Molecular architecture *via* coordination: quasi-octahedral macrocycles of rhodium and iridium bearing a pentamethylcyclopentadienyl group

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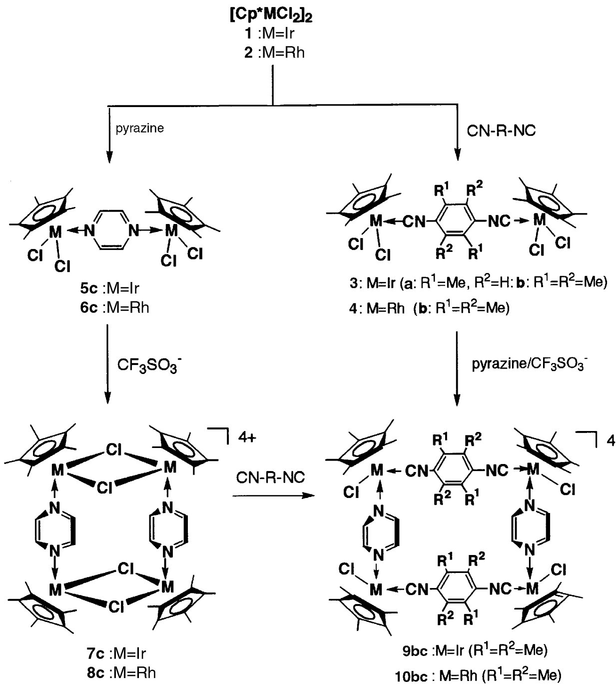
Reactions of $[Cp^*MCl_2]_2$ (M = Rh, Ir) with bidentate ligand (L = pyrazine; L′ = diisocyanide) gave $[Cp^*MCl_2(L\ or\ L')]_2$, which were converted into tetranuclear complexes $[Cp^*_2M_2Cl_2(L)(L')]_2\ (OTf)_4$ containing different ligands on treatment with Ag(OTf).

Metal-containing supramolecules and coordination polymers have attracted interest in recent years since there are many promising metal fragments which can be used for construction of novel supramolecular materials.[1] In particular, square planar complexes of platinum and palladium are attractive as building blocks which occupy vertices. For example, diphosphine and diamine derivatives as ligands in metallic building blocks have been used extensively by many groups.[2] We are interested in supramolecular complexes, based on quasi-octahedral geometries, bearing arene and cyclopentadienyl groups and their derivatives, since new types of supramolecular series would be developed by introduction of these organic moieties. Octahedral building blocks can be applied to form cubic or ladder-shaped structures. As our first report of this study, we report here, the stepwise assembly of tetranuclear rhodium and iridium supramolecules bearing pentamethylcyclopentadienyl and binary ligands. Complexes constructed here are novel because they contain 2-D architectures with two different ligand 'edges', *i.e.* molecular rectangles. Self-assembled supramolecules bearing pentamethylcyclopentadienyl groups, to our knowledge, have been reported only by Rauchfuss and coworkers;[3,4] $[Cp_4Cp^*_4Co_4Rh_4(CN)_{12}]^{4+}$, $[Cp^*_7Rh_7(CN)_{12}]^{2+}$ and $[Cp^*_7Rh_3Ir_4(CN)_{12}]^{2+}$ ($Cp^* = C_5Me_5$).

When bis[dicloro(pentamethylcyclopentadienyl)iridium] **1** was treated with 1,4-diisocyano-2,5-dimethylbenzene (**a**) or 1,4-diisocyano-2,3,4,5-tetramethylbenzene (**b**) in a 1 : 1 molar ratio at room temperature (Scheme 1), yellow crystals, formulated as $[Cp^*IrCl_2]_2[CN–R–NC]$ (**3a**: R = 2,5-$Me_2C_6H_2$; **3b**: R = 2,3,5,6-Me_4C_6) by FAB mass spectrometry, were formed in high yields.† Their IR spectra showed a strong band at *ca.* 2140 cm^{-1} owing to terminal isocyanide groups. In the ^1H NMR spectra two singlet resonances due to the Cp* and Me protons appeared at δ *ca.* 1.86 and 2.40. These spectroscopic data suggested dimeric structures for **3a** and **3b**, where the Ir centers are connected by a μ-diisocyanide ligand. X-Ray crystal analysis of **3a** confirmed the dimeric structure.‡ The Ir–C(11) and average Ir–Cl bond lengths are 1.96 and 2.401 Å, respectively, and the two Ir atoms are separated by 11.6 Å. The analogous rhodium compound $[Cp^*RhCl_2]_2[\mu\text{-}1,4\text{-}(NC)_2\text{-}2,3,5,6\text{-}Me_4C_6]$ **4b**, was prepared as orange crystals in 80% yield by the reaction of $[Cp^*RhCl_2]_2$ **2** with **b**.†

Treatment of **1** or **2** with pyrazine (**c**) also generated dinuclear complexes, $[(Cp^*MCl_2)_2(\mu\text{-}C_4H_4N_2)]$ (**5c**, M = Ir; **6c**, M = Rh), according to FAB mass spectrometry.† In the ^1H NMR spectra in dmso-d_6, two singlets appeared at δ *ca.* 1.62 and 8.65, due to the Cp* and pyrazine protons, respectively. When **6c** was reacted with AgOTf (Tf = CF_3SO_2) in a 1 : 2 ratio in CH_2Cl_2–MeCN at room temperature, reddish orange crystals of $[(Cp^*RhCl)_4(pyz)_2](OTf)_4$ **8c** (pyz = pyrazine) were produced, and FAB mass spectrometry showed a peak at *m/z* 1254 ([M + $1]^+$).† The ^1H NMR spectrum consists of two characteristic singlets at δ 1.61 and 8.65 in a 60 : 8 intensity ratio, suggesting a symmetric tetranuclear structure. Indeed, X-ray crystallographic analysis revealed that the complex cation has a rectangular structure bridged by four Cl atoms and pyrazine molecule with Rh···Rh separations of 3.68 and 7.02 Å (Fig. 1).‡ The crystal contains MeOH as crystal solvent. Both Rh(1)Rh(2)Cl(1)Cl(2) and pyrazine least-squares planes are perpendicular to the Rh(1)Rh*(1)Rh(2)Rh*(2) plane. The average Rh–N bond length is 2.413 Å. A tetranuclear iridium complex **7c** was obtained from **5c** and AgOTf in a similar manner to the rhodium analog.† The ^1H NMR spectrum showed two types of resonances for each of the Cp* and pyrazine ligands; at δ 1.58 and 1.74 for the former and at δ 8.84 and 8.97 for the latter, suggesting the presence of configurational isomers.



Scheme 1 Reactions of $[Cp^*MCl_2]_2$ (**1**: R = Ir and **2**: M = Rh) with pyrazine or isocyanides.

When μ-chloro-bridged complex **7c** was treated with 2 equiv. of **b**, the Cl bridges were replaced by **b** to produce yellow crystals formulated as $[(Cp^*IrCl)_4(pyz)_2\{1,4\text{-}(NC)_2\text{-}2,3,5,6\text{-}Me_4C_6\}_2](OTf)_4$ **9bc**.† This complex can also be obtained from the reaction between **3b** and pyrazine in the presence of Ag(OTf). In the IR spectrum, the CN band appeared at 2176 cm^{-1} while the ^1H NMR spectrum showed three singlets at δ 1.94, 2.42 and 8.65 in a 30 : 12 : 4 intensity ratio, due to Cp*, isocyanide and pyrazine protons, respectively. In addition, the

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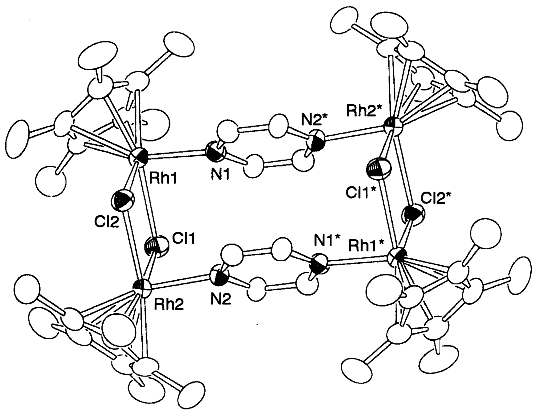

Fig. 1 Molecular structure of $[(Cp^*{}_4Rh_4Cl_4)(\mu\text{-}Cl)_4(\mu\text{-}pyz)_2](CF_3SO_3)_4$ **8c** (CF_3SO_3 anions omitted for clarity). Selected bond lengths (Å) and angles (°): Rh(1)–Cl(1) 2.466(3), Rh(1)–Cl(2) 2.467(2), Rh(1)–N(1) 2.133(7), Rh(2)–Cl(2) 2.474(3), Rh(2)–Cl(2) 2.459(2), Rh(2)–N(2) 2.153(8); Cl(1)–Rh(1)–Cl(2) 83.50(8), Cl(1)–Rh(1)–N(1) 88.0(2), Cl(2)–Rh(1)–N(1) 87.8(2), Cl(1)–Rh(2)–Cl(2) 83.47(8), Cl(1)–Rh(2)–N(2) 88.5(2), Cl(2)–Rh(2)–N(2) 88.5(2).

structure was determined by single crystal X-ray analysis (Fig. 2).‡ An asymmetric unit of the crystal of **9bc** consists of two halves of the molecules, each having a crystallographically imposed inversion center in the middle of the Ir···Ir* vector. Each iridium atom is surrounded by isocyanide, pyrazine, Cl and Cp*. The complex has a tetranuclear rectanglar structure with Ir···Ir* lengths of 6.986(1), 7.9145(9), 11.6459(9) and 11.668(1) Å. The dihedral angles between the Ir_4 plane and pyrazine are 49.44, 48.82° and those between Ir_4 plane and phenyl rings are 83.55, 83.58° and 75.75, 75.95°. The average Ir–C and Ir–Cl bond lengths are 1.97 and 2.388 Å, similar to those of **3a**. The average Ir–N bond length of 2.12 Å is somewhat shorter than that of **8c**. A rhodium analog **10bc** was obtained in 45% yield from the direct reaction of **4b** with pyrazine in the presence of AgOTf.†

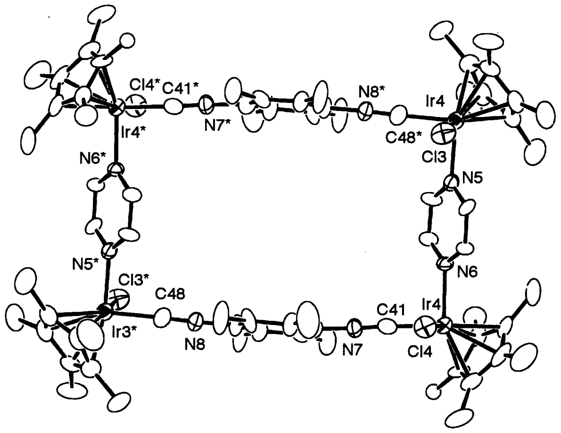

Fig. 2 Molecular structure of $[(Cp^*{}_4Ir_4Cl_4)\{\mu\text{-}1,4\text{-}(NC)_2\text{-}2,3,5,6\text{-}Me_4C_6\}_2(\mu\text{-}pyz)_2](CF_3SO_3)_4$ **9bc** (CF_3SO_3 anions omitted for clarity). Selected bond lengths (Å) and angles (°): Ir(1)–Cl(1) 2.379(5), Ir(1)–N(1) 2.12(1), Ir(1)–C(12) 1.92(2), C(12)–N(4) 1.18(2), Ir(2)–Cl(2) 2.368(5), Ir(2)–N(2) 2.11(1), Ir(2)–C(5) 1.96(2), C(5)–N(3) 1.14(2), Ir(3)–Cl(3) 2.408(5), Ir(3)–N(5) 2.11(1), Ir(3)–C(48) 1.98, C(48)–N(8) 1.14(2), Ir(4)–Cl(4) 2.395(4), Ir(4)–N(6) 2.12(1), Ir(4)–C(41) 1.98(2), C(41)–N(7) 1.13(2); Cl(1)–Ir(1)–N(1) 87.5(4), Cl(1)–Ir(1)–C(12) 86.7(6), N(1)–Ir(1)–C(12) 87.2(6), Cl(2)–Ir(2)–N(2) 86.5(4), Cl(2)–Ir(2)–C(5) 87.7(5), N(2)–Ir(2)–C(5) 90.8(6), Cl(3)–Ir(3)–N(5) 86.0(4), Cl(3)–Ir(3)–C(48) 88.8(5), N(5)–Ir(3)–C(48) 90.5(6), Cl(4)–Ir(4)–N(6) 86.0(4), Cl(4)–Ir(4)–C(41) 87.8(5), N(6)–Ir(4)–C(41) 93.2(6).

Studies on the self-assembly of cubic or ladder-shaped complexes by this synthetic methodology and the use of molecular materials are now in progress.

Notes and references

† Satisfactory analytical data were obtained for new complexes: **3a** (yellow, 75%): IR(Nujol): 2137 cm^{-1}. $\delta_H(CDCl_3)$: 1.86 (s, Cp*, 30H), 2.42 (s, Me, 6H), 7.29 (s, Ph, 2H). Calc. for $C_{30}H_{38}N_2Cl_4Ir_2$: C, 37.81; H, 4.02; N, 2.94. Found: C, 37.26; H, 4.04; N, 2.97%. **3b** (orange, 86%): FAB mass: *m/z* 981 (M + 1). IR(Nujol): 2150 cm^{-1}. $\delta_H(CDCl_3)$: 1.86 (s, Cp*, 30H), 2.39 (s, Me, 12H). Calc. for $C_{32}H_{42}N_2Cl_4Ir_2$: C, 39.18; H, 4.32; N, 2.86. Found: C, 38.67; H, 4.26; N, 2.95%. **4b** (orange, 73%): FAB mass: *m/z* 802 (M). IR(Nujol): 2176 cm^{-1}. $\delta_H(CDCl_3)$: 1.83 (s, Cp*, 30H), 2.40 (s, Me, 12H). Calc. for $C_{32}H_{42}N_2Cl_4Rh_2$: C, 47.90; H, 5.28; N, 3.49. Found: C, 48.26; H, 5.46; N, 4.24%.

5c (yellow, 83%): δ_H(dmso-d_6): 1.62 (s, Cp*, 60H), 8.65 (s, pyz, 8H). Calc. for $C_{24}H_{34}N_2Cl_4Ir_2$: C, 32.88; H, 3.91; N, 3.20. Found: C, 32.51; H, 3.81; N, 3.27%. **6c** (orange, 82%): δ_H(dmso-d_6): 1.61 (s, Cp*, 30H), 8.66 (s, pyz, 4H). Calc. for $C_{24}H_{34}N_2Cl_4Rh_2H_2O$: C, 40.25; H, 5.07; N, 3.91. Found: C, 40.29; H, 4.84; N, 4.04%. **7c** (yellow, 64%): δ_H(dmso-d_6): 1.58 (s, Cp*, 30H), 1.74 (s, Cp*, 30H), 2.05 (s, pyz, 12H), 8.84 (s, pyz, 4H), 8.97 (s, pyz, 4H). Calc. for $C_{60}H_{80}N_8Cl_4F_{12}O_{12}S_4Ir_4$: C, 30.43; H, 3.23; N, 4.73. Found: C, 30.24; H, 3.48; N, 4.59%. **8c** (reddish orange, 67%): δ_H(dmso-d_6): 1.61 (s, Cp*, 60H), 8.65 (s, pyz, 8H). Calc. for $C_{52}H_{68}N_4Cl_4F_{12}O_{12}S_4Rh_2$: C, 33.75; H, 3.70; N, 3.03. Found: C, 33.55; H, 3.67; N, 3.19%.

9bc (yellow, 65%): IR(Nujol): 2176 cm^{-1} (N≡C). δ_H(dmso-d_6): 1.94 (s, Cp*, 60H), 2.42 (s, Me, 24H), 8.66 (s, pyz, 8H). Calc. for $C_{76}H_{92}N_8Cl_4F_{12}O_{12}S_4Ir_4$: C, 34.78; H, 3.53; N, 4.27. Found: C, 34.87; H, 3.71; N, 4.61%.

10bc (orange, 49%): IR (nujol): 2186 cm^{-1} (N≡C). δ_H(dmso-d_6): 1.88 (s, Cp*, 60H), 2.43 (s, Me, 24H), 8.65 (s, pyz, 8H). Calc. for $C_{76}H_{92}N_8Cl_{10}F_{12}O_{12}S_4Rh_4$: C, 38.35; H, 3.99; N, 4.53. Found: C, 38.30; H, 4.39; N, 4.20%.

‡ *Crystal data*: for **3a**: $C_{30}H_{38}N_2Cl_4Ir_2$, M = 952.9, monoclinic, space group $P2_1/n$ (no. 14), a = 7.54(1), b = 16.571(7), c = 12.800(7) Å, β = 95.69(7)°, V = 1590(2) Å^3, D_c = 1.989 g cm^{-3} (Z = 2) at 27 °C, μ = 87.4 cm^{-1}; $R1$ = 0.041 and R_w = 0.111.

For **8c**: $C_{54}H_{76}N_4O_{14}S_4F_{12}Cl_4Rh_4$, M = 1914.9, monoclinic, space group $P2_1/n$ (no. 14), a = 13.245(7), b = 20.417(6), c = 14.419(4) Å, β = 108.31(2)°, V = 3701(1) Å^3, D_c = 1.718 g cm^{-3} (Z = 2) at 28 °C, μ = 12.20 cm^{-1}; $R1$ = 0.050 and R_w = 0.100.

For **9bc**: $C_{78}H_{98}N_8Cl_4F_{12}O_{14}S_4Ir_4$, M = 2638.6, triclinic, space group $P\bar{1}$ (no. 2), a = 13.1339(9), b = 16.203(1), c = 26.309(2) Å, α = 73.953(2), β = 87.9327(7), γ = 81.7369(6)°, V = 5324.7(6) Å^3, D_c = 1.646 g cm^{-3} (Z = 2) at −90 °C, μ = 52.1 cm^{-1}; $R1$ = 0.086 and R_w = 0.089.

CCDC 182/1743. See http://www.rsc.org/suppdata/cc/b0/b003416i/ for crystallographic files in .cif format.

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