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Reactivity of [HC{(C(Me)N(Dipp))}$_2$-Ca{N(SiMe$_3$)$_2$}(THF)] (Dipp = C$_6$H$_3$^{i}Pr$_2$-2,6) with C–H acids: Synthesis of heteroleptic calcium η^5-organometallics

Anthony G. Avent [b], Mark R. Crimmin [a], Michael S. Hill [a,*], Peter B. Hitchcock [b]

[a] *Department of Chemistry, Imperial College London, Exhibition Road, South Kensington, London SW7 2AZ, UK*
[b] *The Chemistry Laboratory, University of Sussex, Falmer, Brighton, East Sussex, BN1 9QJ, UK*

Abstract

A series of heteroleptic calcium η^5-C$_5$R$_5$ cyclopentadienides supported by an *N*-Dipp (Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$)-substituted β-diketiminate ligand have been synthesised by selective protonolysis of the readily available reagent [HC{(C(Me)N(Dipp))}$_2$Ca{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$_5$Me$_4$H)], [CaH(C$_{13}$H$_9$)] and [CaH(C$_9$H$_7$)] 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))}$_2$Ca(μ-OSiMe$_3$)]$_2$.
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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$_2'$Ae (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

* Corresponding author. Tel.: +44 0 207 594 5709; fax: +44 0 20 7594 5804.
E-mail address: mike.hill@imperial.ac.uk (M.S. Hill).

Scheme 1.

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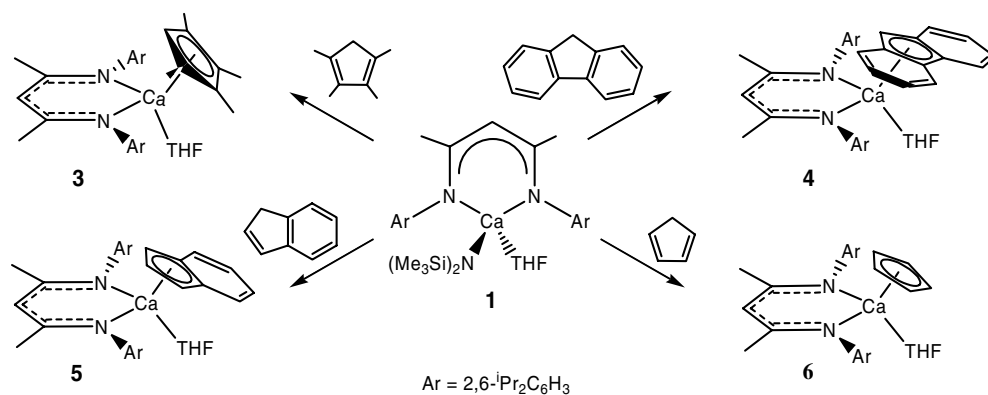
a variety of cyclopentadiene C–H acids. Although use of calcium silazides for the synthesis of homoleptic calcocenes has been reported previously [11], this study is the first communication of this protolytic route in the synthesis of *heteroleptic* calcium cyclopentadienides.

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 ^1H 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 ^1H 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
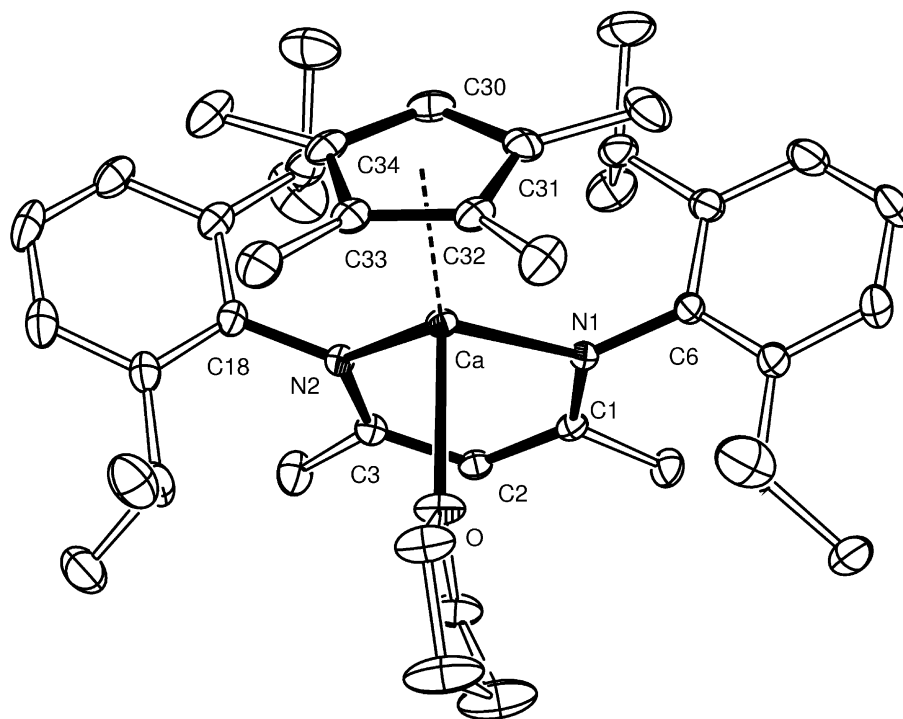
Fig. 1. Thermal ellipsoid plot of **3** (30% ellipsoids). Hydrogen atoms removed for clarity.

Table 1
Selected data collection parameters for compounds **3–5** and **10**

	3	4	5	10
Chemical formula	$C_{42}H_{62}CaN_2O$	$C_{46}H_{58}CaN_2O \cdot 0.5(C_7H_8)$	$C_{42}H_{56}CaN_2O$	$C_{71}H_{108}Ca_2N_4O_2Si_2$
Formula weight	651.02	741.09	644.97	1185.95
T (K)	173(2)	173(2)	173(2)	173(2)
Crystal size (mm^3)	$0.3 \times 0.3 \times 0.1$	$0.08 \times 0.04 \times 0.04$	$0.3 \times 0.3 \times 0.2$	$0.15 \times 0.15 \times 0.10$
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a (Å)	19.3334(3)	9.2543(4)	17.6249(6)	10.9314(2)
b (Å)	9.2435(2)	19.8708(5)	11.1317(4)	13.2443(4)
c (Å)	22.4387(5)	23.7231(1)	20.0954(5)	13.2472(4)
α (°)	90	90	90	97.727(1)
β (°)	97.932(1)	97.473(2)	105.328(2)	101.680(2)
γ (°)	90	90	90	108.283(2)
Z	4	4	4	1
V (Å^3)	3971.62(14)	4325.4(3)	3802.4(2)	1742.50(8)
d_c (Mg m^{-3})	1.09	1.14	1.13	1.13
μ (mm^{-1})	0.19	0.18	0.20	0.24
θ Range (°)	3.72–25.04	3.77–25.00	3.81–25.01	3.73–25.05
R_1, wR_2 [$I > 2\sigma(I)$]	0.050, 0.107	0.071, 0.140	0.053, 0.116	0.056, 0.138
R_1, wR_2 (all data)	0.074, 0.118	0.151, 0.172	0.096, 0.136	0.074, 0.150
Measured/independent reflections/R_{int}	50 949/6981/0.068	24 189/7531/0.088	42 305/6669/0.080	22 098/6117/0.047
Reflections with $I > 2\sigma(I)$	5286	4192	4430	4866

that the unique methine carbon centre is directed towards the β-diketiminate ligand and steric interactions between the ring methyl groups and the flanking *N*-Dipp substituents are minimised. As a result of this crowding (vide infra), however, the Ca–C(30) methine distance [2.640(2) Å] is significantly shorter than the remaining Ca–cyclopentadienyl distances, particularly those of the 3- and 4-CMe centres of the ligand [Ca–C(32), 2.761(2); Ca–C(33), 2.773(2) Å]. The Ca–centroid distance [2.436(2) Å] is, how-

ever, typical of those observed previously in heteroleptic calcium compounds containing substituted cyclopentadienyl groups such as the acetylide complex [(Cp^{4i})Ca{C≡CPh}(THF)]$_2$ [2.432 Å] (Cp^{4i} = ^{i}Pr$_4$C$_5$H) and [(Me$_4$EtC$_5$)-Ca(μ-NSiMe$_2$CH$_2$CH$_2$SiMe$_2$)]$_2$ [2.418, 2.413 Å] [10c,10b]. The crowding of the metal centre is also apparent from the O–Ca–N(1) [96.08(6)°] and O–Ca–N(2) [97.82(6)°] angles which are more acute than those observed in previous heteroleptic THF-solvated calcium complexes

Table 2
Selected bond lengths (Å) for compounds 3–5 and 10

	3	4	5	10[r]
Ca–O	2.364(2)	2.332(3)	2.3459(18)	2.2857(19)[s]
Ca–N(1)	2.385(2)	2.352(3)	2.347(2)	2.353(2)
Ca–N(2)	2.371(2)	2.360(3)	2.341(2)	2.424(2)
Ca–centroid	2.436(2)	2.503(4)	2.421(3)	–
Ca–C(30)	2.640(2)	2.652(4)	2.664(3)[h]	–
Ca–C(31)	2.694(2)	2.777(4)	2.677(3)[i]	–
Ca–C(32)	2.761(2)	2.889(4)[a]	2.701(3)[j]	–
Ca–C(33)	2.773(2)	2.849(4)[b]	2.747(3)[k]	–
Ca–C(34)	2.711(2)	2.733(4)[c]	2.713(3)[l]	–
N(1)–C(1)	1.330(3)	1.3339(4)	1.324(3)	1.336(4)
N(1)–C(6)	1.436(3)	1.448(4)	1.434(3)	1.438(3)
N(2)–C(3)	1.326(3)	1.326(4)	1.329(3)	1.329(4)
N(2)–C(18)	1.438(3)	1.434(4)	1.439(3)	1.437(3)
C(1)–C(2)	1.404(3)	1.401(5)	1.406(4)	1.405(4)
C(1)–C(4)	1.517(3)	1.515(5)	1.521(4)	1.514(4)
C(2)–C(3)	1.409(3)	1.412(5)	1.406(4)	1.411(4)
C(3)–C(5)	1.515(3)	1.518(5)	1.523(4)	1.519(4)
C(30)–C(34)	1.412(3)	1.422(6)[d]	1.407(5)[m]	–[t]
C(30)–C(31)	1.416(3)	1.421(7)	1.375(5)[n]	–
C(31)–C(32)	1.407(3)	1.442(6)[e]	1.379(4)[o]	–
C(31)–C(35)	1.508(3)	1.418(6)[f]	1.416(4)[p]	–
C(32)–C(33)	1.418(3)	1.433(6)[g]	1.441(4)[q]	–

  [a] Ca–C(36).
  [b] Ca–C(37).
  [c] Ca–C(42).
  [d] C(30)–C(42).
  [e] C(31)–C(36).
  [f] C(36)–C(37).
  [g] C(37)–C(42).
  [h] Ca–C(40).
  [i] Ca–C(41).
  [j] Ca–C(42).
  [k] Ca–C(34).
  [l] Ca–C(39).
  [m] C(39)–C(40).
  [n] C(40)–C(41).
  [o] C(41)–C(42).
  [p] C(42)–C(34).
  [q] C(34)–C(39).
  [r] Symmetry transformations used to generate equivalent atoms: $-x$, $-y + 1$, $-z + 1$.
  [s] Ca–O′, 2.2509(19).
  [t] Si–O, 1.625(2) Å.

Table 3
Selected bond angles (°) for compounds 3–5 and 10

	3	4	5	10[k]
O–Ca–N(1)	96.08(6)	101.04(10)	96.65(7)	120.08(8)[l]
O–Ca–N(2)	97.82(6)	98.74(10)	100.06(7)	127.52(7)[m]
N(2)–Ca–N(1)	79.78(6)	80.49(10)	81.25(7)	80.60(8)
O–Ca–centroid	115.57(7)	111.0(1)	118.71(9)	–
N(2)–Ca–centroid	129.31(7)	131.0(1)	129.91(9)	–
N(1)–Ca–centroid	128.95(7)	127.5(1)	120.74(9)	–
C(1)–N(1)–C(6)	117.97(18)	118.0(3)	121.0(2)	118.4(2)
C(1)–N(1)–Ca	122.08(14)	123.8(2)	122.91(16)	121.76(18)
C(6)–N(1)–Ca	119.30(13)	117.5(2)	115.95(15)	119.13(16)
C(3)–N(2)–C(18)	119.15(17)	118.5(3)	119.0(2)	119.7(2)
C(3)–N(2)–Ca	123.09(14)	123.9(2)	121.48(16)	120.57(18)
C(18)–N(2)–Ca	116.61(12)	117.2(2)	118.20(14)	119.27(16)
N(1)–C(1)–C(2)	125.06(19)	124.8(3)	123.7(2)	124.3(2)
N(1)–C(1)–C(4)	120.12(19)	120.5(3)	121.2(2)	120.6(2)
C(2)–C(1)–C(4)	114.81(19)	114.6(3)	115.1(2)	115.1(2)
C(1)–C(2)–C(3)	130.9(2)	130.7(3)	131.4(2)	131.8(3)
N(2)–C(3)–C(2)	124.26(19)	124.5(3)	124.8(2)	125.0(2)
C(34)–C(30)–C(31)	109.0(2)	107.4(4)[a]	108.1(3)[f]	–[n]
C(32)–C(31)–C(30)	107.1(2)	108.7(4)[b]	118.3(3)[g]	–
C(31)–C(32)–C(33)	108.6(2)	107.1(4)[c]	107.0(3)[h]	–
C(34)–C(33)–C(32)	108.0(2)	108.2(4)[d]	108.3(3)[i]	–
C(33)–C(34)–C(30)	107.4(2)	108.5(4)[e]	110.2(3)[j]	–

  [a] C(42)–C(30)–C(31).
  [b] C(30)–C(31)–C(36).
  [c] C(37)–C(36)–C(31).
  [d] C(36)–C(37)–C(42).
  [e] C(30)–C(42)–C(37).
  [f] C(39)–C(40)–C(41).
  [g] C(38)–C(39)–C(34).
  [h] C(42)–C(34)–C(39).
  [i] C(41)–C(42)–C(34).
  [j] C(40)–C(41)–C(42).
  [k] Symmetry transformations used to generate equivalent atoms: $-x$, $-y + 1$, $-z + 1$.
  [l] O′–Ca–N(1), 109.68(8).
  [m] O′–Ca–N(2), 141.76(8).
  [n] O′–Ca–O, 80.31(7); Si–O–Ca, 122.16(10); Si–O–Ca′, 137.54(11); Ca–O–Ca′ 99.70(7).

supported by this β-diketiminate ligand. For example, the corresponding angles in 1 are 113.79(5)° and 91.25(5)° [1], while those of the mononuclear anilide, [HC{(C(Me)-N(Dipp))}₂Ca{NH(Dipp)}(THF)] are 98.20(6)° and 101.73(6)° [2b]. Although the bond lengths and bond angles about the NCCCN chelate are typical of those observed in hetero- and homoleptic calcium complexes, similar steric compression is likely to be the reason for the lack of reactivity of 1 with pentamethylcyclo pentadiene.

In solution, the fluorenyl derivative, 4, displays similar features to those outlined for 3. Restricted rotation about the N-Dipp bond was again apparent at 258 K, giving rise to two isopropyl methine and four isopropyl methyl environments which were correlated by selective decoupling experiments and found to be subject to mutual chemical

exchange by spin saturation transfer. Further assignments, including those of the fluorenyl ring methines were achieved by nOe experiments. This assignment in solution was consistent with the results of an X-ray structural analysis (Fig. 2) performed upon crystals of 4 isolated from concentrated hexane solution. Details are provided in Table 1, while selected bond lengths and bond angles are given in Tables 2 and 3, respectively.

The gross structural features of compound 4 are similar to those described for compound 3. The Ca–C bond distances to the η⁵-fluorenyl substituent [Ca–C(30)–Ca–C(37)] (Table 2) are again indicative of a canting of the ligand away from the bidentate β-diketiminato ligand, while the calcium centre sits below the plane of the planar NCCCN fragment. This folding is characterised by the angle formed between the N1C1C2C3N2 and N1CaN2 least-squares planes [25.77°]. Differences between the remaining important bond lengths and bond angles in 3 and the corresponding parameters in 4 may be ascribed to the differing steric demands and topologies of the hydrocarbon ligands. Although a homoleptic calcium fluorenyl
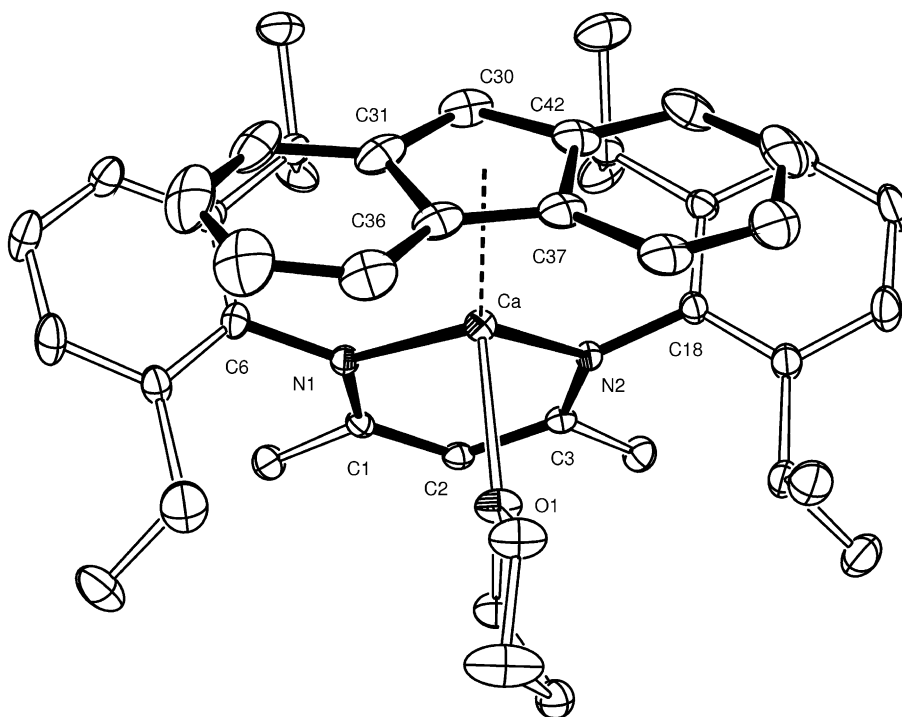
Fig. 2. Thermal ellipsoid plot of **4** (30% ellipsoids). Hydrogen atoms removed for clarity.

derivative has been described and a trimethylsilylated fluorenyl ligand has been crystallographically characterised [10e,10f,13], **4** represents the first example of a structurally well-defined calcium complex of the parent hydrocarbon ligand.

^{1}H NMR analysis of the indenyl complex, **5**, in d_8-toluene was consistent with the expected formulation. A similar splitting of the ligand environments to that noted for **3** and **4** was observed on lowering the temperature to 238 K. At elevated temperatures (338 K) no evidence of restricted *N*-Dipp rotation was observed. Reduction of the temperature to 298 K resulted in a splitting of isopropyl methyl environments, which were shown to be exchanging on the NMR timescale by spin saturation transfer experiments. Irradiation of the backbone methyl resonance of the β-diketiminate ligand produced enhancements in the resonances ascribed to the coordinated THF and indenyl ligands, as well as an nOe to the proximal β-diketiminate backbone methine. This latter feature shows the integrity of the molecule in hydrocarbon solution and confirms the mononuclear constitution of the complex. A further feature of the room temperature spectrum is the diastereotopic disposition of the protons of the methylene groups α- to the oxygen donor of the coordinated THF molecule. The appearance of these signals as a pair of broadened multiplets at 3.42 and 2.44 ppm may be explained if the solution structure is similar to that observed in the solid state (vide infra) and the C_6 carbon ring of the ligand is unsymmetrically disposed with respect to the β-diketiminato chelate. These peaks coalesce at 318 K and we postulate that the indenyl ligand, despite the inherent steric pressure provided

by the bulky β-diketiminate ligand, is free to rotate about the Ca–centroid axis at this temperature with $\Delta G^{\ddagger} = 61.8 \text{ kJ mol}^{-1}$.

The solid-state structure of **5** is illustrated in Fig. 3. There is no plane of symmetry perpendicular to the N(1)C(1)C(2)C(3)N(2) plane and it is the retention of this structure on the NMR timescale that is postulated as the source of the asymmetry in the variable temperature NMR data. Although again within the normal range for Ca–cyclopentadienyl bonding, the Ca–C contacts to the tertiary carbon centres C(40) [2.664(3) Å], C(41) [2.677(3) Å] and C(42) [2.701(3) Å] are shorter than those to the quaternary C(34) and C(39) atoms of the C_6 indenyl ring (vide infra). The O–Ca–N bond angles within **5** [O–Ca–N(1), 96.65(7)°; O–Ca–N(2) 100.06(7)°], which were similar in both **3** and **4**, also reflect this loss of symmetry, but in general do not indicate a greatly diminished crowding compared to that provided by tetramethylcyclopentadienyl or fluorenyl.

The above structural descriptions attribute the observed variations in Ca–C bond lengths within the structures of **3**–**5** to the steric pressure provided by the bulky β-diketiminate ligand. In order to test this hypothesis we have undertaken DFT calculations performed on the model complexes [CaH(C₅Me₄H)], **6**, [CaH(C₁₃H₉)] (**7**) and [CaH(C₉H₇)] (**8**) and implemented in GAUSSIAN 03 [14]. A single hydride was selected as co-ligand in order to minimise steric interactions between the C_5 substituent and to maximise possible stereoelectronic influences upon calcium-substituent binding. Table 4 presents the results provided by the fully optimised structures and illustrates the variation of the Ca–C
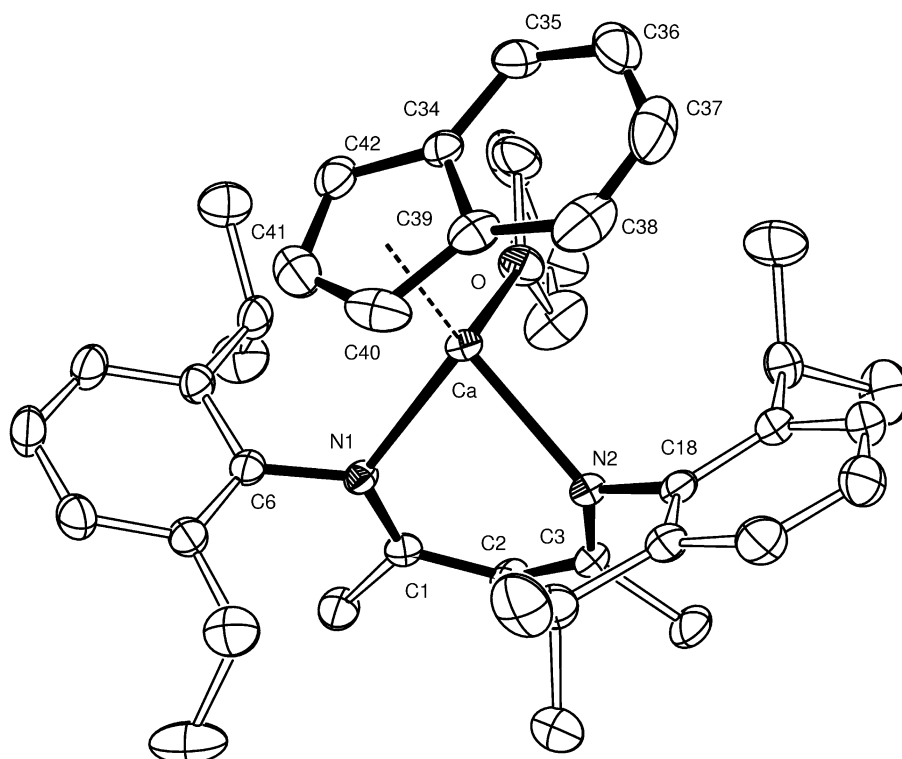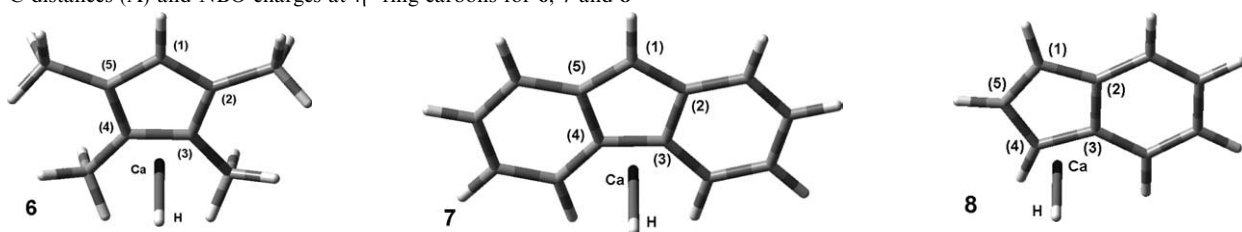
Fig. 3. Thermal ellipsoid plot of **5** (30% ellipsoids). Hydrogen atoms removed for clarity.

Table 4
Calculated Ca–C distances (Å) and NBO charges at η^5-ring carbons for **6**, **7** and **8**

	6	**7**	**8**
C(1)	2.706; −0.443	2.706; −0.502	2.761; −0.567
C(2)	2.744; −0.183	2.784; −0.130	2.766; 0.127
C(3)	2.764; −0.214	2.818; −0.183	2.766; 0.127
C(4)	2.706; −0.443	2.706; −0.502	2.763; −0.566
C(5)	2.744; −0.183	2.784; −0.130	2.790; −0.316

distances along with the calculated NBO charges borne by each carbon centre. The variation in Ca–C distances is similar to that observed within the solid-state structures of **3–5**. Bonding within all three calculated structures is revealed to be largely ionic [NBO charges at Ca, ca. +1.5], whilst the carbon centre bearing the greatest negative charge displays the shortest (largely electrostatic) contact to calcium. It is noteworthy that in each case a similar trend is observed in the corresponding β-diketiminate complexes, **3–5** and that the variation between shortest and longest Ca–C contacts (ca. 3%) is of a similar magnitude in both the experimentally determined and calculated structures bearing the same η^5-coordinated ligand. Our data indicate, therefore,

that the precise structures of these complexes are dictated not only by steric interactions but also by steroelectronic influences that result from the differing constitution of the hydrocarbon ligands.

Attempts to isolate the simplest heteroleptic complex of this general type [HC{C(Me)N(Dipp)}$_2$Ca{η^5-C$_5$H$_5$}-(THF)] (**9**) in pure form were not successful and the spectroscopic data listed in Section 3 relate entirely to the in situ reaction referred to previously. Although **9** is apparently formed in a stoichiometric quantity, its solubility and stability are limited by the reduced steric protection provided by the considerably less bulky cyclopentadienyl substituent and a commensurate increase in sensitivity to

electrophilic reagents. This latter quality is emphasised by our attempts to produce single crystals of **9**, which resulted in the isolation of a small amount of material suitable for an X-ray analysis. The results of this analysis are illustrated in Fig. 4 and revealed the structure of the centrosymmetric calcium siloxide, **10**. Although the data provided by this analysis were of a high quality, no other spectroscopic or characterising data are available due to the small amount of material isolated. It has long been known that poly-diorganosiloxanes may react with strongly nucleophilic bases such as alkyl lithiums to form metal triorganosilanolates [15]. The siloxide substituent of **7** was, most likely therefore, introduced in the form of silicone grease employed to provide an air-tight seal about the Quick-fit™ joints of our glassware and may be cited as circumstantial evidence that the reactivity of the sterically unencumbered calcium cyclopentadienyl compounds is greater than that of the substituted derivatives.

Details of the crystallographic analysis are provided in Table 1 and selected bond lengths and bond angles within **10** are displayed in Tables 2 and 3, respectively. Although metal siloxides have been studied since the 1870s [16], the chemistry of calcium siloxides is rather undeveloped and relevant structural data are scarce. The calcium centres within **7** are four-coordinate and feature bridging trimethylsiloxide ligands. The Ca–O [2.2857(19) Å] and Ca–O′ [2.2509(19) Å] bonds are sufficiently dissimilar to allow classification of these interactions as inter- and intramolecular, respectively. Both of these distances are, however,

similar to the shorter bridging Ca-(μ-OSiPh$_3$) distances [range, 2.255(5)–2.334(5) Å] observed in the dimeric calcium siloxide [Ca$_2$(OSiPh$_3$)$_4$(NH$_3$)$_4$] despite the reduced coordination number (4 versus 6) observed in the structure of **10** [17]. Despite an expected reduction in the overall crowding about calcium, the N(1)–Ca–N(2) bond angle [80.30(7)°] and Ca–N distances are similar to those observed in **3**–**5** and in previously reported calcium species containing this ligand [1–3,6]. We have previously commented that the apparent invariance of this angle is determined by the size of the Ca^{2+} cation within the β-diketiminato ligand 'bite'.

These results emphasise the utility of sterically demanding β-diketiminato ligands in the study of well-defined organocalcium and calcium coordination complexes. The use of calcium cyclopetadienyls in subsequent metathetical reactions with alkali metal alkyls and amides is precedented [10a]. We are, therefore, continuing to examine the reactivity of the readily accessible reagents **3**–**5** and will report the results of these studies in subsequent publications.

3. Experimental

All manipulations involving alkaline earth metals were carried out using standard Schlenk and glovebox techniques under an inert atmosphere of either dinitrogen or argon. All solvents were distilled under dinitrogen and dried with conventional drying agents. Cyclopentadiene reagents were freeze–thaw degassed prior to use. ^{1}H
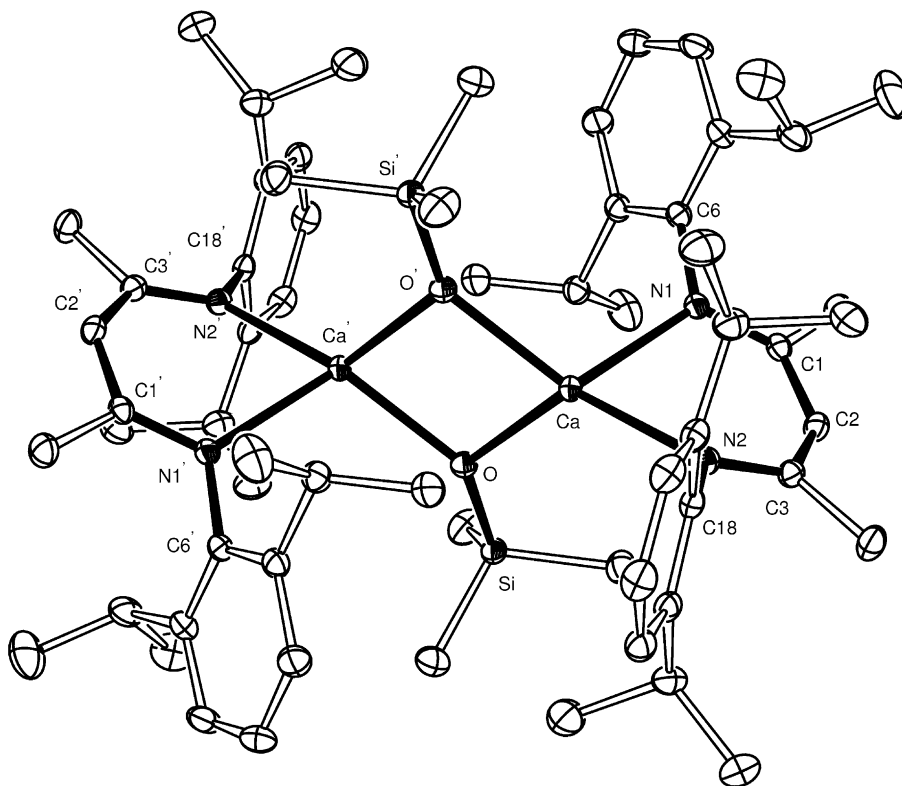

Fig. 4. Thermal ellipsoid plot of **10** (30% ellipsoids). Hydrogen atoms removed for clarity.

NMR spectra were recorded at 270 or 500 MHz from samples in either C_6D_6 or d_8-toluene; chemical shifts are given relative to $SiMe_4$. The NMR data cited for **9** were obtained from an NMR-scale reaction of **1** and cyclopentadiene. Repeated attempts to accumulate mass spectral data on isolated compounds were unsuccessful due to their air- and moisture- sensitivity as were attempts to obtain accurate microanalytical data (Mr. S. Boyer, University of North London) for compounds **3** and **4**. Compounds **1** and **2** were synthesised by the literature procedures [1,12]. Calcium iodide and $KN(SiMe_3)_2$ were purchased from Sigma-Aldrich and used as received.

3.1. $[\{HC(C(Me)_2N$-$2,6$-$^iPr_2C_6H_3)_2\}Ca\{\eta^5$-$(Me)_4C_5H\}$-$(THF)]$ (3)

Tetramethylcyclopentadiene (0.18 g, 1.45 mmol) in hexane was added to a hexane solution of **1**, (1.00 g, 1.45 mmol). The resultant solution was heated at 60 °C for 48 h. Compound **3** was isolated as colourless fine needles when this solution was allowed to cool to room temperature (0.38 g, 46%). ^{1}H NMR (d_8-toluene, 298 K): δ 1.16 (d, 12H, $CH(Me)_2$), 1.38 (s, 6H, 2,5-Me, $(Me)_4C_5H$), 1.49 (s, 6H, $NC(Me)$) 1.54 (d, 12H, $CH(Me)_2$), 1.76 (s, 6H, 3,4-Me, $(Me)_4C_5H$), 2.04 (m, 4H, THF), 3.05 (m, 4H, $CH(Me)_2$), 3.60 (m, 4H, THF), 4.56 (s, 1H, $C(Me)CH$), 5.50 (s, 1H, $(Me)_4C_5H$), 6.91–7.12 (m, 6H, ArH).

3.2. $[\{HC(C(Me)_2N$-$2,6$-$^iPr_2C_6H_3)_2\}Ca\{\eta^5$-$C_{13}H_9\}$-$(THF)]$ (4)

To a stirred solution of **1** (0.40 g, 0.58 mmol) in a minimum volume of toluene was added a stoichiometric quantity of fluorene in the same solvent. The resultant solution was refluxed for 48 h and **4** was isolated a colourless needles when this hot solution was allowed to cool to 5 °C (0.11 g, 30%). ^{1}H NMR (d_8-toluene, 298 K): δ 0.40 (d, 12H, $CH(Me)_2$), 1.02 (d, 12H, $CH(Me)_2$), 1.30 (m, 4H, THF), 1.35 (s, 6H, $NC(Me)$), 2.25 (m, 4H, $CH(Me)_2$), 3.49 (m, 4H, THF), 4.45 (s, 1H, $C(Me)CH$), 6.20 (s, 1H, $C_{13}H_9$), 6.65 (m, 2H, $C_{13}H_9$), 6.83 (m, 2H, $C_{13}H_9$), 7.00–7.25 (m, 6H, ArH), 7.76 (d, 2H, $C_{13}H_9$).

3.3. $[\{HC(C(Me)_2N$-$2,6$-$^iPr_2C_6H_3)_2\}Ca\{\eta^5$-$C_9H_7\}$-$(THF)]$ (5)

This compound was synthesised by the same method as that described for **3** and isolated as pale yellow crystals from hexane (40%). Anal. Calc. for $C_{42}H_{56}CaN_2O$: C, 78.79; H, 8.77; N, 2.17. Found: C, 78.50; H, 8.40; N, 2.00%. ^{1}H NMR (d_8-toluene, 298 K): δ 0.85 (d, 12H, $CH(Me)_2$), 1.15 (m, 4H, THF), 1.43 (s, 6H, $NC(Me)$), 1.61 (d, 12H, $CH(Me)_2$), 2.41 (m, 4H, $CH(Me)_2$), 2.44 3.42 (m, 2H, THF), 4.48 (s, 1H, $C(Me)CH$), 5.92 (d, 2H, C_9H_7), 6.25 (t, 1H, C_9H_7), 6.60 (dd, 2H, C_9H_7), 7.05 (m, 2H, ArH), 7.10 (dd, 2H, C_9H_7), 7.15 (m, 4H, ArH).

3.4. Attempted synthesis of 9: isolation of 10

Addition of a stoichiometric quantity of cyclopentadiene to a hexane solution of **1** gave an immediate colourless precipitate. This was heated to aid dissolution, however the only crystalline material isolated was shown to be the dimeric siloxide, **10**, by an X-ray crystallographic analysis. In situ NMR data for **9**: ^{1}H NMR (C_6D_6, 298 K): δ 1.15 (d, 12H, $CH(Me)_2$), 1.60 (s, 6H, $NC(Me)$), 2.18 (d, 12H, $CH(Me)_2$), 3.18 (m, 4H, $CH(Me)_2$), 4.87 (s, 1H, $C(Me)CH$), 5.80 (s, 5H, C_5H_5), 7.05–7.20 (m, 6H, ArH).

3.5. Crystal structure determinations

Data were collected at 173 K on a Nonius kappa CCD diffractometer, λ (Mo Kα) = 0.71073 Å; details are given in Table 1. An absorption correction (MULTI-SCAN) was applied for **3**–**5** and **10**. For **4**, the disordered toluene solvate the H atoms were omitted and for **7** the toluene solvate molecule is disordered about an inversion centre and was included with isotropic C atoms, SADI constraints, and H atoms omitted. The structures were solved by direct methods (SHELXS-97) [18] and refined by full-matrix least-squares (SHELXL-97) [19] with non-H atoms anisotropic and H atoms included in riding mode.

Appendix A. Supplementary data

ORTEP figure **2**. Crystallographic data for **2**–**5** and **10** in CIF format. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Reference Nos. 285285–285289. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.11.065.

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