A New Mechanistic Path in the Reaction of Ruthenium Trichloride with Silylated Cyclopentadienes. Ionic Transition Metal Halides as Desilylating Agents

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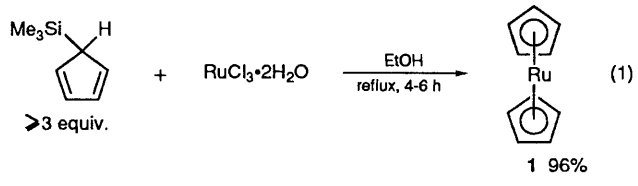
The reaction of hydrated ruthenium trichloride with mono-, bis- and tris-(trimethylsilyl)cyclopentadiene in alcohol solvents leads to high yields of ruthenocene; these processes proceed through an unprecedented chloride ion-induced desilylation of the silylated cyclopentadienes followed by reaction of Ru^{III} ion with cyclopentadiene, rather than the mechanistically distinct carbon–silicon bond cleavage that has been observed in other transition metal halide systems.

The reaction of transition metal halides with silylated or stannylated cyclopentadienes represents a particularly efficient route to certain cyclopentadienyl complexes.[1,2] Advantages of these reagents include the fact that reduction of the metal does not generally occur, that silylated and stannylated reagents can afford different products than the corresponding lithiated analogues, and that these transformations often afford high yields of cyclopentadienyl complexes under very mild conditions. In all such reactions reported to date, treatment of the metal halide with a silylated cyclopentadiene $C_5(SiMe_3)_nH_{6-n}$ (n = 1–3) results in a single desilylation event per cyclopentadiene to afford a complex that contains a cyclopentadienyl ligand containing one less trimethylsilyl substituent, along with the liberation of halogenotrimethylsilane. In the course of our studies,[2] we have discovered an initially puzzling series of reactions that occur by a very different mechanistic pathway. We now report results concerning the reaction of ruthenium trichloride with silylated cyclopentadienes, which affords high yields of ruthenocene and occurs by an unprecedented chloride ion-induced desilylation path.

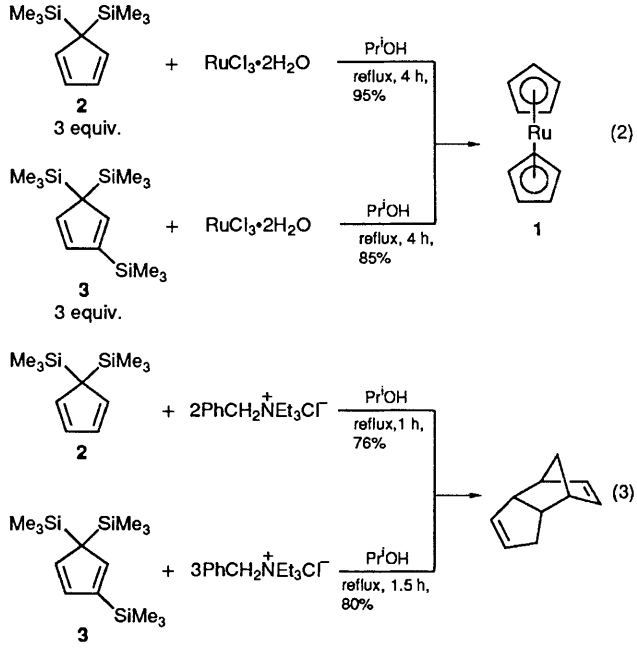
It was initially envisaged that reaction of silylated cyclopentadienes with ruthenium trichloride might afford monocyclopentadienylruthenium dichloride complexes,[3] which would then serve as synthetic precursors to half-sandwich ruthenium complexes. However, reaction of 3–4 equivalents of (trimethylsilyl)cyclopentadiene with ruthenium trichloride in refluxing ethanol for 4–6 h, followed by workup, instead afforded ruthenocene **1** in 96% yield [eqn. (1)]. Ironically, this is the highest yield yet reported for a preparation of this metallocene.[4] The transformation could be achieved in either ethanol or propan-2-ol solvent; methanol gave much lower yields. Reaction in a variety of polar aprotic solvents [acetone, tetrahydrofuran (THF), CH_2Cl_2, benzene] afforded low yields (<50%) of **1**. An excess of (trimethylsilyl)cyclopentadiene (≥3 equiv.) was required to achieve the maximum yields. When the reaction was conducted using 2.0 equivalents of (trimethylsilyl)cyclopentadiene, the yields of **1** ranged from 43 to 47%.

The reaction of ruthenium trichloride with 3 equivalents of bis(trimethylsilyl)cyclopentadiene **2**[5] and tris(trimethylsilyl)-cyclopentadiene **3**[5] was examined next. Surprisingly, both of these reactions afforded **1** in high yield [eqn. (2)]. There was no evidence for the desired 1,1′-bis(trimethylsilyl)ruthenocene and 1,1′,3,3′-tetrakis(trimethylsilyl)ruthenocene. An experiment was performed in which ruthenium trichloride reacted with 3.0 equivalents of **3** (99.8% pure by GLC) in refluxing propan-2-ol for 0.5 h. Analysis of this solution by GLC and GLC–MS showed that when the reaction was about 25% complete, a 93 : 7 ratio of **3** : **2** was present. Additionally, **1** and (trimethylsilyl)ruthenocene had been produced in a 97 : 3 ratio. These results strongly implied that the silylated cyclopentadienes were being desilylated by a species present in the reaction mixture.



In order to understand better the desilylation process, **2** and **3** were treated with a source of ionic chloride under conditions similar to those in the preparation of ruthenocene. Treatment of **2** with benzyltriethylammonium chloride (2 equiv.) in refluxing propan-2-ol for 1 h led to complete conversion to cyclopentadiene dimer [76%, eqn. (3)]. GLC analysis after 0.5 h showed a 13 : 40 : 47 mixture of **2** : (trimethylsilyl)-cyclopentadiene : dicyclopentadiene. A similar reaction of **3** and benzyltriethylammonium chloride (3 equiv.) required 1.5 h for complete conversion to dicyclopentadiene [80%, eqn. (3)], with GLC analysis after 1.0 h affording a 24 : 1 : 6 : 69 mixture of **3** : **2** : (trimethylsilyl)cyclopentadiene : dicyclopentadiene. Refluxing **3** in propan-2-ol for 4 h gave 5–10% reaction, which indicates that alcohols are sufficiently nucleophilic to desilylate **3**, although such a reaction is sluggish relative to that of chloride ion. Hence, **2** and **3** are desilylated by chloride ion in a stepwise manner ultimately to afford dicyclopentadiene. Moreover, ruthenium trichloride reacts much faster with cyclopentadiene than with the silylated cyclopentadienes.

It is clear that the reaction of ruthenium trichloride with silylated cyclopentadienes deviates from the pathway expected by analogy with other metal halides.[1,2] Rather, the polysilylated cyclopentadienes are desilylated by chloride ion to form cyclopentadiene (and its dimer), which then react to form ruthenocene.[4] Halogen promoted cleavage of C(sp³)–Si bonds is precedented;[6] the transition states for reaction of the silylated cyclopentadienes with chloride ion presumably contain considerable aromatic stabilization, which lowers the



energy barrier for the desilylations. Ruthenium trichloride is well known to react in polar protic solvents to form a variety of complexes with chloride counterions;[7] this provides the chloride ion for the desilylation. Furthermore, ruthenium trichloride has been reported to react with cyclopentadiene in refluxing methanol to afford **1** in 80% yield.[4] The alcohol solvent serves as a proton source for the intermediate cyclopentadienide, a reducing agent for Ru^{III},[8] and as a trap for the chlorotrimethylsilane that is produced. Thus, a dichotomy of pathways exists in the reactions of silylated cyclopentadienes with transition metal halides. In early transition metals and other systems where the metal–halogen bond is not highly dissociated, silicon–carbon cleavage occurs to afford a cyclopentadienyl complex containing one less trimethylsilyl substituent than was present in the starting material. However, in the later transition metal halides and in polar solvents, where appreciable ionization of the metal–halogen bond can occur, multiple desilylations ensue, which can lead to complexes containing unsubstituted cyclopentadienyl ligands from polysilylated precursors. The present results provide a mechanistic basis for understanding the various pathways exhibited in reactions of silylated cyclopentadienes with ionizable transition metal halides.

The authors thank the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work and Professor Robert D. Bach for helpful discussions.

Received, 6th March 1991; Com. 1/01051D

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