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Synthesis of η^5-1,2,3,4,5-pentamethylcyclopentadienyl-platinum complexes *

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Abstract

Reaction of K_2PtCl_4 with pentamethylcyclopentadiene gave the *exo*-H isomer (**1b**, 25%) as well as the *endo*-H isomer (**1a**, 75%) of $[Pt(\eta^4\text{-}C_5Me_5H)Cl_2]$. The mixture reacted with $AgBF_4$ in acetone at −78°C to give the mixed *endo*-H, *exo*-H isomeric dication solvate complexes $[Pt(\eta^4\text{-}C_5Me_5H)(acetone)_x]^{2+}(BF_4^-)_2$ (**2a,b**), which decompose at room temperature to give $[Pt(\eta^4\text{-}C_5Me_5H)(\eta^5\text{-}C_5Me_5)]^+BF_4^-$ (**3**). The same reaction of **1a,b** in the presence of dienes (pentamethylcyclopentadiene, cyclopentadiene, 1,3-cyclohexadiene, and 1,5-cyclooctadiene) occurs with spontaneous deprotonation to give the monocationic complexes, **3**, $[Pt(\eta^4\text{-}C_5Me_5H)(\eta^5\text{-}C_5Me_5)]^+BF_4^-$ (**4a,b**), $[Pt(\eta^4\text{-}C_6H_8)(\eta^5\text{-}C_5Me_5)]^+BF_4^-$ (**5**), and $[Pt(\eta^4\text{-}C_8H_{12})(\eta^5\text{-}C_5Me_5)]^+BF_4^-$ (**6**), respectively, in high yield. The products from the reaction depend on the ability of the coordinated diene to undergo deprotonation in an intermediate, in the order, η^4-1,3-cyclohexadiene ~ η^4-1,5-cyclooctadiene < η^4-*endo*-pentamethylcyclopentadiene < η^4-*exo*-pentamethylcyclopentadiene < η^4-cyclopentadiene. The solvent complexes $[M(\eta^5\text{-}C_5Me_5)(acetone)_3]^{2+}(BF_4^-)_2$ (M = Rh, Ir) react with C_5Me_5H to give decamethyl-rhodocenium and -iridocenium salts.

Key words: Platinum; Cyclopentadienyl; Rhodocenium; Iridocenium

1. Introduction

Pentamethylcyclopentadienyl complexes of platinum have been far less studied than those of other transition metals. The main method of synthesis involves interaction of C_5Me_5M (M = Li [1], Na [1], MgCl [2,3]) with platinum halides, but these reactions are often accompanied by nucleophilic addition of $C_5Me_5^-$ to hydrocarbon ligands [1] and cannot be used to make cationic compounds. Recent attempts to prepare pentamethylcyclopentadienyl platinum derivatives starting from $[Pt_2(R)_2(L)_2(\mu\text{-}OH)_2]$ and pentamethylcyclopentadiene were unsuccessful [4]. Pentamethylcyclopentadienyl platinum complexes of the type $[Pt(\eta^5\text{-}C_5Me_5)X_n]$ that could be convenient sources of $[Pt(\eta^5\text{-}C_5Me_5)]^+$ fragments are largely unknown [5]. The only exception is the material which, from its microanalysis and NMR spectrum, was identified as the Pt(IV) salt, $[Pt_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}Br_3)]Br_3$, and which was obtained by reaction of the *endo*-H isomer of $[Pt(\eta^4\text{-}C_5Me_5H)Cl_2]$ with bromine [6].

We here report a simple and more general synthesis of η^5-C_5R_5Pt(II) complexes involving use of dicationic solvent species.

2. Results and Discussion

2.1. The generation of $[Pt(\eta^4\text{-}C_5Me_5H)(acetone)_x]^{2+}(BF_4^-)_2$

Only the *endo*-H isomer of $[Pt(\eta^4\text{-}C_5Me_5H)Cl_2]$ was isolated from direct interaction of platinum(II) salts with hexamethyl "Dewar-benzene" (hexamethyl-

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* With best wishes to Professor Helmut Werner on his 60th birthday.

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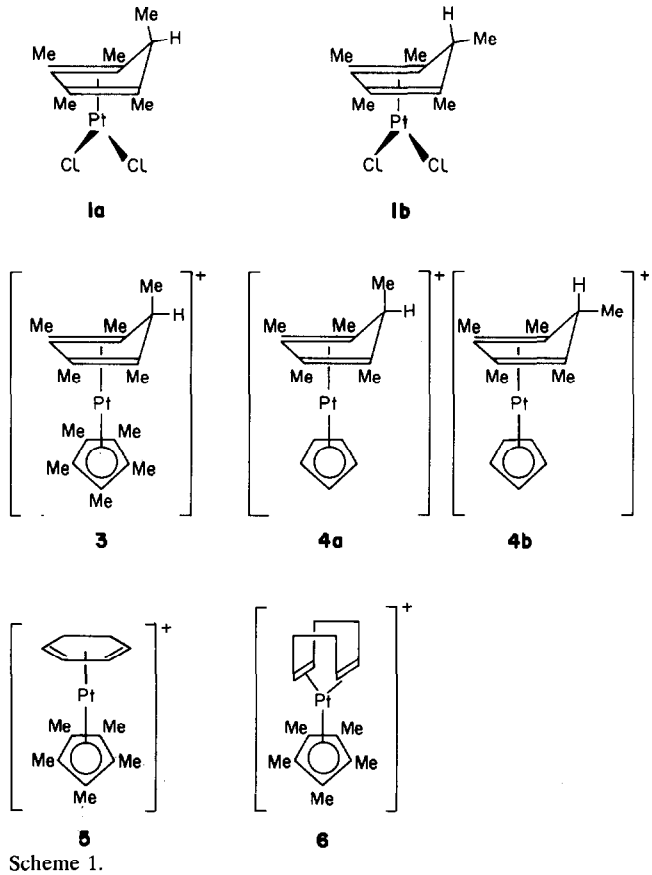

Scheme 1.

bicyclo[2.2.0]hexadiene) in methanol solution in the presence of $SnCl_2$ [7]. By contrast, the reaction of pentamethylcyclopentadiene with K_2PtCl_4 in methanol in the presence of $SnCl_2$ gave a mixture which was shown to contain the *exo*-H isomer (**1b**, 25%) in addition to the major product, the *endo*-H isomer (**1a**, 75%).

$$K_2PtCl_4 + C_5Me_5H \longrightarrow [Pt(\eta^4\text{-}endo\text{-}C_5Me_5H)Cl_2] \quad \mathbf{1a}$$
$$+ [Pt(\eta^4\text{-}exo\text{-}C_5Me_5H)Cl_2] \quad \mathbf{1b}$$

The ^1H NMR spectrum of the mixture of **1a** and **1b** showed two singlets for each isomer arising from the methyl groups on the co-ordinated diene at δ 1.40 (J(Pt–H) = 9.4), 2.23 (J(Pt–H) = 39.2) (**1a**) and 1.26 (J(Pt–H) = 10.5), 2.26 (J(Pt–H) = 37.6 Hz) (**1b**). The methyls and the H on the sp^3 carbons were observed at 0.99 (d, CH_3, J = 6.6) and 3.41 (q, H_{endo}, J = 6.6) for isomer **1a**, and at 1.58 (d, CH_3, J = 7.2) and 2.34 (q, H_{exo}, J = 7.2 Hz) for **1b**. The resonances of **1a** were assigned by comparison with those of the authentic material [7]; from this comparison it is evident that in the *endo*-H isomer the sp^3 C–Me comes at higher field (lower frequency, typically $\delta < 1.0$) and the C–H at lower field (higher frequency) than in the *exo*-H isomer. The structures proposed for other complexes of this type are based on extensions of this relationship.

The interaction of the mixed isomers **1a,b** with silver tetrafluoroborate in acetone at −78°C gave the dicationic solvent complexes **2a,b**,

$$[Pt(\eta^4\text{-}endo\text{-}C_5Me_5H)Cl_2] + [Pt(\eta^4\text{-}exo\text{-}C_5Me_5H)Cl_2] + 2AgBF_4 \longrightarrow$$
$$[Pt(\eta^4\text{-}endo\text{-}C_5Me_5H)(acetone)_x]^{2+}(BF_4^-)_2 \quad \mathbf{2a}$$
$$+ [Pt(\eta^4\text{-}endo\text{-}C_5Me_5H)(acetone)_x]^{2+}(BF_4^-)_2 \quad \mathbf{2b}$$

Complexes **2a,b** were very unstable and were characterised only by ^1H NMR spectroscopy at −50°C; they were formed in the same ratio (**2a**:**2b** = 3:1) as **1a** and **1b**. The spectrum of **2a,b** is very similar to that of **1a,b**, with a small downfield shift, to 4.00 ppm, for the *endo*-H resonance in **2a**. The signal of the *exo*-H was not observed due to its low concentration and the instability of **2b**. The methyl groups of **2a** and **2b** have almost the same chemical shifts as in **1a** and **1b**, but J(Pt–H) has increased from 10 to 40 Hz.

The solution of **2a,b** decomposed rapidly at room temperature, presumably with liberation of pentamethylcyclopentadiene, and the monocationic complex $[Pt(\eta^4\text{-}C_5Me_5H)(\eta^5\text{-}C_5Me_5)]^+BF_4^-$ (**3**) was isolated in low yield.

2.2. The interaction of $[Pt(\eta^4\text{-}C_5Me_5H)(acetone)_x]^{2+}(BF_4^-)_2$ (2a,b) with dienes

2.2.1. Pentamethylcyclopentadiene

When **2a,b** was generated from $[Pt(\eta^4\text{-}C_5Me_5H)Cl_2]$ (**1a,b**) and $AgBF_4$ in the presence of pentamethylcyclopentadiene at room temperature the monocationic sandwich complex **3** was formed in 76% yield; this supports the reaction path suggested above.

$$\mathbf{1a,b} + AgBF_4 + C_5Me_5H \longrightarrow [Pt(\eta^4\text{-}C_5Me_5H)(\eta^5\text{-}C_5Me_5)]^+BF_4^- \quad \mathbf{3}$$

The rhodium and iridium complexes $[M(\eta^5\text{-}C_5Me_5)(solvent)_3]^{2+}$ react with dienes to give dicationic species which undergo spontaneous deprotonation and give enyl compounds [8], and it is probable that **3** is formed by similar path.

$$\mathbf{2a,b} + C_5Me_5H \longrightarrow [Pt(\eta^4 - C_5Me_5H)_2](BF_4)_2 \longrightarrow \mathbf{3}$$

The ^{1}H NMR spectrum of **3** shows only one isomer. The C(Me)H resonances of the η^4-C_5Me_5H ligand were observed at δ 0.68 (d, 3 H, J 6.4), which was assigned to the CH_{3exo}, and at 3.59 ppm (q, 1 H, J(Pt–H) 54.8 Hz) assigned to H_{endo}; thus **3** is presumed to have the *endo*-H structure [9]. The reason that only one isomer was obtained from the isomeric mixture **2a,b**, is presumably due to the different reactivities of the *endo*-H and *exo*-H atoms, with the *exo*-H isomer in the intermediate dication being more easily deprotonated. A higher reactivity of the *exo*-H relative to the *endo*- has been previously noted for η^4-pentamethylcyclopentadiene rhodium complexes [9].

2.2.2. Cyclopentadiene

Cyclopentadiene has been found to react with the dicationic solvent complexes of rhodium [8], iridium [8], and palladium [10] and to give η^5-cyclopentadienyl complexes. It was found that on reaction with **2a,b**, cyclopentadiene gave a mixture of two isomers (again in the ratio 3 : 1), which are assigned to the *endo*-H and *exo*-H isomers **4a,b**, respectively, on the basis of the chemical shifts of CH_{3exo} and CH_{3endo} (δ 0.70 and 1.41 respectively). Deprotonation of C_5Me_5H and formation of η^5-C_5Me_5 complexes was not observed, probably because of the higher C–H acidity of cyclopentadiene ($pK_a = 18.0$) than of pentamethylcyclopentadiene ($pK_a = 26.1$) [11]. Thus in the intermediate $[Pt(\eta^4\text{-}C_5H_6)(\eta^4\text{-}C_5Me_5H)]^{2+}(BF_4^-)_2$ the η^4-C_5H_6 rather than the η^4-C_5Me_5H is deprotonated.

1a,b + $AgBF_4$ + C_5H_6 ⟶

$$[Pt(\eta^4\text{-}endo\text{-}C_5Me_5H)(\eta^5\text{-}C_5H_5)]^+BF_4^- \quad \mathbf{4a}$$

$$+\,[Pt(\eta^4\text{-}exo\text{-}C_5Me_5H)(\eta^5\text{-}C_5H_5)]^+BF_4^- \quad \mathbf{4b}$$

The ^{1}H NMR spectrum for **4a,b** is very similar to that of **1a,b**, except for the additional signals from the η^5-C_5H_5 rings at δ 6.18 (s, J(Pt–H) 25.2 Hz) (**4a**) and 6.21 (s, J(Pt–H) 24.2 Hz) (**4b**). The resonance of the *exo*-H in **4b** is shifted downfield to 5.70 (q, J 6.6, J(Pt–H) 140.3 Hz); similar large downfield shifts of *exo*-H's have previously been reported for η^4-C_5H_6 complexes of the third row transition metals iridium [9,12] and rhenium [13]. In the ^{13}C NMR spectrum of **4a,b** the resonances of the η^4-*endo*-C_5Me_5H and η^4-*exo*-C_5Me_5H ligands are very close to those of **1a,b**; on the other hand a large difference (20 p.p.m.) is observed for chemical shifts of the high field *C*Me atoms on going from **1a,b** to **4a,b**. This may be due to higher back donation from $[Pt(\eta^5\text{-}C_5H_5)]^+$ than from $PtCl_2$ [12].

2.2.3. 1,3-cyclohexadiene and 1,5-cyclooctadiene

1,3-Cyclohexadiene and 1,5-cyclooctadiene were also successfully used to make pentamethylcyclopentadienyl complexes, and gave the cationic compounds **5** and **6** in high yield when they were treated with **2a,b**

1a,b + $AgBF_4$ + diene ⟶

$$[Pt(\eta^4\text{-diene})(\eta^5\text{-}C_5Me_5)]^+BF_4^-$$

5, diene = 1,3-cyclohexadiene
6, diene = 1,5-cyclooctadiene

The ^{1}H NMR spectrum of **5** shows δ 1.50-1.90 (m, 4 H, CH_2CH_2), 4.43 (m, 2 H, J(Pt–H) 34 Hz), 6.12 (m, 2 H, J(Pt–H) 42.4 Hz) (η^4-1,3-C_6H_8) and the spectrum of **6** is similar to that reported earlier [1]. No evidence of any isomerisation of the dienes was observed.

Presumably the interaction of **2a,b** with these dienes also leads to the formation of bis-diene dicationic intermediates $[Pt(\eta^4\text{-diene})(\eta^4\text{-}C_5Me_5H)]^{2+}(BF_4^-)_2$, which undergo spontaneous deprotonation. The type of complex isolated will therefore depend on the relative abilities of the various coordinated dienes to undergo spontaneous deprotonation, and these can be assumed to increase in the order, η^4-1,3-cyclohexadiene ~ η^4-1,5-cyclooctadiene < η^4-*endo*- pentamethylcyclopentadiene < η^4-*exo*-pentamethylcyclopentadiene < η^4-cyclopentadiene. This agrees with the relative C–H acidities of pentamethylcyclopentadiene and cyclopentadiene; unfortunately no data are available for the others.

2.3. Synthesis of decamethylrhodocenium and -iridocenium salts

This investigation has shown that $[Pt(\eta^4\text{-}C_5Me_5H)Cl_2]$ (**1a,b**) can be used as a source for $[Pt(\eta^5\text{-}C_5Me_5)]^+$ and $[Pt(\eta^4\text{-}C_5Me_5H)]^+$. The ability of pentamethylcyclopentadiene to undergo spontaneous deprotonation has also been used in the synthesis of decamethylrhodocenium and -iridocenium salts,

$$[M(\eta^5\text{-}C_5Me_5)(acetone)_3]^{2+}(BF_4^-)_2$$

$$+\,C_5Me_5H \longrightarrow [M(\eta^5\text{-}C_5Me_5)_2]^+BF_4^-$$

The last reaction, as well as that of **2a,b** with pentamethylcyclopentadiene, shows that a pentamethylcyclopentadienyl ligand can be introduced into transition metal complexes without using its organometallic derivatives.

3. Experimental details

All experiments were carried out using Schlenk techniques under argon. Solvents were purified by standard methods. ^{1}H and ^{13}C NMR spectra were

obtained with Bruker WP-200SY and Varian VXR 300 spectrometers in $CDCl_3$ and $(CD_3)_2CO$ solutions. All chemicals shifts are reported in ppm (δ) relative to TMS.

3.1. Preparation of $[Pt(\eta^4\text{-}C_5Me_5H)Cl_2]$ (1a,b)

Pentamethylcyclopentadiene (0.5 cm^3, 0.42 mmol) and solution of $SnCl_2xH_2O$ (0.03 g, 0.2 mmol) in concentrated hydrochloric acid (6 cm^3) were added to a suspension of K_2PtCl_4 in methanol (25 cm^3). The mixture was refluxed (4 h), cooled (to 20°C) and concentrated *in vacuo*. The yellow solid was filtered off, washed with methanol and diethyl ether, dried *in vacuo* and crystallised from CH_2Cl_2/Et_2O. Yield 0.33 g (82%). Anal. Calc. for $C_{10}H_{16}Cl_2Pt$: C, 29.8; H, 4.0; Cl, 17.6. Found C, 29.8; H, 4.1; Cl, 17.6. ^1H NMR ($(CD_3)_2CO$) δ 0.99 (d, 3 H, CH_{3exo}, J 6.6 Hz), 1.40 (s, 6 H 6H, $2CH_3$, J(Pt–H) 9.4 Hz), 2.23 (s, 6 H, $2CH_3$, J(Pt–H) 39.2 Hz), 3.41 (q, H_{endo}, J 6.6 J(Pt–H) 2.5 Hz) **1a**; 1.26 (s, 6 H, $2CH_3$, J(Pt–H) 10.5 Hz), 1.58 (d, 3 H, CH_{3endo}, J 7.2 Hz), 2.26 (s, 6 H, $2CH_3$, J(Pt–H) 37.6 Hz), 2.34 (q, 1 H, H_{exo} J 7.2 Hz) **1b**. ^{13}C NMR ($CDCl_3$) δ 10.0 (2*Me*, J(Pt–C) 20 Hz), 13.0 (2*Me*, J(Pt–C) 3 Hz), 21.9 (Me_{exo}, J(Pt–C) 57.8 Hz), 58.0 (*C*HMe, J(Pt–C) 100 Hz), 103.4 (2*C*Me, J(Pt–C) 118 Hz), 110.0 (2*C*Me, J(Pt–C) 115 Hz) (**1a**); 9.8 (2*Me*), 12.6 (2*Me*), 29.8 (Me_{endo}), 55.4 (*C*HMe), 101.3 (2*C*Me), 110.0 (2*C*Me) (**1b**). (Coupling constants J(Pt–C) for **1b** have not been determined because of the poor solubility of the complex.)

3.2. Reaction of 1a,b with $AgBF_4$ to give $[Pt(\eta^4\text{-}C_5Me_5H)(acetone)_x]^{2+}(BF_4^-)_2$ (2a,b)

A solution of the isomer mixture **1a,b** (40 mg, 0.1 mmol) in $(CD_3)_2CO$ (2.0 cm^3) was cooled to −78°C and $AgBF_4$ (40 mg, 0.2 mmol) was added. The mixture was stirred (20 min/ − 78°C) and then filtered quickly. The ^1H NMR spectrum of the solution was recorded at −50°C δ 0.99 (d, 3 H, CH_{3exo}, J 6.5 Hz), 1.38 (s, 6 H, $2CH_3$, J(Pt–H) 41.0 Hz), 2.40 (s, 6 H, $2CH_3$, J(Pt–H) 39.0 Hz), 4.00 (q, 1 H, H_{endo}, J 6.5 Hz), **2a**; 1.23 (s, 6 H, 2 CH_3, J(Pt–H) 42.1 Hz), 1.74 (d, 3 H, CH_{3endo}, J 7.3), 2.41 (s, 6 H, $2CH_3$, J(Pt–H) 41.2 Hz) **2b**. The solution was allowed to warm to room temperature, stirred for 4 h, and then evaporated to dryness *in vacuo*. The residue was washed with diethyl ether and crystallised from $CH_2Cl_2Et_2O$. Yield 8 mg (29%) of complex **3**, identified by its NMR spectrum. ^1H NMR ($(CD_3)_2CO$) δ 0.68 (d, 3 H, CH_{3exo}, J 6.4) 1.58 (s, 6 H, $2CH_3$, J(Pt–H) 30.5 Hz), 1.99 (s, 15 H, C_5Me_5, J(Pt–H) 19.8 Hz), 2.33 (s, 6 H, $2CH_3$, J(Pt–H) 23.6 Hz), 3.59 (q, 1 H, H_{endo}, J(Pt–H) 54.8 Hz).

3.3. Reaction of 2a,b with dienes (general procedure) (3–6)

Silver tetrafluoroborate (0.39 g, 2.0 mmol) was added to a solution of **1a,b** (0.40 g, 1.0 mmol) and the diene (4.0 mmol) in acetone (15 cm^3); The mixture was stirred (2 h, 20°C) and then filtered. The filtrate was concentrated, and diethyl ether (30 cm^3) was added, to give a precipitate that was filtered off, washed with ether, crystallised from CH_2Cl_2/Et_2O and dried under *vacuo*.

3.3.1. $[Pt(\eta^4\text{-}C_5Me_5H)(\eta^5\text{-}C_5Me_5)]^+BF_4^-$ (3)

Yield 0.42 g (76%). Anal. Calc. for $C_{20}H_{31}BF_4Pt$: C, 43.4; H, 5.6; F, 13.7. Found C, 43.0; H, 5.4; F, 13.4%. ^1H NMR ($(CD_3)_2CO$) δ 0.68 (d, 3 H, CH_{3exo}, J 6.4), 1.58 (s, 6 H, $2CH_3$, J(Pt–H) 30.5 Hz), 1.99 (s, 15 H, C_5Me_5, J(Pt–H) 19.8 Hz), 2.33 (s, 6 H, $2CH_3$, J(Pt–H) 23.6 Hz), 3.59 (q, 1 H, H_{endo}, J(Pt–H) 54.8 Hz). ^{13}C NMR ($CDCl_3$) δ 8.1 (C_5Me_5, J(Pt–C) 9 Hz), 8.6 (2*Me*, J(Pt–C) 22 Hz), 10.6 (2*Me*, J(Pt–C) 23 Hz), 26.8 (Me_{exo}, J(Pt–C) 126 Hz), 58.6 (*C*HMe, J(Pt–C) 128 Hz), 77.7 (2*C*Me, J(Pt–C) 203 Hz), 99.7 (2*C*Me, J(Pt–C) 95 Hz), 104.2 (C_5Me_5, J(Pt–C) 49 Hz).

3.3.2. $[Pt(\eta^4\text{-}C_5Me_5H)(\eta^5\text{-}C_5H_5)]^+BF_4^-$ (4a,b)

Yield 0.39 g. Anal. Calc. for $C_{15}H_{21}BF_4Pt$: C, 37.6; H, 4.3; F, 15.7. Found C, 37.1; H, 4.0; F, 15.7%. ^1H NMR ($(CD_3)_2CO$) δ 0.70 (d, 3 H, CH_{3exo}, J 6.4), 1.96 (s, 6 H, $2CH_3$, J(Pt–H) 36.2 Hz), 2.67 (s, 6 H, $2CH_3$, J(Pt–H) 28.4 Hz), 3.90 (q, 1 H, H_{endo}, J 6.4, J(Pt–H) 53.0 Hz), 6.18 (s, 5 H, C_5H_5, J(Pt–H) 25.2 Hz) (**4a**); 1.41 (d, 3 H, CH_{3endo}, J 6.6, J(Pt–H) 56.0 Hz), 1.67 (s, 6 H, $2CH_3$, J(Pt–H) 36.2 Hz), 2.70 (s, 6 H, $2CH_3$, J(Pt–H) 28.0 Hz), 5.70 (q, 1 H, H_{exo}, J 6.6, J(Pt–H) 140.3 Hz), 6.21 (s, 5 H, C_5H_5, J(Pt–H) 24.2 Hz) (**4b**). ^{13}C NMR ($CDCl_3$) δ 10.6 (2*Me*, J(Pt–C) 22 Hz), 14.5 (2*Me*, J(Pt–C) 18 Hz), 27.9 (Me_{exo}, J(Pt–C) 12 Hz), 59.9 (CMe_{exo}, J(Pt–C) 123 Hz), 82.0 (2*C*Me, J(Pt–C) 189 Hz), 94.1 (C_5H_5, J(Pt–C) 41 Hz), 104.7 (2*C*Me, J(Pt–C) 105 Hz) (**4a**); 10.4 (2*Me*, J(Pt–C) 22 Hz), 14.4 (2*Me*, J(Pt–C) 15 Hz), 18.2 (Me_{endo}, J(Pt–C) 54 Hz), 54.3 (CMe_{endo}, J(Pt–C) 123 Hz), 82.0 (2*C*Me, J(Pt–C) 189 Hz), 94.1 (C_5H_5, J(Pt–C) 41 Hz), 105.1 (2CMe, J(Pt–C) 105 Hz) (**4b**).

3.3.3. $[Pt(\eta^4\text{-}C_6H_8)(\eta^5\text{-}C_5Me_5)]^+BF_4^-$ (5)

Yield 0.33 g (66%). Anal. Calc. for $C_{16}H_{23}BF_4Pt$: C, 38.6; H, 4.7; F, 15.3. Found C, 38.4; H, 4.7; F, 15.65%. ^1H NMR ($(CD_3)_2CO$) δ 1.50–1.90 (m, 4 H, CH_2CH_2), 2.32 (s, 15 H, C_5Me_5, J(Pt–H) 20.8 Hz), 4.43 (m, 2H, J(Pt–H) 34.0 Hz), 6.12 (m, 2 H, J(Pt–H) 42.4 Hz).

3.3.4. [Pt(η^4-C_8H_{12})(η^5-C_5Me_5)]$^+BF4^-$ (6)

Yield 0.42 g (82%). Anal. Calc. for $C_{18}H_{27}BF_4Pt$: C, 41.1; H, 5.4; F, 14.45. Found C, 40.8; H, 5.1; F, 14.9%. ^{1}H NMR ($(CD_3)_2CO$) δ 2.15 (s, 15 H, C_5Me_5, J(Pt–H) 14.0 Hz), 2.54 (m, 8 H, $4CH_2$), 4.71 (m, 4 H, 4CH, J(Pt–H) 78.0 Hz).

3.3.5. Preparation of [Rh(η^5-C_5Me_5)$_2$]$^+BF_4^-$

Silver tetrafluoroborate (0.39 g, 2 mmol) was added to a suspension of [Rh(η^5-C_5Me_5)Cl_2]$_2$ in acetone (10 cm^3) and the mixture stirred (15 min, 20°C) and then filtered. The solid was washed with acetone (2 × 5 cm^3) and pentamethylcyclopentadiene (0.5 cm^3, 0.42 mmol) was added to the combined acetone solutions. The solution was stirred (1 h, 20°C); and then concentrated, and diethyl ether added. The precipitate was filtered off, washed with diethyl ether and dried *in vacuo*. Yield 0.39 g (78%). Anal. Calc. for $C_{20}H_{30}BF_4Rh$: C, 52.2; H, 6.6. Found C, 51.5; H, 6.7. ^{1}H NMR ($(CD_3)_2CO$) δ 1.78 s.

The complex [Ir(η^5-C_5Me_5)$_2$]$^+BF_4^-$ was prepared, by the method used for as decamethylrhodocenium, from [Ir(η^5-C_5Me_5)Cl_2]$_2$ (0.40 g, 0.5 mmol). Yield 0.46 g, 83%. Anal. Calc. for $C_{20}H_{30}BF_4Ir$: C, 43.7; H, 5.5. Found C, 43.7; H 5.5%. ^{1}H NMR ($(CD_3)_2CO$) δ 1.92 s.

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