Electronic Supporting Information

Unprecedented Silicon(II)→Calcium Complexes with N-Heterocyclic Silylenes

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1. Selected NMR and ESI-MS spectra.

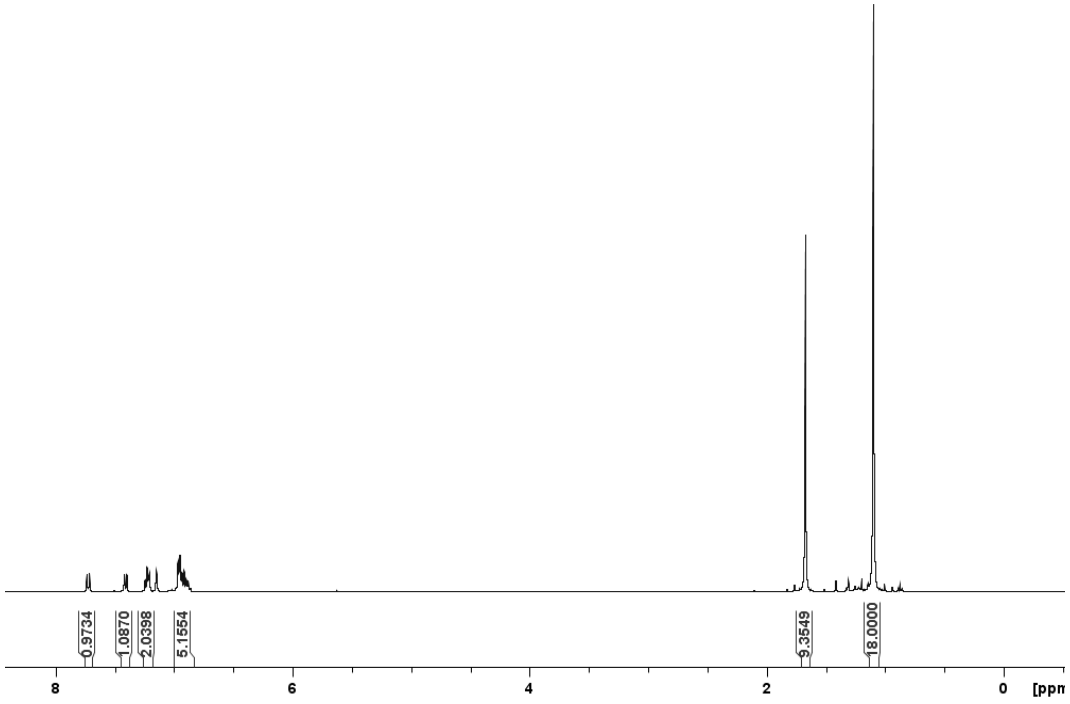

Fig. S1 ^{1}H NMR spectrum of the free NHSi **5** in C_6D_6 at 298 K.

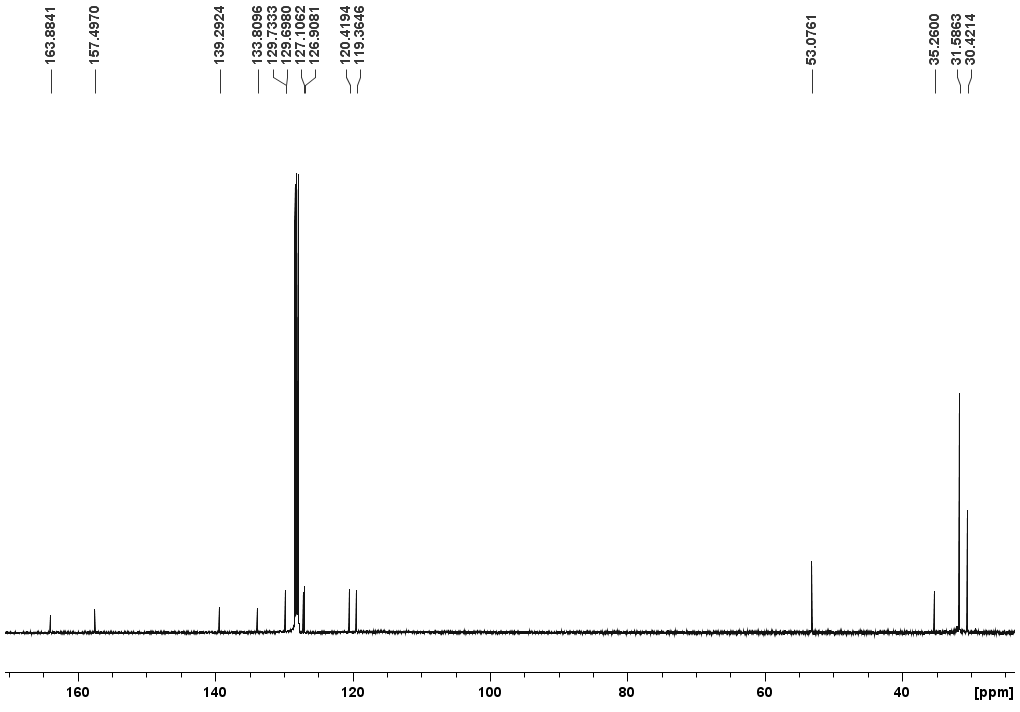

Fig. S2 $^{13}C\{^{1}H\}$ NMR spectrum of the free NHSi **5** in C_6D_6 at 298 K.

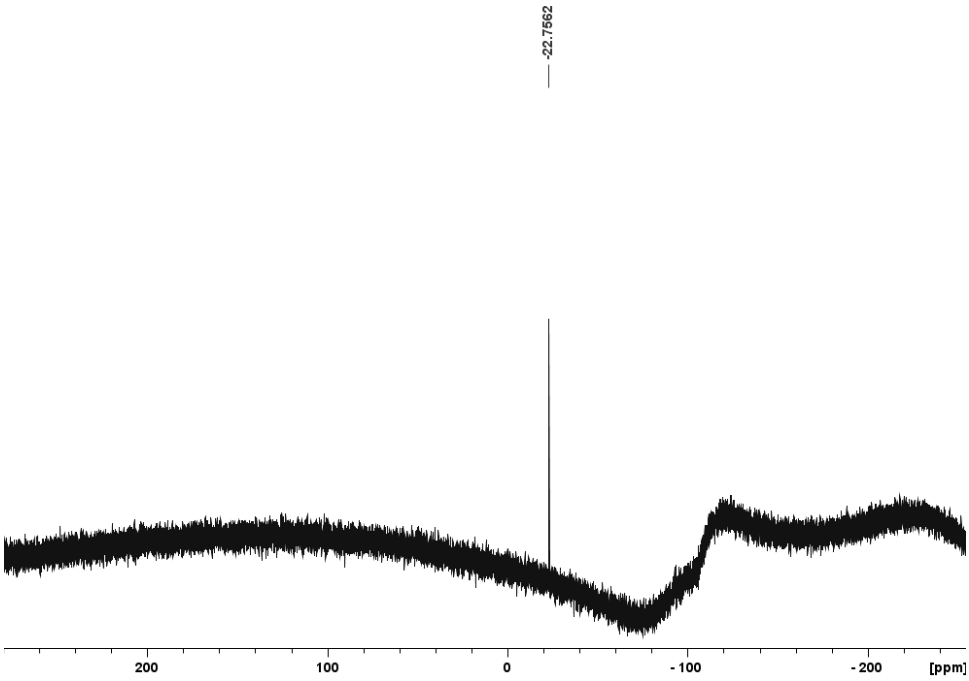

Fig. S3 $^{29}Si\{^{1}H\}$ NMR spectrum of the free NHSi **5** in C_6D_6 at 298 K.

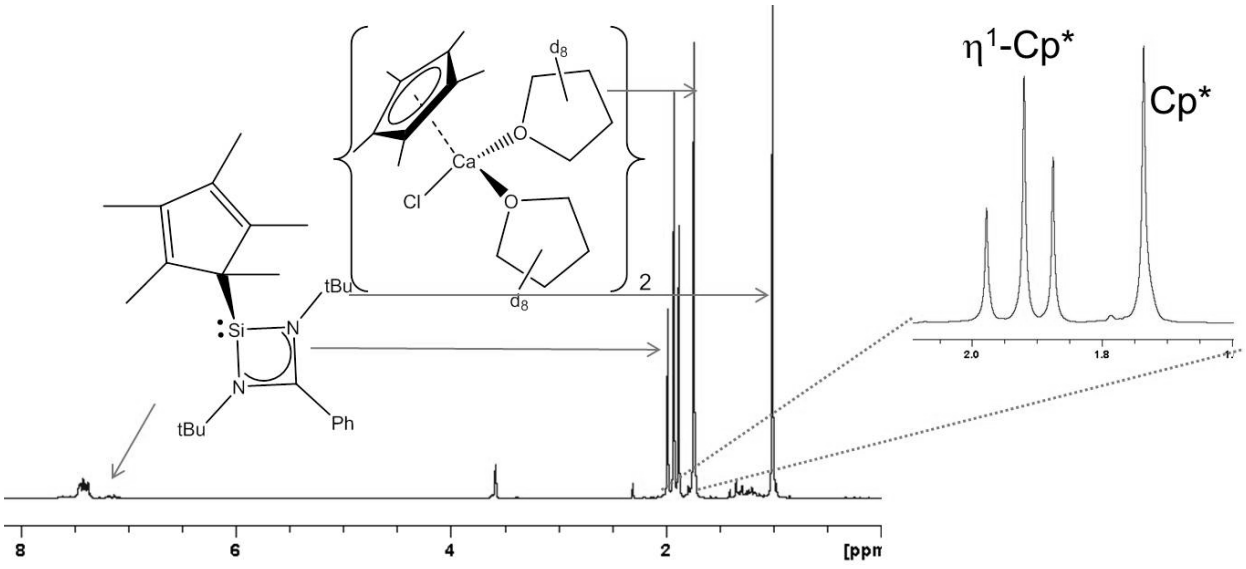

Fig. S4 ^{1}H NMR spectrum of the mixture of $[(\eta^5\text{-}C_5Me_5)CaCl(thf\text{-}d_8)_2]_2$ and :Si(Cp*)(PhC(N^{t}Bu)$_2$) in THF-d_8 resulting from the reaction of compound **2** with chlorosilylene **1**.

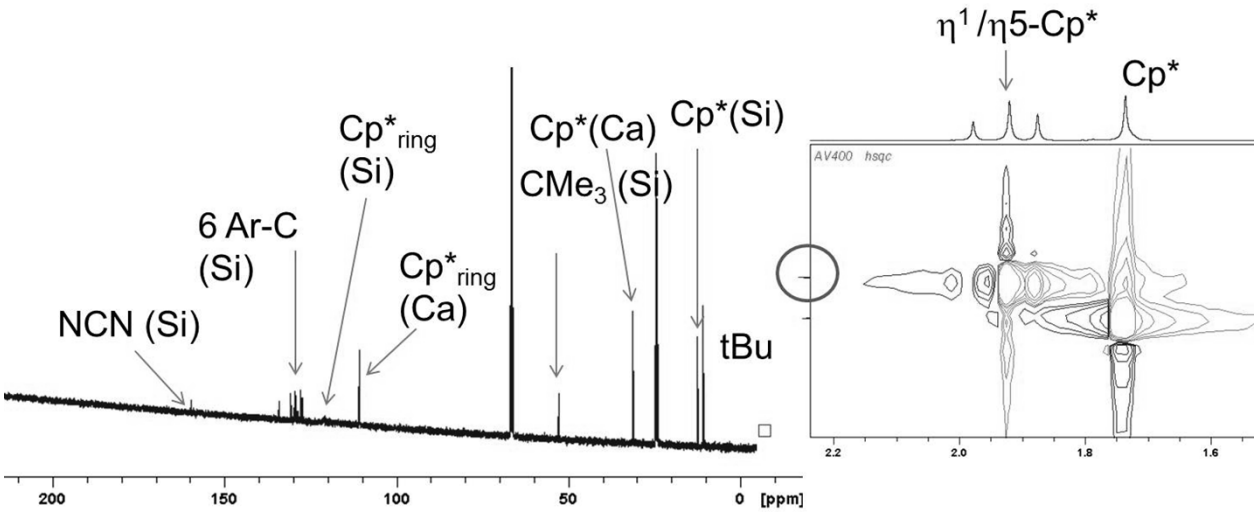

Fig. S5 $^{13}C\{^1H\}$ NMR spectrum of the mixture of $[(\eta^5\text{-}C_5Me_5)CaCl(thf\text{-}d_8)_2]_2$ and :Si(Cp*)(PhC(N^{t}Bu)$_2$) in THF-d_8 resulting from the reaction of compound **2** with chlorosilylene **1**. The expansion on the right shows the HSQC spectrum where the Cp* in coordinated to Si in a η^5 fashion due to only one cross peak for the CH_3 groups.

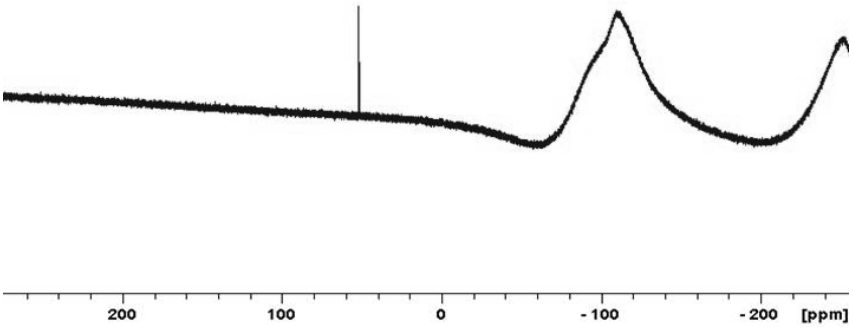

Fig. S6 $^{29}Si\{^1H\}$ NMR spectrum of :Si(Cp*)(PhC(N^{t}Bu)$_2$) in THF-d_8 at 298 K. The resonance signal is at δ = 52.4 ppm.

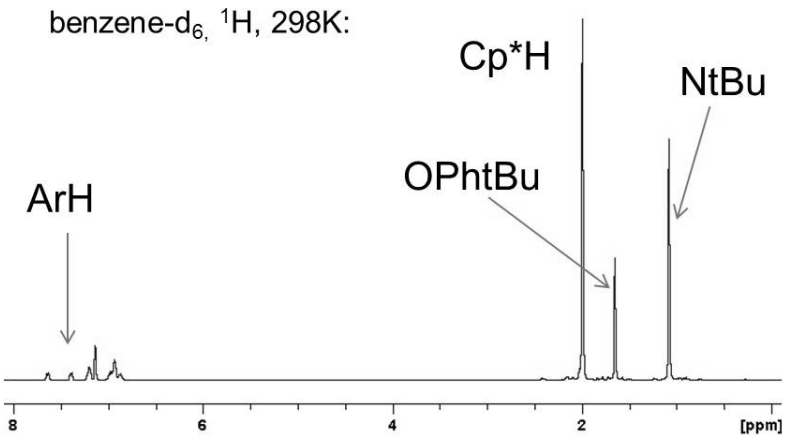

Fig. S7 ^{1}H NMR spectrum of $[(\eta^5\text{-}C_5Me_5)_2Ca\leftarrow\text{:}Si(O\text{-}C_6H_4\text{-}2\text{-}^tBu)\{(N^tBu)_2CPh\}]$ (**6**) in C_6D_6 at 298 K.

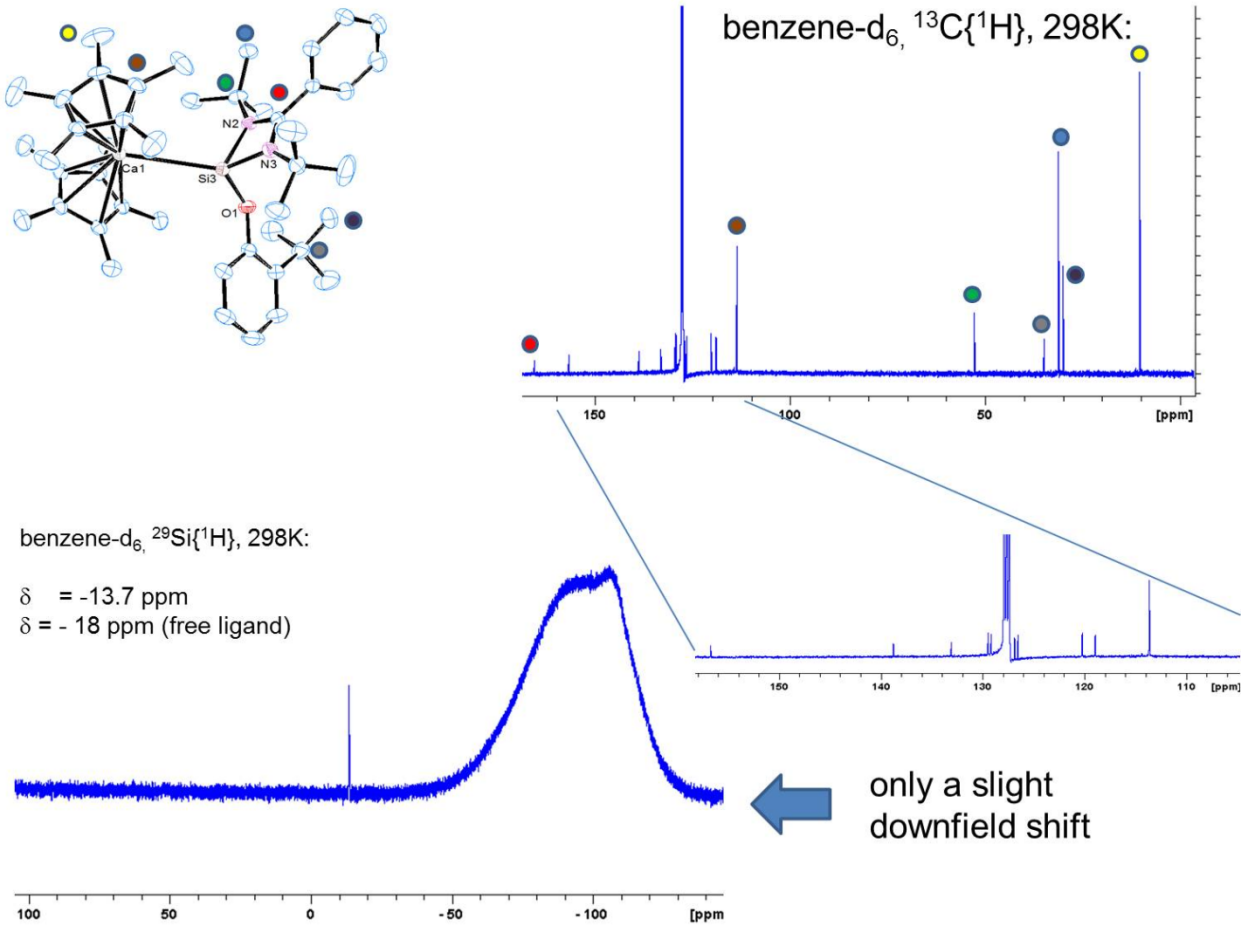

Fig. S8 $^{13}C\{^{1}H\}$ (with partial assignment shown) and ^{29}Si NMR spectrum of $[(\eta^5\text{-}C_5Me_5)_2Ca\leftarrow\text{:}Si(O\text{-}C_6H_4\text{-}2\text{-}^tBu)\{(N^tBu)_2CPh\}]$ (**6**) in C_6D_6 at 298 K. The resonance signal of the Si is only shifted by 4.3 ppm downfield relative to the free ligand.

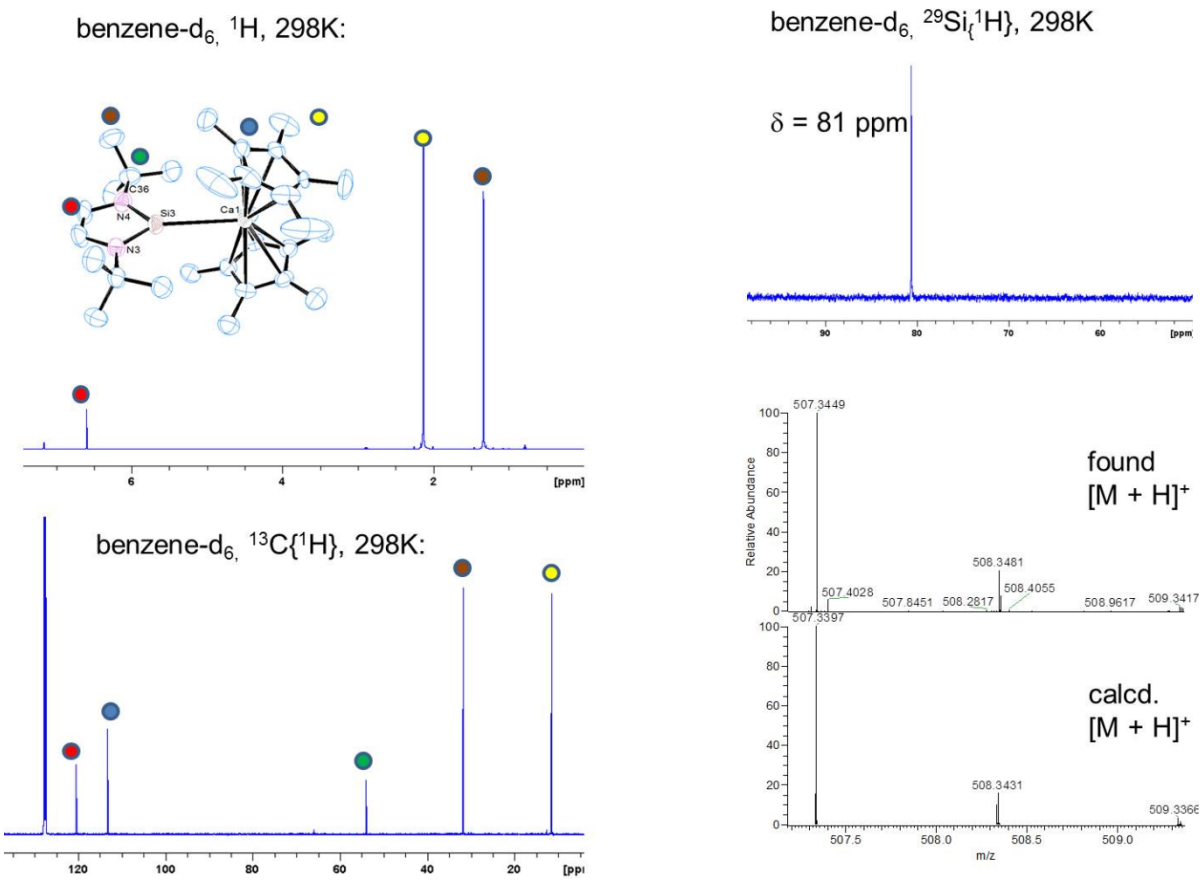

Fig. S9 ^{1}H, $^{13}C\{^{1}H\}$ (with full assignment shown), ^{29}Si NMR spectrum; and ESI-MS of $[M+H]^+$ of compound (**7**) in C_6D_6 at 298 K.

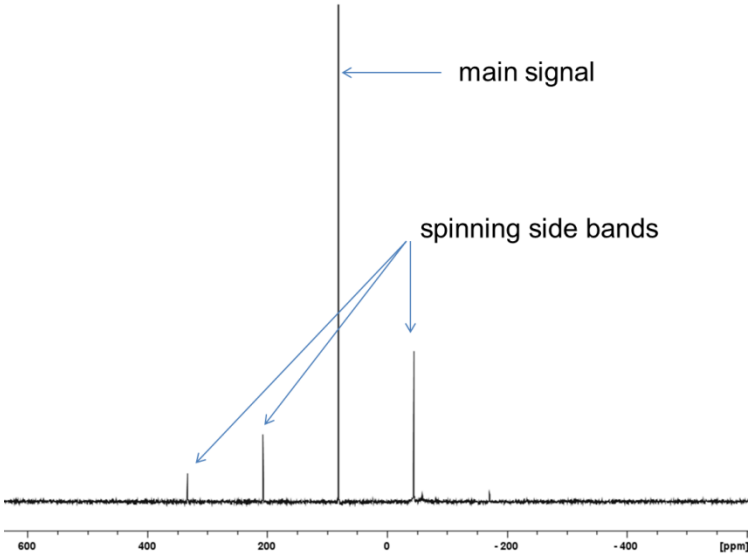

Fig. S10 ^{29}Si-MAS-NMR of compound **7** in the solid state. δ = 81.4 ppm (corresponds to chemical shift in solution).

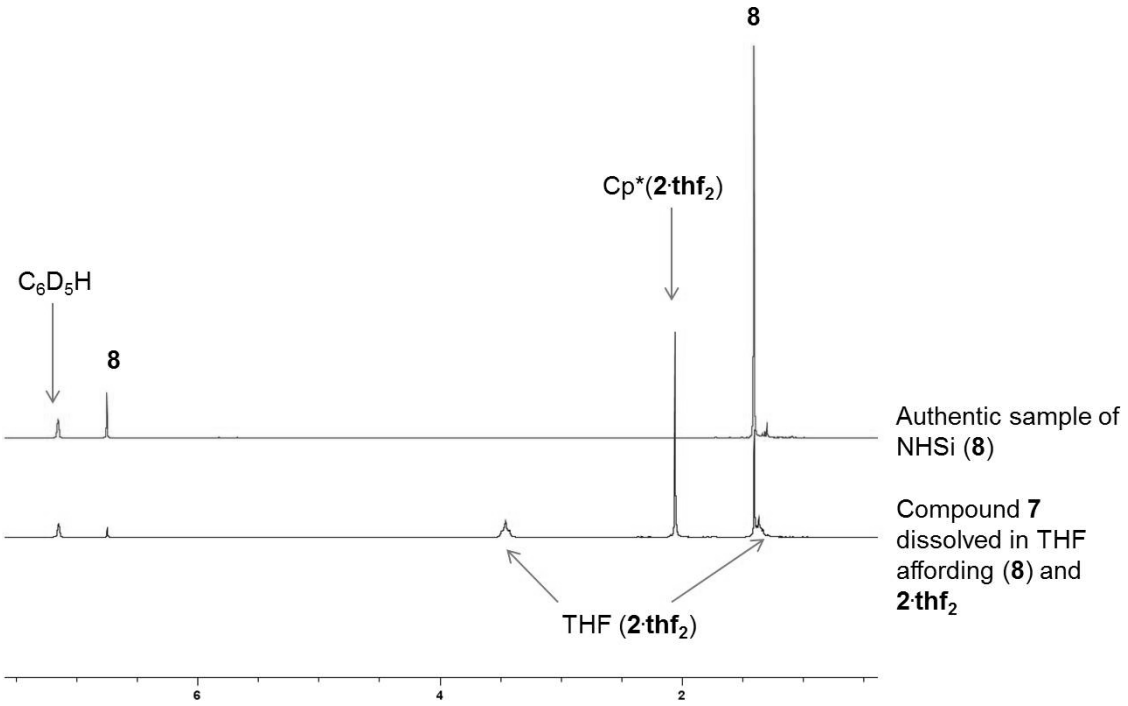

Fig. S11 Comparison of an authentic sample of NHSi **8** (top) and the NMR spectrum of compound **7** dissolved in THF, then dried *in vacuo* (both recorded in C_6D_6) (below) clearly showing free NHSi (8) and concomitant formation of **2·thf$_2$**. (The shifts match those reported in the literature. See: M. J. McCormick, S. C. Stockwell, C. E. H. Davies, T. P. Hanusa, J. C. Huffmann, *Organometallics* 1989, **8**, 2044.)

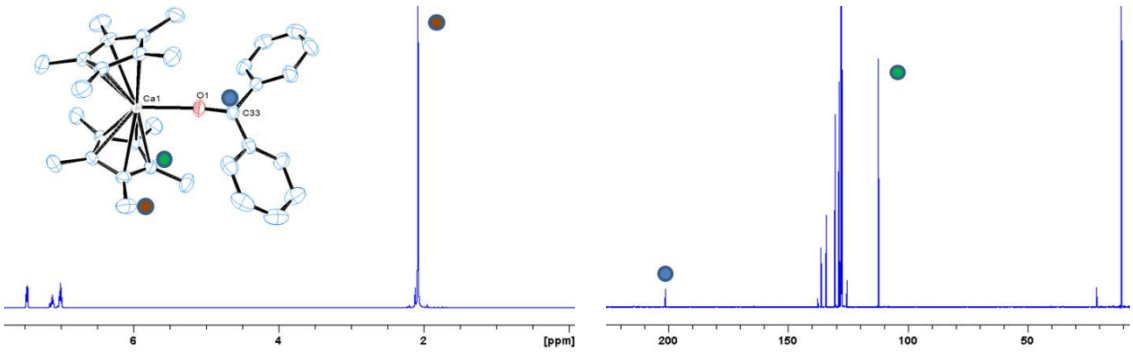

Fig. S12 ^{1}H NMR spectrum of isolated **10** in C_6D_6 at 298 K (left) and $^{13}C\{^{1}H\}$ NMR spectrum of **10** at 298 K (right) showing partial assignment.

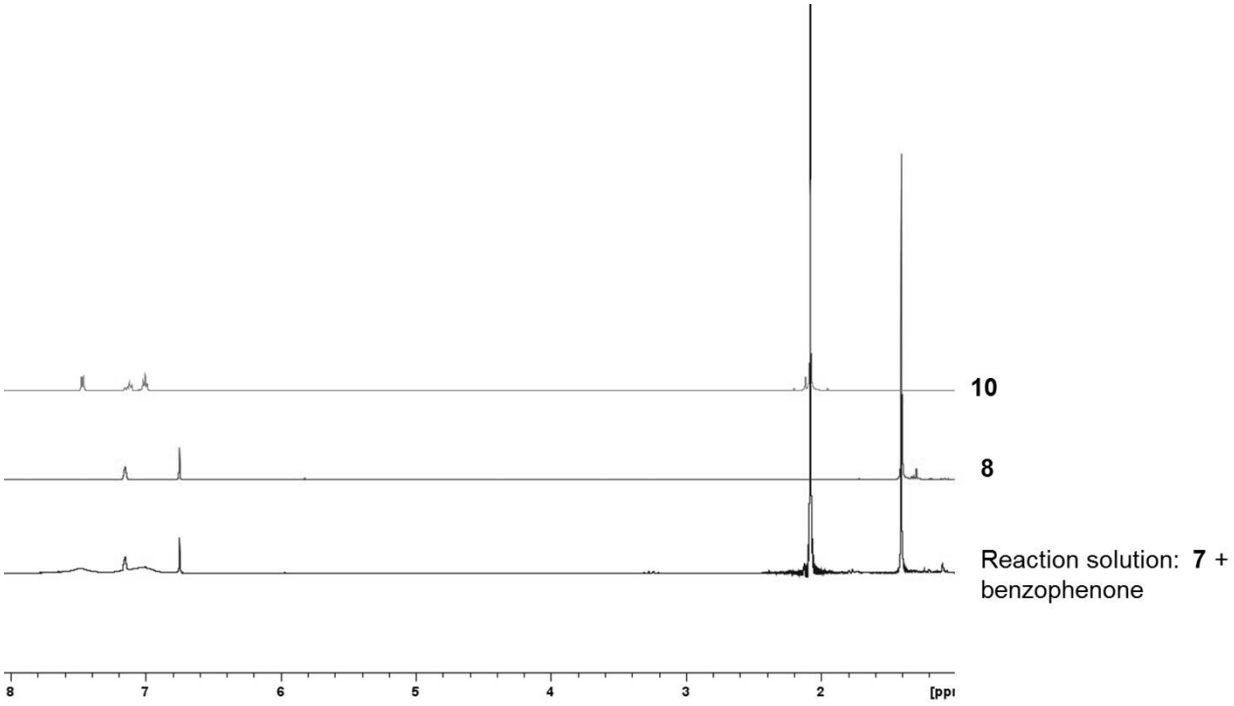

Fig. S13 Comparative ^{1}H NMR (in C_6D_6) spectra of the reaction solution of compound **7** with benzophenone (bottom); an authentic sample of NHSi **8** (middle) and isolated **10** (top).

2. Crystal data and refinement of compounds 3-5.

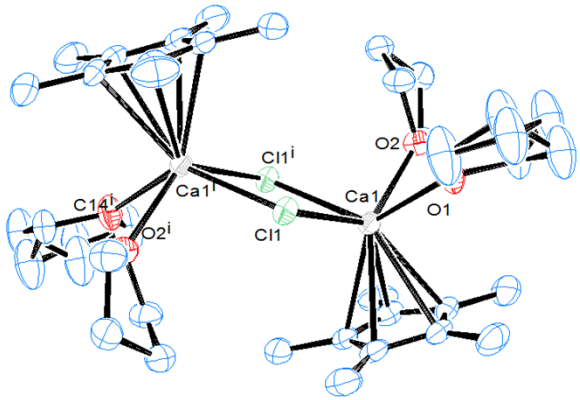

Fig. S14 Ortep representation of the molecular structure of dimer **3** in the solid state. Thermal ellipsoids are set at the 50 % probability interval and H atoms are omitted for clarity.

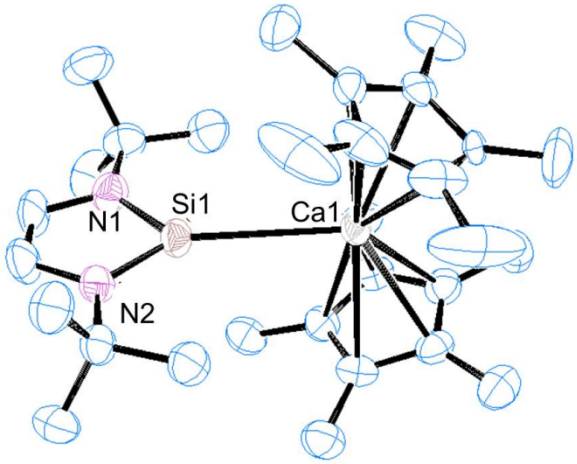

Fig. S15 Ortep representation of the molecular structure of compound **7** in the solid state. Thermal ellipsoids are set at the 50 % probability interval and H atoms are omitted for clarity. The crystal data is only of medium quality but the structural motif is definite.

Table 1s. Crystal Data and Structure Refinement for **3**, **6**, **7** and **10**. [a]

	1/2·**3**	**6**	2·**7**	**10**·0.5 toluene
formula	$C_{18}H_{31}CaClO_2$	$C_{45}H_{66}CaN_2OSi$	$C_{60}H_{100}Ca_2N_4Si_2$	$C_{36.50}H_{44}CaO$
formula weight	354.96	719.17	1013.78	538.80
crystal system	Triclinic	Orthorhombic	Monoclinic	Monoclinic
space group	*P*-1	$P2_12_12_1$	$P2_1/n$	$P2_1/c$
a/Å	9.0963(6)	10.74110(10)	19.1465(8)	9.91840(10)
b/Å	13.5005(9)	14.40170(10)	15.7739(9)	14.12280(10)
c/Å	17.6543(13)	27.9573(2)	21.0187(12)	23.6163(3)
α/deg	80.412(6)			
β/deg	76.114(6)		93.404(5)	101.9090(10)
γ/deg	70.938(6)			
V/Å^3	1980.1(2)	4324.72(6)	6336.8(6)	3236.87(6)
Z	4	4	4	4
ρ_{calcd}/g·cm^{-3}	1.191	1.105	1.063	1.106
μ/mm^{-1}	3.997	1.758	2.190	1.843
F(000)	768	1568	2224	1164
crystal size/mm^3	0.15 x 0.09 x 0.08	0.43 x 0.25 x 0.12	0.21 x 0.16 x 0.13	0.39 x 0.32 x 0.11
θ range/deg	2.59–67.48	3.16–67.48	3.03–67.48	3.67–67.48
collected data	13210	27936	24037	21947
unique data	7128 (R_{int} = 0.0376)	7792 (R_{int} = 0.0304)	11406 (R_{int} = 0.0708)	5811 (R_{int} = 0.0226)
completeness to θ	100.0%	100.0%	100.0%	100.0%
data/restraints/parameters	7128 / 54 / 425	7792 / 0 / 470	11406 / 18 / 670	5811 / 92 / 390
GOF on F^2	1.094	1.034	1.923	1.128
final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0497	R_1 = 0.0309	R_1 = 0.1855	R_1 = 0.0513
	wR_2 = 0.1248	wR_2 = 0.0853	wR_2 = 0.5168	wR_2 = 0.1442
R indices (all data)	R_1 = 0.0648	R_1 = 0.0314	R_1 = 0.2158	R_1 = 0.0521
	wR_2 = 0.1365	wR_2 = 0.0857	wR_2 = 0.5336	wR_2 = 0.1445
Largest diff peak/hole (e·Å^{-3})	0.598/–0.371	0.350/–0.274	2.262/–0.608	0.490/–0.372

[a] All data were collected at 173(2) K using Mo K_α (λ = 0.71073 Å) radiation. $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]\}^{2\}^{1/2}$, GOF = $\{\sum[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

Table 2s. Selected bond (Å) and angles (°) for **3**.

Cl(2)-Ca(2)#1	2.7346(9)
Cl(2)-Ca(2)	2.7393(10)
Ca(2)-O(4)	2.417(2)
Ca(2)-O(3)	2.418(2)
Ca(2)-C(23)	2.664(3)
Ca(2)-C(19)	2.673(3)
Ca(2)-C(22)	2.678(3)
Ca(2)-C(21)	2.694(3)
Ca(2)-C(20)	2.700(3)
Ca(2)-Cl(2)#1	2.7346(9)
Ca(2)-Ca(2)#1	4.1570(12)
Cl(1)-Ca(1)	2.7298(10)
Cl(1)-Ca(1)#2	2.7545(9)
Ca(1)-O(2)	2.404(2)
Ca(1)-O(1)	2.435(2)
Ca(1)-C(5)	2.654(3)
Ca(1)-C(4)	2.666(3)
Ca(1)-C(1)	2.683(3)
Ca(1)-C(2)	2.693(3)
Ca(1)-C(3)	2.694(3)
Ca(1)-Cl(1)#2	2.7545(9)
Ca(1)-Ca(1)#2	4.1894(12)
O(1)-C(14)	1.437(5)
O(1)-C(11)	1.443(4)
O(2)-C(15)	1.445(4)
O(2)-C(18)	1.470(4)
C(1)-C(5)	1.410(5)
C(1)-C(2)	1.417(5)

C(1)-C(6)	1.502(5)
C(2)-C(3)	1.404(5)
C(2)-C(7)	1.516(5)
C(3)-C(4)	1.416(5)
C(3)-C(8)	1.511(5)
C(4)-C(5)	1.409(5)
C(4)-C(9)	1.512(5)
C(5)-C(10)	1.511(5)
C(11)-C(12A)	1.459(12)
C(11)-C(12)	1.538(11)
C(12)-C(13)	1.55(2)
C(13)-C(14)	1.395(17)
C(12A)-C(13A)	1.60(2)
C(13A)-C(14)	1.477(15)
C(15)-C(16)	1.511(5)
C(16)-C(17)	1.525(5)
C(17)-C(18)	1.497(5)
O(3)-C(29)	1.444(4)
O(3)-C(32)	1.454(4)
O(4)-C(33)	1.441(4)
O(4)-C(36)	1.443(4)
C(19)-C(20)	1.408(5)
C(19)-C(23)	1.414(5)
C(19)-C(24)	1.502(5)
C(20)-C(21)	1.418(5)
C(20)-C(25)	1.503(5)
C(21)-C(22)	1.407(5)
C(21)-C(26)	1.508(5)
C(22)-C(23)	1.411(5)
C(22)-C(27)	1.505(5)

C(23)-C(28)	1.505(5)
C(29)-C(30)	1.525(6)
C(30)-C(31)	1.481(6)
C(31)-C(32)	1.513(5)
C(33)-C(34)	1.525(5)
C(34)-C(35)	1.519(6)
C(35)-C(36)	1.513(5)

Ca(2)#1-Cl(2)-Ca(2)	98.83(3)
O(4)-Ca(2)-O(3)	74.46(8)
O(4)-Ca(2)-C(23)	109.16(10)
O(3)-Ca(2)-C(23)	139.76(10)
O(4)-Ca(2)-C(19)	87.46(9)
O(3)-Ca(2)-C(19)	114.01(10)
C(23)-Ca(2)-C(19)	30.72(11)
O(4)-Ca(2)-C(22)	137.44(9)
O(3)-Ca(2)-C(22)	123.85(10)
C(23)-Ca(2)-C(22)	30.62(10)
C(19)-Ca(2)-C(22)	50.44(10)
O(4)-Ca(2)-C(21)	128.01(10)
O(3)-Ca(2)-C(21)	94.65(10)
C(23)-Ca(2)-C(21)	50.44(11)
C(19)-Ca(2)-C(21)	50.27(10)
C(22)-Ca(2)-C(21)	30.38(11)
O(4)-Ca(2)-C(20)	97.69(10)
O(3)-Ca(2)-C(20)	89.30(9)
C(23)-Ca(2)-C(20)	50.53(11)
C(19)-Ca(2)-C(20)	30.38(11)
C(22)-Ca(2)-C(20)	50.34(10)
C(21)-Ca(2)-C(20)	30.48(11)

O(4)-Ca(2)-Cl(2)#1	130.52(6)
O(3)-Ca(2)-Cl(2)#1	80.44(6)
C(23)-Ca(2)-Cl(2)#1	117.42(8)
C(19)-Ca(2)-Cl(2)#1	141.98(8)
C(22)-Ca(2)-Cl(2)#1	91.89(7)
C(21)-Ca(2)-Cl(2)#1	95.53(8)
C(20)-Ca(2)-Cl(2)#1	124.17(8)
O(4)-Ca(2)-Cl(2)	84.13(6)
O(3)-Ca(2)-Cl(2)	130.93(6)
C(23)-Ca(2)-Cl(2)	88.80(8)
C(19)-Ca(2)-Cl(2)	108.40(9)
C(22)-Ca(2)-Cl(2)	101.81(8)
C(21)-Ca(2)-Cl(2)	132.18(8)
C(20)-Ca(2)-Cl(2)	137.75(8)
Cl(2)#1-Ca(2)-Cl(2)	81.17(3)
O(4)-Ca(2)-Ca(2)#1	111.10(6)
O(3)-Ca(2)-Ca(2)#1	108.81(6)
C(23)-Ca(2)-Ca(2)#1	106.81(8)
C(19)-Ca(2)-Ca(2)#1	136.57(9)
C(22)-Ca(2)-Ca(2)#1	99.01(7)
C(21)-Ca(2)-Ca(2)#1	120.39(8)
C(20)-Ca(2)-Ca(2)#1	149.01(8)
Cl(2)#1-Ca(2)-Ca(2)#1	40.630(19)
Cl(2)-Ca(2)-Ca(2)#1	40.544(19)
Ca(1)-Cl(1)-Ca(1)#2	99.61(3)
O(2)-Ca(1)-O(1)	74.71(8)
O(2)-Ca(1)-C(5)	126.31(10)
O(1)-Ca(1)-C(5)	134.71(10)
O(2)-Ca(1)-C(4)	96.84(10)
O(1)-Ca(1)-C(4)	125.82(10)

C(5)-Ca(1)-C(4)	30.71(11)
O(2)-Ca(1)-C(1)	141.86(9)
O(1)-Ca(1)-C(1)	106.42(10)
C(5)-Ca(1)-C(1)	30.63(11)
C(4)-Ca(1)-C(1)	50.60(11)
O(2)-Ca(1)-C(2)	115.72(10)
O(1)-Ca(1)-C(2)	84.79(10)
C(5)-Ca(1)-C(2)	50.42(10)
C(4)-Ca(1)-C(2)	50.30(10)
C(1)-Ca(1)-C(2)	30.56(11)
O(2)-Ca(1)-C(3)	91.49(9)
O(1)-Ca(1)-C(3)	95.29(10)
C(5)-Ca(1)-C(3)	50.55(10)
C(4)-Ca(1)-C(3)	30.62(11)
C(1)-Ca(1)-C(3)	50.40(10)
C(2)-Ca(1)-C(3)	30.21(11)
O(2)-Ca(1)-Cl(1)	127.95(6)
O(1)-Ca(1)-Cl(1)	85.14(6)
C(5)-Ca(1)-Cl(1)	101.99(8)
C(4)-Ca(1)-Cl(1)	132.68(9)
C(1)-Ca(1)-Cl(1)	89.61(8)
C(2)-Ca(1)-Cl(1)	109.37(8)
C(3)-Ca(1)-Cl(1)	138.53(8)
O(2)-Ca(1)-Cl(1)#2	80.90(6)
O(1)-Ca(1)-Cl(1)#2	134.49(7)
C(5)-Ca(1)-Cl(1)#2	90.62(7)
C(4)-Ca(1)-Cl(1)#2	94.47(8)
C(1)-Ca(1)-Cl(1)#2	116.31(8)
C(2)-Ca(1)-Cl(1)#2	140.70(8)
C(3)-Ca(1)-Cl(1)#2	123.49(8)

Cl(1)-Ca(1)-Cl(1)#2	80.39(3)
O(2)-Ca(1)-Ca(1)#2	107.26(6)
O(1)-Ca(1)-Ca(1)#2	113.93(6)
C(5)-Ca(1)-Ca(1)#2	98.19(7)
C(4)-Ca(1)-Ca(1)#2	119.53(8)
C(1)-Ca(1)-Ca(1)#2	106.68(8)
C(2)-Ca(1)-Ca(1)#2	136.46(8)
C(3)-Ca(1)-Ca(1)#2	148.33(8)
Cl(1)-Ca(1)-Ca(1)#2	40.410(19)
Cl(1)#2-Ca(1)-Ca(1)#2	39.975(19)
C(14)-O(1)-C(11)	108.3(3)
C(14)-O(1)-Ca(1)	125.2(2)
C(11)-O(1)-Ca(1)	126.5(2)
C(15)-O(2)-C(18)	108.2(3)
C(15)-O(2)-Ca(1)	128.1(2)
C(18)-O(2)-Ca(1)	110.54(19)
C(5)-C(1)-C(2)	107.4(3)
C(5)-C(1)-C(6)	127.2(3)
C(2)-C(1)-C(6)	125.4(3)
C(5)-C(1)-Ca(1)	73.57(18)
C(2)-C(1)-Ca(1)	75.13(19)
C(6)-C(1)-Ca(1)	118.5(2)
C(3)-C(2)-C(1)	108.5(3)
C(3)-C(2)-C(7)	126.0(3)
C(1)-C(2)-C(7)	125.4(3)
C(3)-C(2)-Ca(1)	74.91(18)
C(1)-C(2)-Ca(1)	74.31(18)
C(7)-C(2)-Ca(1)	119.8(2)
C(2)-C(3)-C(4)	107.8(3)
C(2)-C(3)-C(8)	126.6(3)

C(4)-C(3)-C(8)	125.4(4)
C(2)-C(3)-Ca(1)	74.88(18)
C(4)-C(3)-Ca(1)	73.60(18)
C(8)-C(3)-Ca(1)	122.0(2)
C(5)-C(4)-C(3)	107.9(3)
C(5)-C(4)-C(9)	125.5(4)
C(3)-C(4)-C(9)	126.5(4)
C(5)-C(4)-Ca(1)	74.19(19)
C(3)-C(4)-Ca(1)	75.77(19)
C(9)-C(4)-Ca(1)	118.7(2)
C(4)-C(5)-C(1)	108.4(3)
C(4)-C(5)-C(10)	125.0(3)
C(1)-C(5)-C(10)	126.6(4)
C(4)-C(5)-Ca(1)	75.10(19)
C(1)-C(5)-Ca(1)	75.80(19)
C(10)-C(5)-Ca(1)	116.6(2)
O(1)-C(11)-C(12A)	105.6(5)
O(1)-C(11)-C(12)	105.7(5)
C(12A)-C(11)-C(12)	29.9(7)
C(11)-C(12)-C(13)	95.2(8)
C(14)-C(13)-C(12)	106.1(13)
C(11)-C(12A)-C(13A)	106.7(11)
C(14)-C(13A)-C(12A)	97.3(9)
C(13)-C(14)-O(1)	105.6(7)
C(13)-C(14)-C(13A)	19.2(11)
O(1)-C(14)-C(13A)	112.0(7)
O(2)-C(15)-C(16)	106.4(3)
C(15)-C(16)-C(17)	101.5(3)
C(18)-C(17)-C(16)	102.2(3)
O(2)-C(18)-C(17)	105.8(3)

C(29)-O(3)-C(32)	109.1(3)
C(29)-O(3)-Ca(2)	127.6(2)
C(32)-O(3)-Ca(2)	110.2(2)
C(33)-O(4)-C(36)	104.3(2)
C(33)-O(4)-Ca(2)	124.6(2)
C(36)-O(4)-Ca(2)	131.0(2)
C(20)-C(19)-C(23)	108.5(3)
C(20)-C(19)-C(24)	127.1(4)
C(23)-C(19)-C(24)	124.0(4)
C(20)-C(19)-Ca(2)	75.86(19)
C(23)-C(19)-Ca(2)	74.31(19)
C(24)-C(19)-Ca(2)	121.6(2)
C(19)-C(20)-C(21)	107.5(3)
C(19)-C(20)-C(25)	126.5(4)
C(21)-C(20)-C(25)	125.8(4)
C(19)-C(20)-Ca(2)	73.75(19)
C(21)-C(20)-Ca(2)	74.53(19)
C(25)-C(20)-Ca(2)	121.1(2)
C(22)-C(21)-C(20)	108.1(3)
C(22)-C(21)-C(26)	125.5(4)
C(20)-C(21)-C(26)	126.2(4)
C(22)-C(21)-Ca(2)	74.19(19)
C(20)-C(21)-Ca(2)	74.99(19)
C(26)-C(21)-Ca(2)	120.7(3)
C(21)-C(22)-C(23)	108.2(3)
C(21)-C(22)-C(27)	125.1(4)
C(23)-C(22)-C(27)	126.5(4)
C(21)-C(22)-Ca(2)	75.43(19)
C(23)-C(22)-Ca(2)	74.17(19)
C(27)-C(22)-Ca(2)	119.9(2)

C(22)-C(23)-C(19)	107.6(3)
C(22)-C(23)-C(28)	126.8(4)
C(19)-C(23)-C(28)	125.4(4)
C(22)-C(23)-Ca(2)	75.21(19)
C(19)-C(23)-Ca(2)	74.97(19)
C(28)-C(23)-Ca(2)	119.4(2)
O(3)-C(29)-C(30)	104.3(3)
C(31)-C(30)-C(29)	102.4(4)
C(30)-C(31)-C(32)	103.5(3)
O(3)-C(32)-C(31)	105.9(3)
O(4)-C(33)-C(34)	105.5(3)
C(35)-C(34)-C(33)	104.3(3)
C(36)-C(35)-C(34)	104.0(3)
O(4)-C(36)-C(35)	103.5(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+2,-z #2 -x+1,-y+1,-z+1

Table 3s. Selected bond lengths (Å) and angles (°) for **6**.

Ca(1)-C(19)	2.6466(15)
Ca(1)-C(18)	2.6538(15)
Ca(1)-C(30)	2.6621(16)
Ca(1)-C(29)	2.6674(16)
Ca(1)-C(26)	2.6673(17)
Ca(1)-C(28)	2.6828(15)
Ca(1)-C(20)	2.6859(15)
Ca(1)-C(17)	2.6889(16)
Ca(1)-C(27)	2.6920(16)
Ca(1)-C(16)	2.7022(16)

Ca(1)-Si(1)	3.2732(5)
Si(1)-O(1)	1.6893(12)
Si(1)-N(1)	1.8632(13)
Si(1)-N(2)	1.8831(14)
Si(1)-C(1)	2.3310(16)
N(1)-C(1)	1.334(2)
N(1)-C(12)	1.484(2)
N(2)-C(1)	1.334(2)
N(2)-C(8)	1.487(2)
O(1)-C(36)	1.3715(19)
C(1)-C(2)	1.490(2)
C(2)-C(7)	1.384(2)
C(2)-C(3)	1.387(2)
C(3)-C(4)	1.387(3)
C(4)-C(5)	1.383(3)
C(5)-C(6)	1.378(3)
C(6)-C(7)	1.388(2)
C(8)-C(10)	1.510(3)
C(8)-C(9)	1.516(2)
C(8)-C(11)	1.545(3)
C(12)-C(14)	1.517(3)
C(12)-C(13)	1.529(3)
C(12)-C(15)	1.529(2)
C(16)-C(17)	1.409(2)
C(16)-C(20)	1.421(2)
C(16)-C(21)	1.505(2)
C(17)-C(18)	1.416(2)
C(17)-C(22)	1.504(3)
C(18)-C(19)	1.420(2)
C(18)-C(23)	1.504(2)

C(19)-C(20)	1.421(2)
C(19)-C(24)	1.508(2)
C(20)-C(25)	1.505(2)
C(26)-C(30)	1.409(3)
C(26)-C(27)	1.414(3)
C(26)-C(31)	1.508(3)
C(27)-C(28)	1.414(2)
C(27)-C(32)	1.501(3)
C(28)-C(29)	1.413(2)
C(28)-C(33)	1.497(2)
C(29)-C(30)	1.409(2)
C(29)-C(34)	1.500(3)
C(30)-C(35)	1.508(3)
C(36)-C(37)	1.387(2)
C(36)-C(41)	1.407(2)
C(37)-C(38)	1.384(2)
C(38)-C(39)	1.374(3)
C(39)-C(40)	1.384(3)
C(40)-C(41)	1.399(2)
C(41)-C(42)	1.535(3)
C(42)-C(45)	1.536(3)
C(42)-C(43)	1.536(3)
C(42)-C(44)	1.542(3)

C(19)-Ca(1)-C(18)	31.07(5)
C(19)-Ca(1)-C(30)	165.16(5)
C(18)-Ca(1)-C(30)	145.39(5)
C(19)-Ca(1)-C(29)	134.50(5)
C(18)-Ca(1)-C(29)	125.32(5)
C(30)-Ca(1)-C(29)	30.67(5)

C(19)-Ca(1)-C(26)	152.67(6)
C(18)-Ca(1)-C(26)	121.61(6)
C(30)-Ca(1)-C(26)	30.66(6)
C(29)-Ca(1)-C(26)	50.63(5)
C(19)-Ca(1)-C(28)	117.36(5)
C(18)-Ca(1)-C(28)	97.42(5)
C(30)-Ca(1)-C(28)	50.60(5)
C(29)-Ca(1)-C(28)	30.62(5)
C(26)-Ca(1)-C(28)	50.56(5)
C(19)-Ca(1)-C(20)	30.89(5)
C(18)-Ca(1)-C(20)	50.88(5)
C(30)-Ca(1)-C(20)	162.23(5)
C(29)-Ca(1)-C(20)	161.13(5)
C(26)-Ca(1)-C(20)	148.17(5)
C(28)-Ca(1)-C(20)	147.17(5)
C(19)-Ca(1)-C(17)	50.95(5)
C(18)-Ca(1)-C(17)	30.73(5)
C(30)-Ca(1)-C(17)	136.29(5)
C(29)-Ca(1)-C(17)	138.41(5)
C(26)-Ca(1)-C(17)	105.66(6)
C(28)-Ca(1)-C(17)	108.12(5)
C(20)-Ca(1)-C(17)	50.48(5)
C(19)-Ca(1)-C(27)	125.16(5)
C(18)-Ca(1)-C(27)	95.56(5)
C(30)-Ca(1)-C(27)	50.53(5)
C(29)-Ca(1)-C(27)	50.49(5)
C(26)-Ca(1)-C(27)	30.59(6)
C(28)-Ca(1)-C(27)	30.51(5)
C(20)-Ca(1)-C(27)	141.39(5)
C(17)-Ca(1)-C(27)	91.02(5)

C(19)-Ca(1)-C(16)	50.85(5)
C(18)-Ca(1)-C(16)	50.59(5)
C(30)-Ca(1)-C(16)	143.28(6)
C(29)-Ca(1)-C(16)	166.25(5)
C(26)-Ca(1)-C(16)	117.96(6)
C(28)-Ca(1)-C(16)	138.03(5)
C(20)-Ca(1)-C(16)	30.58(5)
C(17)-Ca(1)-C(16)	30.31(5)
C(27)-Ca(1)-C(16)	115.78(5)
C(19)-Ca(1)-Si(1)	97.09(4)
C(18)-Ca(1)-Si(1)	128.16(4)
C(30)-Ca(1)-Si(1)	83.88(4)
C(29)-Ca(1)-Si(1)	88.01(4)
C(26)-Ca(1)-Si(1)	110.22(4)
C(28)-Ca(1)-Si(1)	117.45(4)
C(20)-Ca(1)-Si(1)	84.25(4)
C(17)-Ca(1)-Si(1)	133.39(4)
C(27)-Ca(1)-Si(1)	133.99(4)
C(16)-Ca(1)-Si(1)	104.43(4)
O(1)-Si(1)-N(1)	96.54(6)
O(1)-Si(1)-N(2)	98.79(6)
N(1)-Si(1)-N(2)	69.77(6)
O(1)-Si(1)-C(1)	100.20(6)
N(1)-Si(1)-C(1)	34.88(6)
N(2)-Si(1)-C(1)	34.91(6)
O(1)-Si(1)-Ca(1)	125.94(4)
N(1)-Si(1)-Ca(1)	110.44(4)
N(2)-Si(1)-Ca(1)	133.95(5)
C(1)-Si(1)-Ca(1)	128.71(4)
C(1)-N(1)-C(12)	132.02(14)

C(1)-N(1)-Si(1)	92.11(9)
C(12)-N(1)-Si(1)	134.42(11)
C(1)-N(2)-C(8)	130.13(14)
C(1)-N(2)-Si(1)	91.22(10)
C(8)-N(2)-Si(1)	138.06(11)
C(36)-O(1)-Si(1)	130.56(11)
N(2)-C(1)-N(1)	106.85(13)
N(2)-C(1)-C(2)	127.31(15)
N(1)-C(1)-C(2)	125.82(14)
N(2)-C(1)-Si(1)	53.87(8)
N(1)-C(1)-Si(1)	53.01(8)
C(2)-C(1)-Si(1)	178.78(12)
C(7)-C(2)-C(3)	120.50(16)
C(7)-C(2)-C(1)	121.54(15)
C(3)-C(2)-C(1)	117.93(16)
C(2)-C(3)-C(4)	119.26(19)
C(5)-C(4)-C(3)	120.40(19)
C(6)-C(5)-C(4)	120.03(18)
C(5)-C(6)-C(7)	120.17(19)
C(2)-C(7)-C(6)	119.64(17)
N(2)-C(8)-C(10)	112.07(16)
N(2)-C(8)-C(9)	106.42(13)
C(10)-C(8)-C(9)	110.14(18)
N(2)-C(8)-C(11)	109.92(15)
C(10)-C(8)-C(11)	110.8(2)
C(9)-C(8)-C(11)	107.29(16)
N(1)-C(12)-C(14)	108.71(14)
N(1)-C(12)-C(13)	106.15(14)
C(14)-C(12)-C(13)	109.19(18)
N(1)-C(12)-C(15)	114.38(14)

C(14)-C(12)-C(15)	110.21(17)
C(13)-C(12)-C(15)	108.03(15)
C(17)-C(16)-C(20)	108.13(15)
C(17)-C(16)-C(21)	124.85(16)
C(20)-C(16)-C(21)	126.42(16)
C(17)-C(16)-Ca(1)	74.32(9)
C(20)-C(16)-Ca(1)	74.07(9)
C(21)-C(16)-Ca(1)	124.55(11)
C(16)-C(17)-C(18)	108.20(15)
C(16)-C(17)-C(22)	124.48(16)
C(18)-C(17)-C(22)	126.41(16)
C(16)-C(17)-Ca(1)	75.37(9)
C(18)-C(17)-Ca(1)	73.26(9)
C(22)-C(17)-Ca(1)	125.97(12)
C(17)-C(18)-C(19)	108.08(14)
C(17)-C(18)-C(23)	126.34(16)
C(19)-C(18)-C(23)	125.37(16)
C(17)-C(18)-Ca(1)	76.01(9)
C(19)-C(18)-Ca(1)	74.19(9)
C(23)-C(18)-Ca(1)	120.07(11)
C(18)-C(19)-C(20)	107.74(14)
C(18)-C(19)-C(24)	125.60(15)
C(20)-C(19)-C(24)	126.58(15)
C(18)-C(19)-Ca(1)	74.74(9)
C(20)-C(19)-Ca(1)	76.08(8)
C(24)-C(19)-Ca(1)	117.86(10)
C(19)-C(20)-C(16)	107.85(14)
C(19)-C(20)-C(25)	126.58(16)
C(16)-C(20)-C(25)	124.93(15)
C(19)-C(20)-Ca(1)	73.03(8)

C(16)-C(20)-Ca(1)	75.34(9)
C(25)-C(20)-Ca(1)	124.71(10)
C(30)-C(26)-C(27)	108.13(15)
C(30)-C(26)-C(31)	125.9(2)
C(27)-C(26)-C(31)	125.7(2)
C(30)-C(26)-Ca(1)	74.47(9)
C(27)-C(26)-Ca(1)	75.67(10)
C(31)-C(26)-Ca(1)	120.31(13)
C(28)-C(27)-C(26)	107.78(15)
C(28)-C(27)-C(32)	126.03(19)
C(26)-C(27)-C(32)	125.4(2)
C(28)-C(27)-Ca(1)	74.39(9)
C(26)-C(27)-Ca(1)	73.74(9)
C(32)-C(27)-Ca(1)	125.48(13)
C(29)-C(28)-C(27)	107.93(15)
C(29)-C(28)-C(33)	125.69(17)
C(27)-C(28)-C(33)	125.82(17)
C(29)-C(28)-Ca(1)	74.09(9)
C(27)-C(28)-Ca(1)	75.10(9)
C(33)-C(28)-Ca(1)	123.49(11)
C(30)-C(29)-C(28)	108.08(15)
C(30)-C(29)-C(34)	127.09(17)
C(28)-C(29)-C(34)	124.76(16)
C(30)-C(29)-Ca(1)	74.46(9)
C(28)-C(29)-Ca(1)	75.30(9)
C(34)-C(29)-Ca(1)	118.74(11)
C(26)-C(30)-C(29)	108.07(15)
C(26)-C(30)-C(35)	126.75(19)
C(29)-C(30)-C(35)	124.92(19)
C(26)-C(30)-Ca(1)	74.87(10)

C(29)-C(30)-Ca(1)	74.87(9)
C(35)-C(30)-Ca(1)	120.96(11)
O(1)-C(36)-C(37)	120.21(15)
O(1)-C(36)-C(41)	118.66(15)
C(37)-C(36)-C(41)	121.13(15)
C(38)-C(37)-C(36)	121.14(17)
C(39)-C(38)-C(37)	119.02(18)
C(38)-C(39)-C(40)	119.91(17)
C(39)-C(40)-C(41)	122.91(19)
C(40)-C(41)-C(36)	115.88(17)
C(40)-C(41)-C(42)	121.66(17)
C(36)-C(41)-C(42)	122.44(15)
C(45)-C(42)-C(41)	110.79(17)
C(45)-C(42)-C(43)	109.86(18)
C(41)-C(42)-C(43)	109.27(16)
C(45)-C(42)-C(44)	106.99(19)
C(41)-C(42)-C(44)	112.02(17)
C(43)-C(42)-C(44)	107.8(2)

Symmetry transformations used to generate equivalent atoms:

Table 4s. Selected bond lengths (Å) and angles (°) for **10**.

Ca(1)-O(1)	2.2925(19)
Ca(1)-C(2)	2.632(3)
Ca(1)-C(3)	2.633(3)
Ca(1)-C(9)	2.634(3)
Ca(1)-C(10)	2.641(3)
Ca(1)-C(4)	2.644(3)
Ca(1)-C(1)	2.646(3)
Ca(1)-C(8)	2.652(3)

Ca(1)-C(5)	2.668(3)
Ca(1)-C(6)	2.670(3)
Ca(1)-C(7)	2.680(3)
O(1)-C(33)	1.238(3)
C(1)-C(2)	1.410(4)
C(1)-C(5)	1.415(4)
C(1)-C(11)	1.505(4)
C(2)-C(3)	1.413(4)
C(2)-C(12)	1.511(4)
C(3)-C(4)	1.418(4)
C(3)-C(13)	1.509(4)
C(4)-C(5)	1.418(4)
C(4)-C(14)	1.503(4)
C(5)-C(15)	1.511(4)
C(6)-C(7)	1.410(4)
C(6)-C(10)	1.417(4)
C(6)-C(19)	1.508(4)
C(7)-C(8)	1.418(4)
C(7)-C(18)	1.506(4)
C(8)-C(9)	1.413(4)
C(8)-C(17)	1.506(4)
C(9)-C(10)	1.406(4)
C(9)-C(16)	1.508(4)
C(10)-C(20)	1.511(4)
C(21)-C(22)	1.390(4)
C(21)-C(26)	1.391(4)
C(21)-C(33)	1.481(4)
C(22)-C(23)	1.375(5)
C(23)-C(24)	1.378(5)
C(24)-C(25)	1.388(5)

C(25)-C(26)	1.383(4)
C(27)-C(32)	1.389(4)
C(27)-C(28)	1.397(4)
C(27)-C(33)	1.477(4)
C(28)-C(29)	1.372(5)
C(29)-C(30)	1.381(5)
C(30)-C(31)	1.378(5)
C(31)-C(32)	1.387(4)
C(34)-C(39)	1.369(9)
C(34)-C(35)	1.380(10)
C(34)-C(40)	1.494(12)
C(35)-C(36)	1.359(10)
C(36)-C(37)	1.329(10)
C(37)-C(38)	1.388(11)
C(38)-C(39)	1.391(10)

O(1)-Ca(1)-C(2)	125.69(8)
O(1)-Ca(1)-C(3)	130.05(8)
C(2)-Ca(1)-C(3)	31.13(9)
O(1)-Ca(1)-C(9)	84.77(8)
C(2)-Ca(1)-C(9)	130.89(9)
C(3)-Ca(1)-C(9)	145.09(9)
O(1)-Ca(1)-C(10)	84.30(8)
C(2)-Ca(1)-C(10)	148.37(8)
C(3)-Ca(1)-C(10)	137.17(9)
C(9)-Ca(1)-C(10)	30.90(9)
O(1)-Ca(1)-C(4)	100.19(8)
C(2)-Ca(1)-C(4)	51.45(9)
C(3)-Ca(1)-C(4)	31.17(8)
C(9)-Ca(1)-C(4)	171.09(9)

C(10)-Ca(1)-C(4)	141.61(9)
O(1)-Ca(1)-C(1)	94.78(8)
C(2)-Ca(1)-C(1)	30.98(8)
C(3)-Ca(1)-C(1)	51.37(9)
C(9)-Ca(1)-C(1)	136.04(9)
C(10)-Ca(1)-C(1)	166.93(9)
C(4)-Ca(1)-C(1)	51.40(9)
O(1)-Ca(1)-C(8)	113.46(9)
C(2)-Ca(1)-C(8)	101.86(9)
C(3)-Ca(1)-C(8)	115.03(9)
C(9)-Ca(1)-C(8)	31.01(9)
C(10)-Ca(1)-C(8)	51.18(9)
C(4)-Ca(1)-C(8)	146.05(9)
C(1)-Ca(1)-C(8)	118.38(9)
O(1)-Ca(1)-C(5)	80.57(8)
C(2)-Ca(1)-C(5)	51.06(8)
C(3)-Ca(1)-C(5)	51.17(8)
C(9)-Ca(1)-C(5)	157.89(9)
C(10)-Ca(1)-C(5)	159.13(9)
C(4)-Ca(1)-C(5)	30.97(9)
C(1)-Ca(1)-C(5)	30.89(9)
C(8)-Ca(1)-C(5)	149.22(9)
O(1)-Ca(1)-C(6)	112.69(8)
C(2)-Ca(1)-C(6)	121.59(9)
C(3)-Ca(1)-C(6)	106.50(9)
C(9)-Ca(1)-C(6)	50.98(8)
C(10)-Ca(1)-C(6)	30.95(8)
C(4)-Ca(1)-C(6)	120.11(9)
C(1)-Ca(1)-C(6)	152.52(9)
C(8)-Ca(1)-C(6)	50.92(8)

C(5)-Ca(1)-C(6)	150.91(9)
O(1)-Ca(1)-C(7)	133.49(8)
C(2)-Ca(1)-C(7)	97.49(9)
C(3)-Ca(1)-C(7)	95.51(8)
C(9)-Ca(1)-C(7)	50.94(8)
C(10)-Ca(1)-C(7)	50.92(8)
C(4)-Ca(1)-C(7)	122.06(9)
C(1)-Ca(1)-C(7)	125.67(9)
C(8)-Ca(1)-C(7)	30.84(9)
C(5)-Ca(1)-C(7)	145.94(8)
C(6)-Ca(1)-C(7)	30.57(9)
C(33)-O(1)-Ca(1)	174.4(2)
C(2)-C(1)-C(5)	107.9(2)
C(2)-C(1)-C(11)	125.6(3)
C(5)-C(1)-C(11)	126.5(3)
C(2)-C(1)-Ca(1)	73.95(15)
C(5)-C(1)-Ca(1)	75.41(15)
C(11)-C(1)-Ca(1)	116.41(19)
C(1)-C(2)-C(3)	108.3(2)
C(1)-C(2)-C(12)	125.0(3)
C(3)-C(2)-C(12)	126.5(3)
C(1)-C(2)-Ca(1)	75.06(15)
C(3)-C(2)-Ca(1)	74.47(15)
C(12)-C(2)-Ca(1)	120.06(19)
C(2)-C(3)-C(4)	108.0(2)
C(2)-C(3)-C(13)	126.2(3)
C(4)-C(3)-C(13)	125.5(3)
C(2)-C(3)-Ca(1)	74.40(15)
C(4)-C(3)-Ca(1)	74.84(15)
C(13)-C(3)-Ca(1)	121.97(19)

C(3)-C(4)-C(5)	107.6(2)
C(3)-C(4)-C(14)	125.2(3)
C(5)-C(4)-C(14)	127.0(3)
C(3)-C(4)-Ca(1)	73.99(15)
C(5)-C(4)-Ca(1)	75.46(16)
C(14)-C(4)-Ca(1)	119.89(19)
C(1)-C(5)-C(4)	108.1(2)
C(1)-C(5)-C(15)	125.8(3)
C(4)-C(5)-C(15)	125.9(3)
C(1)-C(5)-Ca(1)	73.70(15)
C(4)-C(5)-Ca(1)	73.56(15)
C(15)-C(5)-Ca(1)	123.09(18)
C(7)-C(6)-C(10)	108.0(2)
C(7)-C(6)-C(19)	125.0(3)
C(10)-C(6)-C(19)	126.8(3)
C(7)-C(6)-Ca(1)	75.11(16)
C(10)-C(6)-Ca(1)	73.42(15)
C(19)-C(6)-Ca(1)	121.26(19)
C(6)-C(7)-C(8)	108.0(2)
C(6)-C(7)-C(18)	125.1(3)
C(8)-C(7)-C(18)	126.3(3)
C(6)-C(7)-Ca(1)	74.32(15)
C(8)-C(7)-Ca(1)	73.49(15)
C(18)-C(7)-Ca(1)	125.2(2)
C(9)-C(8)-C(7)	107.7(2)
C(9)-C(8)-C(17)	126.2(3)
C(7)-C(8)-C(17)	125.8(3)
C(9)-C(8)-Ca(1)	73.82(15)
C(7)-C(8)-Ca(1)	75.67(15)
C(17)-C(8)-Ca(1)	121.7(2)

C(10)-C(9)-C(8)	108.4(2)
C(10)-C(9)-C(16)	126.5(3)
C(8)-C(9)-C(16)	125.0(3)
C(10)-C(9)-Ca(1)	74.82(15)
C(8)-C(9)-Ca(1)	75.17(16)
C(16)-C(9)-Ca(1)	119.60(18)
C(9)-C(10)-C(6)	107.9(2)
C(9)-C(10)-C(20)	125.9(3)
C(6)-C(10)-C(20)	126.2(3)
C(9)-C(10)-Ca(1)	74.28(15)
C(6)-C(10)-Ca(1)	75.62(15)
C(20)-C(10)-Ca(1)	116.81(18)
C(22)-C(21)-C(26)	119.1(3)
C(22)-C(21)-C(33)	120.2(3)
C(26)-C(21)-C(33)	120.4(3)
C(23)-C(22)-C(21)	121.0(3)
C(22)-C(23)-C(24)	119.7(3)
C(23)-C(24)-C(25)	120.2(3)
C(26)-C(25)-C(24)	120.1(3)
C(25)-C(26)-C(21)	119.9(3)
C(32)-C(27)-C(28)	118.8(3)
C(32)-C(27)-C(33)	121.0(3)
C(28)-C(27)-C(33)	120.1(2)
C(29)-C(28)-C(27)	121.1(3)
C(28)-C(29)-C(30)	119.3(3)
C(31)-C(30)-C(29)	120.8(3)
C(30)-C(31)-C(32)	119.9(3)
C(31)-C(32)-C(27)	120.0(3)
O(1)-C(33)-C(27)	119.4(3)
O(1)-C(33)-C(21)	119.4(3)

C(27)-C(33)-C(21)	121.1(2)
C(39)-C(34)-C(35)	118.9(7)
C(39)-C(34)-C(40)	123.5(8)
C(35)-C(34)-C(40)	117.6(7)
C(36)-C(35)-C(34)	119.3(7)
C(37)-C(36)-C(35)	123.0(8)
C(36)-C(37)-C(38)	119.1(8)
C(37)-C(38)-C(39)	118.9(7)
C(34)-C(39)-C(38)	120.7(8)

Symmetry transformations used to generate equivalent atoms:

3. Computational Details

We have used density functional theory in the Kohn−Sham formulation as implemented in the Turbomole 6.4 program [1] to locate minima on the potential energy surface of the systems studied. A recent implementation of Grimme's D3 dispersion parameters [2] in Turbomole has paved the way for calculations on large organometallic systems that include dispersive interactions. To account for these forces we optimised all stationary points at the BP86-D3 level of theory, which contains Grimme's D3 dispersion parameters. The double ζ-quality basis set DZP [3] as well as the multipole-accelerated resolution of the identity approximation MARI-J with suitable fitting basis sets [4] were used in these computations. All stationary points were fully optimised. Molecular orbitals were drawn with Molden 4.8 [5] using ± 0.03 au isosurfaces for the orbital plots. A natural population analysis (NPA)[6] and resulting Wiberg bond indices (WBI)[7] were used for a detailed study of the electronic structure and bonding in some cases. Instead of the distances, WBIs describe the bond strengths, allowing the limitation of looking only at bond lengths to be overcome. The Gaussian 09 software package[8] was used at this stage.

4. Z-Matrices and optimized structures

Structure **6**

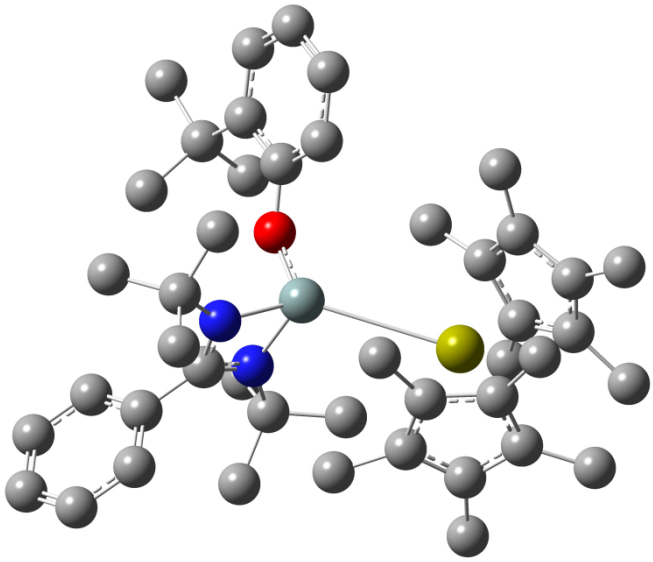

Fig. S16 Geometry optimized structure of compound **6**.

```
  116
FINAL HEAT OF FORMATION = -2905.301420
Ca    -0.346715    -0.163854    -2.563001
 O     0.747484    -1.232751     1.540727
Si    -0.249758    -0.232405     0.526279
 N     0.460978     1.411368     1.176401
 N    -1.358048     0.494390     1.925614
 C     1.833041    -1.713366    -2.381196
 C    -2.451616     0.011520     2.798653
 C     0.673141    -2.558418     1.834038
 C    -0.549111     1.561337     2.049309
 C     0.789294    -2.498188    -2.979247
 C    -1.619776     3.747929     2.719442
 H    -2.236657     3.709094     1.810550
 C    -0.322934    -4.763836     1.450631
 H    -1.029022    -5.399954     0.895494
 C    -1.859503     1.176156    -4.284708
 C     1.373886    -0.831538    -4.481748
 C     0.100978     2.757270     4.140560
 H     0.802976     1.934400     4.342605
 C    -2.725322     0.225117    -3.651202
 C     1.525259    -3.085597     2.852328
 C    -0.231570    -3.399091     1.148728
 H    -0.855585    -2.960407     0.354733
 C    -0.902347     4.889245     4.747558
 H    -0.976527     5.745889     5.434556
 C     0.508543    -1.955498    -4.276807
 C    -0.710856     2.706021     2.988502
```

C	-2.874088	0.606915	-2.280326
C	2.185092	-0.678929	-3.312145
C	1.575201	2.289365	0.769211
C	0.131345	-3.728153	-2.406956
H	0.550595	-3.996864	-1.418737
H	0.263327	-4.609323	-3.072359
H	-0.969131	-3.609986	-2.270320
C	2.581340	-2.031828	-1.113271
H	3.549643	-2.537284	-1.327932
H	2.008659	-2.700053	-0.442562
H	2.828294	-1.125820	-0.521478
C	-1.710065	4.838448	3.598108
H	-2.413914	5.656068	3.381337
C	1.575201	-0.045039	-5.748128
H	2.555949	-0.286658	-6.217214
H	1.575902	1.052223	-5.571880
H	0.793534	-0.255855	-6.501806
C	2.576170	-2.202223	3.559959
C	1.394113	-4.461398	3.135676
H	2.025281	-4.909208	3.914669
C	-2.102700	1.796271	-2.060857
C	0.490545	-5.298482	2.458499
H	0.430878	-6.365671	2.719304
C	-1.460955	2.137576	-3.298243
C	1.831065	1.991891	-0.721253
H	2.014664	0.910029	-0.883166
H	2.724632	2.533063	-1.085564
H	0.967062	2.305290	-1.344030
C	3.348824	0.273227	-3.215419
H	4.142557	0.014533	-3.952521
H	3.823677	0.253652	-2.214860
H	3.061988	1.326489	-3.427110
C	-0.437234	-2.564658	-5.276533
H	-0.774622	-1.828279	-6.033017
H	-1.347336	-2.975865	-4.793945
H	0.036356	-3.405935	-5.832036
C	-3.764617	-0.090493	-1.289307
H	-3.619895	-1.193596	-1.292861
H	-4.844453	0.082458	-1.498969
H	-3.571846	0.258189	-0.256249
C	1.278722	3.793968	0.935482
H	0.326258	4.074152	0.444541
H	2.093949	4.373132	0.458067
H	1.224534	4.100847	1.996047
C	-2.123503	2.642877	-0.816818
H	-1.125209	3.048862	-0.557575
H	-2.469710	2.062873	0.060882
H	-2.804908	3.517526	-0.923612
C	3.609977	-1.736397	2.504132
H	4.135104	-2.606354	2.061212
H	4.368501	-1.069668	2.965633
H	3.115598	-1.188623	1.681941
C	-3.459950	-0.912209	-4.309900
H	-3.062952	-1.131809	-5.319207
H	-4.544639	-0.688844	-4.424946
H	-3.396725	-1.854490	-3.722649
C	-2.864428	-1.375130	2.268910
H	-3.147968	-1.327551	1.198988
H	-3.736610	-1.754269	2.836510

H	-2.042583	-2.108703	2.384465
C	1.909370	-0.972872	4.232341
H	1.383332	-0.344359	3.491608
H	2.679475	-0.352009	4.737218
H	1.178855	-1.297422	5.001643
C	-0.609956	3.354981	-3.557806
H	-1.143720	4.119169	-4.166485
H	0.323482	3.110255	-4.110629
H	-0.308651	3.854437	-2.614362
C	-3.664382	0.965097	2.745588
H	-3.418629	1.957142	3.168760
H	-4.503447	0.544446	3.335584
H	-4.012234	1.103576	1.702789
C	3.335865	-2.973455	4.660031
H	2.654992	-3.340019	5.455584
H	4.076635	-2.300737	5.138432
H	3.895041	-3.840380	4.253528
C	-1.579807	1.275563	-5.758524
H	-2.390977	1.827251	-6.285530
H	-1.502693	0.280831	-6.241117
H	-0.635953	1.814967	-5.967717
C	0.000108	3.846158	5.019863
H	0.630925	3.881344	5.920856
C	-1.947849	-0.140933	4.250301
H	-1.040483	-0.775477	4.273990
H	-2.727822	-0.620040	4.875634
H	-1.705185	0.839266	4.704066
C	2.818463	1.904225	1.599230
H	2.639443	2.096098	2.675825
H	3.701464	2.494600	1.281537
H	3.049605	0.829186	1.481149

Structure **7**

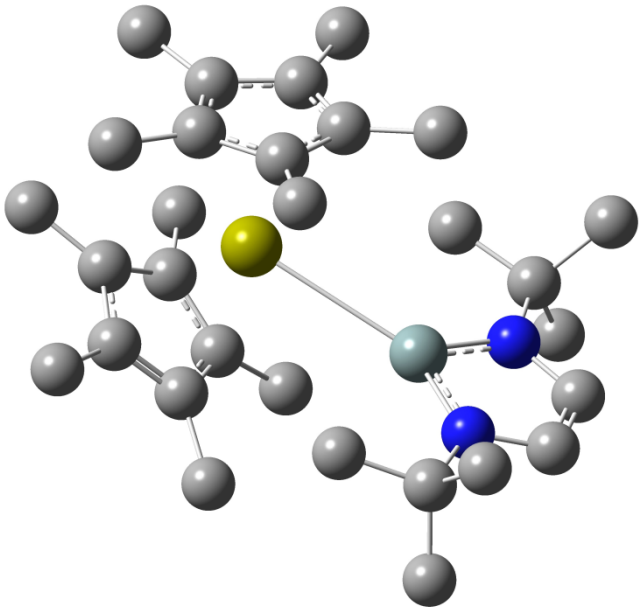

Fig. S17 Geometry optimized structure of compound **7**. Calculated d(Ca-Si) = 3.090 Å.

```
   84
FINAL HEAT OF FORMATION = -2249.201890
Ca    -0.942642     0.592913    -0.544730
Si     1.462311    -0.644233     0.793773
 C    -3.520502     0.364441    -0.124212
 C    -2.279081    -1.491356     0.503795
 C    -3.085830    -0.938030    -0.544689
 N     2.436905    -0.701667     2.290489
 C    -0.875587     3.000229    -1.566587
 C    -0.163600     1.315730    -2.997938
 C    -1.279776     2.144824    -2.645409
 C     2.368095     1.210583    -2.290912
 H     2.809415     0.876114    -1.326087
 H     3.019664     2.026196    -2.675789
 H     2.465845     0.364645    -3.000836
 C    -2.961374     0.623569     1.172081
 C     0.938848     1.669518    -2.153020
 C    -1.770772    -2.905155     0.609009
 H    -0.741277    -2.953683     1.024921
 H    -1.759505    -3.423128    -0.371437
 H    -2.413097    -3.516988     1.282282
 C     3.279137    -1.810087     2.331395
 H     3.947401    -1.991872     3.182729
 C    -0.175821     0.327233    -4.135502
 H    -0.373435     0.825687    -5.110407
 H    -0.967109    -0.446853    -4.017399
 H     0.789562    -0.207446    -4.234515
 C     3.181898    -2.615729     1.224728
 H     3.763510    -3.532260     1.064612
 C    -1.699058     4.082334    -0.918771
 H    -1.506629     5.082477    -1.368306
 H    -1.483713     4.176888     0.166647
 H    -2.786531     3.889512    -1.016693
 N     2.258865    -2.163856     0.286830
 C     1.970633    -0.403096     4.705956
 H     0.955827    -0.829625     4.581698
 H     1.944930     0.324044     5.542245
 H     2.657674    -1.223830     4.993205
 C     2.425667     0.291020     3.404554
 C     3.368048    -2.786990    -1.831639
 H     3.623930    -1.725257    -2.019846
 H     3.248755    -3.298790    -2.807731
 H     4.219855    -3.258198    -1.301964
 C     0.922036    -2.216028    -1.790940
 H    -0.038294    -2.283768    -1.241652
 H     0.783837    -2.720593    -2.766591
 H     1.144957    -1.151489    -2.003203
 C    -2.563710     2.197248    -3.427420
 H    -2.397452     2.630219    -4.439744
 H    -3.332246     2.818431    -2.930752
 H    -3.005545     1.190672    -3.587557
 C    -2.205860    -0.527311     1.565132
 C     3.838519     0.890247     3.571883
 H     4.582602     0.120275     3.857208
 H     3.836123     1.665061     4.364545
 H     4.172879     1.358427     2.624376
 C     1.699731    -4.357831    -0.736809
 H     2.513355    -4.900067    -0.215962
 H     1.508550    -4.883413    -1.693632
```

H	0.785817	-4.421237	-0.114482
C	2.067153	-2.883612	-1.005792
C	1.439683	1.421781	3.056903
H	1.752189	1.966783	2.144068
H	1.396345	2.151807	3.888899
H	0.414656	1.031160	2.896539
C	0.491107	2.697785	-1.256476
C	1.357773	3.424936	-0.263007
H	2.209875	2.797121	0.071337
H	0.794761	3.732883	0.643792
H	1.796006	4.355607	-0.690716
C	-1.628705	-0.804027	2.927630
H	-0.643905	-1.315747	2.874822
H	-2.298933	-1.464986	3.523063
H	-1.490820	0.122259	3.521129
C	-4.539369	1.232480	-0.810371
H	-5.539544	1.128010	-0.332619
H	-4.662330	0.968856	-1.877718
H	-4.279280	2.310144	-0.764406
C	-3.458558	-1.621362	-1.835489
H	-2.694590	-2.365218	-2.144358
H	-3.560236	-0.898379	-2.671926
H	-4.426878	-2.166045	-1.765756
C	-3.218438	1.856684	1.998962
H	-4.172117	1.789245	2.569945
H	-3.289874	2.767873	1.369393
H	-2.412703	2.035291	2.741223

5. Bader Atoms in Molecules (AIM) Analysis

The Bader atoms in molecules (AIM) analysis was conducted on the geometry optimized complex **7**, using the freely available computer program Multiwfn.[9] Only the relevant parameters at the (3, -1) bond critical point (BCP) for the Ca-Si bond are shown below.

========== CP 155, Type (3,-1) ==========

Position (Bohr): 0.21424610794047 0.12062972200135 0.10406095133013

Density of all electrons: 0.1746582940E-01

Density of Alpha electrons: 0.8732914700E-02

Density of Beta electrons: 0.8732914700E-02

Spin density of electrons: 0.0000000000E+00

Lagrangian kinetic energy G(r): 0.1406783355E-01

Hamiltonian kinetic energy K(r): -0.2345620396E-02

Potential energy density V(r): -0.1172221315E-01

Energy density (H): 0.2345620396E-02

Laplacian of electron density: 0.6565381578E-01

Electron localization function (ELF): 0.5437688397E-01

Localized orbital locator (LOL): 0.1935287937E+00

Local information entropy: 0.6078567283E-03

Reduced density gradient (RDG): 0.4225128518E-15

Sign(lambda2)*rho: -0.1746582940E-01

Corr. hole for alpha, ref.: 0.00000 0.00000 0.00000 : -0.8305892971E-02

Source function, ref.: 0.00000 0.00000 0.00000 : -0.1956867271E-01

Wavefunction value for orbital 1 : 0.2667098916E-04

Average local ionization energy: 0.5483134849E+00

User defined real space function: 0.1000000000E+01

ESP from nuclear charges: 0.4605267389E+02

ESP from electrons: -0.4579494080E+02

Total ESP: 0.2577330870E+00 a.u. (0.7013274E+01 J/C, 0.1617172E+03 kcal/mol)

Note: Below information are for electron density

Components of gradient in x/y/z are:

-0.1153997687E-16 0.2281906760E-17 0.1401839528E-17

Norm of gradient is: 0.1184665855E-16

Components of Laplacian in x/y/z are:

0.5317552493E-01 0.3885135376E-02 0.8593155482E-02

Total: 0.6565381578E-01

Hessian matrix:

0.5317552493E-01 -0.3225423983E-01 0.3679313903E-01

-0.3225423983E-01 0.3885135376E-02 -0.1903850472E-01

0.3679313903E-01 -0.1903850472E-01 0.8593155482E-02

Eigenvalues of Hessian: λ_3 = 0.9015781911E-01 λ_2 = -0.1295523378E-01 λ_1 = -0.1154876955E-01

Eigenvectors(columns) of Hessian:

0.7977608581E+00 -0.5369751486E-01 -0.6005782131E+00

-0.3981780537E+00 0.7010536496E+00 -0.5915893997E+00

0.4528044288E+00 0.7110839312E+00 0.5378919892E+00

Determinant of Hessian: 0.1348914326D-04

Ellipticity of electron density: 0.121785

eta index: 0.143695

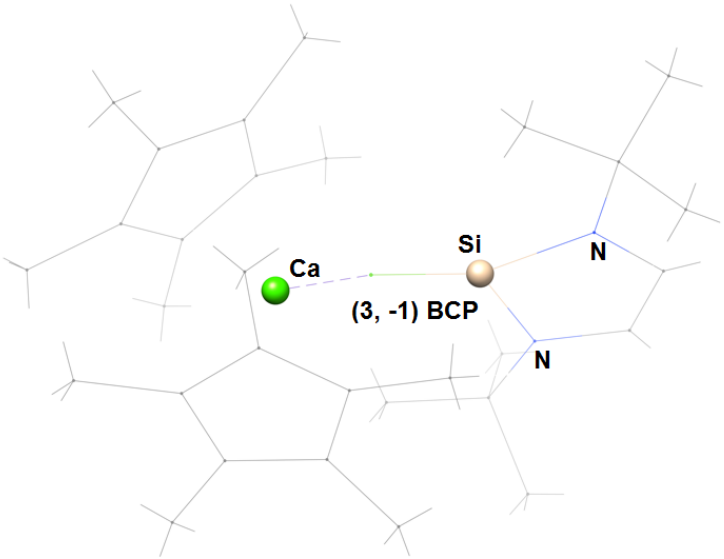

Fig. S18 Graphical representation of the (3,-1) BCP between the calcium and Si centres in compound **7**. (All other BCPs in the molecule have been removed for clarity)

6. References

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