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Synthesis, Crystal Structures and Redox Properties of Mixed-Sandwich Complexes of Ruthenium(II) with Cyclopentadienyl and Tris(pyrazolyl)methane Ligands

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New mixed-sandwich ruthenium(II) complexes have been prepared by treatment of either [RuCp(acn)$_3$][PF$_6$] or [RuCp*(acn)$_3$][PF$_6$] (Cp = η^5-cyclopentadienyl; Cp* = η^5-pentamethylcyclopentadienyl, acn = CH$_3$CN) with tris(pyrazolyl)methane (^{H}Tpm) and tris(3,5-dimethylpyrazolyl)methane (^{Me}Tpm), respectively. [RuCp(^{H}Tpm)][PF$_6$] (**1**), [RuCp*(^{H}Tpm)][PF$_6$] (**2**) and [RuCp(^{Me}Tpm)][PF$_6$] (**3**) have been examined by single-crystal X-ray diffraction (**1**, **2**) and 2D NMR experiments, which reveal discrete units of cationic mixed-sandwich complexes of the composition [RuCp$^{(*)}$(^{R}Tpm)]$^+$ featuring η^5-cyclopentadienyl and κ^3N-coordinated ^{R}Tpm ligands. The air-sensitive salt [RuCp*(acn)(^{Me}Tpm)][PF$_6$] (**4**) exhibits a κ^2N-coordinated ^{Me}Tpm and one remaining acetonitrile ligand, presumably due to steric interactions between the sterically more bulky Cp* and ^{Me}Tpm ligands. Cyclic voltammetric studies of the symmetric mixed-sandwich complexes **1**–**3** in acetonitrile show quasi-reversible oxidation processes centred at $E^0{}_{1/2}$ = +0.38 (**1**), +0.15 V (**2**) and +0.35 V (**3**) vs. Fc/Fc$^+$. These values are mainly affected by the different nature of the Cp ligands; the differently substituted ^{R}Tpm entities have very little influence.

Introduction

Tris(pyrazolyl)methane ligands (^{R}Tpm) have received a great deal of attention since their introduction by Trofimenko in the late 1960s.[1] Recent improvements in the synthesis of ring-substituted tris(pyrazolyl)methane derivatives by Reger et al.[2] have provided a suitable entry point for a fruitful coordination chemistry, which has been summarised in two recent review articles.[3] Several "sandwich"[4] like transition metal complexes of the general formula [M(^{R}Tpm)$_2$]$^{n+}$ have been published.[3] Surprisingly, only a limited number of "mixed-sandwich" complexes of the type [MCp$^{(*)}$(^{R}Tpm)]$^{(n-1)+}$ featuring η^5-cyclopentadienyl and κ^3N-coordinated ^{R}Tpm ligands are known (Scheme 1).

The first mixed-sandwich complexes were reported by O'Sullivan and Lalor in 1973.[5] The complex salt [CoCp*(^{H}Tpm)](I)$_2$ was obtained by reaction of [CoCp*(CO)I$_2$] with ^{H}Tpm, and the closely related Rh^{III} complex [RhCp*(^{H}Tpm)][PF$_6$]$_2$ by treatment of [{RhCp*Cl$_2$}$_2$] with ^{H}Tpm. Recently, O'Hare and coworkers reported the synthesis of a series of mixed-sandwich complexes of cyclopentadienyl and ^{H}Tpm or tris(pyrazolyl)hydroborate (Tp) ligands, respectively.[6] The Co^{III} salt [CoCp(^{H}Tpm)][PF$_6$]$_2$ ($E^0{}_{1/2}$ = –0.30 V vs. Fc/Fc$^+$) can be reduced with [Cp$_2$Co] to yield the Co^{II} species [CoCp(^{H}Tpm)][PF$_6$], partially contaminated with [Cp$_2$Co][PF$_6$]. The corresponding iron(II) complex [FeCp*(^{H}Tpm)][PF$_6$] could be obtained by reaction of the ^{H}Tpm ligand with [FeCp*(acn)$_3$][PF$_6$] (acn = CH$_3$CN) but turned out to be unstable in solution.[6]

In order to probe the accessibility and stability of this type of complex, we focused on the synthesis of the analogous Ru^{II} complexes, which, much to our surprise, were not known in the literature. Only some closely related, neutral poly(pyrazolyl)borate complexes [RuCp$^{(*)}$(Tp^{R})] had been reported previously.[7] In this contribution we present a straightforward procedure for the preparation of various mixed-sandwich complexes of Ru^{II} consisting of cyclopentadienyl or pentamethylcyclopentadienyl (Cp or Cp*) and a tris(pyrazolyl)methane ligand (^{H}Tpm or ^{Me}Tpm). We are interested in this type of complex because they are synthetically valuable precursor compounds for the synthesis of novel zwitterionic mixed-sandwich metal complexes of tris(pyrazolyl)methanides [^{R}Tpmd][8] – a meanwhile well-established class of multifunctional ligands comprising dual functionality, which can either seperately or simultaneously act as κ^1C- or κ^3N-donor.[9]

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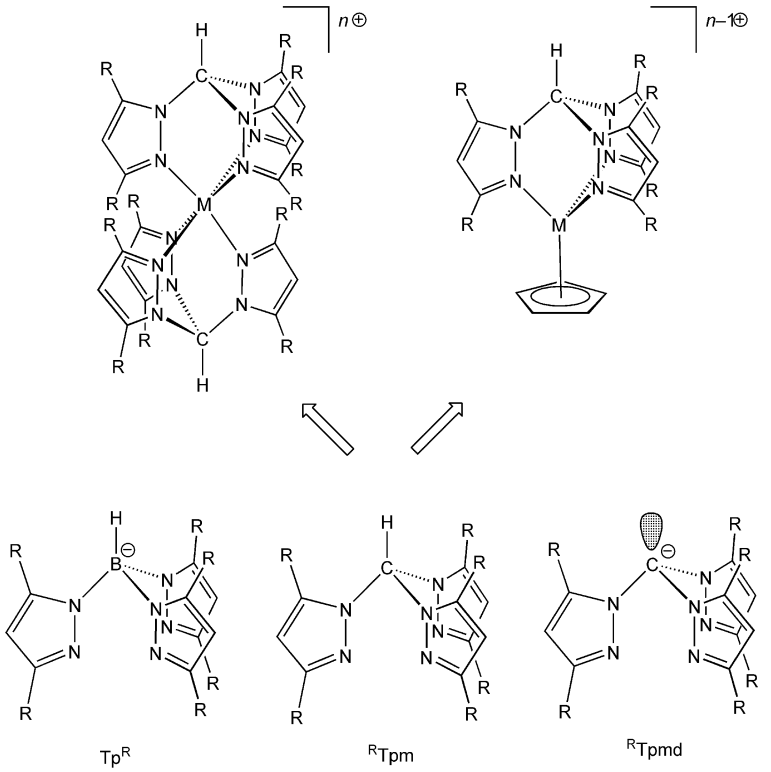


Scheme 1. Schematic drawing of common "sandwich" $[M(^{R}Tpm)_2]^{n+}$ and comparably rare "mixed-sandwich" $[MCp^{(*)}(^{R}Tpm)]^{(n-1)+}$ metal complexes of neutral tris(pyrazolyl)methane ligands (^{R}Tpm); anionic analogues of the latter: tris(pyrazolyl)hydroborate (Tp^{R}) and tris(pyrazolyl)methanides (^{R}Tpmd).

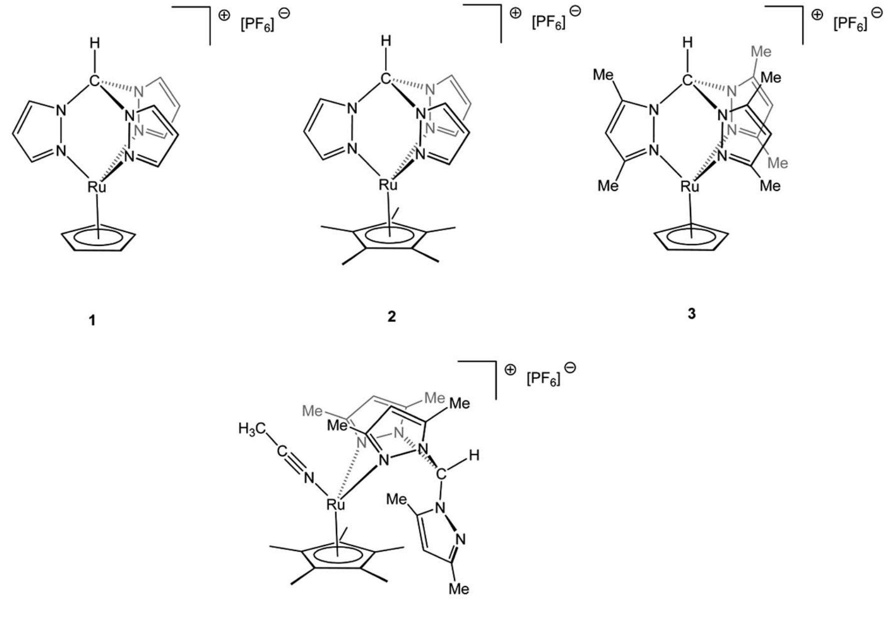
Results and Discussion

Synthesis

We chose the acetonitrile salts $[RuCp^{(*)}(acn)_3][PF_6]$ [$Cp^{(*)}$ = Cp* and Cp] as suitable starting materials to introduce $[Ru^{II}Cp^{(*)}]^+$ moieties into the desired complexes. These compounds are readily available following established literature procedures.[10,11] In most cases, replacement of the three acetonitrile ligands is easily achieved by simply treating the starting materials with the tripodal ^{R}Tpm ligands (R = Me or H; Scheme 2). For instance, the complex $[RuCp(^{H}Tpm)][PF_6]$ (**1**) was obtained by treating $[RuCp(acn)_3][PF_6]$ with ^{H}Tpm in acetonitrile.

The first reactions in this series were performed in CH_2Cl_2, but the formation of insoluble by-products and low yields meant our focus turned to polar solvents such as thf and acetonitrile. Recrystallisation of the crude product from acetonitrile/diethyl ether afforded analytically pure and crystalline **1** in 91% yield. The Cp* derivative $[RuCp^*(^{H}Tpm)][PF_6]$ (**2**) precipitates during the analogous reaction of $[RuCp^*(acn)_3][PF_6]$ with ^{H}Tpm in thf. Likewise, the corresponding complex $[RuCp(^{Me}Tpm)][PF_6]$ (**3**), which contains the hexamethyl-substituted ^{Me}Tpm ligand, is also insoluble in thf. The target compounds can thus easily be isolated by filtration and subsequent washing with thf in analytically pure quality and good to very good yields [56% (**2**), 86% (**3**)]. Only the acetonitrile adduct $[RuCp^*(acn)(^{Me}Tpm)][PF_6]$ (**4**) could obtained in very low and non-constant isolated yield, and with varying analytical purity, from the reaction between the sterically more crowded starting materials, namely $[RuCp^*(acn)_3][PF_6]$ and ^{Me}Tpm. All efforts to improve the yield or the synthetic protocol failed. For example, the use of different solvents (acetone, acetonitrile, thf) and prolonged reaction times showed no improvements. Furthermore, the remaining acetonitrile donor ligand in **4** cannot be removed in vacuo or by prolonged heating of the reaction mixture in dichloroethane. The latter procedure gave only decomposition products. Yellow solutions of **4** in various solvents are highly sensitive to oxygen and/or moisture, which becomes immediately apparent by the colour change of the solution from yellow to deep red when exposed to air. By contrast, compounds **1** to **3**, which are yellow solids and form deep orange crystals when recrystallised from acetonitrile and diethyl ether, are all thermally stable (m.p./dec. above 300 °C) and are not sensitive to air. The solution UV/Vis spectra of these complexes in acetonitrile show characteristic absorptions. While we detected a broad shoulder around λ = 370 nm for the ^{H}Tpm complexes **1** and **2**, a bathochromically shifted, well-defined maximum at λ_{max} = 382 nm (ε = 1597 L mol^{-1} cm^{-1}) was observed for the ^{Me}Tpm complex **3** (see Supporting Information).

The highly symmetrical complexes **1**–**3** give simple signal sets in their ^{1}H and ^{13}C NMR spectra, consistent with three equivalent pyrazolyl rings and an unhindered rotation of the $Cp^{(*)}$ ring on the NMR time scale. The precise assignments of the ^{1}H and ^{13}C NMR resonance signals were carried out on the basis of various 2D NMR experiments



1 2 3

4

Scheme 2. Compilation of the complexes investigated in this contribution: κ^3*N*- vs. κ^2*N*-coordinated ^{R}Tpm ligands in the mixed-sandwich compounds **1**–**4**.

(HMQC, HMBC or NOESY). In particular, the NOEs between the apical C*H* moiety and the protons (or methyl groups) in the 5-position of the pz ring, and between the Cp$^{H/Me}$ ring protons and the corresponding protons (or methyl groups) in the 3-position, are powerful tools for corroborating the preservation of the mixed-sandwich structure in solution. For a typical example (**3**) see Figure 1.

The NMR spectrum of complex **4** differs from those mentioned above as the proton resonances in the ^{1}H NMR spectrum are considerably broadened, which is indicative of a fluxional process in solution. In [D$_8$]THF, the resonances appear at δ = 7.61 (CH$_{apical}$), 6.24 ($W_{1/2}$ = 40 Hz, CH$_{pz}$), 2.46 ($W_{1/2}$ = 85 Hz, 3,5-Me$_2$pz) and 1.35 ppm ($W_{1/2}$ = 16 Hz, Cp*). Furthermore, a singlet for one additional acetonitrile molecule is present at a chemical shift of δ = 2.29 ppm. The same set of broadened signals, although with slightly different chemical shifts, was observed in CD$_2$Cl$_2$ (see Experimental Section). These NMR findings are in agreement with a fluxional κ^2*N*-coordination of the ^{Me}Tpm ligand, which means that the coordinated and uncoordinated pz nitrogen donors are in exchange in solution and that the remaining coordination site around ruthenium is occupied by one acetonitrile donor molecule.[12] This solution behaviour of **4** contrasts the findings of Mann et al. for the related complex [Ru(CO)Cp(Tp^{Me})], which also contains a κ^2*N*-coordinated Tp^R ligand.[7a] In this case, distinct

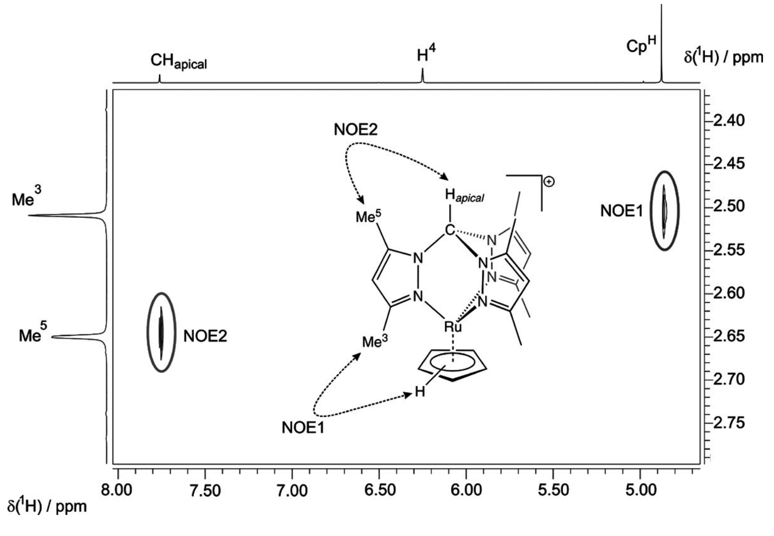


Figure 1. Section of the ^{1}H NOESY NMR spectrum of [RuCp(^{Me}Tpm)][PF$_6$] (**3**; 400.1 MHz, 298 K, [D$_6$]acetone, mixing time 300 ms). Me^3 and Me^5 denote the methyl groups in the positions 3 and 5 of the pz ring, respectively.

resonances for the coordinated and uncoordinated pz ligands were observed in the ^{1}H NMR spectrum at room temperature.

Molecular Structures

The crystal structure determination of the ^{H}Tpm complexes **1** and **2** (Figure 2) confirmed the formation and preservation of the mononuclear complex salts in the solid state (space group *Cmca* for **1** and $P\bar{1}$ for **2**).[13] Table 1 summarises and compares relevant structural parameters. The single crystals obtained for complex **3** were only of poor quality; all attempts to improve their quality and/or size failed. The ruthenium cation in **1** and **2** is coordinated by three pyrazole nitrogen atoms (κ^3N-^{R}Tpm) and one cyclopentadienyl anion (η^5-Cp$^{(*)}$). The same coordination environment around ruthenium is found in the corresponding Tp^{R} complexes [RuCp$^{(*)}$(Tp^{R})].[7] Crystallographically characterised ^{R}Tpm analogues, however, are only available for the cobalt salts mentioned above.[6]

Both mixed-sandwich complexes adopt a "staggered" arrangement of both ligand entities. While complex **1** contains a crystallographic mirror plane, the analogue **2** is slightly distorted from an ideal C_s-symmetric structure. The torsion of the Cp* ring consisting of an intrinsic fivefold symmetry with respect to the ^{H}Tpm ligand (C_3 axis) in **2** can be seen from the top views of both complexes in Figure 2. The mean Ru–N distances of 211.1 (**1**) and 214.5 pm (**2**) are similar to the average Ru–N distance found for the Tp complex [RuCp$^{(*)}$(Tp^{R})] (212.8 pm).[7] The Ru–N distances are slightly longer in **2** than in **1**, presumably due to steric interactions. The distances of the Cp$^{(*)}$ centroid (Cp$_{cent}$) to the Ru atom (**1**: 176.4 pm; **2**: 178.2 pm) resemble

Table 1. Selected bond lengths [pm] and angles [°] for **1**, **2**, and **4** (Cp$_{cent}$ denotes the centroid of the cyclopentadienyl ligand; N$_{cent}$ denotes the centroid of the plane spanned by the three nitrogen atoms coordinated to Ru).

Value	1	2	4
Ru1–N2	211.5(3)	215.4(3)	217.5(8)
Ru1–N4	210.3(4)	213.4(3)	217.0(9)
Ru1–N6[a]	211.5(3)	214.8(3)	–
Ru1–N99	–	–	207.8(9)
Ru1–Cp$_{cent}$	176.4	178.2	180.4
C1···Ru1	316.6	320.5	346.2
N2–Ru1–N4	83.1(1)	82.8(1)	83.1(3)
N2–Ru1–N6[a]	81.9(2)	81.5(1)	–
N4–Ru1–N6[a]	83.1(1)	80.8(1)	–
N2–Ru1–N99	–	–	83.2(3)
N4–Ru1–N99	–	–	83.2(3)
Cp$_{cent}$–Ru1–N2	130.4	130.4	132.1
Cp$_{cent}$–Ru1–N4	130.1	130.7	132.0
Cp$_{cent}$–Ru1–N6[a]	130.4	131.7	–
Cp$_{cent}$–Ru1–N99	–	–	125.6
Cp$_{cent}$–Ru1···C1	179.8	179.0	132.4
C1–N–N–Ru1[b]	0.6, 0, 0.6	1.5, 3.7, 2.7	5.1, 10.3
N···N (mean)[c]	278.9	280.5	288.1
N$_{cent}$···Ru1	136.6	140.6	–
N$_{cent}$···C1	180.1	179.9	–

[a] N2′ for **1**. [b] Absolute value of the torsion angle. [c] Average distance between the nitrogen atoms coordinated to Ru, i.e. nitrogen atoms of κ^3N-^{H}Tpm for **1** and **2** and those of κ^2N-^{Me}Tpm and acetonitrile for **4**.

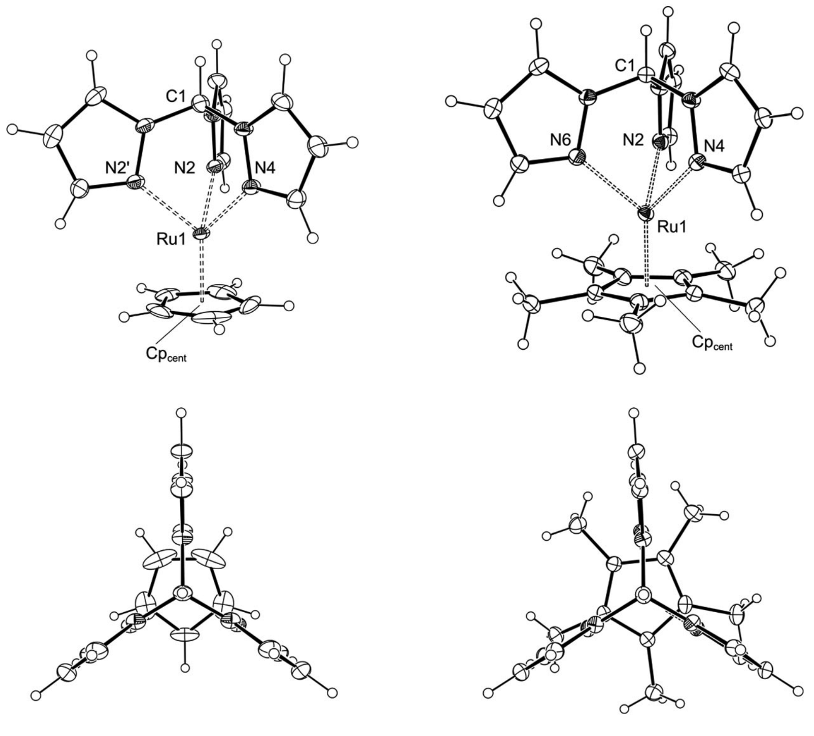


Figure 2. Molecular structures (side and top views) for [RuCp(^{H}Tpm)][PF$_6$] (**1**; left) and [RuCp*(^{H}Tpm)][PF$_6$] (**2**; right). Displacement ellipsoids are drawn at the 30% probability level. [PF$_6$]$^-$ anions have been omitted for clarity. Cp$_{cent}$ denotes the centroid of the cyclopentadienyl ligand; equivalent atoms of **1** denoted with a prime generated by $-x + 1$, y, z.

the distances found for other Ru cyclopentadienyl compounds.[14] Again, the Ru–Cp_{cent} separation was found to be slightly longer for the Cp* complex **2**.

As expected from the NMR investigations, the molecular structure of **4** (space group $P\bar{1}$, Table 1)[13] was found to be different from those of **1** and **2** (Figure 3) as the *N*-donor ligand ^{Me}Tpm is coordinated to Ru^{II} in a κ^2*N*-fashion and one uncoordinated, terminal pz ring remains in an *exo* position, presumably due to steric reasons. The coordination sphere around ruthenium is completed by the η^5-bound Cp* entity and one acetonitrile donor ligand. A comparable structural motif has been found, for instance, in the ruthenium(II) arene complex $[Ru(C_6H_6)(\kappa^2N\text{-}^{Me}Tpm)Cl][PF_6]$.[15]

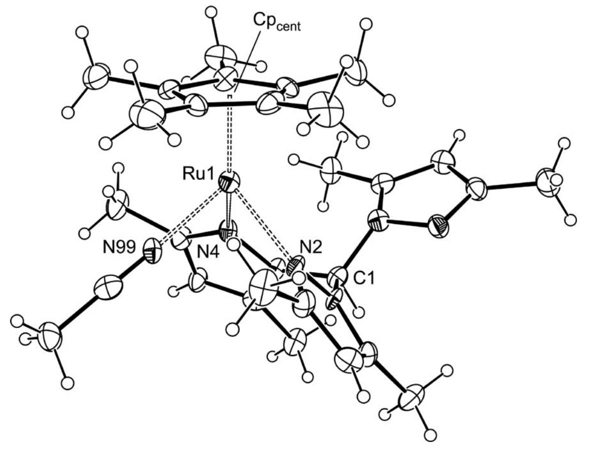


Figure 3. Molecular structure of $[RuCp^*(acn)(^{Me}Tpm)][PF_6]$ (**4**). Displacement ellipsoids are drawn at the 30% probability level. The $[PF_6]^-$ anion has been omitted for clarity; Cp_{cent} denotes the centroid of the cyclopentadienyl ligand.

Due to steric crowding in **4**, the separation between the Cp_{cent} and the ruthenium atom (180.4 pm) is slightly longer than those found for **1** or **2** (176.4 and 178.2 pm, respectively). This is also apparent from the elongated Ru–N_{pz} distances [av. 217.3 pm (**4**) vs. 211.1 (**1**) and 214.5 pm (**2**)], with the ruthenium–acetonitrile interaction of 207.8 pm being significantly shorter. In analogy to the arene complex $[Ru(C_6H_6)(\kappa^2N\text{-}^{Me}Tpm)Cl][PF_6]$,[15] the uncoordinated *exo*-pyrazolyl ring of the ^{Me}Tpm ligand is arranged in close spatial proximity to the ruthenium(II) atom and the Cp* ligand.

Electrochemistry

Similar to the mixed-sandwich Tp^R complexes of Ru^{II} prepared by Mann,[7a] the title compounds **1**–**3** also resemble the electrochemical behaviour of ferrocene rather than ruthenocene.[16] Thus, complexes **1**–**3** show one quasi-reversible oxidation process in acetonitrile centred at $E^0_{1/2}$ = +0.38 (**1**), +0.15 (**2**) and +0.35 V (**3**) vs. Fc/Fc$^+$ (see Figure 4).[17] The differences of the peak potentials ($\Delta\phi_p = \phi_p{}^a - \phi_p{}^c$) between the anodic and cathodic half-wave potentials was found to be 73 (**1**), 78 (**2**) and 77 mV (**3**) at 100 mV s^{-1} with the expected scan-rate dependence.

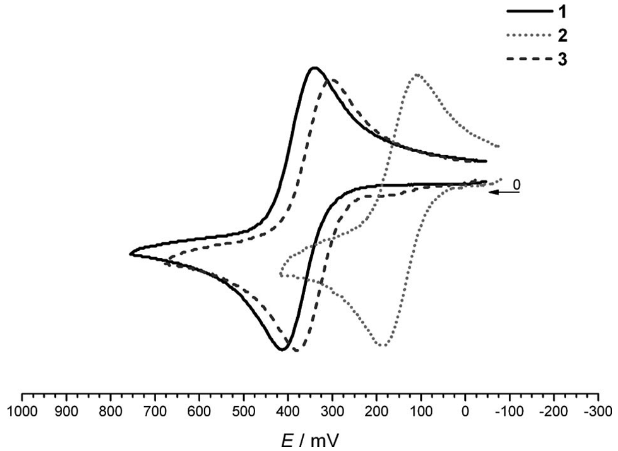


Figure 4. Cyclic voltammetry of $[RuCp(^{H}Tpm)][PF_6]$ (**1**, solid black line), $[RuCp^*(^{H}Tpm)][PF_6]$ (**2**, dotted grey line) and $[RuCp(^{Me}Tpm)][PF_6]$ (**3**, dashed dark grey line) at room temperature in acetonitrile vs. the ferrocene/ferrocenium couple (Fc/Fc$^+$).[23] Scan rate: 100 mV s^{-1}; Pt/$[nBu_4N][PF_6]$/Ag. The intensities of the current peak potentials have been scaled for comparison. All redox waves show exactly the same behaviour in a second CV cycle; only one is shown here for clarity.

Most importantly, the oxidation potentials show very little dependence on the substituents (Me vs. H) on the ^{R}Tpm moieties [$|\Delta E(\mathbf{1},\mathbf{3})|$ = 0.03 V] but are significantly affected by variations in the Cp^R ring. The same tendency has been observed for mixed-sandwich Tp^R complexes of ruthenium(II).[7a] The more electron-donating Cp* ligand yields a more negative $E^0_{1/2}$ value of +0.15 V for **2** [$|\Delta E(\mathbf{1},\mathbf{2})|$ = 0.23 V]. The Cp* species **2** is much more easily oxidised than the analogous Cp complexes because the oxidised form of **2** is stabilised by the electron-donating Cp* ligand. These cationic ^{R}Tpm compounds are more difficult to oxidise than the corresponding, though zwitterionic, mixed-sandwich Ru^{II} Tp^R complexes mentioned above.[7a] This is in good agreement with the electrochemical behaviour of the ^{R}Tpm, Tp^R and ^{R}Tpmd sandwich complexes of iron(II), which show the same correlation: the dicationic complex $[Fe(^{Me}Tpm)_2]^{2+}$ is more difficult to oxidise ($E^0_{1/2}$ = +0.70 V)[18] than its neutral analogues $[Fe(Tp^{Me})_2]$ ($E^0_{1/2}$ = –0.44 V)[19] or $[Fe(^{Me}Tpmd)_2]$ ($E^0_{1/2}$ = –0.32 V).[8h]

Conclusions

We have presented a straightforward procedure for the preparation of mixed-sandwich complexes of ruthenium(II) containing tris(pyrazolyl)methane (^{R}Tpm) and cyclopentadienyl ligands [$Cp^{(*)}$]. The obtained salts $[RuCp(^{H}Tpm)][PF_6]$ (**1**), $[RuCp^*(^{H}Tpm)][PF_6]$ (**2**), $[RuCp(^{Me}Tpm)][PF_6]$ (**3**) and $[RuCp^*(acn)(^{Me}Tpm)][PF_6]$ (**4**) have been characterised by various methods. The X-ray structures of complexes **1**, **2** and **4** reveal two different coordination modes for the ^{R}Tpm ligand. Thus, while the symmetric mixed-sandwich complexes **1**–**3** show κ^3*N*-coordinated ^{R}Tpm ligands, **4** is only available as an air-sensitive acetonitrile adduct consisting of a κ^2*N*-coordinated ^{Me}Tpm ligand.

The hexafluorophosphate salts **1**–**3** can be oxidised (quasi) reversibly to the corresponding dications, as shown by cyclic voltammetry. It appears that only the substituents attached to the Cp rings influence the redox potentials of these complexes to a significant extent, while those of ^{R}Tpm have very little influence.

Experimental Section

General Considerations: All reactions and manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques. Thf was dried with potassium/benzophenone, diethyl ether and *n*-hexane were dried with sodium-potassium alloy/benzophenone, CH_2Cl_2 and acetonitrile over CaH_2 and acetone over $CaSO_4$ and molecular sieves (3 Å). Air-sensitive compounds were stored and weighed in glove boxes (Braun MB150 G-I and Unilab system). Elemental analyses and mass spectroscopic analyses were carried out in the institutional technical laboratories. Satisfactory elemental analysis could not be obtained for some complexes (**1** and **2**) due to the relatively high fluorine concentration. UV/Vis spectra were obtained with a Varian Cary 100 Scan UV/Vis spectrophotometer in acetonitrile. Solution NMR spectra were recorded using a Bruker Avance instrument operating at ^{1}H Larmor frequencies of 300 and 400 MHz and are referenced according to IUPAC recommendations.[20] Chemical shifts are given relative to TMS for ^{13}C and ^{1}H. Coupling constants (*J*) are given in Hertz as positive values regardless of their real individual signs. The UV/Vis spectra of **1**–**3** (Figure S1) can be found in the Supporting Information.

Materials and Reagents: [RuCp(acn)$_3$][PF$_6$],[10] [RuCp*(acn)$_3$][PF$_6$],[11] tris(1-pyrazolyl)methane (^{H}Tpm)[2] and tris(3,5-dimethylpyrazolyl)methane (^{Me}Tpm)[2] were prepared according to literature methods.

Synthesis

[RuCp(^{H}Tpm)][PF$_6$] (1): [RuCp(acn)$_3$][PF$_6$] (800 mg, 1.84 mmol) and ^{H}Tpm (395 mg, 1.84 mmol) were dissolved in thf (50 mL) and stirred overnight. The resulting orange solution was evaporated to dryness and the yellow residue dried in vacuo. Yield 886 mg (1.69 mmol, 91 %). Recrystallisation from acetonitrile/diethyl ether afforded deep orange crystals; m.p. (sealed tube under argon) 310 °C (dec.). ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 9.23 (d, $^{4}J_{\text{H,H}}$ = 0.6 Hz, 1 H, CH_{apical}), 8.60 (dt, $^{3}J_{\text{H,H}}$ = 2.2, $^{4}J_{\text{H,H}}$ = 0.6 Hz, 3 H, 3-*H*pz), 8.34 (dd, $^{3}J_{\text{H,H}}$ = 2.8, $^{4}J_{\text{H,H}}$ = 0.7 Hz, 3 H, 5-*H*pz), 6.58 (dd, $^{3}J_{\text{H,H}}$ = 2.8, $^{3}J_{\text{H,H}}$ = 2.2 Hz, 3 H, 4-*H*pz), 4.64 (s, 5 H, C_5H_5) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, [D$_6$]acetone): δ = 149.5 (s, 3-*C*pz), 134.1 (s, 5-*C*pz), 109.9 (s, 4-*C*pz), 77.0 (s, HC_{apical}), 70.4 (s, C_5H$_5$) ppm. ^{19}F NMR (376.5 MHz, [D$_6$]acetone): δ = –72.2 (d, $^{1}J_{\text{F,P}}$ = 708 Hz) ppm. ^{31}P NMR (162.0 MHz, [D$_6$]acetone): δ = –144.1 (sept, $^{1}J_{\text{P,F}}$ = 708 Hz) ppm.

[RuCp*(^{H}Tpm)][PF$_6$] (2): [RuCp*(acn)$_3$][PF$_6$] (800 mg, 1.59 mmol) and ^{H}Tpm (340 mg, 1.59 mmol) were dissolved in thf (40 mL) and stirred overnight. The resulting orange suspension was filtered (P3), and the yellow residue washed with thf (2 × 10 mL) and dried in vacuo. Yield 530 mg (0.89 mmol, 56 %). Recrystallisation from acetonitrile/diethyl ether afforded deep orange crystals; m.p. (sealed tube under argon): 298 °C. ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 9.31 (d, $^{4}J_{\text{H,H}}$ = 0.5 Hz, 1 H, CH_{apical}), 8.44 (dd, ^{3}J = 2.6, $^{4}J_{\text{H,H}}$ = 0.6 Hz, 3 H, 5-*H*pz), 8.42 (d, $^{3}J_{\text{H,H}}$ = 2.2 Hz, 3 H, 3-*H*pz), 6.60 (dd, $^{3}J_{\text{H,H}}$ = 2.8, $^{3}J_{\text{H,H}}$ = 2.3 Hz 3 H, 4-*H*pz), 1.83 (s, 15 H, C_5Me_5) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, [D$_6$]acetone): δ = 146.4 (s, 3-*C*pz), 134.5 (s, 5-*C*pz), 110.0 (s, 4-*C*pz), 78.76 (s, C_5Me$_5$), 76.6 (s, CH_{apical}), 11.2 (s, C$_5$*Me*$_5$) ppm. ^{19}F NMR (376.5 MHz, [D$_6$]acetone): δ = –72.1 (d, $^{1}J_{\text{F,P}}$ = 708 Hz) ppm. ^{31}P NMR (162.0 MHz, [D$_6$]acetone): δ = –144.0 (sept, $^{1}J_{\text{P,F}}$ = 708 Hz) ppm.

[RuCp(^{Me}Tpm)][PF$_6$] (3): [RuCp(acn)$_3$][PF$_6$] (1.60 g, 3.60 mmol) and ^{Me}Tpm (1.10 g, 3.60 mmol) were dissolved in thf (50 mL) and stirred overnight. The resulting orange suspension was filtered (P3), and the yellow solid washed with thf (20 mL) and dried in vacuo. Yield 1.89 g (3.11 mmol, 86 %). Microcrystalline material was obtained from acetonitrile/diethyl ether; m.p. (sealed tube under argon): 338 °C (dec.). $C_{21}H_{27}F_6N_6PRu$ (609.51): calcd. C 41.38, H 4.46, N 13.79; found C 40.73, H 4.31, N 13.66. ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 7.75 (s, 1 H, CH_{apical}), 6.25 (s, 3 H, 4-*H*pz), 4.87 (s, 5 H, C$_5$*H*$_5$), 2.64 (s, 9 H, 5-*Me*pz), 2.50 (s, 9 H, 3-*Me*pz) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, [D$_6$]acetone): δ = 158.5 (s, 3-*C*pz), 143.2 (s, 5-*C*pz), 111.2 (s, 4-*C*pz), 68.6 (s, CH_{apical}), 65.6 (s, C_5H$_5$), 17.3 (s, 3-*Me*pz), 11.6 (s, 5-*Me*pz) ppm. ^{19}F NMR (376.5 MHz, [D$_6$]acetone): δ = –72.5 (d, $^{1}J_{\text{F,P}}$ = 708 Hz) ppm. ^{31}P NMR (162.0 MHz, [D$_6$]acetone): δ = –144.1 (sept, $^{1}J_{\text{P,F}}$ = 708 Hz) ppm.

[RuCp*(acn)(^{Me}Tpm)][PF$_6$] (4): [RuCp*(acn)$_3$][PF$_6$] (200 mg, 397 µmol) and ^{Me}Tpm (118 mg, 397 µmol) were dissolved in thf (20 mL) and stirred for 2 h. The orange solution was evaporated to dryness, dissolved in CH_2Cl_2 (8 mL) and layered with *n*-hexane (35 mL) to afford some yellow-orange crystals. ^{1}H NMR (400.1 MHz, CD_2Cl_2): δ = 7.39 (s, 1 H, CH_{apical}), 6.18 (br. s, $J = W_{1/2}$ = 11 Hz, 3 H, 4-*H*pz), 2.43 (br. s, $J = W_{1/2}$ = 19 Hz, 18 H, 3,5-*Me*$_2$pz), 2.25 (s, 3 H, CH_3CN), 1.35 (br. s, $J = W_{1/2}$ = 6 Hz, 15 H, C$_5$*Me*$_5$) ppm. ^{1}H NMR (400.1 MHz, [D$_8$]THF): δ = 7.61 (s, 1 H, CH_{apical}), 6.24 (br. s, $W_{1/2}$ = 40 Hz, 3 H, 4-*H*pz), 2.46 (br. s, $W_{1/2}$ = 85 Hz, 18 H, 3,5-*Me*$_2$pz), 2.29 (s, 3 H, CH_3CN) 1.35 (br. s, $W_{1/2}$ = 16 Hz, 15 H, C$_5$*Me*$_5$) ppm.

Electrochemical Measurements: Cyclic voltammetry measurements were performed with an EG&G potentiostat (PAR-model 263A) and an electrochemical cell for sensitive compounds.[21] We used a freshly polished Pt disk working electrode, a Pt wire as counter electrode, and an Ag wire as reference electrode {[*n*Bu$_4$N][PF$_6$] (0.1 M) as electrolyte}. Potentials were calibrated against the Fc/Fc$^+$ couple,[22] which has a potential of $E^{0}_{1/2}$ = 0.352 V vs. Ag/AgCl. We have not discussed rate constants and thermodynamic parameters in detail because uncompensated solution resistance R_u and other factors of our experimental setup have a strong influence.

Crystal Data, X-ray Data Collection and Structure Determination: Crystals of **1**, **2** and **4** suitable for X-ray diffraction were obtained from acetonitrile/diethyl ether (**1**), [D$_6$]benzene (**2**) or CH_2Cl_2/*n*-hexane (**4**; Table 2). In order to avoid quality loss, all single crystals were mounted in perfluoropolyalkyl ether oil on top of a glass fibre and then placed in the cold nitrogen stream of a low-temperature device so that the oil solidified. Data collection for the X-ray structure determinations were performed on a Stoe STADI 4 (**1**, **2**) or Bruker CCD1k (**4**) diffractometer fitted with a CCD area detector, a graphite-monochromated Mo-K_α (0.71073 Å) radiation source and a low temperature device. The calculations were performed using SHELXTL[23] (ver. 6.12) and SHELXL-97.[24] The structure was solved by direct methods and successive interpretation of the difference Fourier maps, followed by full-matrix least-squares refinement (against F^2). The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. Upon convergence, the final Fourier difference map of the X-ray structures showed only some residual electron density located close to the ruthenium atoms. Numerical absorption corrections did not lead to improved datasets. The fluorine atoms of the [PF$_6$]$^-$ counter anion in **1** were seen to have abnormally large

Table 2. Crystallographic data.

Compound	**1**	**2**	**4**
Empirical formula	$C_{15}H_{15}F_6N_6PRu$	$C_{20}H_{25}F_6N_6PRu\cdot 0.5C_6H_6$	$C_{28}H_{40}F_6N_7PRu$
M	525.37	634.55	720.71
Crystal system	orthorhombic	triclinic	triclinic
Space group[13]	*Cmca*	$P\bar{1}$	$P\bar{1}$
a [pm]	1314.7(3)	998.9(2)	834.4(1)
b [pm]	1726.7(4)	1178.9(2)	1318.3(2)
c [pm]	1593.8(2)	1192.6(2)	1531.5(2)
α [°]		82.53(3)	85.26(1)
β [°]		86.97(3)	77.95(1)
γ [°]		65.87(3)	89.22(1)
V [10^6 pm^3]	3617(1)	1270.7(4)	1641.7(4)
μ [mm^{-1}]	1.030	0.749	0.590
$D_{calcd.}$ [g cm^{-3}]	1.929	1.658	1.458
Crystal dimensions	$0.10 \times 0.25 \times 0.25$	$0.10 \times 0.12 \times 0.32$	$0.01 \times 0.32 \times 0.40$
Z	8	2	2
T [K]	150	110	200
$2\theta_{max}$ [°]	52.76	52.40	46.50
Reflections measured	13384	9195	4343
Reflections unique	1925 (R_{int} = 0.041)	4690 (R_{int} = 0.087)	3286
Param./restraints	177/57	339/0	402/36
$R1$ [$I \geq 2\sigma(I)$]	0.0445	0.0533	0.0690
$wR2$ (all data)	0.1097	0.1348	0.1819
Max./min. residual e$^-$ density [e 10^{-6} pm^{-3}]	1.286/–1.007	1.229/–1.732	0.894/–1.261

displacement parameters, indicative of disorder. This anion was modelled as being disordered (four F atoms over 12 positions), representing slightly different orientations of the F atoms. The coordinates, anisotropic displacement parameters and site occupancies of the disordered F atoms were refined to loose restraints on the associated distances and displacement parameters.

CCDC-714246 (for **1**), -714247 (for **2**) and -714248 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Electronic spectra of **1**–**3** in acetonitrile.

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