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η^3-, η^4- and η^6-Co-ordination complexes of the weakly co-ordinating anion tetrakis[3,5-bis(trifluoromethyl)phenyl]borate

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Single-crystal X-ray diffraction has established η^3-, η^4- and η^6-co-ordination of the anion tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB) in the complexes Ag(TFPB)(2,2′-bipy) (2,2′-bipy = 2,2′-bipyridine), Ag(TFPB)(1,2-$C_6H_4I_2$) and Rh(TFPB)(cod) (cod = cycloocta-1,5-diene) respectively.

Very weakly nucleophilic anions are of interest for a variety of applications which require the ‘stabilization’ of highly reactive cationic species.[1,2] Particularly useful in this regard is the anion tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB)[3,4] and a recent example of its use is the isolation and structural characterization of *trans*-[PtH(η^1-ClCH$_2$Cl) (PPr$^i_3$)][TFPB] containing the exceptionally weakly co-ordinating dichloromethane ligand.[5] We here report the synthesis and structural characterization by single-crystal X-ray diffraction of two silver and one rhodium compound of the type $M\{B[3,5\text{-}C_6H_3(CF_3)_2]_4\}L_2$ which are the first examples of complexes in which the TFPB is co-ordinated to the metal.[†]

The silver complexes Ag(TFPB)L_2 [L_2 = 1,2-$C_6H_4I_2$ **1**, 2,2′-bipyridine **2** (2,2′-bipy) and 1,2-bis(diphenylphosphino)ethane (dppe)] were readily obtained as white crystalline products according to equation (1).[‡]

$$AgPF_6 + L_2 + Na[TFPB] \xrightarrow{CH_2Cl_2} Ag(TFPB)L_2 + NaPF_6\downarrow \quad (1)$$

The rhodium complex Rh(TFPB)(cod) **3** (cod = cycloocta-1,5-diene) was similarly obtained from the reaction of [RhCl(cod)]$_2$ with stoichiometric amounts of $AgPF_6$ and Na[TFPB] in CH_2Cl_2 solution. The molecular structures of complexes **1**–**3** as determined by single-crystal X-ray diffraction, together with selected bond lengths are shown in Figs. 1–3. In the silver complexes **1** and **2** the TFPB ligand adopts bidentate bonding modes. In **1** two of the aryl rings are each η^2-bonded to silver *via* the *ipso* carbon and an adjacent *ortho* carbon in a fairly symmetrical manner. The 1,2-diiodobenzene ligand also functions as a reasonably symmetrical bidentate ligand in contrast to the unsymmetrical bonding modes observed in [Ag(1,2-$C_6H_4I_2$)$_3$]PF$_6$ and [Ag(NO$_3$)(1,2-$C_6H_4I_2$)]$_n$.[7] In the 2,2′-bipyridine complex **2** the TFPB ligand exhibits a less symmetrical η^3-bonding mode comprized of an η^2-interaction with an *ipso* and *ortho* carbon atom at one aromatic ring together with a weaker η^1-interaction with the *ipso* carbon of a second aromatic ring. The Ag–C bond distances for the η^2-interaction in **2** [2.424(3) and 2.493(3) Å] are significantly shorter than the corresponding distances in **1** [2.507(3)–2.686(3) Å]. The *ipso* carbon–silver distance of these η^2-interactions is the shorter distance in **2** but the longer one in **1**. The change in co-ordination geometry of the TFPB ligand on going from **1** to **2** may well be a consequence of the increased steric requirements of the 2,2′-bipyridine ligand *vis-à-vis* the 1,2-diiodobenzene ligand. In this regard it is noteworthy that the single-crystal X-ray diffraction studies of the complex Ag(TFPB)(dppe) have shown it to have the ionic structure [Ag$_2$(dppe)$_2$][TFPB]$_2$.[8] Presumably the steric size of the ligand now precludes co-

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[†] Crystal data for complex **1**. $C_{38}H_{52}AgBF_{24}I_2$, M = 1300.99, monoclinic, a = 10.3372(11), b = 17.8488(12), c = 22.607(2) Å, β = 94.214(8)°, U = 4159.8(6) Å^3, T = 173(2) K, space group $P2_1/c$ (no. 14), graphite-monochromated Mo-Kα radiation, λ = 0.71071 Å, Z = 4, D_c = 2.077 g cm^{-1}, F(000) = 2472, colourless fragment with dimensions 0.46 × 0.43 × 0.38, μ = 21.07 cm^{-1}, no absorption correction; Siemens P4 diffractometer using ω scan mode, 2θ = 52.00°, h −10 to 12, k −7 to 22, l −27 to 27, no intensity decay from three standards measured every 97 reflections; 8577 measured, 8111 unique (R_{int} = 0.020). The structure was solved and refined (on F^2 using all data with negative intensities included) using SHELXTL.[6] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as riding atoms. The final weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.0592P)^2 + 1.27P]$ where $P = (F_o^2 + 2F_c^2)/3$. The final $R1[I > 2\sigma(I)]$ = 0.0343 (for 6686 reflections) and $wR2$ (all data) = 0.0997 for 597 parameters, goodness of fit = 1.042. Maximum and minimum peaks in final Fourier-difference were 0.704 and −0.822 e Å^{-3}.

Crystal data for complex **2**. $C_{42}H_{20}AgBF_{24}N_2{\cdot}CH_2Cl_2$, M = 1212.21, monoclinic, a = 12.3777(14), b = 17.334(2), c = 21.539(2) Å, β = 97.695(9)°, U = 4579.6(8) Å^3, T = 173(2) K, space group $P2_1/n$ (no. 14), graphite-monochromated Mo-Kα radiation, λ = 0.71071 Å, Z = 4, D_c = 1.758 g cm^{-1}, F(000) = 2384, colourless fragment with dimensions 0.43 × 0.36 × 0.28, μ = 6.91 cm^{-1}, absorption correction using ψ-scan data (minimum and maximum transmission 0.2570 and 0.9495); Siemens P4 diffractometer using ω-scan mode, 2θ = 50.00°, h 0 to 14, k 0 to 18, l −25 to 25, no intensity decay from three standards measured every 97 reflections; 8264 measured, 7886 unique (R_{int} = 0.026). The structure was solved and refined (on F^2 using all data with negative intensities included) using SHELXTL.[6] All non-hydrogen atoms were refined anistropically and hydrogen atoms were treated as riding atoms. The final weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.0708P)^2 + 2.49P]$ where $P = (F_o^2 + 2F_c^2)/3$. The final $R1[I > 2\sigma(I)]$ = 0.0469 (for 6028 reflections) and $wR2$ (all data) = 0.1329 for 664 parameters, goodness of fit = 1.042. Maximum and minimum peaks in final Fourier-difference were 0.705 and −0.835 e Å^{-3}. The F atoms of two CF$_3$ groups are disordered over two sites. The structure contains one disordered CH_2Cl_2 molecule.

Crystal data for complex **3**. $C_{40}H_{24}BF_{24}Rh{\cdot}0.87CH_2Cl_2$, M = 1148.11, monoclinic, a = 13.542(2), b = 24.403(4), c = 13.840(3) Å, β = 90.06(1)°, U = 4573.9(13) Å^3, T = 173(2) K, space group $P2_1/n$ (no. 14), graphite-monochromated Mo-Kα radiation, λ = 0.71071 Å, Z = 4, D_c = 1.667 g cm^{-1}, F(000) = 2266, colourless fragment with dimensions 0.23 × 0.32 × 0.34, μ = 6.03 cm^{-1}, absorption correction using ψ-scan data (minimum and maximum transmission 0.6418 and 0.9562); Siemens P4 diffractometer using ω-scan mode, 2θ = 50.00°, h 0 to 16, k 0 to 29, l −16 to 16, no intensity decay from three standards measured every 97 reflections; 8264 measured, 7886 unique (R_{int} = 0.026). The structure was solved and refined (on F^2 using all data with negative intensities included) using SHELXTL.[6] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as riding atoms. The final weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.0424P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. The final $R1[I > 2\sigma(I)]$ = 0.0467 (for 5725 reflections) and $wR2$ (all data) = 0.1315 for 652 parameters, goodness of fit = 0.959. Maximum and minimum peaks in final Fourier-difference were 0.902 and −0.868 e Å^{-3}. The F atoms of one of the CF$_3$ groups are disordered over two sites. The structure contains a partial occupancy, disordered CH_2Cl_2 molecule. CCDC reference number 186/760.

[‡] Satisfactory elemental analyses were obtained for complexes **1** and **2** (Found for **1**: C, 34.85; H, 3.94; I, 19.84. Calc. for $C_{38}H_{52}AgBF_{24}I_2$: C, 35.08; H, 4.03; I, 19.51%. Found for **2**: C, 42.30; H, 1.67; N, 2.05. Calc. for $C_{42}H_{20}AgBF_{24}N_2{\cdot}CH_2Cl_2$: C, 42.61; H, 1.83; N, 2.31%). Complex **3** was not very stable. Solutions of **3** in CH_2Cl_2 at 20 °C decomposed to unidentified products in a matter of hours.

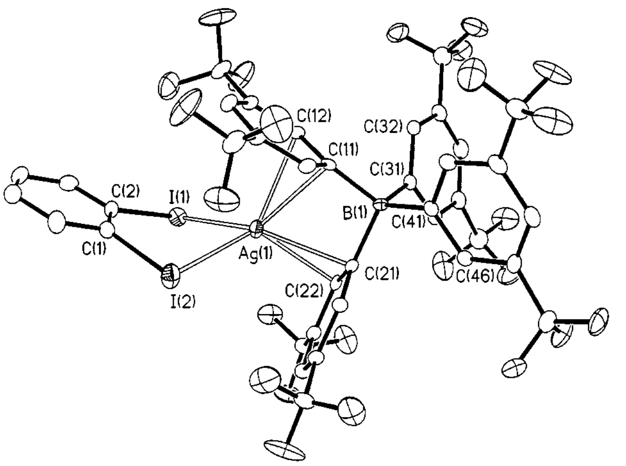

Fig. 1 Molecular structure of the complex Ag(η^4-TFPB)($C_6H_4I_2$) **1**. Selected bond lengths (Å): Ag(1)–I(1) 2.7984(4), Ag(1)–I(2) 2.8080(5), Ag(1)–C(11) 2.686(3), Ag(1)-C(12) 2.581(3), Ag(1)–C(21) 2.571(3), Ag(1)–C(22) 2.507(3)

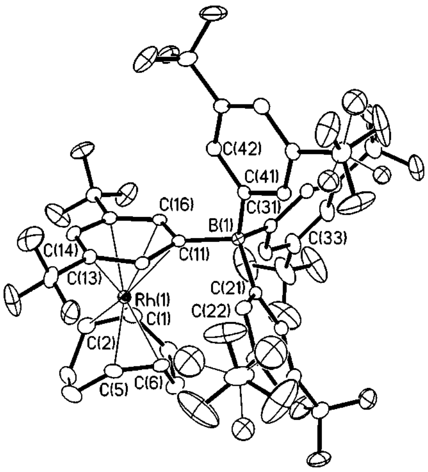

Fig. 3 Molecular structure of the complex Rh(η^6-TFPB)(cod) **3**. Selected bond lengths (Å): Rh(1)–C(11) through to Rh(1)–C(16) 2.430(4), 2.251(4), 2.297(4), 2.324(4), 2.256(4), 2.253(4)

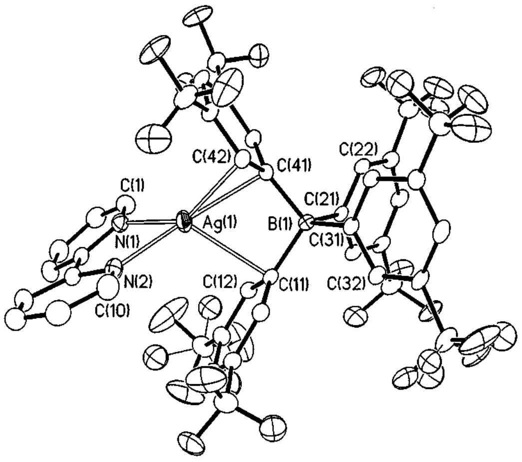

Fig. 2 Molecular structure of the complex Ag(η^3-TFPB)(2,2′-bipy) **2**. Selected bond lengths (Å): Ag(1)–C(11) 2.640(3), Ag(1)–C(41) 2.424(3), Ag(1)–C(42) 2.493(3), Ag(1)–N(1) 2.292(3), Ag(1)–N(2) 2.281(3)

ordination of the TFPB anion. In the rhodium complex **3** the TFPB co-ordinates *via* an η^6-interaction with one of the aromatic rings in a manner that is similar to that observed in several η^6-BPh_4 rhodium complexes.[9]

These studies indicate that the very poor co-ordinating property of the TFPB anion is primarily steric in origin and that metal complexes with two available co-ordination sites and complementary ligands with small steric profiles may result in co-ordination of the TFPB anion.

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