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Reactivity of $[HC\{(C(Me)N(Dipp))\}_2Ca\{N(SiMe_3)_2\}(THF)]$ (Dipp = $C_6H_3{}^iPr_2$-2,6) with C–H acids: Synthesis of heteroleptic calcium η^5-organometallics

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Abstract

A series of heteroleptic calcium η^5-C_5R_5 cyclopentadienides supported by an *N*-Dipp (Dipp = 2,6-$^iPr_2C_6H_3$)-substituted β-diketiminate ligand have been synthesised by selective protonolysis of the readily available reagent $[HC\{(C(Me)N(Dipp))\}_2Ca\{N(SiMe_3)_2\}(THF)]$ with tetramethylcyclopentadiene, fluorene, indene or cyclopentadiene. No reaction was observed with pentamethylcyclopentadiene, presumably for steric reasons. The tetramethylcyclopentadienyl, fluorenyl and indenyl compounds were characterised by variable temperature ^{1}H NMR and X-ray crystallography. Each complex was found to exist as a mononuclear species both in solution and in the solid state and to be highly sterically crowded, as evidenced by the variable temperature NMR studies. DFT (B3LYP/LANL2DZ) calculations on the model complexes $[CaH(C_5Me_4H)]$, $[CaH(C_{13}H_9)]$ and $[CaH(C_9H_7)]$ indicate that the precise structures of such heteroleptic compounds are a result of both stereoelectronic and steric influences. Attempts to isolate the unsubstituted cyclopentadienyl were unsuccessful, but resulted in the crystallographic analysis of the dimeric calcium siloxide $[HC\{(C(Me)N(Dipp))\}_2Ca(\mu\text{-}OSiMe_3)]_2$.

Keywords: Calcium; Cyclopentadienides; Synthesis; Structural characterisation

1. Introduction

We have recently reported the application of the β-diketiminato calcium amide (**1**) (Scheme 1), in the synthesis of heteroleptic calcium primary amides and acetylides from polydentate alkyl or aryl amines or terminal acetylenes, more acidic than the conjugate base of hexamethyldisilizane [1–3]. These compounds are of interest as models for proposed intermediates during the intramolecular hydroamination of a variety of aminoalkynes and -alkenes catalysed by **1** and provided information about the solution structures and structural dynamics occurring in our proposed catalytic cycle in hydrocarbon solvents [4]. The success of this chemistry is dependent upon the coordinative stability of the *N*-Dipp substituted β-diketiminate in the presence of less sterically demanding substituents [5–7]. A wider use of heavier group 2 (Ae) metals in (polymerisation and molecular) catalytic applications will require the controlled synthesis of further examples of heteroleptic complexes, LAeX, in which L is a supporting ligand inert to Schlenk-type redistribution equilibria. Heavier alkaline earth cyclopentadienyls have been central to the development of a true organometallic chemistry of these elements [8]. The majority of these compounds may be classed as 'true' metallocenes Cp'_2Ae (Cp′ = cyclopentadienyl or substituted cyclopentadienyl) and, although stimulating important debate over the nature of the bonding within these largely ionic complexes [9], have not enabled widespread studies of Ae–X reactivity [10]. As part of our attempts to elaborate further calcium derivatives of this general form, we now report the use of **1** to synthesise heteroleptic calcium cyclopentadienides through reaction with

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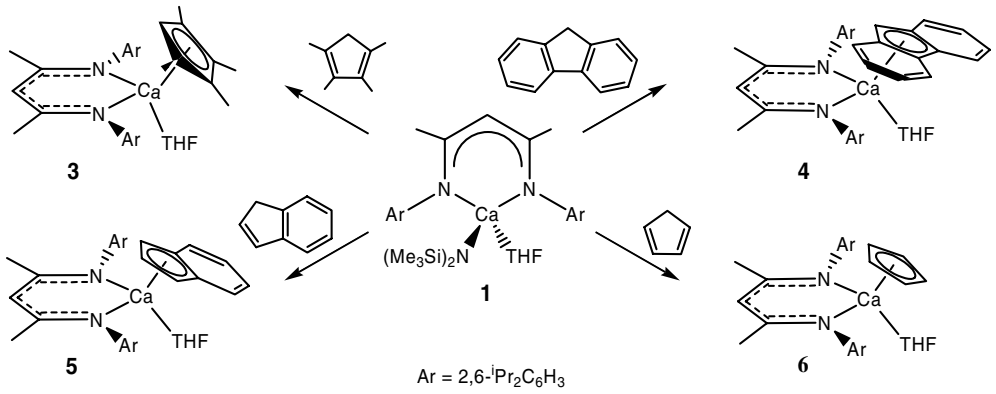

Scheme 1.

a variety of cyclopentadiene C–H acids. Although use of calcium silazides for the synthesis of homoleptic calcocenes has been reported previously [11], this study is the first communication of this protolytic route in the synthesis of *heteroleptic* calcium cyclopentadienides.

2. Results and discussion

Compound **1** was synthesised as described in the literature [1]. A key intermediate in the synthesis is the β-diketiminato potassium derivative $[HC\{(C(Me)N(Dipp))\}_2K]$ (**2**), which was previously reported by Mair and co-workers and structurally characterised as a toluene solvate [12]. During the course of this study, we have obtained the X-ray crystal structure of an unsolvated form of this compound, performed upon crystals grown from hexane solution. In this structure the monomers are arranged in polymeric chains along the 2_1 screw axis propagated by weak K···aryl intermolecular interactions. The metrical parameters are similar to those of the previously reported structure and are not further discussed here. Full structural details and a thermal ellipsoid plot are provided in the Supplementary Information.

A series of NMR scale experiments were conducted to assess the suitability of **1** as a precursor to heteroleptic calcium cyclopentadienides. Stoichiometric reactions of **1** with freshly cracked cyclopentadiene, pentamethylcyclopentadiene, tetramethyl-cyclopentadiene, indene, fluorene or triphenylmethane in C_6D_6 were monitored. Although all of these substrates are sufficiently acidic to protonate the hexamethyldisilazide anion, this did not occur in every case. Hence, the success of the protonolysis reaction, as well as the product stability, was dependent upon the steric demands of the hydrocarbon substrate. Cyclopentadiene and indene reacted with **1** at room temperature with stoichiometric liberation of $HN(SiMe_3)_2$, whilst tetramethylcyclopentadiene and fluorene required prolonged reaction times at elevated temperatures. Furthermore, no reaction was observed between **1** and pentamethylcyclopentadiene, even after extended periods at 90 °C or between **1** and the C–H acidic bond of triphenylmethane under similar conditions. In both cases, **1** was observed to be unstable to deleterious and irreversible Schlenk-type equilibria to the known homoleptic species $[HC\{(C(Me)N(Dipp))\}_2]_2Ca$ [1a,6]. This observed reactivity is consistent with the facile deprotonation of sterically accessible methylene groups by **1**. The more hindered methine groups do not undergo deprotonation even under forcing conditions.

The readily accessible compounds **3**–**5** were synthesised on a preparative scale in either hexane or toluene (Scheme 1), employing slightly longer reaction times than those in the NMR experiments, and isolated by fractional crystallisation.

The tetramethylcyclopentadienyl derivative, **3**, slowly decomposes to tetramethyl cyclopentadiene and, as yet unknown, calcium-containing products in solution. At 258 K in d_8-toluene, however, the ^{1}H NMR spectrum was consistent with the mononuclear formulation indicated in Scheme 1. The methine resonances of the Dipp-isopropyl groups appeared as two separate multiplets at 2.75 and 3.39 ppm and were correlated with the respective doublet methyl resonances at 1.54 and 1.16 ppm by selective decoupling experiments. The diasterotopic nature of these signals may be attributed to hindered rotation about the *N*-Dipp substituents due to the steric demands and resultant crowding of the metal centre induced by the bulky tetramethylcyclopentadienyl co-ligand. The 2,5-methyl and 3,4-methyl groups of the tetramethylcyclopentadienyl substituent appear as singlet resonances at 1.38 and 1.83 ppm and were assigned on the basis of nuclear Overhauser effect measurements and the relative signal enhancement induced in the (Me_4C_5H) methine proton signal at 5.50 ppm. Although the ^{1}H NMR signals sharpened at elevated temperature (338 K), no major structural rearrangements in solution could be inferred. The results of a single crystal X-ray diffraction study are illustrated in Fig. 1 and are consistent with the molecular structure inferred from the solution studies. Details of the crystallographic analysis are provided in Table 1, while selected bond lengths and bond angles are given in Tables 2 and 3, respectively.

The coordination environment about calcium in **3** is provided by the η^5-cyclopentadienyl substituent, the bidentate β-diketiminate and a molecule of THF from the starting material, **1**. The bulky cyclopentadienyl is oriented so