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(η^5-Pentamethylcyclopentadienyl)rhodium and -iridium Complexes with Weakly and Strongly Coordinating Anions: Isolation and First X-ray Molecular Structures of the Tris(solvent) Complexes $[(C_5Me_5)M(acetone)_2(H_2O)][BF_4]_2$ (M = Rh, Ir)

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Several novel pentamethylcyclopentadienyl complexes of general formula $[(C_5Me_5)IrL_3][BF_4]_2$ were prepared including the tris(solvent) precursors $[(C_5Me_5)M(acetone)_2(H_2O)][BF_4]_2$ (M = Rh, Ir) (**1a**,**b**). The X-ray molecular structures of **1a,b** were determined at low temperature. Complexes **1a,b** are isostructural, and both compounds crystallize in the monoclinic space group $P2_1/c$ with a = 10.157(3) Å, b = 14.038(9) Å, c = 16.335(2) Å, β = 99.73(2)°, and Z = 4 for **1a** and with a = 10.107(9) Å, b = 13.994(16) Å, c = 15.996(34) Å, β = 99.61(12)°, and Z = 4 for **1b**. The coordinated water molecule is hydrogen bonded to both BF_4^- anions. Reaction of **1a,b** with pyridine (py) afforded the related tris(pyridine) complexes $[(C_5Me_5)M(\eta^1\text{-(N)-py})_3][BF_4]_2$ (M = Rh, Ir) (**2a,b**). Complex **2b** was characterized by X-ray crystallography, monoclinic space group $P2_1/c$ with a = 8.665(3) Å, b = 19.687(7) Å, c = 18.408(5) Å, β = 94.17(3)°, and Z = 4. Moreover, we prepared the novel neutral compounds $(C_5Me_5)M(\eta^2\text{-}NO_3)(\eta^1\text{-}NO_3)$ (M = Rh, Ir) (**4a,b**) where the anions are bonded to the metal center instead of a coordinating solvent as confirmed by X-ray study on the iridium complex **4b**. The latter crystallizes in the orthorhombic space group *Pcab* with a = 13.032(4) Å, b = 14.370(11) Å, c = 14.839(18) Å, and Z = 8.

Introduction

Supramolecular chemistry will be enhanced by rapid versatile construction of architectures by rational use of coordination chemistry.[1] Thus, metal complexes of different predictable geometrical structures, exhibiting specific predictable reactivity, are crucial tools for the preparation of supermolecules.[2] We recently reported the preparation of rhodio- and iridocryptands/cryptates (Scheme 1) and showed that these supramolecular systems act as hosts to encapsulate polyfluoranions such as BF_4^-.[3] These metallocryptates were obtained in good yield by treatment of the tris(solvent) complexes $[(\eta^5\text{-}C_5Me_5)M(S)_3][BF_4]_2$ (M = Rh, Ir; S = acetone) prepared in situ with the appropriate bridging diamine ligands. The solvated complexes can be regarded as "tripod connectors" in which the η^5-C_5Me_5 ligand remains firmly attached, whereas three weakly bound solvent molecules occupy the three legs of the tripod. The coordinated solvent molecules can be displaced by a wide range of donor ligands under extremely mild conditions.[4] Due to their high reactivity, these compounds were never isolated or characterized. In contrast, in this paper we report the X-ray molecular

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(2) (a) Leininger, S.; Olenyuk, B.; Stang, P. T. *Chem. Rev.* **2000**, *100*, 853−908 and references. (b) Fujita, M. *Chem. Soc. Rev.* **1998**, *27*, 417−425. (c) Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* **1999**, *32*, 975−982.

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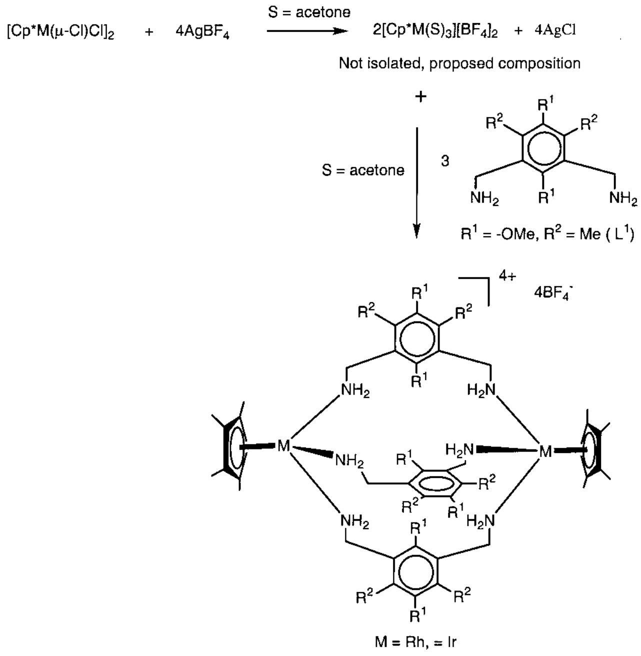
Scheme 1. General Synthetic Strategy for Metallocryptands



structures of the tris(solvent)rhodium and -iridium complexes $[(\eta^5\text{-}C_5Me_5)M(acetone)_2(H_2O)][BF_4]_2$ [M = Rh (**1a**); M = Ir (**1b**)] and show that these compounds possess piano-stool structures. As indicated by displacements of loosely bound solvent molecules in **1a,b** by arenes, pyridine, and 4,4′-bipyridine, these complexes show promise as building blocks for supramolecular chemistry.

Results and Discussion

Synthesis, NMR, and X-ray Molecular Structures of $[(C_5Me_5)M(acetone)_2(H_2O)][BF_4]_2$ (1a,b). The tris(solvent) complexes $[(C_5Me_5)M(S)_3][BF_4]_2$ $\{(S)_3 = (acetone)_2(H_2O)\}$ were prepared in 90% yield from the reaction of $[(C_5Me_5)M(\mu\text{-}Cl)Cl]_2$ and $AgBF_4$ in acetone. The solvent was concentrated under vacuum, and subsequent slow crystallization from acetone/ether mixture[5] at low temperature provided **1a** as orange crystals and **1b** as orange-red crystals (Scheme 2). The IR spectrum of **1a,b** showed a strong band attributed to the free BF_4^- anions at 1080 cm^{-1} (**1a**) and 1083 cm^{-1} (**1b**). Significantly bands attributed to the bound acetone and water molecules were obvious at 1636 and 1634 cm^{-1} (medium intensity, **1a** and **1b**) and at 3457 and 3461 cm^{-1} (strong absorption for **1a** and **1b**). The ^{1}H NMR spectra of **1a,b** recorded in acetone-d_6 exhibited two singlets; for instance, the methyl protons of the η^5-C_5Me_5 appeared at δ 1.81 ppm for **1a** and at δ 1.71 ppm for **1b**, and the coordinated acetone molecules showed a signal at δ 2.09 ppm for **1a** and at δ 2.08 ppm for **1b**. (At this time, we do not know whether the acetone ligands on **1a,b** exchange with deuterated acetone or not.) These chemical shifts were solvent dependent; for instance, in CD_2Cl_2 the η^5-C_5Me_5 appeared at δ 1.56 ppm and the bonded acetone at δ 2.12 ppm for **1a** and at δ 1.55 and 2.11 ppm for **1b**. The empirical formulas of these rhodium and iridium precursors were confirmed by X-ray analysis.

X-ray Molecular Structures of $[(C_5Me_5)M(acetone)_2(H_2O)][BF_4]_2$ (M = Rh, Ir) (1a,b). Suitable crystals of the tris(solvent)rhodium and -iridium complexes $[(C_5Me_5)M(acetone)_2(H_2O)][BF_4]_2$ (**1a,b**) were obtained separately by slow evaporation of Et_2O into an acetone solution of either **1a** or **1b** (Scheme 2). Both compounds crystallize in the monoclinic unit cell space group $P2_1/c$. Crystallographic data for **1a,b** are shown in Table 1. Selected bond distances and angles for **1a,b** are shown in Tables 2 and 3. Complexes **1a,b** are isostructural; only the Cameron view of **1b** is shown (Figure 1). The structure of either compound reveals the three-legged piano-stool coordination mode. Furthermore, it clearly shows the presence of two molecules of acetone bonded to the metal center via the oxygen atoms, while the third site is occupied by one molecule of water. The Ir(1)−

Scheme 2

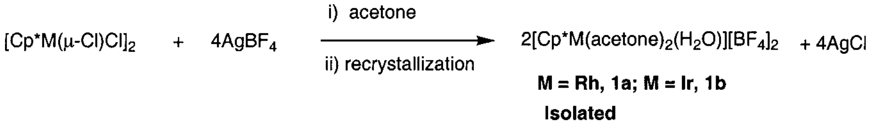


Table 1. Crystal Data and Structure Refinement for **1a**, **1b**, **2b**, and **4b**

	1a	1b	2b	4b
empirical formula	$C_{16}H_{29}O_3Rh(BF_4)_2$	$C_{16}H_{29}O_3Ir(BF_4)_2$	$C_{25}H_{30}N_3IrCH_2Cl_2(BF_4)_2$	$C_{10}H_{15}IrN_2O_6$
fw	545.92	635.23	823.29	451.46
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	Pcab
a (Å)	10.157(3)	10.107(9)	8.655(3)	13.032(4)
b (Å)	14.038(9)	13.994(16)	19.687(7)	14.370(11)
c (Å)	16.335(2)	15.996(34)	18.408(5)	14.839(18)
β (deg)	99.73(2)	99.61(12)	94.17(3)	
V (Å^3)	2295(2)	2231(6)	3128(2)	2779(6)
Z	4	4	4	8
ρ_{calcd} (g·cm^{-3})	1.58	1.89	1.75	2.16
temp (°C)	−10	−40	22	22
λ(Mo Kα) (Å)	0.71069	0.71069	0.71069	0.71069
μ (cm^{-1})	8.22	60.65	45.1	96.32
$R(F_o)^a$	0.1063	0.0643	0.0724	0.0402
$R_w(F_o)^b$	0.1135	0.0745	0.0762	0.0475

$^a R = [\Sigma(|F_o| - |F_c|)/\Sigma F_o$. $^b R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

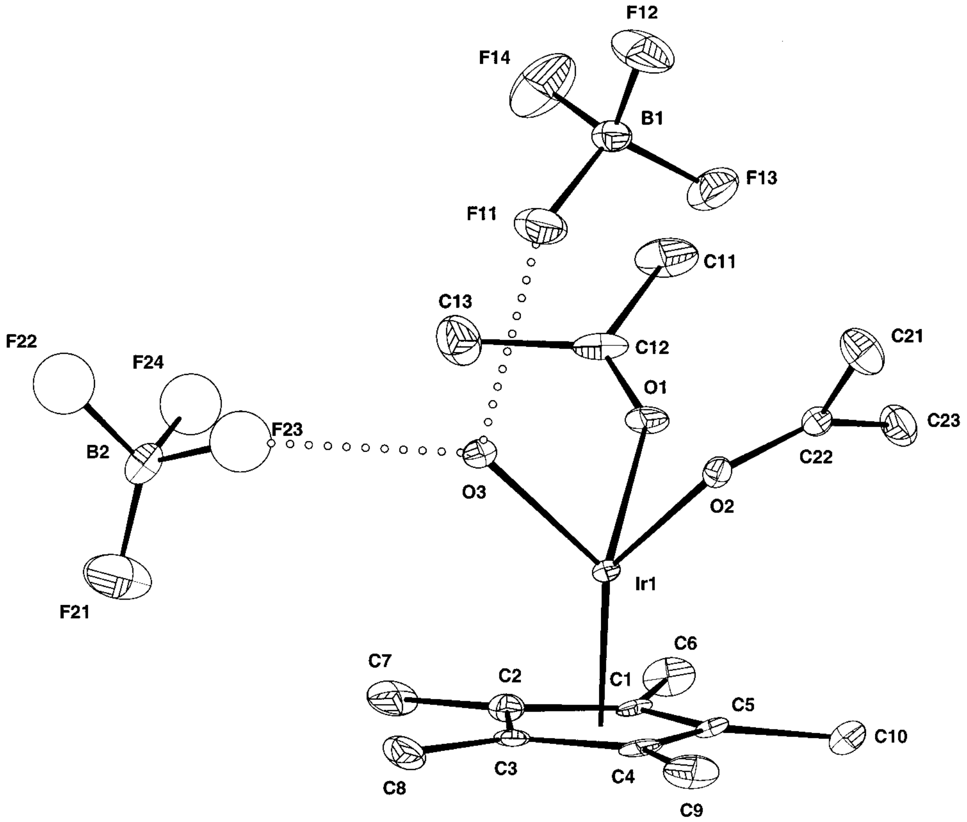


Figure 1. Crystal view of the cationic part of **1b** with the atom numbering system. Hydrogens have been omitted for clarity. Dotted lines indicate hydrogen bonding between the oxygen atom of the aqua ligand and neighboring F atoms of BF_4^- anions.

Table 2. Selected Atomic Distances (Å) and Angles (deg) for **1a**

Rh(1)−C(1) = 2.13(1)
Rh(1)−C(2) = 2.114(11)
Rh(1)−C(3) = 2.130(11)
Rh(1)−C(4) = 2.107(12)
Rh(1)−C(5) = 2.12(1)
Rh(1)−O(1) = 2.089(9)
Rh(1)−O(2) = 2.169(7)
Rh(1)−O(3) = 2.179(8)
C(11)−C(12) = 1.50(2)
C(12)−C(13) = 1.46(2)
C(12)−O(1) = 1.257(15)
C(21)−C(22) = 1.491(18)
C(22)−C(23) = 1.474(19)
C(22)−O(2) = 1.204(13)

C(11)−C(12)−O(1) = 119.9(14)
C(11)−C(12)−C(13) = 118.1(14)
C(13)−C(12)−O(1) = 122.0(14)
C(21)−C(22)−O(2) = 119.4(12)
C(21)−C(22)−C(23) = 116.0(12)
C(23)−C(22)−O(2) = 124.6(12)

Table 3. Selected Atomic Distances (Å) and Angles (deg) for **1b**

Ir(1)−C(1) = 2.144(9)
Ir(1)−C(2) = 2.131(11)
Ir(1)−C(3) = 2.131(9)
Ir(1)−C(4) = 2.109(8)
Ir(1)−C(5) = 2.117(8)
Ir(1)−O(1) = 2.105(7)
Ir(1)−O(2) = 2.130(7)
Ir(1)−O(3) = 2.165(7)
C(11)−C(12) = 1.474(19)
C(12)−C(13) = 1.55(2)
C(12)−O(1) = 1.170(15)
C(21)−C(22) = 1.500(18)
C(22)−C(23) = 1.470(17)
C(22)−O(2) = 1.228(12)

C(11)−C(12)−O(1) = 125.1(17)
C(11)−C(12)−C(13) = 116.5(14)
C(13)−C(12)−O(1) = 118.4(13)
C(21)−C(22)−O(2) = 118.6(10)
C(21)−C(22)−C(23) = 116.6(10)
C(23)−C(22)−O(2) = 124.7(10)

O(1) and Rh(1)−O(1) bond distances are 2.105(7) and 2.089(9) Å, and those of Ir(1)−O(2) and Rh(1)−O(2) are 2.130(7) and 2.169(7) Å, while the distances between the metal centers and the oxygen atom of the water molecule, Ir(1)−O(3) and Rh(1)−O(3), are, respectively, 2.165(7) and 2.179(8) Å. Interestingly the bonded water molecule in either complex interacts with the two BF_4^- free anions through hydrogen bonding with O(3)−F(23) and O(3)−F(11) distances of 2.647(11) and 2.820(30) Å in **1b** and 2.693(14) and 2.886(29) Å in **1a**. Such interactions have been previously observed by other rhodium and iridium aqua complexes.[6] We also note that several X-ray structures of pentamethylcyclopentadienylrhodium and -iridium complexes incorporating one, two, or three aqua ligands have been reported;[7] however, to our knowledge complexes **1a,b** are the first examples reported for (C_5Me_5)Rh and (C_5Me_5)Ir compounds incorporating weakly bonded acetone mol-

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[5] We feel that the water molecule comes from the acetone solvent used. Although acetone was distilled over K_2CO_3 for several hours, pure dried acetone is extremely difficult to obtain, and the presence of a part per million amount of H_2O in distilled acetone is sufficient to coordinate to the metal center. H_2O is a better nucleophile than acetone; besides it hydrogen bonds with free anions, which may stabilize the whole species.

[6] (a) Hughes, R. P.; Lindner, D. C.; Rheingold, A. L.; Liable-Sands, L. M. *J. Am. Chem. Soc.* **1997**, *119*, 11544−11545. (b) Hughes, R. P.; Lindner, D. C.; Smith, J. M.; Zhang, D.; Incarvito, Ch. D.; Lam, K.-C.; Liable-Sands, L. M.; Sommer, R. D.; Rheingold, A. L. *J. Chem. Soc., Dalton Trans.* **2001**, 2270−2278.

Table 4. Selected Atomic Distances (Å) and Angles (deg) for **2b**

Ir(1)−C(1) = 2.142(14)
Ir(1)−C(2) = 2.172(14)
Ir(1)−C(3) = 2.147(12)
Ir(1)−C(4) = 2.155(12)
Ir(1)−C(5) = 2.172(11)
Ir(1)−N(1) = 2.13(1)
Ir(1)−N(2) = 2.158(11)
Ir(1)−N(3) = 2.104(13)
C(11)−C(12) = 1.474(19)

N(1)−Ir(1)−N(2) = 85.7(4)
N(1)−Ir(1)−N(3) = 83.1(5)
N(1)−Ir(1)−N(3) = 94.6(5)

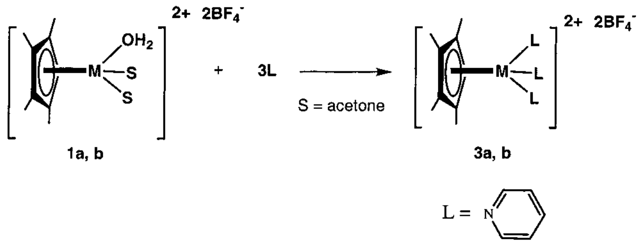
ecules. The only known iridium complex possessing two coordinated acetone molecules identified structurally is the dihydride complex $[IrH_2(acetone)_2(PPh_3)_2][BF_4]$ reported by Crabtree et al.[8] In this complex the Ir−O distances are 2.220(5) and 2.235(5) Å longer than those found in the Cp*M-solvated complexes **1a,b**, presumably the result of the *trans*-directing hydrides in this species.

Compounds **1a,b** can be stored in a cold place under argon for a long period of time. However, they hydrolyze when exposed to air for a short period of time. To check their reactivity, we treated **1b** with *o*-cresol in acetone, followed by NEt_3, to afford the known π-arene complex $[(C_5Me_5)Ir(\eta^5\text{-}(CH_3{-}C_6H_4O))][BF_4]$[9] as a white microcrystalline powder in quantitative yield. Similar results were obtained for the rhodium precursor **1a**. Therefore, these isolated species provide an easy systematic procedure to prepare other (η^5-pentamethylcyclopentadienyl)rhodium and -iridium complexes comparable to the in situ complexation procedure known as the Maitlis reaction.[10]

One might expect that, in acetone solvent, precursors **1a,b** may exist in equilibrium with the hypothetical tris(acetone) species $[(C_5Me_5)M(acetone)_3][BF_4]_2$; however, this remains a pure assumption, in the absence of any experimental data. However, it is clear from our results described below that all the ligands can be easily displaced by N-centered nucleophiles.

Reaction with Pyridine and X-ray Molecular Structure of $[(C_5Me_5)Ir(\eta^1\text{-}(N)\text{-}C_6H_5N)_3][BF_4]_2$ (2b). The tris(solvent) precursors reacted with pyridine (py) in acetone for 30 min, during which the initial orange-red color turned to yellow. Reaction workup afforded yellow crystals identified by spectroscopic data as tris[(η^1-N)-pyridine]rhodium and -iridium complexes $[(C_5Me_5)M(\eta^1\text{-}(N)\text{-}py)_3][BF_4]_2$ [M = Rh (**2a**); M = Ir (**2b**)] (Scheme 3). The hexafluorophosphate salt analogue complexes $[(C_5Me_5)M(\eta^1\text{-}(N)\text{-}py)_3][PF_6]_2$ were reported previously;[4a] however, no X-ray structure was determined. Crystals of **2b** were obtained from CH_2Cl_2/Et_2O by a slow evaporation method. Compound **2b** crystallizes in the monoclinic unit cell space group $P2_1/c$. Crystallographic data for **2b** are shown in Table 1. Selected bond distances and angles for **2b** are shown in Table 4. The Cameron view of this complex is shown in Figure 2. The structure exhibits the usual three-legged piano-stool coordination displayed by such complexes. The structure shows clearly that the three sites are occupied by pyridine; each molecule is N-bonded to the iridium center. The Ir(1)−N(1−3) bond distances are 2.130(10), 2.158(11), and 2.104(13) Å, respectively.

Scheme 3



Unlike the tris(solvent) complexes **1a,b**, compounds **2a,b** are stable in air, and they can be stored indefinitely under argon; this is no doubt related to the strong coordination displayed by the bound pyridine molecules.

In an attempt to prepare the supramolecular iridium and rhodium cubes (Scheme 4), we treated the tris(solvent) complexes **1a,b** with 4,4′-bipyridine (bpy) in a molar ratio of 8:12 in nitromethane, and the reactions were monitored by ^{1}H NMR over a period of time. After 1 h, in addition to unreacted **1a,b**, the tris-N-bonded complexes $[(C_5Me_5)M(\eta^1\text{-}(N)\text{-}bpy)_3][BF_4]_2$ [M = Rh (**3a**); M = Ir (**3b**)] were formed as identified by NMR data, similar to those obtained for **2a,b**. For instance, the methyl protons of the η^5-Cp* appeared as a singlet at δ 1.66 for **3a** and at δ 1.58 ppm for **3b**. Meanwhile, the η^1-(N)-bonded bpy displayed four doublets at δ 7.72, 7.91, 8.64, and 8.69 ppm for **3a** and δ 7.73, 7.93, 8.65, and 8.79 ppm for **3b**. Unlike the corresponding pyridine analogues **2a,b**, these compounds are very unstable toward hydrolysis in coordinating solvent, and hence attempts to isolate a pure sample of either **3a** or **3b** were unsuccessful. The reaction was allowed to proceed for several weeks, but no significant changes were observed in the ^{1}H NMR spectra, such as the formation of a symmetric pattern as one would expect for a supramolecular iridium or rhodium cube. In this context we note that self-assembly of a supramolecular cube was achieved by treating the organometallic precursor $[([9]ane\ S_3)Ru(DMSO)Cl_2]$ with 4,4′-bpy in nitromethane for 4 weeks.[11] The product was identified by NMR analysis and mass spectroscopy, but no X-ray

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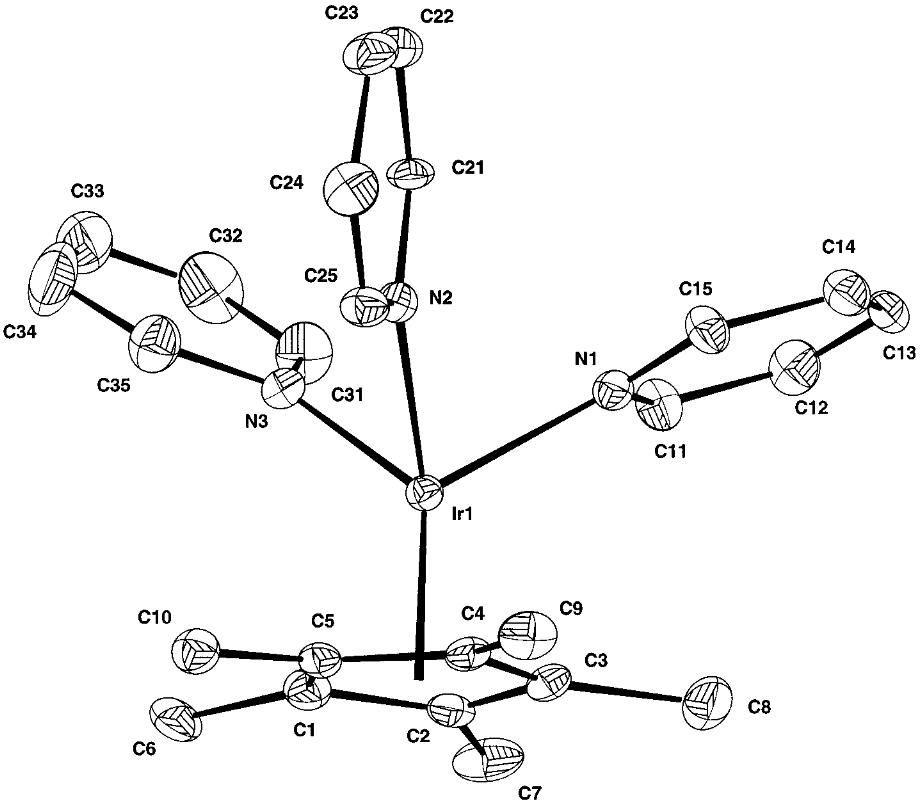
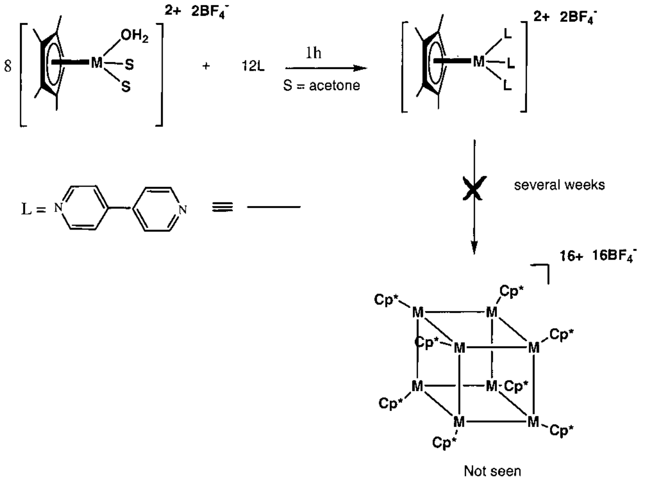


Figure 2. Crystal view of the cationic part of **2b** with the atom numbering system. Hydrogens have been omitted for clarity.

Scheme 4. Tentative Self-Assembly of Molecular Cubes Incorporating Only "(C_5Me_5M)" Units



structure was reported. Rauchfuss et al. have elegantly reported the preparation of supramolecular cubes incorporating (C_5Me_5)M and (C_5H_5)M units in an alternating fashion (M = Rh, Ir, and Co) but using CN^- ions as bridging ligands, which maintain the whole system firmly stable in solution.[12] In particular, the supramolecular cube $[(C_5H_5)_4(C_5Me_5)_4Rh_4Co_4(CN)_{12}][PF_6]_4$ was identified by spectroscopic data, and a related complex was ascertained by X-ray analysis and shows beautifully that the metal centers occupy the eight corners.[12b] The success of this approach is related to the nature of the bridging ligand used, an anionic cyanide. Furthermore, when a mixture of (C_5Me_5)M and (C_5H_5)M units is used, it appears that mixed cubes form selectively because (C_5Me_5)−(C_5Me_5) interactions impede the formation of molecular boxes containing only large C_5Me_5 units.[12b] Therefore, in our case, the neutral ligand 4,4′-bpy = L−L may not hold the system firmly in solution, and steric hindrance caused by eight close neighbors of (C_5Me_5)M units may inhibit the assembly of supramolecular cubes. Considerable efforts are now directed to employ the desired bridging ligand as well as the metal ion of proper geometry.

Synthesis, Characterization, and X-ray structure of (C_5Me_5)M(η^2-NO_3)(η^1-NO_3) (M = Rh, Ir). To quantify the electrophilicity of the metal ions in the pentamethylcyclopentadienyl complexes **1a,b**, we decided to prepare the analogous precursors but incorporating a nitrate anion instead of the BF_4^-. Our choice is also based on the fact that the *cis*-protected square-planar metals M(en)$(NO_3)_2$ (M = Pt, Pd; en = ethylenediamine) have been extensively used in the literature as corner connectors with a variety of ligands to build up several supramolecular systems of different shapes.[13] Hence, the analogous tripod connectors (C_5Me_5)M$(NO_3)_2$ (M = Rh, Ir) (**4a,b**) may also be useful precursors to prepare supramolecular systems.

Thus, treatment of the $[(C_5Me_5)M(\mu\text{-}Cl)Cl]_2$ (M = Rh, Ir) with 4 equiv of $AgNO_3$ in acetone provided after reaction

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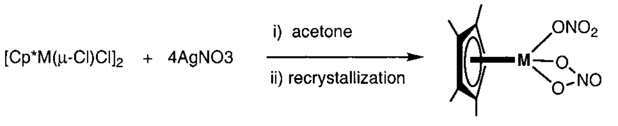
(13) For a recent review see: Fujita, M.; Umemoto, K.; Yoshizawa, M.; Fujita, N.; Kusukawa, T.; Biradha, K. *Chem. Commun.* **2001**, 509−518 and references therein.

Table 5. Selected Atomic Distances (Å) and Angles (deg) for **4b**

Ir(1)−C(1) = 2.13(1)   Ir(1)−C(2) = 2.14(1)   Ir(1)−C(3) = 2.11(1)
Ir(1)−C(4) = 2.11(1)   Ir(1)−C(5) = 2.13(1)   Ir(1)−O(11) = 2.157(9)
Ir(1)−O(12) = 2.16(1)   Ir(1)−O(21) = 2.12(1)

O(11)−N(1)−O(13) = 123.5(14)   O(12)−N(1)−O(13) = 123.8(14)   O(11)−N(1)−O(12) = 112.7(11)
O(21)−N(2)−O(23) = 117.3(14)   O(22)−N(2)−O(23) = 117.3(14)   O(21)−N(2)−O(22) = 115.8(15)

Scheme 5



M = Rh, 4a; M = Ir, 4b

workup the new pentamethylcyclopentadienyl complexes $(C_5Me_5)M(\eta^2\text{-}NO_3)(\eta^1\text{-}NO_3)$ (M = Rh, Ir) (**4a,b**) identified by spectroscopic data and X-ray structural determination of **4b** (Scheme 5). Crystals of **4b** were conveniently grown from CH_2Cl_2/ether solution. Compound **4b** crystallizes in the orthorhombic unit cell space group *Pcab*. Crystallographic data for **4b** are shown in Table 1. Selected bond distances and angles for **4b** are shown in Table 5. The Cameron view of this complex is shown in Figure 3. The structure exhibits the usual three-legged piano-stool coordination displayed by such compounds, with one of the nitrate anions acting as a bidentate ligand bound to the iridium center through two oxygen atoms, and the other nitrate acting only as a monodentate ligand. The Ir(1)−O(11,12,21) bond distances are 2.157(9), 2.160(10), and 2.120(10) Å, respectively, with a slightly shorter bond distance displayed by the monodentate anion.

As one would expect, no acetone or water molecules were found attached to the metal center. Such a behavior has been reported in the literature; for instance, substitution of water molecules in the tris(aqua)rhodium and -iridium complexes by the NO_3 anions proceeds under mild conditions.[7b]

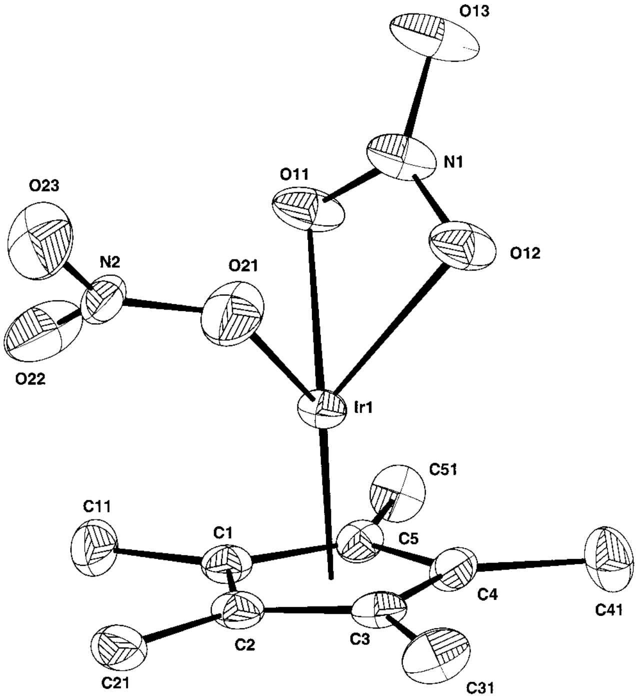


Figure 3. Crystal view of **4b** with the atom numbering system. Hydrogens have been omitted for clarity.

The novel complexes **4a,b** are air stable and soluble in a variety of polar solvents including CH_2Cl_2; however, they are less reactive than the analogous tris(solvent)iridium and -rhodium complexes **1a,b**. For instance, at room temperature **4a,b** did not react with arene ligands to give the related $[(C_5Me_5)Ir(\pi\text{-arene})][NO_3]_2$ complexes, but substitution of the anions by pyridine molecules occurred smoothly, providing the related complexes $[(C_5Me_5)M(\eta^1\text{-(N)-py})_3][NO_3]_2$. In comparison to the well-known $M(en)(NO_3)_2$ (M = Pt, Pd; en = ethylenediamine), we feel that our tripod precursors **4a,b** would be reactive toward rigid polyfunctional N-bonded ligands, and hence, various novel supramolecular architectures will be constructed.

Concluding Remarks

In this paper we report the synthesis and characterization of several new (pentamethylcyclopentadienyl)rhodium and -iridium complexes. In particular, the X-ray molecular structures of the tris(solvent) precursors **1a,b** are presented for the first time. These are the only structurally known complexes of the pentamethylcyclopentadienyl family that show bonded acetone molecules. The acetone and water ligands in **1a,b** are readily displaced by cresol, pyridine, and 4,4′-bipyridine. Similarly, acetone and water ligands are smoothly displaced by nitrate, giving precursors $(C_5Me_5)M(\eta^2\text{-}NO_3)(\eta^1\text{-}NO_3)$ (M = Rh, Ir) (**4a,b**) comparable to the well-known *cis*-protected square-planar metals $M(en)(NO_3)_2$ (M = Pt, Pd; en = ethylenediamine). The latter are systematically employed to construct supramolecular structures. The X-ray molecular structure of **4b** shows that the metal center is bonded to NO_3 anions rather than a coordinating solvent. Finally, the reactivity of **4a,b** toward pyridine was reported.

Experimental Section

General Procedures. All manipulations were carried out under an argon atmosphere using Schlenk techniques. Solvents were purified and dried prior to use by conventional distillation techniques. All reagents obtained from commercial sources were used without further purification. NMR spectra were recorded on Bruker AM 250 and 400 MHz instruments. NMR chemical shifts are reported in parts per million referenced to the residual solvent proton resonance [(^{1}H) CHD_2CN, 1.93; $(CHD_2)_2CO$, 2.05; $CHDCl_2$, 5.33; (^{13}C) CD_3CN, 1.29; CD_3COCD_3, 29.6; CD_2Cl_2, 53.73]. Infrared spectra were obtained on a Bio-rad Win-IR spectrometer version 2.04 A from samples prepared on KBr disks. Elemental analyses were performed by the Microanalytical Laboratory of the University of Paris VI.

Synthesis of $[(\eta^5\text{-}C_5Me_5)Rh(acetone)_2(H_2O)][BF_4]_2$ (1a). A solution of $AgBF_4$ (155 mg, 0.79 mmol) in acetone (10 mL) was added to $[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}Cl)Cl]_2$ (120 mg, 0.194 mmol) in acetone (20 mL), to give rapidly a white precipitate of AgCl. The reaction mixture was stirred for 15 min, and then the resulting orange-red solution was filtered into a dry Schlenk tube kept under argon. The filtrate was reduced to half-volume under vacuum, then to this orange-red solution was layered diethyl ether, and the system was left overnight in the refridgerator to crystallize. Orange-red crystals were obtained. Yield: 90% (182 mg). IR (KBr disk, cm^{-1}): ν(C=O) 1615, $\nu(BF_4^-)$ 1080. ^{1}H NMR [$(CD_3)_2CO$, 400 MHz]: δ 2.09 (s, $-CH_3$, coordinated acetone), 1.81 (s, η^5-C_5Me_5). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 2.12 (s, $-CH_3$, coordinated acetone), 1.53 (s, η^5-C_5Me_5). $^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$, 100.62 MHz]: δ (O=C, coordinated acetone, not observed), 96.06 [$C_5(CH_3)_5$, $-C{=}C-$], 30.44 (s, $-CH_3$, coordinated acetone) 8.98 [$C_5(CH_3)_5$, $-CH_3$]. (O=C, coordinated acetone, not observed). Due to **1a**'s instability, C, H analysis could not be done.

Synthesis of [(η^5-C_5Me_5)Ir(acetone)$_2$(H_2O)][BF_4]$_2$ (1b). The tris-solvated species **1b** was prepared in a manner similar to that of **1a**. **1b** was obtained as orange crystals. Yield: 90% (214 mg). IR (KBr disk, cm^{-1}): ν(C=O) 1615, $\nu(BF_4^-)$ 1083. ^{1}H NMR [$(CD_3)_2CO$, 400 MHz]: δ 2.11 (s, $-CH_3$, coordinated acetone), 1.71 (s, η^5-C_5Me_5). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 2.11 (s, $-CH_3$, coordinated acetone), 1.55(s, η^5-C_5Me_5). $^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$, 100.62 MHz]: δ (O=C, coordinated acetone, not observed), 94.56 [$C_5(CH_3)_5$, $-C{=}C-$], 30.44 (s, $-CH_3$, coordinated acetone) 8.55 [$C_5(CH_3)_5$, $-CH_3$] (O=C, coordinated acetone, not observed). Due to **1b**'s instability, C, H analysis could not be done.

Synthesis of [(η^5-C_5Me_5)Rh(η^1-(N)-C_6H_5N)$_3$][BF_4]$_2$ (2a). A 100 μL sample of distilled pyridine was added to a solution of **1a** (50 mg, 0.091 mmol) in CH_2Cl_2 (20 mL), to rapidly give a yellow solution. The reaction was allowed to proceed for 30 min, and then the solvent was reduced under vaccuum. Subsequent addition of diethyl ether provided a yellow precipitate in quantitative yield (57 mg). Compound **2a** was separated, washed several times with diethyl ether, and then dried under vaccum. **2a** was obtained as a yellow microcrystalline substance. IR (KBr disk, cm^{-1}): $\nu(BF_4^-)$ 1080. ^{1}H NMR [$(CD_3)_2CO$, 400 MHz]: δ 8.68 (d, H_o, 6H), 8.24 (t, H_p, 3H), 7.77 (t, H_m, 6H), 1.63 (s, 15H, η^5-C_5Me_5). $^{13}C\{^1H\}$ NMR [100.61 MHz, $(CD_3)_2CO$]: δ 154.09, 141.41, 128.88 (coordinated pyridine), 100.30 [d, J_{Rh-C} = 8 Hz, $C_5(CH_3)_5$, $-C{=}C-$], 8.59 [$C_5(CH_3)_5$, $-CH_3$]. Anal. Calcd for $C_{25}H_{30}N_3B_2F_8Rh$: C, 46.22; H, 4.62; N, 6.47. Found: C,46.10; H,4.43, N, 6,31.

Synthesis of [(η^5-C_5Me_5)Ir(η^1-(N)-C_6H_5N)$_3$][BF_4]$_2$ (2b). Compound **2b** was prepared in a fashion similar to that of **2a**. **2b** was obtained as a yellow microcrystalline solid in quantitative yield (55 mg). IR (KBr disk, cm^{-1}): $\nu(BF_4^-)$ 1080. ^{1}H NMR [$(CD_3)_2CO$, 400 MHz]: δ 8.75 (d, H_o, 6H), 8.28 (t, H_p, 3H), 7.79 (t, H_m, 6H), 1.55 (s, 15H, η^5-C_5Me_5). $^{13}C\{^1H\}$ NMR [100.61 MHz, $(CD_3)_2CO$]: δ 154.73, 141.76, 129.38 (coordinated pyridine), 92.39 [$C_5(CH_3)_5$, $-C{=}C-$], 8.15 [$C_5(CH_3)_5$, $-CH_3$]. Anal. Calcd for $C_{25}H_{30}N_3B_2F_8Ir$: C, 40.65; H, 4.06; N, 5.69. Found: C, 40.24; H, 3.95, N, 5.41.

Synthesis of (η^5-C_5Me_5)Rh(η^2-NO_3)(η^1-NO_3) (4a). To a Schlenk tube containing 275 mg (1.62 mmol) of $AgNO_3$ and 200 mg (0.32 mmol) of [(C_5Me_5)Rh(μ-Cl)Cl]$_2$ was added 20 mL of acetone, and the reaction mixture was stirrred for 1 h, during which the solution turned orange and a white precipitate was formed. The filtrate was separated, and the volume was reduced to half under vacuum. Addition of diethyl ether provided an orange microcrystalline material, which was isolated and dried under vaccuum. Yield: (quantitative) 230 mg. IR (KBr disk, cm^{-1}): $\nu(NO_3^-)$ 1523, 1278 (chelating bidentate), 1467, 1384 (unidentate).[14] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.76 (s, 15H, η^5-C_5Me_5). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 93.52 [d, J_{Rh-C} = 10 Hz, $C_5(CH_3)_5$, $-C{=}C-$], 9.36 [$C_5(CH_3)_5$, $-CH_3$]. Anal. Calcd for $C_{10}H_{15}RhN_2O_6$: C, 33.17; H, 4.17; N, 7.74. Found: C, 32.91; H, 3.95; N, 7.66

Synthesis of (η^5-C_5Me_5)Ir(η^2-NO_3)(η^1-NO_3) (4b). This complex was prepared in a fashion similar to that of **4a**. **4b** was obtained as a yellow microcrystalline solid. Yield: (quantitative) 220 mg. IR (KBr disk, cm^{-1}): $\nu(NO_3^-)$ 1550, 1273 (chelating bidentate), 1493, 1384 (unidentate).[14] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.69 (s, 15H, η^5-C_5Me_5). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 84.73 [s, $C_5(CH_3)_5$, $-C{=}C-$], 9.79 [$C_5(CH_3)_5$, $-CH_3$]. Anal. Calcld for $C_{10}H_{15}IrN_2O_6$: C, 26.61; H, 3.35; N, 6.21. Found: C, 26.31; H, 3.11; N, 6.49.

X-ray Crystal Structure Determination for 1a, 1b, 2b, and 4b. Suitable crystals of **1a** and **1b** were obtained using slow diffusion techniques from acetone/ether solution but keeping the system in a cold place, while those of **2b** and **4b** were obtained at room temperature by slow diffusion of ether into a saturated solution of the desired sample. The selected crystals of complexes **1a** and **1b** were mounted onto the top of a glass rod at −10 and −40 °C, respectively. As for **2b** and **4b** they were mounted at room temperature. Accurate cell dimensions and orientation matrix were obtained by least-squares refinements of 25 accurately centered reflections on a Nonius CAD4 diffractometer equipped with graphite-monochromated Mo Kα radiation. No significant variations were observed in the intensities of two checked reflections during data collection for **1b** (11%), **2b** (3.2%), and **4b** (4.9%); however, strong decay was observed for **1a** (75%). This decay was corrected according to standards. Complete crystallographic data and collection parameters for **1a** and **1b** are listed in Table 1. The data were corrected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS.[15] The structures of these compounds were refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms excluding the free BF_4^- anions. In **1b** one of the two BF_4^- anions was disordered and was modeled isotropically. Hydrogen atoms were introduced in calculated positions in the last refinements and were allocated an overall refinable isotropic thermal parameter. Fractional parameters, anisotropic thermal parameters, and all bond lengths and angles are given in the Supporting Information for complexes **1a**, **1b**, **2b**, and **4b**.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **1a**, **1b**, **2b**, and **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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