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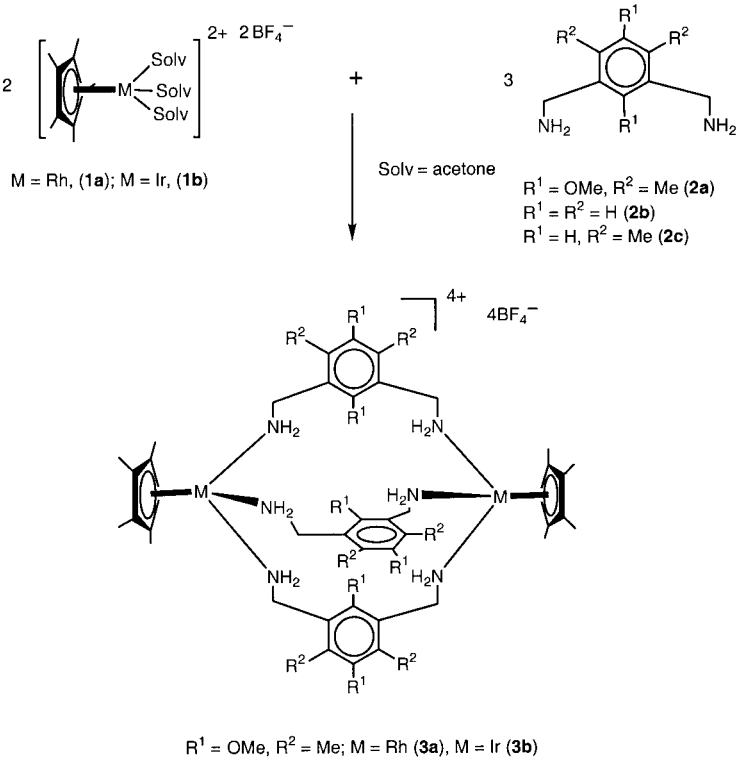
[23] The comments offered in footnote [32] of reference [4b] apply equally well to the present circumstances.

Rational Design and X-ray Molecular Structure of the First Irido-Cryptand and Encapsulation of a Tetrafluoroborate Anion**

Hani Amouri,* Marie Noelle Rager, Florence Cagnol, and Jacqueline Vaissermann

In memory of John A. Osborn

Supramolecular systems obtained by assembling molecular subunits through noncovalent interactions have been the focus of recent intense investigations.[1] In the last decade there has been a blossoming in the preparation of inorganic and organometallic macrocycles which have shown particular promise in the supramolecular chemistry of host–guest interactions.[2] Cryptands, which are the most fascinating macrobicyclic systems, possess intramolecular cavities that are available for the encapsulation of ionic guests.[3] In a spectacular demonstration by Lehn and co-workers a bis-(tren) chelate receptor was used to encapsulate fluoride anions.[4] Recently Bowman-James and co-workers have elegantly shown that a bicyclic polyammonium receptor can encapsulate two nitrate anions.[5] Although the chemistry of organic cryptands is steadily expanding, less is known about metallocryptands.[6] Herein we report a rational high-yield (70–85%) strategy for preparing organometallic cryptands that is based on iridium coordination chemistry (Scheme 1)



Scheme 1. General synthetic strategy for metallocryptands.

and demonstrate their properties as anion hosts. Although the coordination chemistry of cations is well developed, the chemistry of anion encapsulation is still in its infancy:[7] only one example of a metallo-helicate encapsulating a PF_6^- ion has been described by Steel and co-workers and two supramolecular tetrahedron complexes encapsulating a BF_4^- ion have been reported by the groups of Huttner, and Ward and McCleverty.[8] To our knowledge no metallo-cryptate that encapsulates a polyfluoroanion has so far been reported.

The novelty of our work is the use of $[Cp^*M(Solv)_3][BF_4]_2$ ($Cp^* = C_5(CH_3)_5$, M = Rh, Ir, Solv = acetone) (**1a**, **b**) complexes[9] as "tripod connectors". These compounds possess piano-stool structures in which the η^5-Cp* ligand remains firmly attached, whereas three weakly bound acetone molecules occupy the three legs of the tripod. In this work we have used diamines that were designed to coordinate to two different tripod connectors rather than to chelate to a single metal center. We sought the spontaneous and cooperative self-assembly of metallocryptands by combining two metal fragments and three diamines (Scheme 1).

To demonstrate the viability of our strategy we prepared the bidentate ligand 1,3-bis(aminomethyl)-2,5-dimethoxy-4,6-dimethylbenzene (**2a**). Significantly, treatment of three equivalents of the diamine **2a** with two equivalents of tripod connectors **1a** or **1b**, prepared in situ, affords in one-pot reactions the rhodium and iridium cryptands $[(Cp^*M)_2(\mathbf{2a})_3][BF_4]_4$ (**3a** and **3b**), respectively, in 77–85% yield. The ^1H and ^{13}C NMR data recorded in CD_3CN are consistent with the proposed formulas. Most remarkably, the resonances ascribed to the protons of the amino groups appear at very different fields: at $\delta = 5.12$ (td, $J = 11.5$, 4.4 Hz, 1H) and at $\delta = 1.41$ (br t, 1H) for **3a** and at $\delta = 5.91$ (td, $J =$

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11.5, 4.5 Hz, 1H) and at $\delta = 2.40$ (brt, 1H) for **3b.** These different amine resonances are consistent with a rather asymmetric structure. The folding of the ligands was confirmed by a single-crystal X-ray diffraction study (Figure 1).[10] As expected, cryptand **3b** is made up of three connecting

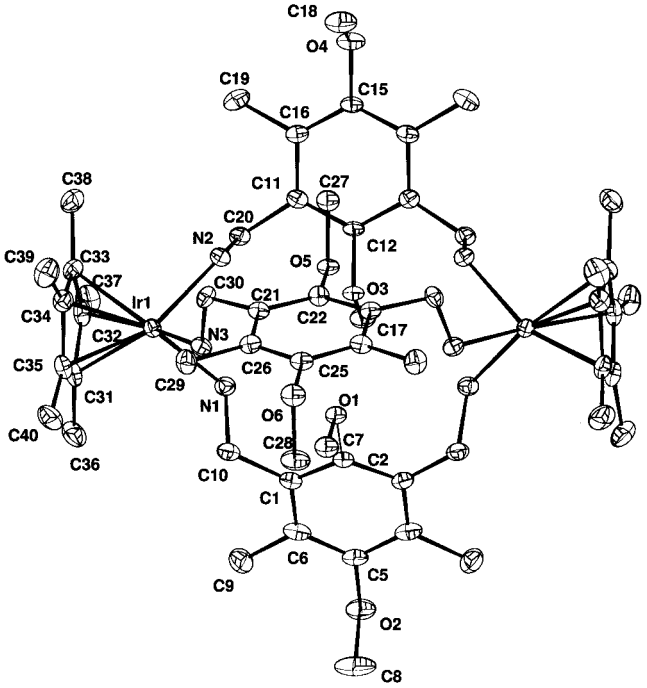

Figure 1. Crystal view of the cationic part of the metallocryptand **3b** with atom numbering system. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir1-N1 2.189(7), Ir1-N2 2.141(7), Ir1-N3 2.143(7), Ir1-C31 2.177(9), Ir1-C32 2.161(9), Ir1-C33 2.188(9), Ir1-C34 2.157(9), Ir1-C35 2.160(9); N1-Ir1-N2 84.1(3), N1-Ir1-N3 81.8(3), N2-Ir1-N3 82.5(3).

diamine ligands **2a** that bridge the two "Cp*Ir" moieties. Each metal center adopts a three-legged piano stool described by the three (-NH_2) groups of **2a** and the (η^5-Cp*) coordinated ligand. It is clear that the three bidentate diamines and the two iridium centers describe an internal cavity, with both extremities are capped by the iridium fragments.

The Ir···Ir distance in **3b** is 8.17 Å, while the average O···O distance between the internal methoxy groups is 3.56 Å. All the BF_4^- ions are located outside the metallomacrocyclic cavity, perhaps because of the steric hindrance presented by the internal methoxy groups. The ^{19}F NMR spectrum of **3b** recorded in CD_3CN showed a sharp singlet at $\delta = -150$ which was attributed to free BF_4^- ions.[8b, 11]

Our next synthetic tactic was to prepare other metallocryptands without methoxy groups on the interior of the cavity, so as to leave more room for anionic guests. Thus, three equivalents of 1,3-bis(aminomethyl)benzene (**2b**) or the methylated derivative (**2c**) were combined with two equivalents of **1b**, prepared in situ, to afford the off-white complexes **4** and **5**, respectively, in 70–75% yield. Complexes **4** and **5** were fully characterized by spectroscopic analyses (^1H, ^{13}C, ^{19}F NMR, IR) and elemental analysis. In contrast to what was seen for **3**, the ^1H NMR spectra of **4** and **5** recorded in CD_3CN showed that the metallomacrocycles are fully symmetric: for example, the protons of the coordinated amino groups resonated as one large triplet at $\delta = 5.24$ for **4** and at $\delta = 5.12$ for **5**. Remarkably, the ^{19}F NMR spectra of both **4** and **5** recorded in CD_3CN showed not only the presence of a singlet at $\delta = -149.5$, which were attributed to free BF_4^- ions (as observed for **3b**; see above), but also another signal at $\delta = -44.7$ for **4** and at $\delta = -46.2$ for **5**. These latter presonances were attributed to an encapsulated and hydrogen-bonded BF_4^- ion, respectively. Most remarkably, the ^{13}C NMR spectra of **4** and **5** showed a doublet at $\delta = 132.7$ ($J_{C-F} = 10.8$ Hz) for **4** and at $\delta = 134$ ($J_{C-F} = 9.4$ Hz) for **5**. These resonances are ascribed to the three aromatic carbon atoms C(2), each of which is concluded to be close to one ^{19}F nucleus of the BF_4^- ion. Thus, selective ^{19}F decoupling experiments were carried out on **4** while recording the $^{13}C\{^{19}F\}$ spectra: when the ^{19}F signal at $\delta = -44.7$ was irradiated, the signal attributed to C(2) in the ^{13}C spectrum became a singlet (Figure 2). Similar results were also obtained for complex **5**.

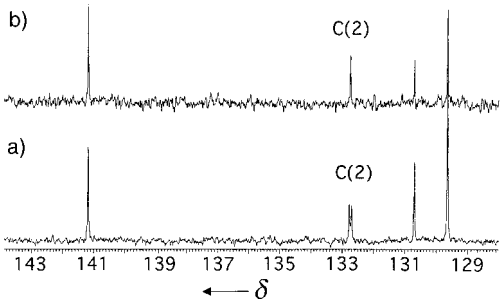

Figure 2. Section of the NMR spectra of **4.** a) $^{13}C\{^1H\}$ and b) $^{13}C\{^{19}F,^1H\}$, showing a direct interaction between C(2)-H and one ^{19}F nucleus of the encapsulated BF_4^- ion.

This observation suggests that on the time scale of the NMR experiment the BF_4^- ion remains encapsulated within the cryptate, but is tumbling within the cavity rather than being locked in one orientation. Although all attempts to obtain diffractable crystals of **4** have so far been unsuccessful, the unusual spectroscopic results and the ^{19}F decoupled experiments, when taken together, suggest strongly the formation of the first iridium cryptates of the formula $[BF_4^- \subset (Cp^*Ir)_2(\mathbf{2b})_3][BF_4]_3$ (**4**) and $[BF_4^- \subset (Cp^*Ir)_2(\mathbf{2c})_3][BF_4]_3$ (**5**; Figure 3).

It is suggested that the BF_4^- ion is strongly held by the polarizable protons of the coordinated amino groups bringing it close to the C(2)-H groups of the bidentate ligand (Figure 3). In this work, crucial ^{13}C, and ^{19}F NMR analyses and decoupling experiments, reveal the details of the supramolecular templation process in solution.

In conclusion, we have reported a rational synthetic strategy for formation of metallocryptands that is based on iridium and rhodium coordination chemistry. The cavity size of these metallocryptands can be varied, depending on the bridging diamine ligands used. Most notably, the synthesis of the cryptate complexes **4** and **5** was made possible by increasing the accessibility of the cavity. Further investigations are ongoing on this and related metallocryptand systems

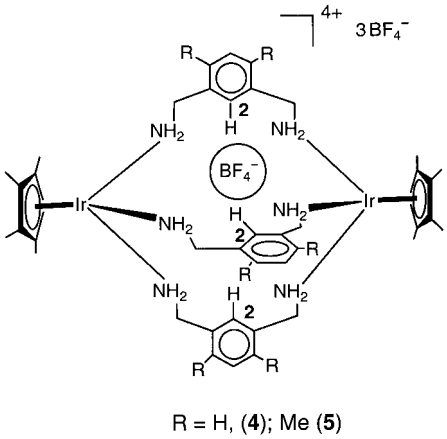

Figure 3. Schematic drawing of the Ir-cyptates **4** and **5**.

to obtain better and more selective hosts for a variety of anionic guests.

Experimental Section

All experimental manipulations were carried out under argon using Schlenk tube techniques

3b: A solution of $AgBF_4$ (195 mg, 1.0 mmol) in acetone (10 mL) was added to $[\{(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}Cl)Cl\}_2]$ (199 mg, 0.25 mmol) in acetone (20 mL). This resulted in the rapid formation of a white precipitate of AgCl. The reaction mixture was stirred for 15 min. then the resulting orange solution of $[(\eta^5\text{-}C_5Me_5)Ir(acetone)_3][BF_4]_2$ was filtered into a dry Schlenk tube kept under argon. A solution of **2a** (110 mg, 0.75 mmol) in $C_2H_4Cl_2$ (10 mL) was then added to this orange solution and the mixture was stirred for 1 h, during which the solution became lighter and a white precipitate was obtained. This compound was separated and washed several times with Et_2O and dried under vacuum, to give 353 mg of **3b** (85% yield). ^{1}H NMR (400 MHz, CD_3CN): $\delta = 5.91$ (td, 6H, NH_2), 4.06 (td, 6H, CH_2), 3.65 (s, 9H, CH_3O), 3.43 (t, 6H, CH_2), 2.82 (s, 3H, CH_3O), 2.46 (s, 18H, CH_3), 2.40 (brt, 6H, NH_2), 1.95 (s, 30H, η^5-$C_5(CH_3)_5$). Elemental analysis calcd for $C_{55}H_{90}O_6N_6Ir_2B_4F_{16}\cdot C_3H_6O$: C 40.48, H 5.62, N 4.88; found: C 41.26, H 5.63, N 5.14.

3a: was prepared in a similar way to that described for **3b**. Yield 77% (276 mg). ^{1}H NMR (400 MHz, CD_3CN): $\delta = 5.12$ (td, 6H, NH_2), 4.01 (td, 6H, CH_2), 3.65 (s, 9H, CH_3O), 3.33 (t, 6H, CH_2), 2.78 (s, 3H, CH_3O), 2.47 (s, 18H, CH_3), 1.93 (s, 30H, η^5-$C_5(CH_3)_5$), 1.41 (brt, 6H, NH_2). Elemental analysis calcd for $C_{55}H_{90}O_6N_6Rh_2B_4F_{16}\cdot C_3H_6O$: C 45.16, H 6.27, N 5.45; found: C 46.06, H 6.45, N 5.55.

4: This irido-cryptate was prepared in acetone at room temperature following the above procedure, but using the diamine ligand **2b**. Yield 70% (247 mg). ^{1}H NMR (400 MHz, CD_3CN): $\delta = 7.39$–7.50 (m, 12H, aromatic-H), 5.24 (brt, 12H, NH_2), 3.91 (brs, 12H, CH_2), 1.85 (s, 30H, η^5-$C_5(CH_3)_5$). Elemental analysis calcd for $C_{44}H_{66}N_6Ir_2B_4F_{16}\cdot C_3H_6O$: C 38.43, H 4.94, N 5.72; found: C 38.66, H 5.17, N 6.16

5 was prepared in a similar fashion to that of **4** but using the diamine ligand **2c**. Yield 75% (280 mg). ^{1}H NMR (400 MHz, CD_3CN): $\delta = 7.26$–7.06 (m, 6H, aromatic-H), 5.12 (brt, 12H, NH_2), 3.83 (brs, 12H, CH_2), 1.84 (s, 30H, η^5-$C_5(CH_3)_5$). Elemental analysis calcd for $C_{50}H_{78}N_6Ir_2B_4F_{16}$: C 40.17, H 5.62, N 5.26; found: C 39.04, H 5.47, N 5.59.

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[10] Light yellow crystals, $C_{56}H_{96}O_9N_6Ir_2B_4F_{16}$, $M_r = 1729$, orthorhombic, space group *Pnma*, $a = 17.671(10)$, $b = 18.639(3)$, $c = 21.489(5)$ Å, $V = 7078(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.62$ g cm^{-3}, $T = 22\,^\circ$C, $R = 0.0505$ ($Rw = 0.0608$) for 4889 observed independent reflections, GOF = 1.02. Crystal dimensions $0.30 \times 030 \times 0.60$ mm; Enraf-Nonius CAD4 diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å) collection range $2\theta = 2$–50°. Absorption correction was applied based on a ψ-scan curve. The structure was determined by direct methods and subsequent difference Fourier syntheses, and refined by full-matrix least-squares on F^2 by using the programs of the PC version of CRYSTALS. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located on a difference-Fourier map and their coordinates were refined with an overall isotropic thermal parameter. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-163552 (**3b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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