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Preliminary Communication

Bis(η^5-pentamethylcyclopentadienyl)- and (η^5-cyclopentadienyl)(η^5-pentamethylcyclopentadienyl)-platinium dications: Pt(IV) metallocenes

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Abstract

Reaction of $[Pt_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}Br)_3]^{3+}(Br^-)_3$ with C_5R_5H (R = H, Me) in the presence of $AgBF_4$ gives the first platinocenium dications, $[Pt(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5R_5)]^{2+}(BF_4^-)_2$. On electrochemical reduction, $[Pt(\eta^5\text{-}C_5Me_5)_2]^{2+}$ yields $[Pt(\eta^4\text{-}C_5Me_5H)(\eta^2\text{-}C_5Me_5)]^+ BF_4^-$.

Key words: Cyclopentadienyl; Metallocenes; Platinum; Electrochemistry

Introduction

Although the 20-electron dicyclopentadienyl–nickel complexes nickelocene, pentamethyl- and decamethylnickelocene are all well known [1], there seem to be no reliable reports of the corresponding metallocenes of either Pd(II) or Pt(II). Attempts to prepare palladocene and platinocene by analogy with nickelocene starting from Pd(II) or Pt(II) salts and metal cyclopentadienides were unsuccessful, probably because of the instability of the metallocenes; the usual products were dimeric monocyclopentadienyls [2]. There also seem to be no reports concerning the corresponding M(III) and M(IV) (M = Pd, Pt) metallocenes. Nickelocene [3], pentamethyl- [4] and decamethyl-nickelocene [5,6] can be oxidised first to 19-electron cation-radicals and then to 18-electron dications; in the case of Cp_2^*Ni, both the Ni(III) and Ni(IV) cations, $[Ni(\eta^5\text{-}C_5Me_5)_2]^+$ and $[Ni(\eta^5\text{-}C_5Me_5)_2]^{2+}$, were isolated and characterised.

On the basis of our expectation that 18-electron platinocenium dications would be more stable than the neutral 20-electron complexes, we undertook the synthesis of such salts. As starting material we used the pentamethylcyclopentadienyl platinum complex $[Pt_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}Br)_3]^{3+}(Br^-)_3$, **1**, which one of us reported earlier [7]. We found that **1** reacted readily with either cyclopentadiene or pentamethylcyclopentadiene in the presence of silver tetrafluoroborate in acetone to give $[Pt(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)]^{2+}(BF_4^-)_2$, **2**, and $[Pt(\eta^5\text{-}C_5Me_5)_2]^{2+}(BF_4^-)_2$, **3**, respectively (in 50% yield).

$$\left[Pt_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}Br)_3\right]^{3+}(Br^-)_3 + 6\,AgBF_4 + 2\,C_5H_5H \longrightarrow \left[Pt(\eta^5 - C_5Me_5)(\eta^5\text{-}C_5R_5)\right]^{2+}(BF_4^-)_2$$

$$(\mathbf{2})\ R = H;\ (\mathbf{3})\ R = Me$$

The platinocenium(II) dications **2** and **3** were characterised by microanalysis and spectroscopically. The complexes were quite stable, both in the solid and as solutions in water, acetone or dichloromethane. ^1H NMR (acetone-d_6), **2**, δ, 2.78 [15H, C_5Me_5, J(Pt–H) 21.0 Hz]; 7.17 [5H, C_5H_5, J(Pt–H) 30.5 Hz], and **3**, δ, 2.39 [30H, 2 C_5Me_5, J(Pt–H) 19.2 Hz]; ^{13}C NMR (acetone-d_6), **2**, δ, 10.2 [$C_5\mathit{Me}_5$, J(Pt–C) 9.1]; 102.1 [C_5H_5, J(Pt–C) 62.6 Hz], and **3**, δ 8.03 [$C_5\mathit{Me}_5$, J(Pt–C) 9.0 Hz]; 114.6 [C_5Me_5, J(Pt–C) 69.1].

Cyclic voltammetry studies of the penta- and decamethylplatinocenium dications **2** and **3** (carbon-glass electrode, 200 mV s^{-1}, $c = 2 \times 10^{-3}$ M l^{-1}, acetone, 0.2 M Bu_4NPF_6, SCE reference) showed that both compounds undergo one-electron reduction processes. Cathodic peaks were observed at -0.26 V for **2** and at -0.60 V for **3**. It should be noted that the reduction potential of **3** is negative, unlike the first reduction potential of $[Ni(\eta^5\text{-}C_5Me_5)_2]^{2+}$ [4]. Both reduction peaks of **2** and **3** are irreversible, even at -60°C, indicating that the 19-electron cation-radicals of **2** and **3** are very unstable.

That the reactivity of the 19-electron rhodocenes is higher than the cobaltocenes has been clearly demonstrated; on reduction, the rhodocenium salts gave either carbon–carbon bonded dimers or pentamethylcyclopenta*diene* complexes [8,9]. The properties of the 19-electron Pt(III) cation-radical $[Pt(\eta^5\text{-}C_5Me_5)_2]^+$ are

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also rather different from those of the $[Ni(\eta^5\text{-}C_5Me_5)_2]^+$ cation-radical. Thus bulk electrolysis of an acetone solution of **3** at −0.7 V gives the monocationic pentamethylcyclopentadiene complex $[Pt(\eta^4\text{-}C_5Me_5H)(\eta^5\text{-}C_5Me_5)]^+$ **4**, (stereochemistry not established) which was obtained earlier by another route [10]. Preparative oxidation of **4** at +1.3 V resulted in regeneration of dication **3**.

$$\underset{\mathbf{3}}{[Pt(\eta^5\text{-}C_5Me_5)_2]^{2+}(BF_4^-)_2} \underset{-e^- - H}{\overset{+e^- + H}{\rightleftharpoons}} \underset{\mathbf{4}}{[Pt(\eta^4\text{-}C_5Me_5H)(\eta^5\text{-}C_5Me_5)]^+ BF_4^-}$$

Complexes **2** and **3** are the first platinum metallocenes, and the 18-electron dications are the most stable.

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