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LETTER

Relative Reactivity of Decamethylsilicocene and Decamethylsamarocene: Reduction of $(C_5Me_5)_2SiCl_2$ by Sm(II) Reagents

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Recently two remarkable, strongly reducing decamethylmetallocenes have been described in the literature: $(C_5Me_5)_2Si$ (1) [1] and $(C_5Me_5)_2Sm$ (2) [2]. Decamethylsilicocene was the first π complex with silicon as a central atom and decamethylsamarocene was the first f-element complex with just two cyclopentadienyl rings as the only ligands, i.e., the first f-element analog of ferrocene. We were interested in examining the relative reactivities of these two divalent species and decided to examine the reduction of $(C_5Me_5)_2SmCl(THF)$ [3] by 1 and the reduction of $(C_5Me_5)_2SiCl_2$ [4] by 2.

$(C_5Me_5)_2SiCl_2$ is cleanly reduced by 2 in toluene within 14 h to form 1 and $[(C_5Me_5)_2SmCl]_3$ [5] as shown in eqn. (1). Given this result, it was not

$$3(C_5Me_5)_2SiCl_2 + 6(C_5Me_5)_2Sm \longrightarrow 3(C_5Me_5)_2Si + 2[(C_5Me_5)_2SmCl]_3 \qquad (1)$$

surprising that $(C_5Me_5)_2SmCl(THF)$ was not reduced by 1. Hence, the divalent samarium complex is the more strongly reducing of the two decamethylmetallocenes.

We also examined the reduction of $(C_5Me_5)_2SiCl_2$ by other Sm(II) reagents. $(C_5Me_5)_2Sm(THF)_2$ [6] reduces $(C_5Me_5)_2SiCl_2$ cleanly in toluene over a 14-h period, as shown in eqn. (2). Equations (1)

$$(C_5Me_5)_2SiCl_2 + 2(C_5Me_5)_2Sm(THF)_2 \longrightarrow (C_5Me_5)_2Si + 2(C_5Me_5)_2SmCl(THF) \qquad (2)$$

and (2) are consistent with the observed similarity of the $(C_5Me_5)_2Sm(THF)_{0-2}$ complexes and alkali metals [7–11] and with the fact that 1 can be prepared by alkali metal naphthalide reduction of $(C_5Me_5)_2SiCl_2$ [1]. However, $(C_5Me_5)_2SiCl_2$ fails to react with the mono(pentamethylcyclopentadienyl)Sm(II) species $[(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$ [6] in toluene/THF over 3 days. Similarly, $SmI_2(THF)_2$ [12] fails to react with $(C_5Me_5)_2SiCl_2$ in either THF (over 5 days) or toluene (over 8 days). $[(Me_3Si)_2N]_2Sm(THF)_2$ [13] also fails to form $(C_5Me_5)_2Si$ from $(C_5Me_5)_2SiCl_2$ in toluene over a 3-day period.

These results suggest that the presence of the two C_5Me_5 rings is important to the reactivity of Sm(II) in these $(C_5Me_5)_2SiCl_2$ reductions. Traditionally, in trivalent organolanthanide chemistry, steric and electrostatic factors rather than metal–ligand covalent interactions are thought to be most important in affecting the chemistry [11, 14]. For Sm(II), the specific nature of the ligands and the metal–ligand interactions may be considerably more important than is found for trivalent lanthanide complexes.

Experimental

The extremely air- and moisture-sensitive complexes 1 and 2 were handled under nitrogen using Schlenk, vacuum line and glove box techniques. All of the reactions were carried out on a scale of 0.04 to 0.26 mmol of $(C_5Me_5)_2SiCl_2$ or $(C_5Me_5)_2SmCl(THF)$ in 10–30 ml of solvent. In a typical reaction, the $(C_5Me_5)_2SiCl_2$ solution was added to the solution containing the appropriate samarium complex and the reaction was stirred for the time described. The solvent was subsequently removed by rotary evaporation and the reaction mixtures were examined by ^1H NMR spectroscopy.

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