H$_{89}$O$_{32}$S$_7$Ir$_4$·12H$_2$O: C, 31.10; H, 4.35. Found: C, 30.80; H, 4.55%.

NMR Titrations. Stock solutions ((1.25−2.5) × 10^{-3} M) of complex **15b** were prepared in D$_2$O. To 0.50 cm^3 of this host solution were added increasing aliquots of 0.25 M solutions of NaX in D$_2$O (X = Cl, Br, I, NO$_3$, H$_2$PO$_4$, CH$_3$CO$_2$, *etc.*) in a 5 mm NMR tube and the volume topped off to 1.00 cm^3 with fresh D$_2$O. For very high anion: host ratios, 2.5 M anion solutions were used in the same way. ^{1}H NMR spectra were recorded in the usual way for between 10 and 20 samples, and the resulting titration curve analyzed by the EQNMR software.[28] For studies carried out at constant ionic strength, 0.25 M NaCF$_3$SO$_3$ solution was used instead of D$_2$O to make up the volume to 1 cm^3.

Crystallography. Crystal data and data collection parameters are summarized in Table 2. Crystals were mounted using silicon grease in thin walled glass capillaries containing a drop of mother liquor where necessary. All crystallographic measurements were carried out with an Enraf-Nonius CAD4 four-circle diffractometer equipped either with graphite monochromated Mo Kα or Cu Kα radiation using the $\omega-2\theta$ scan mode. Data sets were corrected for Lorentz and polarization effects and for the effects of absorption (ψ-scans) and crystal decay where appropriate. Structures were solved using the direct methods option of SHELXS-86[33] and developed using conventional alternating cycles of least-squares refinement (SHELXL-76[34] for **15d** or SHELXL-93[35]) and difference Fourier synthesis. In all cases, all non-hydrogen atoms were refined anisotropically, except disordered atoms in some isopropyl groups and some solvent molecules, while hydrogen atoms were fixed in idealized positions and allowed to ride on the atom to which they were attached. For structures refined with SHELXL-76, all hydrogen atoms were assigned a fixed isotropic displacement factor (U_{iso} 0.08 Å^2), whereas hydrogen atom thermal parameters were tied to those of the atom to which they were attached for **9a**, **10**, **15d**, and

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16a,**c**. All calculations were carried out on an IBM-PC compatible personal computer.

Supporting Information Available: Crystallographic summary for **9a**, **10**, **15d**, and **16a**, including tables of crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters and hydrogen atom coordinates and isotropic displacement parameters (71 pages). See any current masthead page for ordering and Internet access instructions.

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