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Synthesis and structures of metallocene complexes of iron(II) and ruthenium(II) derived from 9,9′-spirobifluorene

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Abstract

Reaction between 9,9′-spirobifluorene and $[CpM]^+$ (where M = Fe and Ru) equivalents gives the complexes $[CpRu(\eta^6\text{-SBF})][PF_6]$ (**1**), $[(CpRu)_2(\eta^6,\eta^6\text{-SBF})][PF_6]_2$ (**2**) and $[(CpFe)_2(\eta^6,\eta^6\text{-SBF})][PF_6]_2$ (**3**), respectively. Single crystal X-ray structures of **1** and **3** show that the metal atoms exhibit distorted η^6-coordination to SBF phenyl moieties primarily as a consequence of steric interactions between Cp and SBF. The structure of **3** contains each of the possible C_2 enantiomers whereas NMR spectroscopy shows signals consistent with a 1:1 mixture of C_2 and C_1 stereoisomers for both **2** and **3**. In conjunction with electrochemical data the observations are consistent with SBF acting as a molecule containing two independent biphenyl moieties.
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1. Introduction

We have recently been interested in the chemistry of 9,9′-spirobifluorene (SBF) (Fig. 1) and its derivatives primarily because of its intriguing electronic properties and aesthetic appeal. SBF can perhaps structurally best be described as two orthogonal biphenyl moieties fused at a central carbon atom. Electronically SBF has been characterised as 'π–σ–π' [1,2], where each biphenyl can be considered essentially independent and this is reflected in the reactivity where, for example, electrophilic substitution occurs regioselectively at the 2,2′ followed by 7,7′ positions [3,4]. The structure and potentially interesting electronic properties have previously prompted the synthesis and study of compounds for molecular electronic and optical applications [5–8], molecular recognition [9,10], and a derivative of SBF has also recently been incorporated into hydrogen-bonded networks that exhibit large porosity [11].

Our initial interest in SBF was to study its potential as a π-arene ligand to metal moieties with the ultimate aim of incorporating this motif into molecular based solids. Metallocene and related half sandwich complexes have been at the vanguard of organometallic chemistry for over 50 years possessing a myriad of uses and applications encompassing synthetic, catalytic, medicinal, and materials science [12]. We therefore initiated a short study to investigate the synthesis of SBF π-complexes to common metallic fragments that exhibit coordination to arenes.

Here, we report reactions between SBF and precursors for the metallic fragments $Cr(CO)_3$, $Mo(CO)_3$, and $[CpM]^+$ (where M = Fe and Ru). Complexes described herein represent the first metal complex derivatives of SBF where SBF acts as a π-ligand.

2. Results and discussion

We initially investigated reactions between 4 equivalents of $M(CO)_6$ (where M = Cr and Mo) and SBF under conditions analogous to those used for the synthesis of $M(CO)_3(\eta^6\text{-arene})$ complexes, including those derived from biphenyl [13–15].

Reaction between $Mo(CO)_6$ and SBF in decane at 150 °C for 48 h lead only to deposition of a metallic deposit

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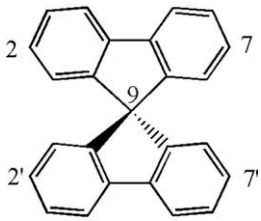

Fig. 1. Structure of 9,9′-spirobifluorene.

and recovery of at least 90% SBF on workup. ^{1}H NMR analysis of crude reaction mixtures did not indicate any SBF containing species other than SBF, and IR spectroscopy showed bands in the carbonyl region corresponding only to $Mo(CO)_6$. Similar results were also obtained using the other common precursor $Mo(CO)_3(C_2H_5CN)_3$ which can be used to coordinate arenes under milder reaction conditions [16].

However, reaction between 4 equivalents of $Cr(CO)_6$ and SBF in refluxing ditertbutyl ether and THF for 3 days did indicate that a π-complex of SBF had formed. Filtration of the reaction mixture to remove metallic deposits gave a yellow supernatant that on addition of hexane, and cooling to −20 °C, precipitated a yellow solid. IR spectroscopy in chloroform showed bands at 1967, 1898 and 1793 cm^{-1} that do not correspond to those of $Cr(CO)_6$ and are indicative of a $Cr(CO)_3$ moiety. In addition to a peak for SBF, mass spectrometry also gave low intensity peaks at *m/z* 452 and 588 that correspond to the compositions $SBFCr(CO)_3$ and $SBF(Cr(CO)_3)_2$, respectively. ^{1}H NMR spectroscopy gave a spectrum containing signals corresponding to SBF and also several low intensity signals spanning the range δ 4.1–8.0 ppm of which the high field signals are indicative of protons from a π-arene complex. Purification was attempted using recrystallisation, sublimation, and column chromatography, however in no case was a sample free from SBF obtained, and as judged by ^{1}H NMR spectroscopy the putative $Cr(CO)_3$ complexes decompose in minutes in solution and over several hours in the solid state.

Due to the problems encountered in the purification and stability of the $M(CO)_3$ derivatives, other metal moieties were sought that are known to coordinate strongly to a range of arene molecules. Arene complexes, including biphenyl, of the fragments $[Cp(Cp^*)M]^+$ (where M = Fe and Ru) have been previously investigated particularly with respect to materials applications [17–21]. Conveniently the complex $[CpRu(CH_3CN)_3][PF_6]$ facilitates coordination of $[CpRu]^+$ under mild conditions [22] and therefore stoichiometric reactions between SBF and 1–4 equivalents of $[CpRu(CH_3CN)_3][PF_6]$ were investigated.

Reaction between 1 equivalent of $[CpRu(CH_3CN)_3][PF_6]$ and SBF in dichloromethane at 50 °C gave, after workup, $[CpRu(\eta^6\text{-SBF})][PF_6]$ (**1**) in good yield. Compound **1** is soluble in chlorinated solvents and acetonitrile and as a solid is stable in air. ^{1}H NMR spectroscopy of **1** showed, in addition to a single resonance at δ 5.22 ppm

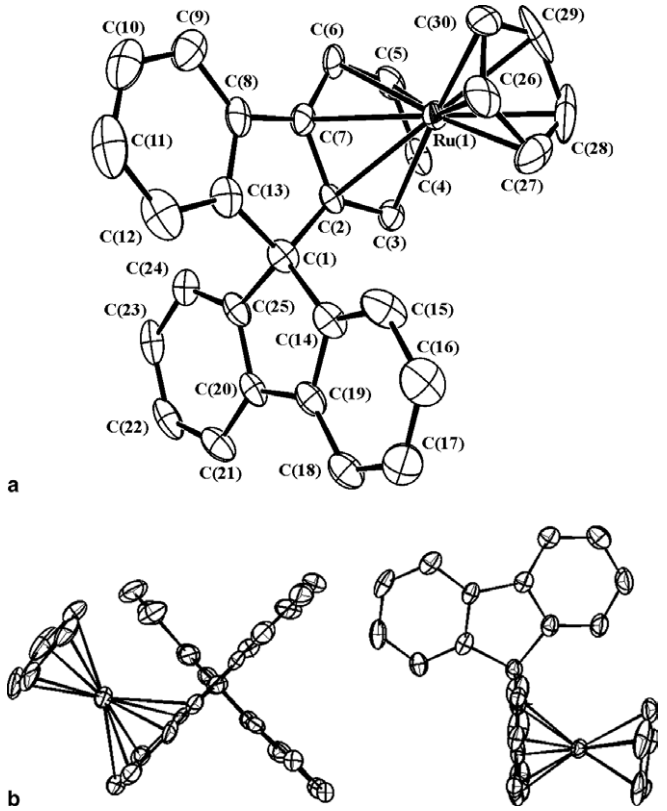

Fig. 2. (a) Molecular structure of a cation of **1**. (b) Views of the cation showing distortion in the SBF moiety. Ellipsoids are at 50% probability and hydrogen atoms have been removed for clarity.

attributable to the Cp moiety, twelve resolved signals of cumulative relative intensity 16H that correspond to the SBF protons. Mass spectrometry gave a single set of peaks centred at 483 with an isotopic distribution pattern consistent with the cation $[CpRu(SBF)]^+$. A single crystal diffraction study also confirmed the proposed formulation. The structure of the cation is shown in Fig. 2 and select data are given in Table 1.

The asymmetric unit of **1** contains two equivalents of the complex, however there is no significant difference between the structures of the two cations. As shown in Fig. 2, SBF is coordinated to the CpRu moiety as η^6-SBF, however as judged by bond lengths and angles there is significant steric congestion between CpRu and SBF moieties. Perhaps the clearest indicators are the $Ru–C_{SBF}$ and $Ru–C_{Cp}$ bond lengths, and the angles about the spiro carbon atom C(1). The Ru–C bonds closest to the phenyl moiety C(14)–C(19) exhibit the greatest bond lengths (cf. Ru(1)–C(2) = 2.251(5) and Ru(1)–C(4) = 2.169(5) Å), and the biphenyl moiety containing C(14)–C(25) is tilted away from the CpRu group (cf. C(2)–C(1)–C(14) = 117.9(4) and C(2)–C(1)–C(25) = 109.4(1)°). In addition the two planes defined by the Cp and C(2)–C(7) phenyl group, respectively, are not parallel, the centroids subtending at an angle of 176.9° at Ru(1).

Reactions were also investigated between >1 equivalent of $[CpRu(CH_3CN)_3][PF_6]$ and SBF. A potential complica-

Table 1
Selected bond lengths (Å) and angles (°) for complex **1**

C(26)–Ru(1)	2.194(6)	C(2)–C(1)–C(14)	117.9(4)
C(27)–Ru(1)	2.198(6)	C(2)–C(1)–C(25)	109.4(4)
C(28)–Ru(1)	2.170(6)	C(13)–C(1)–C(25)	111.8(4)
C(29)–Ru(1)	2.150(6)	C(13)–C(1)–C(14)	115.3(4)
C(30)–Ru(1)	2.167(6)	C(2)–C(1)–C(13)	101.0(4)
C(2)–Ru(1)	2.251(5)	C(14)–C(1)–C(25)	101.7(4)
C(3)–Ru(1)	2.210(5)	$Cp_{centroid}$–Ru(1)–$(C(2)–C(7))_{centroid}$	176.9
C(4)–Ru(1)	2.169(5)		
C(5)–Ru(1)	2.190(5)		
C(6)–Ru(1)	2.215(5)		
C(7)–Ru(1)	2.230(5)		

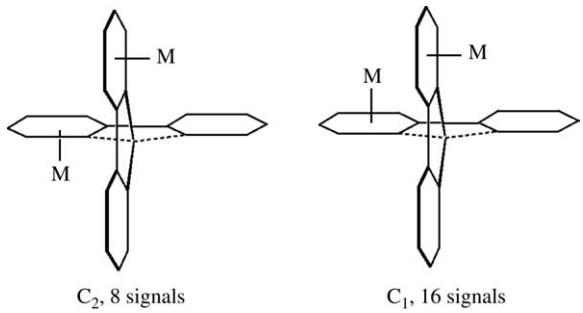

Fig. 3. Physically reasonable isomers resulting from addition of two metal fragments to SBF and the number of signals expected from SBF hydrogen atoms in the ^{1}H NMR spectrum.

tion of multiple addition to SBF is the possible formation of stereoisomers. For example Fig. 3 shows the point group and number of signals expected from SBF in the ^{1}H NMR spectrum of physically reasonable isomers resulting from addition of two metal moieties. The isomers shown in Fig. 3 minimise steric interactions, and are favoured thermodynamically over isomers that have both Lewis acidic metal fragments coordinated to a single biphenyl moiety. It should also be noted that the C_2 isomer is chiral.

Reaction between SBF and 2 equivalents of $[CpRu(CH_3CN)_3][PF_6]$ in dichloromethane at 60 °C for 16 h gave $[(CpRu)_2(\eta^6,\eta^6\text{-SBF})][PF_6]_2$ (**2**) in moderate yield. In chlorinated solvents complex **2** is markedly less soluble than **1** but is reasonably soluble in acetonitrile and as a solid **2** is stable in air for weeks. The ^{1}H NMR spectrum of **2** showed three signals in a 2:1:1 ratio that are assigned to Cp protons, and a complex set of overlapping signals attributable to SBF moieties. With the aid of 2-D homo- and heteronuclear NMR spectroscopy it is possible to distinguish signals corresponding to two SBF containing molecules. Mass spectrometry gave major signals corresponding to $[(CpRu)_2(SBF)][PF_6]^+$ and $[(CpRu)_2(SBF)]^+$ and elemental analysis was consistent with the composition $[(CpRu)_2(SBF)][PF_6]_2$. The data strongly suggests that the product contains a 1:1 mixture of C_1 and C_2 isomers shown in Fig. 3. Numerous attempts to separate the isomers using various chromatography techniques, including ion exchange chromatography, and fractional crystallisation have to date proved fruitless. Growth of single crystals has also proved elusive.

Reaction between SBF and 3 or 4 equivalents of $[CpRu(CH_3CN)_3][PF_6]$ gave complex **2** and excess $[CpRu(CH_3CN)_3][PF_6]$ as judged by ^{1}H NMR spectroscopy and mass spectrometry. Although several examples exist, where both phenyl groups of biphenyls can coordinate η^6 to metal moieties, including $[CpRu]^+$ derivatives [21], these complexes can minimise steric interaction via C_{ipso}–C_{ipso} bond rotation. Therefore, in the case of the rigid SBF motif, tri- and tetra addition is presumably prevented by unfavourable steric interactions between metal and SBF moieties. (vide infra).

In addition to the many complexes of the type $[CpRu(\eta^6\text{-arene})]^+$ some analogous iron complexes are also known including one derived from biphenyl [23–26], however the harsh synthetic routes to this class of complexes has rendered them less well developed. Using a route reported by Astruc [25] for the synthesis of the biphenyl complex $[(CpFe)_2(\eta^6,\eta^6\text{-}C_{12}H_{10})][PF_6]_2$, SBF, ferrocene, Al, and $AlCl_3$ were stirred as a viscous melt at 130 °C for 16 h. On work up and ion exchange the complex $[(CpFe)_2(\eta^6,\eta^6\text{-SBF})][PF_6]_2$ (**3**) was isolated as a yellow powder in good yield. Complex **3** is stable in air, in solution and in the solid state and is soluble in polar organic solvents. ^{1}H NMR spectroscopy, mass spectrometry, and elemental analysis again showed that (**3**) comprised closely to a 1:1 mixture of C_2 and C_1 isomers. Attempts to separate the isomers using column chromatography or recrystallisation did not give appreciable separation, however from recrystallisation of an acetonitrile solution of **3** a few single crystals of complex (**3a**) could be isolated. The structure of a dication is shown in Fig. 4 and select data are given in Table 2.

Fig. 4 shows that each biphenyl moiety of SBF exhibits η^6 coordination to a CpFe group and that the dication is a chiral C_2 enantiomer. The overall structure contains a racemic mixture of both C_2 isomers that are related through a centre of inversion. Inspection of the packing diagram does not reveal any close contacts between cations; the cations being separated by PF_6 anions that exhibit hydrogen bonding between the Cp and SBF hydrogen and fluorine atoms, respectively.

It can be clearly seen from Fig. 4 that the SBF moiety is significantly distorted from its equilibrium molecular structure presumably as a consequence of steric interactions between CpFe and SBF phenyl moieties. The two planes defined by the biphenyl moieties of **3a** are twisted 10° relative to each other, giving an acute angle of 80° (Fig. 4(b)), whereas for **1** these planes are essentially perpendicular (Fig. 2(b)). Furthermore, a tilting distortion similar to **1** is observed, perhaps best exemplified by the compressed angle C(13)–C(1)–C(25) = 101.8° subtended at the spiro carbon C(1). Again similar to **1** the Fe–C_{SBF} and Fe–C_{Cp} bonds also reflect these distortions exhibiting longer Fe–C bonds for carbon atoms closest to the spiro centre.

Attempts to prepare tri and tetra addition complexes of SBF from reaction between **3** and 1 and 2 equivalents of $[CpRu(CH_3CN)_3][PF_6]$, respectively, in chlorinated

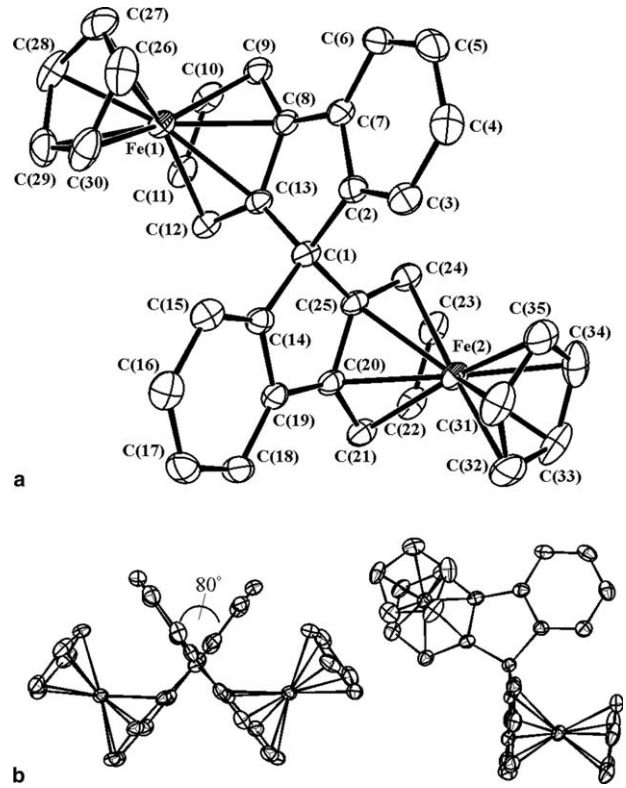

Fig. 4. (a) Molecular structure of complex **3a**. (b) Views of **3a** showing distortions in SBF moiety. Ellipsoids are at 50% probability and hydrogen atoms have been removed for clarity.

Table 2
Selected bond lengths (Å) and angles (°) for complex **3a**

C(26)–Fe(1)	2.058(3)	C(22)–Fe(2)	2.075(3)
C(27)–Fe(1)	2.059(3)	C(23)–Fe(2)	2.088(2)
C(28)–Fe(1)	2.055(3)	C(24)–Fe(2)	2.111(2)
C(29)–Fe(1)	2.054(3)	C(25)–Fe(2)	2.111(2)
C(30)–Fe(1)	2.066(3)	C(2)–C(1)–C(14)	117.5(2)
C(8)–Fe(1)	2.112(2)	C(2)–C(1)–C(25)	116.54(19)
C(9)–Fe(1)	2.087(2)	C(13)–C(1)–C(25)	101.81(19)
C(10)–Fe(1)	2.080(3)	C(13)–C(1)–C(14)	117.96(19)
C(11)–Fe(1)	2.087(3)	C(2)–C(1)–C(13)	101.21(18)
C(12)–Fe(1)	2.114(2)	C(14)–C(1)–C(25)	101.44(18)
C(13)–Fe(1)	2.120(2)	$Cp_{centroid}$–Fe(1)–(C(8)–	176.9
C(31)–Fe(2)	2.058(3)	$C(13))_{centroid}$	
C(32)–Fe(2)	2.052(3)	$Cp_{centroid}$–Fe(2)–(C(20)–	177.5
C(33)–Fe(2)	2.050(3)	$C(25))_{centroid}$	
C(34)–Fe(2)	2.053(3)	$Biphenyl_{Fe(1)}$–$Biphenyl_{Fe(2)}$ twist	80
C(35)–Fe(2)	2.054(3)		
C(20)–Fe(2)	2.112(2)		
C(21)–Fe(2)	2.087(3)		

solvents gave no reaction before decomposition of $[CpRu(CH_3CN)_3][PF_6]$, which is perhaps unsurprising given the steric congestion evident from the structure of **3a**.

The electrochemistry of complexes **1**–**3** was investigated to determine if reversible reduction(s) occur and to probe any potential interaction between metal centres in **2** and **3**. Previous studies on $[(CpRu)(\eta^6\text{-biphenyl})]^+$ and $[(CpFe)_2(\eta^6,\eta^6\text{-biphenyl})]^{2+}$ have shown that at room temperature these complexes exhibit an irreversible reduction and EC process indicative of loss of a CpM moiety at −1.80 and −1.32 V, respectively [21,25]. However, at −38 °C in DMF $[(CpFe)_2(\eta^6,\eta^6\text{-biphenyl})]^{2+}$ does exhibit a reversible two electron process at $E_{1/2} = -1.12$ V [25] and at 25 °C $[(CpRu)_2(\eta^6,\eta^6\text{-biphenyl})]^{2+}$ exhibits a single electron reversible process $E_{1/2} = -1.42$ V but no second reduction down to −2.5 V [21].

Cyclic voltammetry of ruthenium complexes **1** and **2** showed that both exhibit irreversible reduction waves at −1.71 and −1.76 V at scan rates between 10 and 500 mV s^{-1}. It has been reported that for $[(CpM)_n(\eta^6\text{-biphenyl})]^{n+}$ (where M = Fe and Ru) that there is a solvent dependence on the reversibility of electron transfer, however we observed irreversible processes in both MeCN and DMF at 25 and −40 °C for the latter. Complex **3** exhibits a quasi-reversible process at $E_{1/2} = -1.23$ V with $\Delta E_p = 38$ mV at 100 mV s^{-1} that increases slightly with increasing scan rate. In comparison to an internal reference of ferrocene the ΔE_p value and current intensities indicate that this is likely a two electron process similar to that observed for $[(CpFe)_2(\eta^6,\eta^6\text{-biphenyl})]^{2+}$ [25].

3. Conclusions

We have shown that SBF can act as a π-ligand to a select number of transition metals and have structurally characterised complexes resulting from addition of one metal, and an isomer resulting from addition of two metal moieties to SBF, respectively. NMR spectroscopy of products resulting from addition of two $[CpM]^+$ (M = Fe, Ru) units indicates that the synthesis of the two physically reasonable isomers of C_1 and C_2 symmetry (Fig. 3) is unselective. This observation indicates that the addition of one metal does not affect the regioselectivity of addition of the second, which further corroborates the hypothesis that SBF exhibits reactivity and properties reflective of two independent biphenyl groups.

4. Experimental

4.1. General procedures

All manipulations were performed under argon using standard Schlenk techniques unless stated otherwise. All solvents were dried over the appropriate drying agent and distilled under dinitrogen [27]. Reagents and solvents were purchased from Aldrich, Acros or Lancaster and used as supplied. 9,9′-spirobifluorene [2], $Mo(CO)_3(C_2H_5CN)_3$ [28] and $[CpRu(MeCN)_3][PF_6]$ [29] were prepared using literature procedures. IR spectra were recorded on an Avatar 370 FT-IR spectrometer. NMR spectra were recorded at probe temperature on a JEOL (^{1}H, 270 MHz; ^{13}C, 68 MHz), Brüker AMX (^{1}H, 300 MHz), JEOL (^{1}H, 400 MHz; ^{13}C, 100.5 MHz), or DMX (^{1}H, 400 MHz; ^{13}C, 100.5 MHz). Chemical shifts are described in parts per million downfield shift from $SiMe_4$ and are reported consecu-

tively as position (δ_H or δ_C), relative integral, multiplicity (s, singlet; d, doublet; t, triplet; m, multiplet), coupling constant (J/Hz) and assignment. ^{13}C HSQC, PENDANT and Gradient HMBC experiments were performed using standard Brüker pulse sequences. All spin splitting values for ^{1}H NMR spectra are $^3J_{(H-H)}$. Mass spectra were recorded on LCQ Classic or AutoSpec spectrometers. Electrospray ionisation (ESI) was recorded using acetonitrile as the mobile phase. Major fragments were given as percentages of the base peak intensity (100%). Cyclic voltammetry data were collected using a Voltalab radiometer analytical PST050 and Pt working and auxiliary electrodes. Potentials were referenced to SCE separated from the test solution using a fine frit. Test solutions comprised electrolyte (0.1 M $^nBu_4NBF_4$ in DMF) and analyte (10^{-4} mol L^{-1}).

4.2. Synthesis of [(CpRu)(η^6-SBF)][PF_6] (1)

An ampoule was charged with [CpRu(MeCN)$_3$][PF_6] (101 mg, 0.23 mmol), SBF (81 mg, 0.26 mmol) and dichloromethane (20 mL). The resulting solution was stirred at 50 °C for 16 h and the volatiles removed from the resulting solution to give a brown solid. The solid was rinsed with diethyl ether (2 × 20 mL) to give **1** as a grey solid. Yield = 130 mg (93%). Anal. Calc. for $C_{30}H_{21}F_6PRu$: C, 57.42; H, 3.37. Found: C, 57.35; H, 3.41%. MS (ESI); m/z: 483.5 ($M^+ - PF_6$) ^{1}H NMR (270 MHz, CD_3CN) δ 8.02 (d, $J = 10.4$, 2H), 7.94 (d, $J = 9.0$, 1H), 7.60 (t, $J = 8.1$, 1H), 7.54 (t, $J = 8.1$, 1H), 7.45 (t, $J = 8.1$, 1H), 7.39 (m, 2H), 7.07 (m, 3H), 6.75 (d, $J = 8.1$, 1H), 6.49 (d, $J = 8.1$, 1H), 6.17 (t, $J = 6.8$, 1H), 5.85 (t, $J = 6.8$, 1H), 5.62 (d, $J = 6.8$, 1H), 5.22 (s, 5H). ^{13}C NMR (68 MHz, CD_3CN) δ 148.6, 147.8, 147.3, 144.3, 142.9, 141.7, 140.4, 137.0, 131.2, 129.7, 129.1, 129.0, 128.7, 128.0, 124.9, 123.0, 122.7, 121.0, 120.8, 104.3, 83.4, 83.2, 81.4, 81.0(C_{Cp}), 78.3. (C_{spiro} not found).

4.3. Synthesis of [(CpRu)$_2$(η^6,η^6-SBF)][PF_6]$_2$ (2)

An ampoule was charged with [CpRu(MeCN)$_3$][PF_6] (170 mg, 0.23 mmol), SBF (55 mg, 0.17 mmol) and dichloromethane (20 mL). The resulting solution was stirred at 60 °C for 16 h to give a grey precipitate and a dark brown supernatant. The mixture was filtered and the grey residue washed with dichloromethane (2 × 20 mL) that on drying gave **2** as a grey powder. Yield = 95 mg (59.5%). Anal. Calc. for $C_{35}H_{26}F_{12}P_2Ru_2$: C, 44.79; H, 2.79. Found: C, 44.59; H 2.85%. MS (FAB); m/z: 794.9 ($M^+ - (PF_6)$), 648.9 ($M^+ - 2(PF_6)$) ^{1}H NMR (270 MHz, CD_3CN) C_2 isomer δ 8.08 (m, 2H), 7.71 (m, 2H), 7.64 (m, 2H), 7.10 (d, $J = 5.4$, 2H), 7.05 (d, $J = 5.4$, 2H), 6.24 (t, $J = 5.4$, 2H), 5.86 (t, $J = 5.4$, 2H), 5.61 (d, $J = 5.4$, 2H), 5.17 (s, 10 H); C_1 isomer 8.10 (m, 1H), 7.98 (d, $J = 5.4$, 1H), 7.6–7.8 (m, 3H), 7.52 (t, $J = 5.4$, 1H), 7.29 (t, $J = 5.4$, 1H), 7.19 (m, 1H), 7.00 (d, $J = 5.4$, 1H), 6.55 (d, $J = 5.4$, 1H), 6.39 (t, $J = 5.4$, 1H), 6.3–6.15 (m, 2H), 6.05 (d, $J = 5.4$, 1H), 5.85 (m, 1H), 5.58 (d, $J = 5.4$, 1H), 5.38 (s, 5H), 5.22 (s, 5H); ^{13}C (68 MHz, CD_3CN) C_2 isomer 145.2, 139.3, 132.5, 131.9, 126.5, 126.3, 120.2, 104.3, 85.1, 83.3, 83.2 (C_{Cp}), 80.4, 80.7 (C_{spiro} not found). C_1 isomer: poor signal to noise and significant overlap prevented unambiguous determination of ^{13}C signals.

4.4. Synthesis of [(CpFe)$_2$(η^6,η^6-SBF)][PF_6]$_2$(3)

A 50 mL two-necked round-bottomed flask was charged with SBF (0.608 g, 1.92 mmol), Al powder (0.211 g, 7.82 mmol), ferrocene (7.152 g, 38.44 mmol), and $AlCl_3$ (5.128 g, 38.46 mmol). The reactants were then stirred and heated at 130 °C as a viscous melt for 16 h. On cooling to room temperature the dark green solid was hydrolysed with deionised water (80 mL) and concentrated NH_4OH added until pH 10 was obtained giving a white precipitate and yellow supernatant. After filtration the yellow solution was treated with 40% HPF_6 (0.34 mL) to give crude **3** as a yellow precipitate. The precipitate was dissolved in acetonitrile (75 mL) filtered and dried over $MgSO_4$ overnight. The volatiles were removed under reduced pressure and washed with diethyl ether (2 × 20 mL) to give **3** as an orange solid. Yield = 1.453 g (89.1%). Anal. Calc. for $C_{35}H_{26}F_{12}P_2Fe_2$: C, 49.56; H, 3.09. Found: C, 49.65; H, 3.15%. MS (ESI); m/z: 437 ($M^+ - PF_6$), 279 ($M^{2+} - 2(PF_6)$). ^{1}H NMR (270 MHz, CD_3CN) C_2 isomer δ 8.31 (d, $J = 6.3$, 2H), 7.86 (m, 2H), 7.78 (m, 2H), 7.56 (m, 2H), 7.14 (d, $J = 6.3$, 2H), 6.35 (t, $J = 6.3$, 2H), 5.94 (m, 2H), 5.46 (d, $J = 6.0$, 2H), 4.75 (s, 10H); C_1 isomer δ 8.19 (d, $J = 7.0$, 1H), 8.09 (d, $J = 7.0$, 1H), 8.0–7.8 (m, 2H), 7.6–7.7 (m, 3H), 7.3–7.5 (m, 3H), 7.00 (t, $J = 7.0$, 1H), 6.87 (d, $J = 7.0$, 1H), 6.61 (d, $J = 7.0$, 1H), 6.25 (d, $J = 7.0$, 1H), 6.03 (t, $J = 7.0$, 1H), 5.66 (d, $J = 7.0$, 1H) 4.87 (s, 5H), 4.76 (s, 5H). (68 MHz, CD_3CN) C_2 isomer δ 144.3, 139.8, 132.1, 131.5, 126.8, 124.4, 114.0, 102.1, 87.5, 85.9, 82.9, 81.3, 79.0 (C_{Cp}) (C_{spiro} not found); C_1 isomer δ 149.4, 144.2, 141.5, 138.9, 131.0, 130.5, 129.9, 128.4, 128.0, 126.5, 124.6, 124.2, 124.0, 123.8, 121.4, 121.0, 86.3, 85.7, 84.4, 83.8, 83.5, 83.2, 82.6, 81.0, 79.5 (C_{Cp}), 79.1 (C_{Cp}) (C_{spiro} not found).

4.5. Structure determinations

Diffraction data were collected at 115 K on a Bruker Smart Apex diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å) using a SMART CCD camera. Diffractometer control, data collection and initial unit-cell determination was performed using "SMART" (v5.625 Bruker-AXS). Frame integration and unit-cell refinement software was carried out with the "SAINT+" (v6.22, Bruker AXS). Absorption corrections were applied by SADABS (v2.03, Sheldrick). Structures were solved by direct methods using SHELXS-97 (Sheldrick, 1990) and refined by full-matrix least squares using SHELXL-97 (Sheldrick, 1997) [30]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions.

(**1**) Colourless crystals, $C_{30}H_{21}F_6P_1Ru_1$, dimensions $0.15 \times 0.15 \times 0.25$ mm; $M_r = 627.51$; Monoclinic $P2_1/c$, $a = 12.218(6)$, $b = 26.847(12)$, $c = 15.132(7)$ Å, $V = 4964(4)$ Å^3, $Z = 8$, λ(Mo Kα) = 0.71073 Å, $\rho_{calc} = 1.679$ g cm^{-3}, $T = 115(2)$ K, $F(000) = 2512$, θ range for data collection 1.52–25.15 °, limiting indices $-14 \leqslant h \leqslant 13$, $-28 \leqslant k \leqslant 32$, $-13 \leqslant l \leqslant 17$ 27649/8802 collected/unique reflections ($R_{(int)} = 0.0738$), goodness of fit on $F^2 = 0.973$, $\Delta\rho_{max/min} = 2.349/-0.678$ e Å^{-3}, final R indices ($I > 2\sigma(I)$) $R_1 = 0.0455$, $wR_2 = 0.0967$.

(**3a**) Yellow crystals, $C_{35}H_{26}F_{12}Fe_2P_2$, dimensions $0.25 \times 0.20 \times 0.20$ mm; $M_r = 848.20$; Monoclinic $P2_1/c$, $a = 8.8052(8)$, $b = 18.3273(17)$, $c = 20.1367(19)$ Å, $V = 3200.7(5)$ Å^3, $Z = 4$, λ(Mo Kα) = 0.71073 Å, $\rho_{calc} = 1.760$ g cm^{-3}, $T = 115(2)$ K, $F(000) = 1704$, θ range for data collection 1.51–25.03°, limiting indices $-10 \leqslant h \leqslant 10$, $-21 \leqslant k \leqslant 19$, $-23 \leqslant l \leqslant 21$ 17607/5636 collected/unique reflections ($R_{(int)} = 0.0275$), goodness of fit on $F^2 = 1.052$, $\Delta\rho_{max/min} = 0.938/-0.588$ e Å^{-3}, final R indices ($I > 2\sigma(I)$) $R_1 = 0.0378$, $wR_2 = 0.0989$.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 279231 and 279232 for compounds **1** and **3a**, respectively. Copies of this information may be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 2EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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