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Note

Synthesis of cyclopentadienyl ruthenium(II) complexes containing tethered functionalities

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ABSTRACT

The reaction of $[C_5H_4(CH_2)_nX]Tl$ (**1**: $n = 2$, X = NMe_2, OMe, CN; $n = 3$, X = NMe_2) with $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)]_2$, **2**, afforded the sandwich compounds $[\{\eta^5\text{-}C_5H_4(CH_2)_nX\}Ru(\eta^6\text{-}C_6H_6)]PF_6$, **3**, and $[\eta^5\text{-}C_5H_4(CH_2)_nX]_2Ru$, **4**. Photolytic cleavage of **3** in acetonitrile afforded the tethered products $[\{\eta^5{:}\kappa N\text{-}C_5H_4(CH_2)_nX\}Ru(CH_3CN)_2]PF_6$, **5**.

1. Introduction

Ruthenium complexes continue to be of great interest as catalysts for a very wide variety of reactions [1]. A desirable property for a potential molecular catalyst is that it should be able to generate a vacant coordination site which can be "plugged up" readily when not involved in the catalytic reaction. One approach to this is that of hemilabile ligands [2], and the use of cyclopentadienyls substituted with functional groups which can coordinate to the metal centre is an example. We have been interested in this approach and have sought to prepare cyclopentadienylruthenium complexes in which the cyclopentadienyl has an amine or some other functional groups tethered to it. Known examples in the literature include tethered phosphine [3], alkene [4], carborane [5] and amine or pyridine [6]. With the exception of those in which the tether is an N donor, most of these are, however, rather tightly bound to the ruthenium centre. On the other hand, those with O donors appear not to bind [7]. We report here our attempt at the synthesis of such complexes in which the tethered group is NMe_2, OMe or CN.

2. Results and discussion

Our synthesis of the tethered complexes $[\{\eta^5{:}\kappa N\text{-}C_5H_4(CH_2)_nX\}Ru(CH_3CN)_2]PF_6$, **5**, is outlined in Scheme 1. The thallium salts of the substituted cyclopentadienyls **1a–d** were obtainable as spectroscopically pure products after removal of the solvent in vacuo [8]. They were, however, very air-sensitive in solution. Synthesis of the sandwich complexes $[\{\eta^5\text{-}C_5H_4(CH_2)_nX\}\text{-}Ru(\eta^6\text{-}C_6H_6)]PF_6$, **3**, followed that for $[\{\eta^5\text{-}C_5H_4(CH_2)_2NHCbz\}\text{-}Ru(\eta^6\text{-}C_6H_6)]PF_6$ [6a]. They were obtained in moderate yields from the reaction of **1** with $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)]_2$, **2**, and we have found that another product, *viz.*, the substituted ruthenocene $[\eta^5\text{-}C_5H_4(CH_2)_nX]_2Ru$, **4**, was also obtained in variable amounts. The formation of ruthenocene from an analogous reaction with unsubstituted cyclopentadiene has been reported previously [9]. We have also explored alternative routes [9,10] to **3** that obviated the use of thallium but they failed to give the desired product for amine-functionalised cyclopentadiene. The ruthenocenes **4** were identified on the basis of their spectroscopic and analytical data, although **4c** and **4d** were not separable from **3c** and **3d**, respectively. They were obtained as oils, and **4a** formed brown needle-shaped crystals at low temperatures.

The UV photolysis of **3** in acetonitrile solution afforded the tethered complexes **5**. The formation of **5** was indicated by the downfield shifts of the ^1H resonances [11], for example, that for the $N\mathit{Me}_2$ groups in **5a** and **5b** are shifted downfield by 0.43 and 0.34 ppm with respect to those for **3a** and **3b**, respectively. The spectroscopic data are also similar to those for $[\{\eta^5{:}\kappa N\text{-}C_5H_4(CH_2)_2NH_2\}Ru(CH_3CN)_2]PF_6$[6b].

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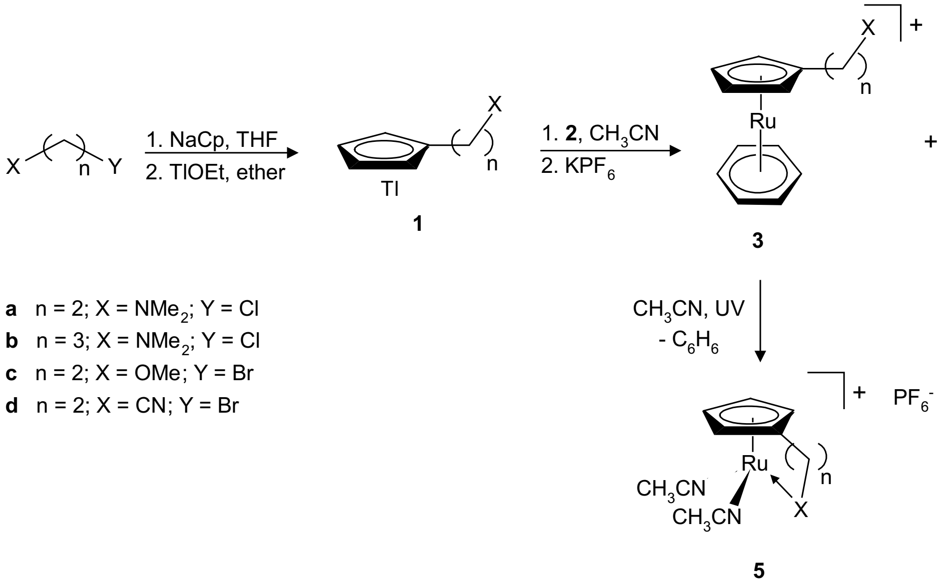

Scheme 1.

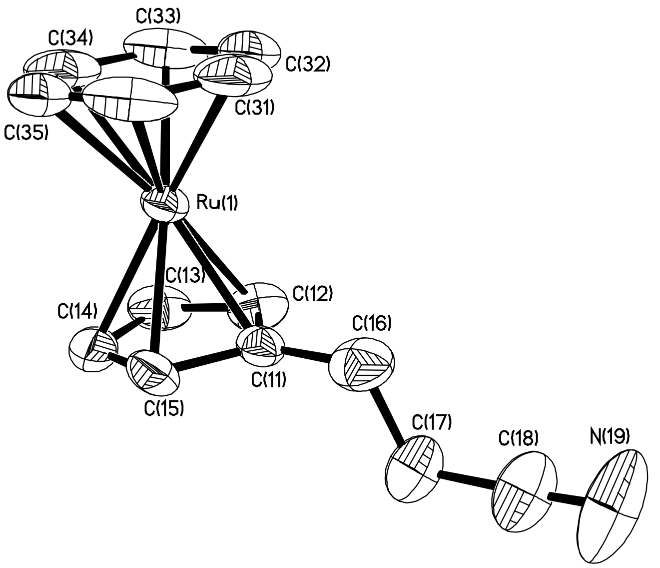

Fig. 1. ORTEP diagram (50% probability thermal ellipsoids) and selected bond lengths (Å) and angles (°) for **3d**. Ru(1)-centroid (C_6) = 1.69(2); Ru(1)-centroid (C_5) = 1.80(2); C(11)–C(16) = 1.51(2); C(16)–C(17) = 1.508(19); C(17)–C(18) = 1.48(2); C(18)–N(19) = 1.12(2); N(19)–C(18)–C(17) = 177.1(19).

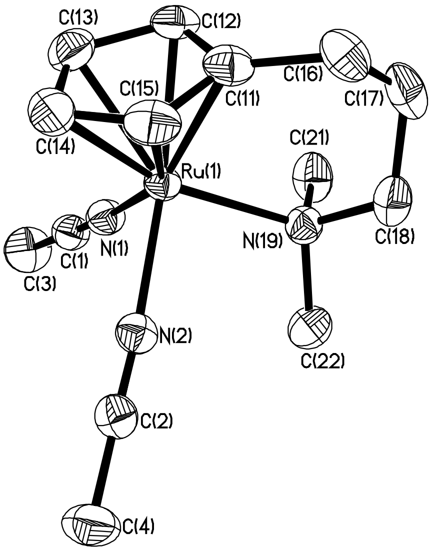

Fig. 2. ORTEP diagram (50% probability thermal ellipsoids) and selected bond lengths (Å) and angles (°) for **5b**. Ru(1)-centroid (C_5) = 1.773(4); Ru(1)–N(1) = 2.080(3); Ru(1)–N(2) = 2.074(3); Ru(1)–N(19) = 2.227(3); C(1)–N(1) = 1.133(4); C(2)–N(2) = 1.132(4); C(18)–N(19) = 1.482(4); C(1)–C(3) = 1.460(5); C(2)–C(4) = 1.450(5); C(11)–C(16) = 1.490(5); C(16)–C(17) = 1.510(7); C(17)–C(18) = 1.523(6); C(1)–N(1)–Ru(1) = 174.4(3); C(2)–N(2)–Ru(1) = 176.1(3); C(18)–N(19)–Ru(1) = 111.8(2); N(1)–C(1)–C(3) = 178.9(4); N(2)–C(2)–C(4) = 179.1(4); N(19)–C(18)–C(17) = 177.1(19).

Crystals of **3d** and **5b** were subjected to single crystal X-ray crystallographic studies. There are two formula units in the asymmetric unit of **3d**. The ORTEP plots and selected bond parameters for one of the cations in **3d** are given in Fig. 1, and for the cation in **5b** in Fig. 2. The two crystallographically distinct molecules in **3d** have largely similar bond parameters; some deviations, such as the C(11)–C(16)–C(17) bond angle (109.5(12)° and 114.3(14)°, for the two molecules) may be attributed to crystal packing forces. The cation of **5b** has a "3-legged piano stool" geometry, with N–Ru(1)–N angles (85.85(11)–89.59(11)°) comparable to those of the cation $[CpRu(CO)_3]^+$ ($\angle C_{CO}$–Ru–C_{CO} = 88.6(2)–94.6(2)°) [12]. The Ru–N bond length (2.227(3) Å) is also comparable to those for some other related compounds (~2.15–2.31 Å) [13].

We have thus shown that the reaction of the thallium salts of substituted cyclopentadienyls with the dimeric species $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)]_2$, **2**, afforded both $[\{\eta^5\text{-}C_5H_4(CH_2)_nX\}Ru(\eta^6\text{-}C_6H_6)]PF_6$, **3**, and the ruthenocene $[\eta^5\text{-}C_5H_4(CH_2)_nX]_2Ru$, **4**. The alternative strategy that would have allowed us to avoid the use of thallium salts failed in our hands. Photolysis of **3** in acetonitrile afforded the tethered complexes $[\{\eta^5{:}\kappa N\text{-}C_5H_4(CH_2)_nX\}\text{- }Ru(CH_3CN)_2]PF_6$, **5**.

3. Experimental

All manipulations were carried out either under argon using standard Schlenk techniques or in a Vacuum Atmospheres Company (VAC) glove box. Photochemical reactions were performed with a Hanovia 450W UV lamp, with a nominal λ_{max} of 254 nm.