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Deprotonation and Subsequent Functionalization of Methyl Groups in Cationic Ruthenium Triple-decker Complexes

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The cationic complex $[(\eta\text{-C}_5\text{Me}_5)\text{Ru}(\mu,\eta\text{-C}_5\text{Me}_5)\text{Ru}(\eta\text{-C}_5\text{Me}_5)]^+$ undergoes deprotonation of the terminal ring methyl groups on treatment with $\text{Bu}^n\text{Li–Bu}^t\text{OK}$ at − 78 °C in tetrahydrofuran; subsequent treatment with EX reagents gives rise to functionalized complexes $[(\eta\text{-C}_5\text{Me}_5)\text{Ru}(\mu,\eta\text{-C}_5\text{Me}_5)\text{Ru}(\eta\text{-C}_5\text{Me}_4\text{CH}_2\text{E})]^+$ (E = Me, Me_3Si, EtS).

The chemistry of triple-decker complexes has been extensively developed since the synthesis of nickel triple-decker complexes $[(\eta\text{-C}_5\text{H}_4\text{R})\text{Ni}(\mu,\eta\text{-C}_5\text{H}_4\text{R})\text{Ni}(\eta\text{-C}_5\text{H}_4\text{R})]^+$ (R = H, Me) by Werner and Salzer in 1972.[1,2] Later, a wide variety of multidecker compounds, based on boron-containing heterocycles, were prepared by other research groups.[3–5] Recently, we have obtained triple-decker complexes of iron group metals with cyclopentadienyl ligands.[6,7] In spite of a considerable number of publications dealing with the synthesis of triple-decker complexes, their properties have not been sufficiently investigated. In the present work we have studied the possibility of deprotonation of the methyl group in cationic ruthenium triple-decker complexes.

It is well known that in cationic complexes such as $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-arene})]^+$ the acidity of the protons at the α-carbon atoms of the arene ligands is enhanced owing to the influence of the positive charge of the complex.[8] More surprising is the relatively high acidity of analogous protons in the cyclopentadienyl ligand, which was first discovered for complex $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{H}_4\text{CHPh}_2)]^+$.[9] This property was recently used for the functionalization of cobalticenium[10] and rhodocenium[11] derivatives as well as of the iridium(III) complex $\text{Ir}(\eta\text{-C}_5\text{H}_5)(\text{CO})\text{MePh}$.[12]

We found that ruthenium complex **1** undergoes deprotonation by a strong base, such as a mixture of $\text{Bu}^n\text{Li–Bu}^t\text{OK}$ at − 78 °C, giving rise to a ruby-red product **2**, which may be represented as a resonance hybrid **2a**↔**2b**. Subsequent treatment with functionalization reagents (MeI, Me_3SiCl, EtSSEt) leads to the modified complexes **3–5** (Scheme 1).†

The ^{1}H NMR data of compounds **3–5**‡ indicate that only the

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† The structures of **3–5** were confirmed by satisfactory results of elemental analysis.

‡ *NMR data* for compound **3**: δ (CDCl_3) 1.53 (s, 6H, $\eta\text{-C}_5\text{Me}_4\text{Et}$), 1.52 (s, 21H, $\eta\text{-C}_5\text{Me}_4\text{Et}$ and $\eta\text{-C}_5\text{Me}_5$), 1.92 (q, 2H, $\text{—CH}_2\text{Me}$, ^3J 7.5 Hz), 0.95 (t, 3H, $\text{—CH}_2\text{Me}$, ^3J 7.5 Hz), 2.15 (s, 15H, $\mu,\eta\text{-C}_5\text{Me}_5$).

For **4**: δ $[(\text{CD}_3)_2\text{CO}]$ 1.61 (s, 6H, $\eta\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_3$), 1.60 (s, 21H, $\eta\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_3$ and $\eta\text{-C}_5\text{Me}_5$), 1.48 (s, 2H, CH_2SiMe_3), − 0.02 (s, 9H, SiMe_3), 2.25 (s, 15H, $\mu,\eta\text{-C}_5\text{Me}_5$).

For **5**: δ $[(\text{CD}_3)_2\text{CO}]$ 1.68, 1.63 (s, 12H, $\eta\text{-C}_5\text{Me}_4\text{CH}_2\text{SEt}$), 1.61 (s, 15H, $\eta\text{-C}_5\text{Me}_5$), 3.29 (s, 2H, $\eta\text{-C}_5\text{Me}_4\text{CH}_2\text{SEt}$), 2.51 (q, 2H, $\text{—CH}_2\text{SCH}_2\text{Me}$, ^3J 7.4 Hz), 1.18 (t, 3H, $\text{—CH}_2\text{SCH}_2\text{Me}$, ^3J 7.4 Hz), 2.31 (s, 15H, $\mu,\eta\text{-C}_5\text{Me}_5$).

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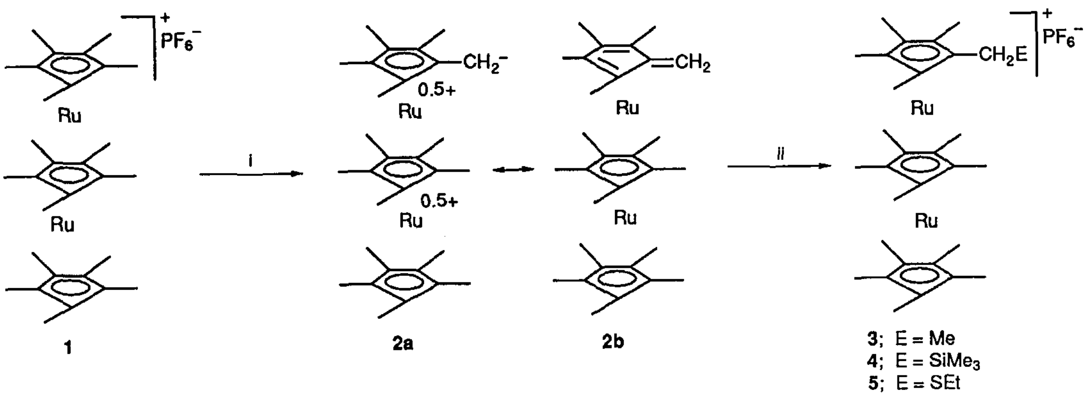

Scheme 1 *Reagents and conditions*: i, Bu^nLi-Bu^tOK, tetrahydrofuran (THF), – 78 °C; ii, EX, – 78 °C

methyl groups of the terminal ring undergo deprotonation. This is rather surprising since, at first sight, deprotronation should occur for the central ring, which is connected to two positively charged ruthenium atoms. This may be explained by the fact that the principle contribution to the stabilization of deprotonation product **2** is made by resonance form **2b**, whereas the realization of an analogous structure with a η^4-tetramethylfulvene ligand in the central position is unlikely.

It should be mentioned that, in contrast to cationic complexes $[M(\eta-C_5H_5)(\eta-C_5Me_5)]^+$ (M = Co, Rh), which are easily deprotonated by $KOBu^t$,[10,11] deprotonation of **1** occurs only on treatment with a much stronger base (Bu^nLi-Bu^tOK). This may be connected with the delocalization of positive charge over a greater number of atoms in the latter case. Using Bu^nLi for deprotonation demands a higher temperature (– 20 to – 30 °C) and is accompanied by partial decomposition.§

We have also investigated the behaviour of the unsymmetrical triple-decker complex $[(\eta-C_5H_5)Ru(\mu,\eta-C_5Me_5)Ru(\eta-C_5Me_5)]^+$ in similar reaction. However, in this case the reaction occurs unselectively. Parallel with deprotonation of the methyl groups in the terminal pentamethylcyclopentadienyl fragment, metallation of the unsubstituted cyclopentadienyl ring also occurs. The ^1H NMR spectrum of the products, obtained after treatment of the reaction mixture with methyl iodide, clearly shows the presence of a monomethylated cyclopentadienyl ring.

Thus, we have investigated the deprotonation of the methyl groups of cationic ruthenium triple-decker complexes and have used this property for their functionalization.

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References

1 H. Werner and A. Salzer, *Synth. Inorg. Met. Org. Chem.*, 1972, **2**, 239.
2 A. Salzer and H. Werner, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 930.
3 R. N. Grimes, *Coord. Chem. Rev.*, 1979, **28**, 47.
4 W. Siebert, *Adv. Organomet. Chem.*, 1980, **18**, 301.
5 G. Herberich, in *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, Pergamon Press, Oxford, 1982, vol. 1, p. 381.
6 A. R. Kudinov, M. I. Rybinskaya, Yu. T. Struchkov, A. I. Yanovskii and P. V. Petrovskii, *J. Organomet. Chem.*, 1987, **336**, 187.
7 M. I. Rybinskaya and A. R. Kudinov, *Metallorg. Khim.*, 1989, **2**, 26 (*Organomet. Chem. USSR*, 1989, **2**, 12).
8 D. Astruc, *Tetrahedron*, 1983, **39**, 4027.
9 J. E. Sheats, W. Miller and T. Kirsch, *J. Organomet. Chem.*, 1975, **91**, 97.
10 D. Gloaguen and D. Astruc, *J. Am. Chem. Soc.*, 1990, **112**, 4607.
11 O. V. Gusev, A. Z. Rubezhov, J. A. Miguel-Garcia and P. M. Maitlis, *Mendeleev Commun.*, 1991, 21.
12 J. A. Miguel-Garcia and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1990, 1472.

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§ Decamethylruthenocene, separated as one of the decomposition products, was identified by its ^1H NMR spectrum.