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Si–H addition followed by C–H bond activation induced by a terminal thorium imido metallocene: a combined experimental and computational study†

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The Si–H bond addition to a terminal actinide imido complex was comprehensively studied. The base-free thorium imido [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th=N(p-tolyl) (**1**) activates Si–H bonds in PhSiH$_3$ or Ph$_2$SiH$_2$ to give the thorium amido hydrido metallocenes [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(H)[N(p-tolyl)SiH$_2$Ph] (**2**) and [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(H)[N(p-tolyl)SiHPh$_2$] (**3**), respectively. Complex **2** readily inserts unsaturated molecules into the Th–H bond, whereas complex **3** reversibly activates an intramolecular aromatic C–H bond to yield [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th[η^2-N,C-{N(p-MeC$_6$H$_3$)(SiHPh$_2$)}] (**4**) and H$_2$. The experimental results have been complemented by density functional theory (DFT) studies and provide a detailed understanding of the observed reactivity. In addition, a comparison between Th and early transition metals reveals that the Th^{4+} behaves more like an actinide than a transition metal.

Introduction

Terminal imido complexes of actinide-metals containing an An=N functionality have received widespread attention over the last 20 years because of their unique structural properties and their potential application in group transfer reactions and catalysis.[1–3] Whereas many uranium imido complexes have been prepared and structurally characterized, only a few of them show significant reactivity.[2h–k,s,t,x,3f,g,j,l,o,y] In contrast, thorium imido complexes have remained rare and not much is known about their reaction chemistry.[2d,3h,k,q] This is surprising since thorium has a $7s^2 6d^2$ ground state electron configuration, and one might expect a similar reactivity to that of group 3 and 4 metals, such as Sc, Ti, Zr and Hf, for which several complexes with M=N bond have been prepared.[4,5] However, the underlying question remains whether 5f-orbitals contribute to the bonding in thorium organometallics and whether Th^{4+} should be considered as a transition metal or as an actinide element.[6] To answer this question we have recently prepared the base-free terminal thorium imido complex [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th=

N(p-tolyl) (**1**).[7,8] Complex **1** shows a rich reaction chemistry such as the activation of elemental sulfur (S$_8$).[7] Furthermore it is an important intermediate in the catalytic hydroamination of internal acetylenes,[7] an efficient catalyst for the trimerization of PhCN,[7] and a useful precursor for the preparation of oxido and sulfido thorium metallocenes [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th=E (E = O, S) by cycloaddition–elimination reactions with Ph$_2$C=E (E = O, S) or CS$_2$.[9] Encouraged by this broad reactivity, we are now focusing on small molecule activation. Herein, the first Si–H bond activations by an actinide imido complex and the reactivity of the resulting thorium amido hydrido complexes are reported. Furthermore, the difference between thorium and early transition metal imido complexes will be addressed.

Experimental

General methods

All reactions and product manipulations were carried out under an atmosphere of dry dinitrogen with rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glove box. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. PhSiH$_3$ and Ph$_2$SiH$_2$ were freshly distilled from CaH$_2$ immediately prior to use. [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th=N(p-tolyl) (**1**) was prepared according to literature methods.[7] All other chemicals were purchased from Aldrich Chemical Co. and Beijing Chemical Co. and used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets on an Avatar 360 Fourier transform spectrometer. [^1]H and [^13]C NMR spectra were recorded on a Bruker AV 400 spectrometer at 400 and 100 MHz, respectively. All chemical shifts are reported in δ units with reference

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to the residual protons of the deuterated solvents, which are internal standards, for proton and carbon chemical shifts. Melting points were measured on an X-6 melting point apparatus and were uncorrected. Elemental analyses were performed on a Vario EL elemental analyzer.

Syntheses

Preparation of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(H)[N(p\text{-tolyl})SiH_2Ph]$ (2a)

Method A. A toluene (5 mL) solution of $PhSiH_3$ (68 mg, 0.622 mmol) was added to a toluene (10 mL) solution of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th=N(p\text{-tolyl})$ (1; 500 mg, 0.622 mmol). After this mixture was stirred at room temperature for one hour, the solvent was removed. The residue was extracted with *n*-hexane (10 mL × 2) and filtered. The volume of the filtrate was reduced to *ca.* 2 mL and colorless crystals of 2a were isolated when this solution stood at room temperature for 2 days. Yield: 465 mg (82%) (found: C, 61.72; H, 8.18; N, 1.63. $C_{47}H_{73}NSiTh$ requires C, 61.88; H, 8.07; N, 1.54%). Mp: 116–118 °C (decomp.). ^1H NMR (C_6D_6): δ 18.07 (s, 1H, Th*H*), 7.59 (d, $J = 5.6$ Hz, 2H, aryl), 7.13 (m, 3H, aryl), 7.06 (d, $J = 5.6$ Hz, 2H, aryl), 7.02 (m, 2H, aryl), 6.14 (d, $J = 3.6$ Hz, 2H, ring C*H*), 6.01 (d, $J = 3.6$ Hz, 2H, ring C*H*), 5.06 (s, 2H, Si*H*$_2$), 2.15 (s, 3H, tolylC*H*$_3$), 1.57 (s, 18H, $(CH_3)_3C$), 1.48 (s, 18H, $(CH_3)_3C$), 1.43 (s, 18H, $(CH_3)_3C$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 143.1 (phenyl *C*), 142.2 (phenyl *C*), 135.9 (phenyl *C*), 135.3 (phenyl *C*), 134.9 (phenyl *C*), 130.0 (phenyl *C*), 129.6 (phenyl *C*), 122.9 (phenyl *C*), 119.0 (ring *C*), 115.7 (ring *C*), 115.5 (ring *C*), 115.3 (ring *C*), 113.7 (ring *C*), 35.1 ($(CH_3)_3C$), 34.6 ($(CH_3)_3C$), 34.1 ($(CH_3)_3C$), 34.0 ($(CH_3)_3C$), 33.7 ($(CH_3)_3C$), 33.2 ($(CH_3)_3C$), 20.4 (CH_3). IR (KBr, cm^{-1}): ν 2959 (s, C–H), 2124 (w, Si–H), 1606 (m, C=C), 1458 (s, C–C), 1385 (s, C–C), 1258 (s, C–N), 1094 (s, C–N), 1019 (s, C–N). The NMR sample was maintained at 70 °C and monitored periodically by ^1H NMR spectroscopy. After 4 days, resonances of the *anti*-isomer $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(H)[N(p\text{-tolyl})SiH_2Ph]$ (2b) (^1H NMR (C_6D_6): δ 16.93 (s, 1H, Th*H*), 8.00 (s, 1H, aryl), 7.92 (d, $J = 6.8$ Hz, 2H, aryl), 7.39 (d, $J = 7.4$ Hz, 2H, aryl), 7.23 (d, $J = 7.4$ Hz, 2H, aryl), 7.13 (m, 2H, aryl), 6.41 (d, $J = 3.2$ Hz, 2H, ring C*H*), 6.20 (d, $J = 3.2$ Hz, 2H, ring C*H*), 5.23 (s, 2H, Si*H*$_2$), 2.38 (s, 3H, tolylC*H*$_3$), 1.39 (s, 18H, $(CH_3)_3C$), 1.38 (s, 18H, $(CH_3)_3C$), 1.36 (s, 18H, $(CH_3)_3C$)) were observed by ^1H NMR spectroscopy (*syn/anti* ratio 1 : 9). However, on prolonged heating some degradation was also observed.

Method B

NMR scale. To a J. Young NMR tube charged with $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th=N(p\text{-tolyl})$ (1; 16 mg, 0.02 mmol) and C_6D_6 (0.5 mL), an excess of $PhSiH_3$ was added. Upon addition complete conversion to 2a was observed by ^1H NMR spectroscopy.

Preparation of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(H)[N(p\text{-tolyl})SiHPh_2]$ (3a)

Method A. This compound was prepared as colorless microcrystals from the reaction of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th=N(p\text{-tolyl})$ (1; 500 mg, 0.622 mmol) and Ph_2SiH_2 (114 mg, 0.622 mmol) in toluene (15 mL) and recrystallization from an *n*-hexane solution by a similar procedure as outlined for the

synthesis of 2a. Yield: 516 mg (84%) (found: C, 64.52; H, 8.02; N, 1.43. $C_{53}H_{77}NSiTh$ requires C, 64.41; H, 7.85; N, 1.42%). Mp: 120–122 °C (decomp.). ^1H NMR (C_6D_6): δ 17.84 (s, 1H, Th*H*), 7.74 (s, 2H, aryl), 7.50 (d, $J = 7.2$ Hz, 2H, aryl), 7.11 (m, 8H, aryl), 7.03 (d, $J = 7.2$ Hz, 2H, aryl), 6.02 (s, 4H, ring C*H*), 5.08 (s, 1H, Si*H*), 2.18 (s, 3H, tolylC*H*$_3$), 1.58 (s, 18H, $(CH_3)_3C$), 1.43 (s, 36H, $(CH_3)_3C$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 136.2 (phenyl *C*), 135.8 (phenyl *C*), 134.5 (phenyl *C*), 131.5 (phenyl *C*), 129.9 (phenyl *C*), 129.7 (phenyl *C*), 129.6 (phenyl *C*), 128.2 (phenyl *C*), 127.8 (ring *C*), 127.5 (ring *C*), 119.0 (ring *C*), 115.5 (ring *C*), 115.2 (ring *C*), 35.0 ($(CH_3)_3C$), 34.8 ($(CH_3)_3C$), 34.4 ($(CH_3)_3C$), 34.1 ($(CH_3)_3C$), 33.3 ($(CH_3)_3C$), 33.1 ($(CH_3)_3C$), 20.5 (CH_3). IR (KBr, cm^{-1}): ν 2961 (s, C–H), 2110 (w, Si–H), 1587 (m, C=C), 1454 (m, C–C), 1384 (s, C–C), 1260 (s, C–N), 1090 (s, C–N), 1018 (s, C–N). The NMR sample was maintained at 70 °C and monitored periodically by ^1H NMR spectroscopy. After 1 h, new resonances of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th[\eta^2\text{-}N,C\text{-}\{N(p\text{-MeC}_6H_3)(SiHPh_2)\}]$ (4) (see below) were observed by ^1H NMR spectroscopy with 20% conversion. After 3 h, 27% conversion was observed. However, no change in this ratio was detected on prolonged heating.

Method B

NMR scale. To a J. Young NMR tube charged with $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th=N(p\text{-tolyl})$ (1; 16 mg, 0.02 mmol) and C_6D_6 (0.5 mL), an excess of Ph_2SiH_2 was added. Complete conversion to 3a was observed by ^1H NMR spectroscopy.

Preparation of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th[\eta^2\text{-}N,C\text{-}\{N(p\text{-MeC}_6H_3)(SiHPh_2)\}]$ (4).

After a toluene (10 mL) solution of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(H)[N(p\text{-tolyl})SiHPh_2]$ (3a; 247 mg, 0.25 mmol) was stirred at 70 °C for three days, the solvent was removed. The residue was extracted with *n*-hexane (10 mL × 2) and filtered. The volume of the filtrate was reduced to *ca.* 1 mL, and yellow crystals of 4 were isolated when this solution stood at room temperature for 2 days. Yield: 197 mg (80%) (found: C, 64.52; H, 7.82; N, 1.43. $C_{53}H_{75}NSiTh$ requires C, 64.54; H, 7.66; N, 1.41%). Mp: 128–130 °C (decomp.). ^1H NMR (C_6D_6): δ 7.97 (m, 5H, aryl), 7.49 (d, $J = 8.0$ Hz, 1H, aryl), 7.25 (m, 4H, aryl), 7.20 (d, $J = 6.8$ Hz, 2H, aryl), 6.81 (d, $J = 8.0$ Hz, 1H, aryl), 6.35 (s, 2H, ring C*H*), 6.18 (d, $J = 3.2$ Hz, 2H, ring C*H*), 5.97 (s, 1H, Si*H*), 2.35 (s, 3H, tolylC*H*$_3$), 1.42 (s, 18H, $(CH_3)_3C$), 1.36 (s, 18H, $(CH_3)_3C$), 1.31 (s, 18H, $(CH_3)_3C$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 190.4 (Th*C*), 144.9 (phenyl *C*), 144.2 (phenyl *C*), 142.6 (phenyl *C*), 142.1 (phenyl *C*), 141.9 (phenyl *C*), 137.8 (phenyl *C*), 136.3 (phenyl *C*), 130.5 (phenyl *C*), 129.6 (phenyl *C*), 129.3 (ring *C*), 127.3 (ring *C*), 118.3 (ring *C*), 116.3 (ring *C*), 115.9 (ring *C*), 35.0 ($(CH_3)_3C$), 34.4 ($(CH_3)_3C$), 34.3 ($(CH_3)_3C$), 34.3 ($(CH_3)_3C$), 34.0 ($(CH_3)_3C$), 32.5 ($(CH_3)_3C$), 21.2 (CH_3). IR (KBr, cm^{-1}): ν 2962 (s, C–H), 2113 (w, Si–H), 1457 (m, C–C), 1384 (s, C–C), 1260 (s, C–N), 1091 (s, C–N), 1019 (s, C–N).

Reaction of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th[\eta^2\text{-}N,C\text{-}\{N(p\text{-MeC}_6H_3)(SiHPh_2)\}]$ (4) with H_2

NMR scale. To a J. Young NMR tube charged with $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th[\eta^2\text{-}N,C\text{-}\{N(p\text{-MeC}_6H_3)(SiHPh_2)\}]$ (4; 20 mg, 0.02 mmol) and C_6D_6 (0.5 mL) an excess of H_2 (at 1 atm) was added. ^1H NMR spectroscopy indicated complete conversion to 3a and 3b (ratio 3a/3b *ca.* 10 : 1; ^1H NMR (C_6D_6): δ 16.84 (s, 1H, Th*H*), 7.84 (d, $J = 6.8$ Hz, 1H, aryl), 7.60 (d, $J = 7.5$ Hz, 2H, aryl), 7.34 (s, 2H, aryl), 7.11 (m, 6H, aryl), 6.95 (s, 1H, aryl H), 6.77 (d, J

= 8.1 Hz, 2H, aryl), 6.21 (d, J = 3.0 Hz, 2H, ring CH), 6.18 (d, J = 3.0 Hz, 2H, ring CH), 5.14 (s, 1H, SiH), 2.19 (s, 3H, tolylCH_3), 1.54 (s, 18H, (CH_3)$_3$C), 1.41 (s, 18H, (CH_3)$_3$C), 1.39 (s, 18H, (CH_3)$_3$C)).

Preparation of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th[N(*p*-tolyl)-C(=NC$_6$H$_{11}$)–N(C$_6$H$_{11}$)] (6)

Method A. A toluene (5 mL) solution of *N,N'*-dicyclohexyl-carbodiimide (DCC; 103 mg, 0.50 mmol) was added to a toluene (10 mL) solution of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(H)[N(*p*-tolyl)SiH$_2$Ph] (2a; 228 mg, 0.25 mmol). After this solution was stirred at room temperature for 2 hours, the solvent was removed. The residue was extracted with *n*-hexane (10 mL × 2) and filtered. The volume of the filtrate was reduced to *ca.* 2 mL, and colorless crystals of 6 were isolated when this solution stood at room temperature for 2 days. Yield 217 mg (86%) (found: C, 64.32; H, 8.58; N, 4.03. C$_{54}$H$_{87}$N$_3$Th requires C, 64.19; H, 8.68; N, 4.16%). Mp: 210–212 °C (decomp.). ¹H NMR (C$_6$D$_6$): δ 7.30 (d, J = 8.0 Hz, 2H, aryl), 7.09 (d, J = 8.0 Hz, 2H, aryl), 6.68 (s, 2H, ring CH), 6.35 (s, 2H, ring CH), 3.84 (m, 1H, NCH), 3.31 (m, 2H, CH_2), 3.24 (m, 1H, NCH), 2.36 (m, 2H, CH_2), 2.25 (s, 3H, tolylCH_3), 2.12 (m, 4H, CH_2), 1.84 (m, 8H, CH_2), 1.53 (m, 4H, CH_2), 1.52 (s, 18H, (CH_3)$_3$C), 1.50 (s, 18H, (CH_3)$_3$C), 1.27 (s, 18H, (CH_3)$_3$C). ¹³C{¹H} NMR (C$_6$D$_6$): δ 152.0 (C=N), 145.9 (phenyl C), 144.2 (phenyl C), 143.6 (phenyl C), 143.6 (phenyl C), 130.8 (ring C), 129.3 (ring C), 127.5 (ring C), 125.9 (ring C), 118.3 (ring C), 62.1 (CHN), 53.8 (CHN), 36.4 ((CH$_3$)$_3$$C$), 35.0 ((CH$_3$)$_3$$C$), 34.9 ((CH$_3$)$_3$$C$), 34.8 ((CH$_3$)$_3$$C$), 34.5 ((CH$_3$)$_3$$C$), 33.2 ((CH$_3$)$_3$$C$), 32.4 ($CH_2$), 31.2 ($CH_2$), 28.0 ($CH_2$), 27.2 ($CH_2$), 27.1 ($CH_2$), 25.6 ($CH_2$), 20.8 ($CH_3$). IR (KBr, cm⁻¹): ν 2961 (s, C–H), 1618 (m, C=N), 1574 (s, C=C), 1448 (s, C–C), 1385 (s, C–C), 1259 (s, C–N), 1093 (s, C–N), 1019 (s, C–N).

Method B

NMR scale. To a J. Young NMR tube charged with [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(H)[N(*p*-tolyl)SiH$_2$Ph] (2a; 18 mg, 0.02 mmol) and C$_6$D$_6$ (0.5 mL), DCC (8.2 mg, 0.04 mmol) was added. Complete conversion to 6 and (C$_6$H$_{11}$)N=CHN(C$_6$H$_{11}$)(SiH$_2$Ph) (5) (¹H NMR (C$_6$D$_6$): δ 7.37 (s, 1H, N=CH), 7.10 (m, 5H, aryl), 4.22 (s, 2H, SiH_2), 3.12 (m, 2H, NCH), 1.84 (m, 16H, CH_2), 1.32 (m, 4H, CH_2)) was observed by ¹H NMR spectroscopy.

Method C

NMR scale. To a J. Young NMR tube charged with [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th=N(*p*-tolyl) (1; 16 mg, 0.02 mmol) and C$_6$D$_6$ (0.5 mL), DCC (4.1 mg, 0.02 mmol) was added. Complete conversion to 6 was observed by ¹H NMR spectroscopy.

Reaction of [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(H)[N(*p*-tolyl)SiH$_2$Ph] (2a) with DCC

NMR scale. To a J. Young NMR tube charged with [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(H)[N(*p*-tolyl)SiH$_2$Ph] (2a; 18 mg, 0.02 mmol) and C$_6$D$_6$ (0.5 mL), DCC (4.1 mg, 0.02 mmol) was added. Resonances due to 6 along with those of 5 and unreacted 2a were observed by ¹H NMR spectroscopy (50% conversion based on 2a).

X-ray crystallography

Single-crystal X-ray diffraction measurements were carried out on a Bruker SMART CCD diffractometer using graphite mono-chromated Mo Kα radiation (λ = 0.71073 Å). An empirical absorption correction was applied using the SADABS program.[10] All structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXL-97 program package.[11] The hydride atom in 2a was located from a difference-Fourier map and refined isotropically. Hydrogen atoms were geometrically fixed using the riding model. Disordered solvents in the voids of 2a and 6 were modeled or removed by using the SQUEEZE program.[12] Crystallographic details for 2a, 4 and 6 are summarized in Table 1.

Computational methods

All calculations were carried out with the Gaussian 09 program (G09),[13] employing the B3PW91 method, plus polarizable continuum model (PCM) and D3 (ref. 14) (denoted as B3PW91-PCM + D3), with standard 6-31G(d) basis set for C, H, N and Si elements and Stuttgart RLC ECP from EMSL basis set exchange (https://bse.pnl.gov/bse/portal) for Th element,[15] to fully opti-mize the geometries of reactants, complexes, transition state, intermediates, and product structures, and to mimic experi-mental toluene-solvent conditions (dielectricity constant ε = 2.379). All stationary points were subsequently characterized by vibrational analyses, from which their respective zero-point (vibrational) energy (ZPE) were extracted and used in the relative energy determinations; in addition to ensure that the reactant, complex, intermediate, product and transition state structures resided at minima and 1st order saddle points, respectively, on their potential energy hyper surfaces.

Results and discussion

Complex 1 reacts rapidly with silanes such as PhSiH$_3$ or Ph$_2$SiH$_2$ to give the amido hydrido metallocenes [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(H)[N(*p*-tolyl)SiH$_2$Ph] (2a) and [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th(H)[N(*p*-tolyl)SiHPh$_2$] (3a), respectively (Scheme 1). Consistent with a Si–H bond addition across the Th=N bond the *syn*-isomer is formed exclusively. However, in contrast to scandium[4f] and titanium[5k,l] imido complexes, the reaction of 1 with silanes is irreversible, which is presumably a consequence of the more polarized actinide imido bond (see ESI†). Previous studies have clearly established that the 5f orbitals play a key role in the bonding of actinide complexes, which results in a very polarized An=E bond, whereas this is not the case for group 4 metal complexes.[6c] Therefore, actinide An=E bonds exhibit different reactivity patterns compared to those of early transition metals, as illustrated by reactivity of imido complexes (M=NR) with silanes, in which the less polarized M=N bond (M is early transition metal) shows a reversible Si–H addition, whereas the more polarized Th=N bond undergoes an irreversible Si–H addition because of a more pronounced thermodynamic stabilization of the Si–H addition products. Heating of 2a at 70 °C for four days forms the *anti*-isomer 2b (*ca.* 10%). Under similar reaction conditions, complex 3a is in equilibrium with the aromatic C–H bond activation product [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th{η^2-*N,C*-{N(*p*-MeC$_6$H$_3$)(SiHPh$_2$)}] (4) and H$_2$ (Scheme 1). Moreover, the addi-tion of H$_2$ (1 atm) to 4 at room temperature results in a mixture

Table 1 Crystal data and experimental parameters for compounds **2a**, **4** and **6**

| Compound	2a	4	6
Formula	$C_{47}H_{73}NSiTh$	$C_{53}H_{75}NSiTh$	$C_{54}H_{87}N_3Th$
Fw	912.19	986.27	1010.31
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	*Pbca*	*P2$_1$/c*	*P($\bar{1}$)*
a (Å)	10.425 (1)	16.578 (3)	10.436 (2)
b (Å)	20.765 (1)	16.572 (3)	15.509 (3)
c (Å)	44.289 (3)	17.515 (3)	20.314 (4)
α (deg.)	90	90	92.79 (1)
β (deg.)	90	97.936 (3)	92.25 (1)
γ (deg.)	90	90	109.07 (1)
V (Å^3)	9587.6 (10)	4765.9 (13)	3098.4 (10)
Z	8	4	2
D_{calc} (g cm^{-3})	1.264	1.375	1.083
μ (Mo/Kα)$_{calc}$ (cm^{-1})	3.164	3.188	2.436
Size (mm)	$0.39 \times 0.21 \times 0.11$	$0.25 \times 0.18 \times 0.10$	$0.45 \times 0.20 \times 0.11$
$F(000)$	3728	2016	1044
2θ range (deg.)	3.92 to 55.34	4.40 to 55.22	3.54 to 50.50
No. of reflns, collected	11 151	26 706	10 908
No. of obsd reflns	8989	7619	9578
No. of variables	528	527	542
Abscorr (T_{max}, T_{min})	0.72, 0.37	0.74, 0.50	0.78, 0.41
R	0.032	0.051	0.078
R_w	0.064	0.121	0.224
R_{all}	0.066	0.146	0.230
Gof	1.10	1.07	1.12
CCDC	977309	977310	977311

of the *syn-/anti*-isomers **3a** and **3b** in a 10 : 1 ratio (Scheme 1), as established by ^{1}H NMR spectroscopy. Although complex **1** reacts rapidly with PhSiH$_3$ or Ph$_2$SiH$_2$, no reaction was observed with tertiary silanes such as Et$_3$SiH and Ph$_3$SiH most likely because of the steric hindrance.

The molecular structure of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(H)[N(p\text{-tolyl})SiH_2Ph]$ (**2a**) is shown in Fig. 1. The cyclopentadienyl rings adopt a nearly eclipsed conformation with an average Th–C (ring) distance of 2.858(3) Å, and a Cp (cent)–Th–Cp (cent) angle of 138.1(3)°. The Th–N distance of 2.387(2) Å is comparable to the values found in $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th[(bipy)(SCPh_2)]$ (2.435(1) Å)[16] and $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th(N\text{-}p\text{-tolyl})_2$ (2.228(3) Å).[7] The Th–H distance is 2.01(3) Å, which is in line with reported terminal and bridging Th–H distances, $(2,6\text{-}^tBu_2C_6H_3O)_6Th_3(\mu_3\text{-H})_2(\mu\text{-H})_4$ (2.0(1)–2.6(1) Å),[17] $[(\eta^5\text{-}C_5Me_5)_2ThH(\mu\text{-H})]_2$ (2.03(1) (terminal)–2.29(3) (bridging) Å),[18] $(\eta^5\text{-}C_5Me_5)_3ThH$ (2.33(13) Å),[19] $[\eta^5\text{-}1,3\text{-}(Me_3C)_2C_5H_3]_3ThH$ (1.99(5) Å),[20] and $(\eta^5\text{-}C_5Me_4H)_4[\mu\text{-}\eta^5\text{-}C_5Me_3H(CH_2)\text{-}\kappa C]_2Th_4(\mu\text{-H})_4(\mu_3\text{-H})_4$ (2.503(4) and 2.508(4) Å).[21]

Fig. 2 shows the molecular structure of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Th[\eta^2\text{-}N,C\text{-}\{N(p\text{-MeC}_6H_3)(SiHPh_2)\}]$ (**4**). The average Th–C (ring) distance is 2.882(6) Å, and the Cp (cent)–Th–Cp (cent) angle is 140.6(2)°. The Th–N distance of 2.310(5) Å is shorter than that (2.387(2) Å) found in **2a**. Furthermore, the Th–C(40) distance of 2.420(3) Å is also significantly shorter than the reported Th–C$_{aryl}$ bond distances (2.548(2)–2.654(14) Å).[22–24] Interestingly, only four structurally characterized thorium aryl complexes have been reported, and in all of them the thorium–aryl bond is supported by chelating ligands.[22–24]

As demonstrated above, complex **1** irreversibly activates Si–H bonds to yield the amido hydrido complexes **2** and **3**. Complex **3** undergoes a reversible intramolecular C–H bond activation to give **4** and H$_2$. DFT calculations were performed at the B3PW91 level of theory to further understand the observed process. To properly describe the observed reactivity it was necessary to include solvent and dispersion effects (see ESI†). The reaction of **1** with Ph$_2$SiH$_2$ to **3a** is exergonic with ΔG (343 K) = −17.6 kcal mol^{-1} and proceeds concerted *via* the 4-membered transition state **TS** formed by the Th=N and Si–H moieties. The Si–N and Th–H bonds in **TS** are 2.343 and 2.299 Å, respectively, and *ca.* 0.61 and 0.23 Å longer than those in the product **3a** (see ESI†). The barrier for this reaction is $\Delta G^{\ddagger} = 16.7$ kcal mol^{-1} (343 K) (15.2 kcal mol^{-1} at 298 K) (Fig. 3); and these values are consistent with the rapid and irreversible formation of **3a** at ambient temperature. The transformation of **3a** to **4** + H$_2$ is more complicated and involves the *anti*-intermediate **3b** and two transition states (**TSa** and **TSb**). The barrier for the conversion of **3a** to **3b** *via* **TSa** is 33.7 kcal mol^{-1} at 343 K and also represents the rate-limiting step in this reaction. The computed barrier is consistent with the experimental observation that this reaction only occurs at elevated temperatures, and it is also in reasonable agreement with the experimentally estimated barrier of 26.8 kcal mol^{-1} (see ESI†). The deviation between the computed and experimental values is mainly attributed to the low solubility of H$_2$ in organic solvent, which complicates the kinetic evaluation because the actual H$_2$ concentration cannot be determined with certainty (see ESI†). However, for **TSa** a closer inspection reveals an interesting
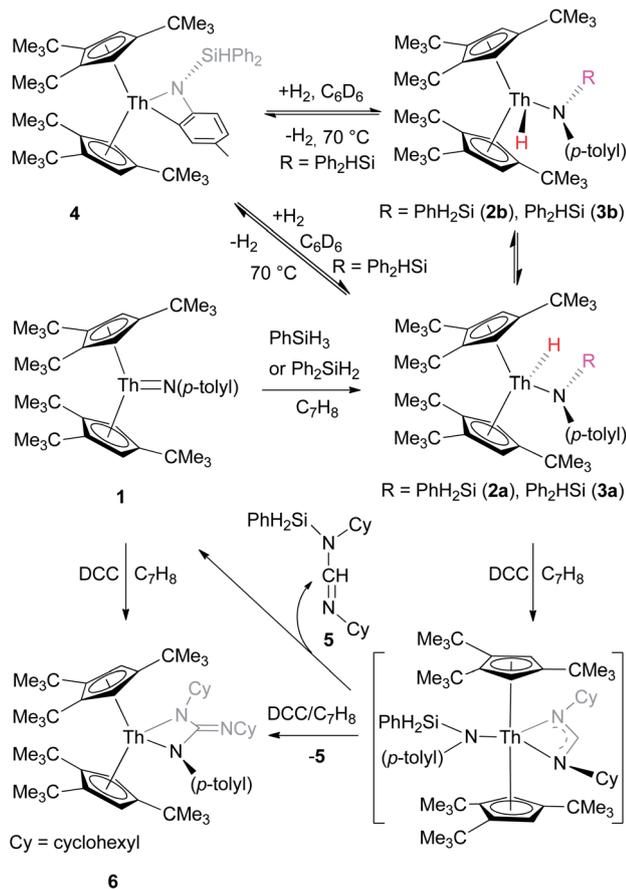
Scheme 1 Synthesis of compounds 2–4 and 6.

Fig. 2 Molecular structure of 4 (thermal ellipsoids drawn at the 35% probability level). Selected bond lengths [Å] and angles [°]: Th–C(Cp) (av.) 2.882(6), Th–C(Cp) (range) 2.803(6) to 2.956(6), Th–Cp (cent) (av.) 2.617(6), Th–N(1) 2.310(5), Th–C(40) 2.420(7), Cp (cent)–Th–Cp (cent) 140.6(2), N(1)–Th–C(40) 61.8(2).
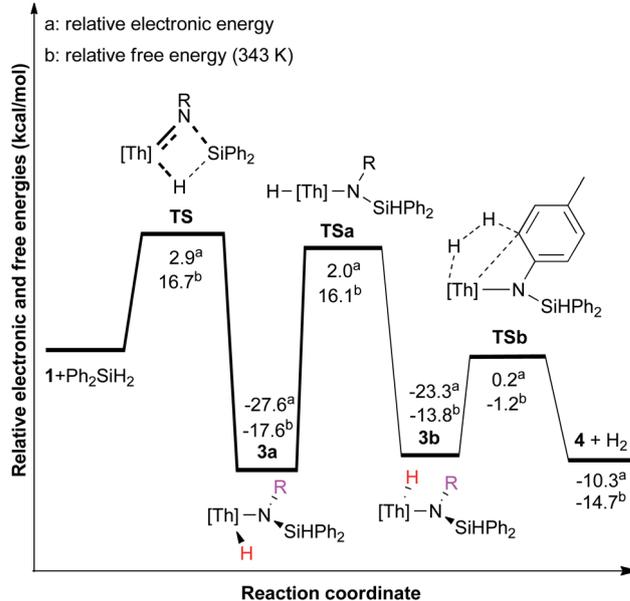
Fig. 3 Energy and free energy profile (kcal mol^{-1}) for the reaction of 1 with Ph$_2$SiH$_2$, obtained with B3PW91-PCM + D3 method. [Th] = [η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Th. R = p-tolyl.
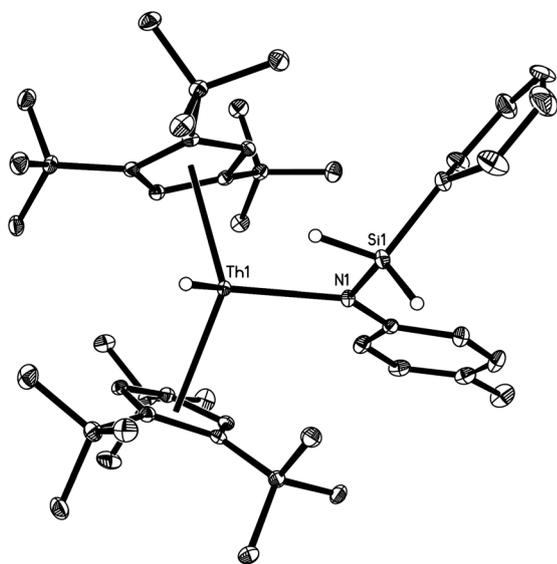

Fig. 1 Molecular structure of 2a (thermal ellipsoids drawn at the 35% probability level). Selected bond lengths [Å] and angles [°]: Th–C(Cp) (av.) 2.858(3), Th–C(Cp) (range) 2.870(3) to 2.946(3), Th–Cp(cent) (av.) 2.592(3), Th–N 2.387(2), Th–H 2.01(3), Th–Si 3.256(1), Cp (cent)–Th–Cp (cent) 138.1(3), N–Th–H 111.9(11).
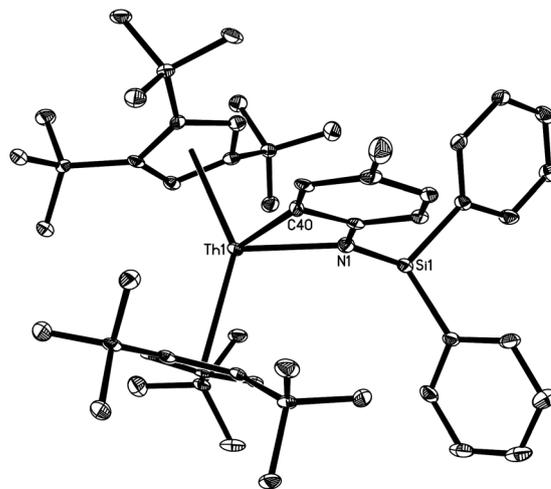
feature, since the *syn-/anti*-intermediates are interconverted not by rotation of the –N(R)(*p*-tolyl) moiety along the Th–N axis, but by a Th–H movement (Fig. 3). This is a direct consequence of the severe steric bulk of the two 1,2,4-(Me$_3$C)$_3$C$_5$H$_2$ ligands, which hinders the rotation along the Th–N axis. Nevertheless, once complex 3b is formed, H$_2$ is released *via* TSb and with a low barrier of 12.6 kcal mol^{-1} (Fig. 3). This makes the *anti*-isomer 3b difficult to isolate, since H$_2$ release from the reaction mixture shifts the equilibrium to the final product 4. On the contrary, H$_2$ addition to complex 4 forms a mixture of 3b and 3a.

Furthermore, similar to the amido hydrido scandium complex,[4f] amido hydrido thorium complexes can also insert unsaturated substrates such as carbodiimides into the Th–H bond. For example, treatment of **2a** with 2 equiv. of *N,N′*-dicyclohexylcarbodiimide (DCC) rapidly forms the metallacycle [η^5-1,2,4-$(Me_3C)_3C_5H_2$]$_2$Th[N(*p*-tolyl)C(=NC$_6$H$_{11}$)–N(C$_6$H$_{11}$)] (**6**) and azomethine (C_6H_{11})N=CHN(C_6H_{11})(SiH$_2$Ph) (**5**) in quantitative conversion (Scheme 1). Furthermore, analogous to group 4 imido complexes,[25] thorium imido **1** can react with DCC to yield metallacycle **6** (Scheme 1), whereas **2a** reacts with 1 equiv. of DCC to give **6** in only 50% conversion. These observations suggest that the insertion product [η^5-1,2,4-$(Me_3C)_3C_5H_2$]$_2$Th [N(*p*-tolyl)SiHPh$_2$][η^3-N(C$_6$H$_{11}$)CHN(C$_6$H$_{11}$)] is unstable and eliminates azomethine **5** to form the imido complex **1**, which then reacts with DCC to the metallacycle **6** by an [2 + 2] cycloaddition reaction (Scheme 1).

The molecular structure of [η^5-1,2,4-$(Me_3C)_3C_5H_2$]$_2$Th[N(*p*-tolyl)C(=NC$_6$H$_{11}$)–N(C$_6$H$_{11}$)] (**6**) is shown in Fig. 4. The Th^{4+} ion is η^5-bound to two Cp-rings and σ-coordinate to the two nitrogen atoms of the [N(*p*-tolyl)C(=NC$_6$H$_{11}$)–N(C$_6$H$_{11}$)] group in a distorted-tetrahedral geometry with an averaged Th–C (ring) distance of 2.877(11) Å. The dihedral angle defined by the planes containing the Cp (cent)–Th–Cp (cent) and N(1)–C(42)–N(3) is 75.2(3)°, and the N(1)–Th(1)–N(3) angle is 58.5(3)°. These metric parameters resemble those found in the alkyne addition complexes [η^5-1,2,4-$(Me_3C)_3C_5H_2$]$_2$Th[N(*p*-tolyl)C(R′)=C(R′)] (R′ = Me, Ph),[7] while the Th–N distances (2.346(9) and 2.337(8) Å) are similar to those found in **2a** and **4**.

Conclusions

In conclusion, the first example of a Si–H bond activation by a terminal actinide imido complex has been comprehensively studied. In contrast to scandium[4f] and titanium[5k,l] imido complexes, silanes such as PhSiH$_3$ and Ph$_2$SiH$_2$ add irreversibly to the thorium imido [η^5-1,2,4-$(Me_3C)_3C_5H_2$]$_2$Th=N(*p*-tolyl) (**1**),

Fig. 4 Molecular structure of **6** (thermal ellipsoids drawn at the 35% probability level). Selected bond lengths [Å] and angles [°]: Th–C(Cp) (av.) 2.877(11), Th–C(Cp) (range) 2.772(10) to 3.024(11), Th–Cp (cent) (av.) 2.613(9), Th–N(1) 2.346(9), Th–N(3) 2.337(8), Cp (cent)–Th–Cp (cent) 128.6(3), N(1)–Th–N(3) 58.5(3).
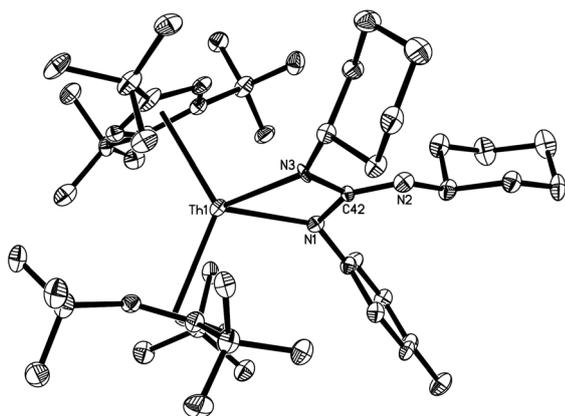
supporting the notion that Th^{4+} behaves more like an actinide than a transition metal.[6c] DFT studies reveal that the 1,2-addition proceeds in a concerted, 4-membered transition state to give amido hydrido complexes **2** and **3**. These compounds are reactive species, as illustrated by the formation of H$_2$ and [η^5-1,2,4-$(Me_3C)_3C_5H_2$]$_2$Th[η^2-*N,C*-{N(*p*-MeC$_6$H$_3$)(SiHPh$_2$)}] (**4**) *via* an intramolecular aromatic C–H bond activation in **3**, and by the insertion of unsaturated substrates such as DCC into the Th–H bond of **2**. The development of new actinide imido complexes and the exploration of thorium amido hydrido complexes in catalysis are ongoing projects in these laboratories.

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