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Deprotonation of 1,2,3,4,5-Pentamethylrhodocenium; a New Route to 1-Substituted-2,3,4,5-tetramethylcyclopentadienylrhodium Complexes

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Reaction of $[Rh(C_5Me_5)(C_5H_5)]^+$ with $KOBu^t$ in tetrahydrofuran gives $[Rh(C_5Me_4CH_2)(C_5H_5)]$; it reacts readily with halides (R—X) to give $[Rh(C_5Me_4CH_2R)(C_5H_5)]X$, which can be converted into $[Rh_2(C_5Me_4CH_2R)_2Cl_4]$.

We have recently reported that the iridium(III) complex $[Ir(\eta^5\text{-}C_5Me_5)(CO)(Me)(Ph)]$ **1** is readily metallated by *sec*-butyllithium at a cyclopentadienyl methyl to give an intermediate which can be converted into substituted complexes such as $[Ir(\eta^5\text{-}C_5Me_4CH_2E)(CO)(Me)(Ph)]$ [E = $SiMe_3$, $PhCH_2$, PhCR(OH)].[1]

Although it has long been known that the ring methyls in rhodium C_5Me_5 complexes are appreciably acidic (for example, $[(C_5Me_5Rh)_2(OH)_3]^+$ readily exchanges with D_2O under basic conditions),[2] previous attempts to carry out preparative syntheses, as well as our attempts to carry out similar reactions on the rhodium analogue of **1** have so far met with little success.

However, we now report that the 1,2,3,4,5-pentamethylrhodocenium cation, $[Rh(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)]PF_6$ **2**, reacts readily with potassium *tert*-butoxide in tetrahydrofuran (THF) to give the deprotonated $[Rh(\eta^4\text{-}C_5Me_4CH_2)(\eta^5\text{-}C_5H_5)]$, **3**, as air-sensitive orange–red crystals (in 60–70% yield). This complex was characterised by microanalysis and spectroscopically: ^1H NMR (C_6D_6) δ 1.50 (s, 2 Me), 1.70 (s, 2 Me), 3.39 (s, CH_2), 4.75 [d, C_5H_5, *J*(Rh—H) 1 Hz]; ^{13}C NMR (C_6D_6) δ 11.9, 12.8 (2 × s, C_5*Me*$_4$), 69.05 (s, CH_2), 70.4 [d, 2 × *C*Me, *J*(Rh—C) 11 Hz], 84.05 [d, Cp, *J*(Rh—C) 5 Hz], 91.5 [d, 2 × *C*Me, *J*(Rh—C) 12 Hz], and 94.3 (s, *C*=CH_2). From the absence of coupling to rhodium of either the carbons or the hydrogens in the exocyclic C=CH_2, we deduce that the $C_5Me_4CH_2$ is probably η^4-bonded to the rhodium through the four ring carbons and that the structure of **3** may be best represented as the tetetramethylfulvene Rh^I **3a** rather than the Rh^{III} zwitterion **3b** (Scheme 1). Fulvene complexes of Rh^I, *e.g.* $[Rh(C_5H_5)(C_5H_4{=}CR_2)]$, made by a different route, have recently been reported.[3]

The most convenient preparative route to the functionalized $C_5Me_4CH_2R$ complexes **4** was by generating **3**, and then carrying out a nucleophilic displacement on the reagent R—X. In this manner a number of 1-substituted 2,3,4,5-tetramethylrhodocenium complexes, $[Rh(C_5Me_4CH_2R)(C_5H_5)]X$ **4** were synthesised, including R = $SiMe_3$, 55% {^1H NMR δ 0.02 ($SiMe_3$), 2.08 (CH_2), 2.12 (2 × Me), 2.15

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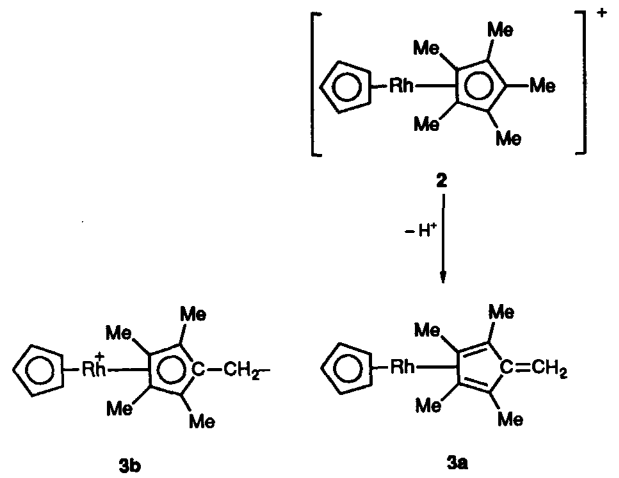
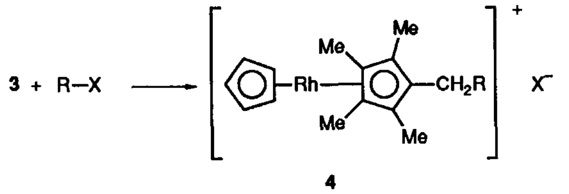


Scheme 1

(2 × Me), 5.46 [d, C_5H_5, J(Rh—H) 1 Hz]}, and R = CH_2Ph, 72% {^1H NMR δ 1.86 (2 × Me), 2.11 (2 × Me), 2.76 (m, CH_2CH_2), 5.48 [d, C_5H_5, J(Rh—H) 1 Hz], 7.15 (m Ph)}.



These complexes are relatively easily converted into $[Rh_2(C_5Me_4CH_2R)_2Cl_4]$; for example, reaction of **4**, R = $SiMe_3$, with phenyllithium followed by hydrolysis and treatment with HCl gave $[Rh_2(C_5Me_4CH_2SiMe_3)_2Cl_4]$; 41% yield, ^1H NMR δ 0.00 ($SiMe_3$), 1.58 (2 × Me), 1.65 (2 × Me), 2.17 (CH_2).

Apart from the C_5Me_5Ir complex just reported,[1] and $C_5Me_5CoC_5H_5{}^+$ which Astruc has very successfully polyalkylated,[4] almost all the other examples of ring—methyl metallation and functionalisation involve methyls on η^6-arene complexes.[5] These reactions on C_5Me_5 complexes thus open up considerable new possibilities for the synthesis of functionalised rhodium complexes which have potential for selective catalysis.[6]

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