

second time. Recrystallization from CH₃CN yielded **2** (62 mg, 50%) as a brown powder.

Complexes **1** and **2** were identified by comparison to the reported spectroscopic data (UV/Vis for both, ¹H NMR for **2**)^[3,4] and by redox titration.

3: Isolated in 50% yield based on **2**. UV/Vis (CH₃OH): λ_{max}(ε) = 618 (140). FAB-MS (calcd. for C₂₄H₂₄N₆O₅Cu₂): 671 ([M⁺ – H]). Crystals: 0.33 × 0.16 × 0.05 mm, triclinic *P* $\bar{1}$, *a* = 11.659(1), *b* = 11.854(1), *c* = 15.695(1) Å, α = 97.48(1), β = 101.75(1), γ = 101.87(1)°, *V* = 2044.5(5) Å³, *Z* = 2, ρ_{calcd} = 1.389 g cm⁻³. Nonius KappaCCD diffractometer, MoKα (λ = 0.7107 Å), 161 K, ω scans, 33764 measured, 7769 independent, 5258 observed reflections [*F* > 3σ(*F*)]. Solved by direct methods (SIR92)^[18] and refined using maXus (MacScience, Japan, 1997). *R* = 0.057 [*F* > 3σ(*F*)], *wR* = 0.068 for 460 parameters, Δρ_{max/min} = 1.49, –0.97 e Å⁻³. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-102174. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Half-Sandwich Alkyl and Hydrido Complexes of Yttrium: Convenient Synthesis and Polymerization Catalysis of Polar Monomers**

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Structurally well characterized organometallic complexes of rare earth metals^[1] such as lanthanocene hydrides and alkyls of the type [(η⁵-C₅R₅)₂LnX₂] (X = H, alkyl) have recently attracted considerable interest as cocatalyst-free homogeneous polymerization catalysts for both nonpolar and polar monomers.^[2] Catalyst systems based on complexes with only one cyclopentadienyl ligand are anticipated to show greater activity towards sterically more demanding monomers.^[3] However, conventional synthesis of mono(cyclopentadienyl) rare earth complexes [(η⁵-C₅R₅)LnX₂(L)_n], where at least one ligand X is a hydride or alkyl, is often hampered by ate-complex formation with concomitant alkali metal salt incorporation.^[3,4] Consequently, only a limited number of this type of half-sandwich complexes has been synthesized, and their catalytic performance still remains unexplored.^[5] We report here a remarkably facile alkane elimination as a route^[6] to yttrium complexes of the type [(η⁵-C₅Me₄SiMe₂X')-YX₂(thf)], as well as preliminary results on the polymerization of *tert*-butyl acrylate and acrylonitrile with these complexes.

Reaction of [Y(CH₂SiMe₃)₃(thf)₂] (**1**)^[7] with (C₅Me₄H)SiMe₂X' (X' = NHCMe₃, Me, Ph, C₆F₅) in pentane at 0 °C for 2 h resulted in the quantitative formation (according to ¹H NMR spectroscopy) of the half-sandwich yttrium complexes [(η⁵:η¹-C₅Me₄SiMe₂NCMe₃)Y(CH₂SiMe₃)(thf)] (**2**) or [(η⁵-C₅Me₄SiMe₂X')Y(CH₂SiMe₃)₂(thf)] (**3**) along with tetramethylsilane (Scheme 1, Table 1). The linked amido-cyclopentadienyl complex **2** was isolated as colorless crystals. Complexes **3a–c** are colorless to slightly yellow crystals which melt below room temperature. All complexes are readily soluble in aliphatic and aromatic hydrocarbons. Remarkably, no formation of the metallocene complex could be observed by ¹H NMR spectroscopy: The excess cyclopentadiene was left unchanged even in the presence of two equivalents of (C₅Me₄H)SiMe₃. The presence of the silicon substituent on cyclopentadiene is crucial for this complexation reaction to be successful. Mixtures of mono- and bis(cyclopentadienyl) complexes were obtained when silicon-free cyclopentadienes such as C₅Me₅H or C₅Me₄H₂ were employed.

When complexes **2** and **3** are in solution at room temperature, the coordinated thf groups are labile on both the chemical and NMR time scale. This is shown by the instantaneous exchange of all coordinated thf molecules upon addition of excess [D₈]THF and the substantial high-field

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Table 1. Selected spectroscopic data of **2**, **3a–c**, and **4**. NMR spectra in [D₆]benzene at 400 MHz (¹H), 100.6 MHz (¹³C), 79.5 MHz (²⁹Si), and 376.4 MHz (¹⁹F) and at 25 °C (unless stated otherwise).

2: ¹H NMR: δ = –0.93 (d, ²*J*(Y,H) = 3.1 Hz, 2H, Y–CH₂), 0.28 (s, 9H, CH₂SiMe₃), 0.74 (s, 6H, SiCH₃), 1.02 (m, 4H, β -CH₂, thf), 1.38 (s, 9H, C(CH₃)₃), 2.04, 2.19 (s, 6H, ring CH₃), 3.30 (m, 4H, α -CH₂, thf); ¹³C NMR: δ = 4.7 (CH₂SiCH₃), 8.4 (NSiCH₃), 11.5, 14.0 (ring CH₃), 24.7 (β -CH₂, thf), 26.2 (d, ¹*J*(Y,C) = 44.9 Hz, YCH₂), 36.0 (C(CH₃)₃), 54.0 (C(CH₃)₃), 70.7 (α -CH₂, thf), 106.6 (ring C at Si), 122.3, 126.4 (ring C); ²⁹Si NMR: δ = –25.0 (NSiMe₂), –2.7 (d, ²*J*(Y,Si) = 1.9 Hz, CH₂SiMe₃)

3a: ¹H NMR: δ = –0.61 (d, ²*J*(Y,H) = 3.1 Hz, 4H, YCH₂), 0.30 (s, 18H, CH₂SiCH₃), 0.41 (s, 9H, SiCH₃), 1.15 (m, 4H, β -CH₂, thf), 1.96, 2.24 (s, 6H, ring CH₃), 3.52 (m, 4H, α -CH₂, thf); ¹³C NMR: δ = 2.6 (SiCH₃), 4.6 (CH₂SiCH₃), 11.5, 14.6 (ring CH₃), 24.8 (β -CH₂, thf), 34.7 (d, ¹*J*(Y,C) = 43.7 Hz, YCH₂), 70.4 (α -CH₂, thf), 115.0 (ring C at Si), 123.3, 126.4 (ring C); ²⁹Si NMR: δ = –10.3 (SiMe₃), –3.2 (d, ²*J*(Y,Si) = 2.1 Hz, CH₂SiMe₃)

3b: ¹H NMR: δ = –0.58 (d, ²*J*(Y,H) = 3.1 Hz, 4H, YCH₂), 0.30 (s, 18H, CH₂SiCH₃), 0.69 (s, 6H, Si(CH₃)Ph), 1.20 (m, 4H, β -CH₂, thf), 1.97, 2.15 (s, 6H, ring CH₃), 3.47 (m, 4H, α -CH₂, thf), 7.17 (m, 3H, C₆H₅), 7.53 (m, 2H, C₆H₅); ¹³C NMR: δ = 1.8 (Si(CH₃)Ph), 4.6 (CH₂SiCH₃), 11.6, 14.8 (ring CH₃), 24.9 (β -CH₂, thf), 34.9 (d, ¹*J*(Y,C) = 43.7 Hz, YCH₂), 70.0 (α -CH₂, thf), 112.6 (ring C at Si), 123.6, 127.1 (ring C), 128.0, 128.8, 134.3 (C₆H₅), 141.6 (*ipso*-C₆H₅); ²⁹Si NMR: δ = –13.8 (SiMe₂Ph), –3.2 (d, ²*J*(Y,Si) = 2 Hz, CH₂SiMe₃)

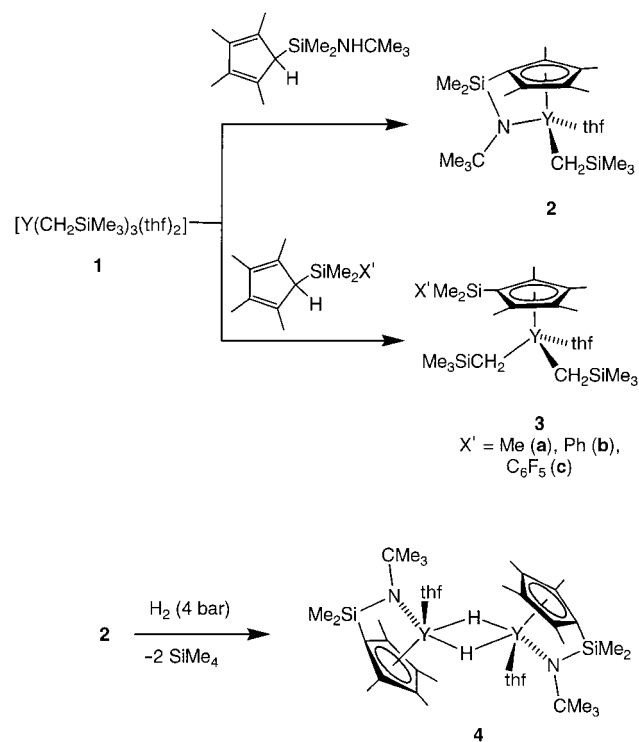
3c: ¹H NMR: δ = –0.65 (d, ²*J*(Y,H) = 3.1 Hz, 4H, YCH₂), 0.28 (s, 18H, CH₂SiCH₃), 0.78 (t, 6H, ³*J*(F,H) = 1.6 Hz, Si(CH₃)C₆F₅), 1.25 (m, 4H, β -CH₂, thf), 1.85, 2.19 (s, 6H, ring CH₃), 3.50 (m, 4H, α -CH₂, thf); ¹³C NMR: δ = 2.6 (Si(CH₃)C₆F₅), 4.5 (CH₂SiCH₃), 11.4, 14.3 (ring CH₃), 25.0 (β -CH₂, thf), 35.0 (d, ¹*J*(Y,C) = 43.7 Hz, YCH₂), 69.9 (α -CH₂, thf), 110.0 (ring C at Si), 112.3 (*ipso*-C₆F₅), 123.9, 126.9 (ring C), 136.2, 147.8, 150.2 (m, C₆F₅); ²⁹Si NMR: δ = –13.8 (SiMe₂C₆F₅), –3.2 (d, ²*J*(Y,Si) = 1.8 Hz, CH₂SiMe₃); ¹⁹F NMR: δ = –105.6 (m, *m*-C₆F₅), –130.7 (t, ³*J*(F,F) = 21 Hz, *p*-C₆F₅), –139.0 (m, *m*-C₆F₅)

4: ¹H NMR ([D₈]toluene, 50 °C): δ = 0.69 (s, 6H, SiCH₃), 1.36 (s, 9H, C(CH₃)₃), 1.46 (brm, 4H, β -CH₂, thf), 2.09, 2.22 (s, 6H, ring CH₃), 3.82 (brm, 4H, α -CH₂, thf), 5.50 (t, 1H, ¹*J*(Y,H) = 28.8 Hz, Y₂H₂); ¹³C NMR ([D₈]toluene, 50 °C): δ = 8.6 (SiCH₃), 12.2, 14.3 (ring CH₃), 25.2 (β -CH₂, thf), 36.8 (C(CH₃)₃), 55.0 (C(CH₃)₃), 72.1 (α -CH₂, thf), 108.5 (ring C at Si), 125.8 (ring C); ²⁹Si NMR ([D₈]toluene, 50 °C): δ = –25.5

4 (major isomer): ¹H NMR ([D₈]toluene, –40 °C): δ = 0.81, 0.95 (s, 3H, SiCH₃), 1.17 (m, 4H, β -CH₂, thf), 1.52 (s, 9H, C(CH₃)₃), 2.02 (s, 6H, ring CH₃), 2.11, 2.54 (s, 3H, ring CH₃), 3.47, 3.85 (brm, 2H, α -CH₂, thf), 5.27 (t, 1H, ¹*J*(Y,H) = 29.0 Hz, Y₂H₂); ¹³C NMR ([D₈]toluene, –40 °C): δ = 8.2, 9.3 (SiCH₃), 12.1, 12.3, 13.9, 14.7 (ring CH₃), 25.0 (β -CH₂, thf), 36.3 (C(CH₃)₃), 54.7 (C(CH₃)₃), 72.7 (α -CH₂, thf), 107.1 (ring C at Si), 119.6, 122.8, 126.0, 126.2 (ring C); ²⁹Si NMR ([D₈]toluene, –40 °C): δ = –25.6

4 (minor isomer): ¹H NMR ([D₈]toluene, –40 °C): δ = 1.20 (m, 4H, β -CH₂, thf), 1.44 (s, 9H, C(CH₃)₃), 2.05, 2.14, 2.20, 2.51 (s, 3H, ring CH₃), 3.78 (brm, 4H, α -CH₂, thf), 5.45 (t, 1H, ¹*J*(Y,H) = 28.6 Hz, Y₂H₂); ¹³C NMR ([D₈]toluene, –40 °C): δ = 8.5, 9.0 (SiCH₃), 11.6, 13.3, 14.1, 15.2 (ring CH₃), 24.9 (β -CH₂, thf), 36.4 (C(CH₃)₃), 55.0 (C(CH₃)₃), 72.4 (α -CH₂, thf), 107.7 (ring C at Si), 119.9, 123.3, 125.8 (ring C); ²⁹Si NMR ([D₈]toluene, –40 °C): δ = –25.7

shift of the signals for the α - and β -protons in the ¹H NMR spectrum at low temperatures. (Decoalescence of the signals into those for free and coordinated thf was observed at –80 °C for **2**.) The temperature dependence of the equilibrium constants was obtained from the chemical shifts of α - and β -CH₂.^[8, 9] The plot of ln *K* versus 1/*T* gave the thermodynamic parameters $\Delta_r H^\circ$ = (24 ± 3) kJ mol^{–1} and $\Delta_r S^\circ$ = (61 ± 12) J K^{–1} mol^{–1} for **2**. The positive reaction entropy and enthalpy is in accordance with a dissociative process. Complex **2** is relatively thermally robust, decomposing by a first-order rate law with a half-life of $t_{1/2}$ = (600 ± 10) min (k_1 = (1.92 ±



Scheme 1.

4) × 10^{–5} s^{–1}) at 50 °C in [D₆]benzene (determined by NMR spectroscopy) to give SiMe₄ and other yet unidentified products of C–H activation. The activation parameters $\Delta H^\ddagger$ = (145 ± 16) kJ mol^{–1} and $\Delta S^\ddagger$ = (110 ± 50) J K^{–1} mol^{–1} were calculated from the temperature dependence of the rate constant of the decomposition of **2**. The bis(alkyl) complexes **3a–c** slowly decompose at room temperature.

Hydrogenolysis of **2** in pentane at room temperature led to the dimeric hydrido complex **4** as a colorless powder in reproducibly good yield (Scheme 1).^[10] The ¹H NMR spectrum of **4** at 50 °C in [D₈]toluene (Figure 1), with only one hydride signal at δ = 5.50 (¹*J*(Y,H) = 28.8 Hz), agrees with a molecule with an internal mirror plane. However, this spectrum is the result of fast interconversion of two asymmetric diastereomers. Their interconversion is slowed down sufficiently at –40 °C, so that a ¹H NMR spectrum containing two triplets for the bridging hydrides (δ = 5.27, 5.45; ¹*J*(Y,H) = 29.0 and 28.6 Hz, respectively) as well as a doublet of all other signals could be obtained. The signal ratio shows that **4** exists as a 4:1 mixture of two asymmetric diastereomers in [D₈]toluene.

An ORTEP diagram of the structure of **4** in the solid state is shown in Figure 2.^[11] The crystal contains racemic pairs of C₂-symmetric homochiral dimers. Thus, the two linked amido-cyclopentadienyl yttrium units are connected by two hydrogen atoms in a *transoid* fashion. The Y₂H₂ core is significantly distorted (considering the well-known problem in the refinement of hydrogen atoms), possibly due to steric repulsion between the two (η^5 : η^1 -C₅Me₄SiMe₂NCMe₃) ligands and due to the strong *trans* influence of the amido ligand (Y1–H1 2.48(4), Y1–H2 1.98(6), Y2–H1 2.39(4), Y2–H2 2.31(6) Å;

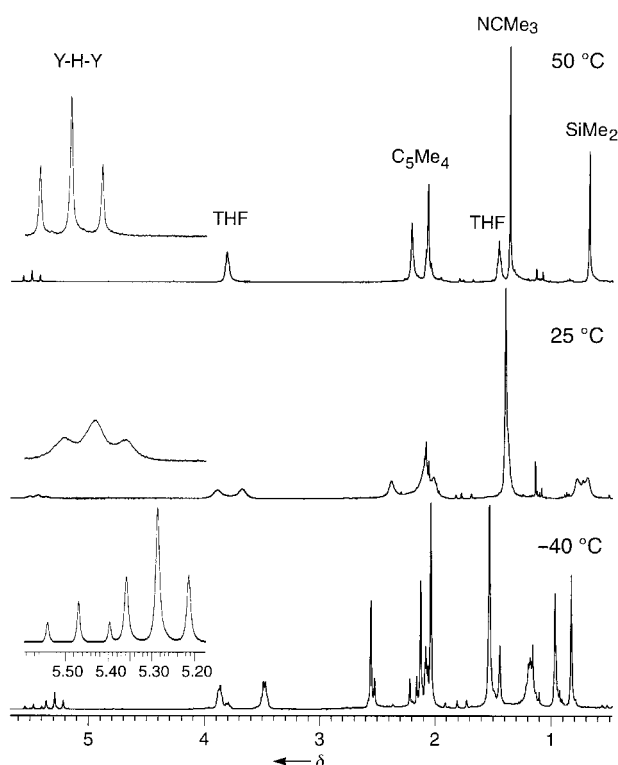


Figure 1. Temperature dependence of the ^1H NMR spectrum of **4** in $[\text{D}_8]\text{toluene}$.

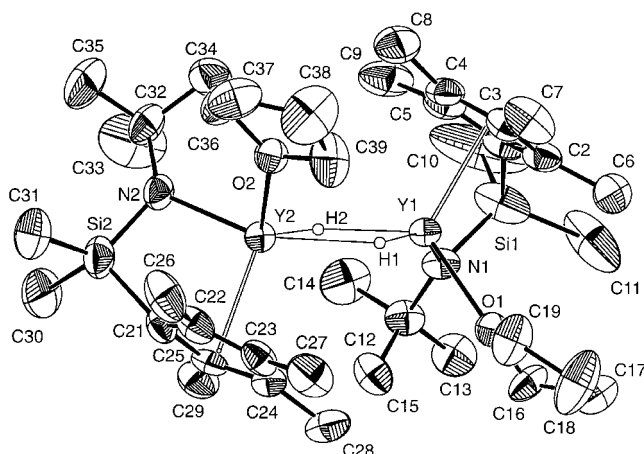


Figure 2. ORTEP diagram of the molecular structure of **4**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms, except for the two bridging hydrides, are omitted for the sake of clarity. Selected bond lengths [Å] and angles [°]: Y1–H1 2.48(4), Y1–H2 1.98(6), Y2–H1 2.39(4), Y2–H2 2.31(6), $\text{Cp}_{\text{cent}}1\text{--Y1}$ 2.351(8), $\text{Cp}_{\text{cent}}2\text{--Y2}$ 2.342(8), Y1–N1 2.250(6), Y2–N2 2.237(6), Y1–O1 2.361(5), Y2–O2 2.378(5), Y1...Y2 3.672(1); Y1–H1–Y2 98(2), Y1–H2–Y2 117(2), H1–Y1–H2 74(2), H1–Y2–H2 71(2), $\text{Cp}_{\text{cent}}1\text{--Y1--N1}$ 97.8(2), $\text{Cp}_{\text{cent}}1\text{--Y1--O1}$ 112.6(2), $\text{Cp}_{\text{cent}}1\text{--Y1--H1}$ 105(2), $\text{Cp}_{\text{cent}}1\text{--Y1--H2}$ 119(2), N1–Y1–O1 93.1(2), N1–Y1–H1 156.8(9), N1–Y1–H2 95(2), $\text{Cp}_{\text{cent}}2\text{--Y2--N2}$ 97.4(2), $\text{Cp}_{\text{cent}}2\text{--Y2--O2}$ 113.5(2), $\text{Cp}_{\text{cent}}2\text{--Y2--H1}$ 103(1), $\text{Cp}_{\text{cent}}2\text{--Y2--H2}$ 118(2), N2–Y2–O2 94.8(2), N2–Y2–H1 160(1), N2–Y2–H2 99(1).

Y1--H2--Y2 117(2), Y1--H1--Y2 98(2)°). The Y...Y distance (3.672(1) Å) is comparable to that of other dimeric yttrium hydrido complexes.^[12] The Y–N bond lengths (2.250(6) and 2.237(6) Å) are significantly shorter than those observed

in the heterobimetallic ytrocenes $\text{Li}[\text{Y}(\eta^5\text{--}\eta^1\text{--C}_5\text{R}_4\text{SiMe}_2\text{NCH}_2\text{CH}_2\text{X})_2]$ ($\text{C}_5\text{R}_4 = \text{C}_5\text{Me}_4$, $\text{C}_5\text{H}_3\text{tBu}$; $\text{X} = \text{OMe}$, NMe_2)^[13a] and the half-sandwich complex $[\text{Li}(\text{thf})][\text{Y}(\eta^5\text{--}\eta^1\text{--C}_5\text{Me}_4\text{SiMe}_2\text{NCH}_2\text{CH}_2\text{OMe})(o\text{--C}_6\text{H}_4\text{CH}_2\text{NMe}_2)\text{Cl}]$,^[13b] but slightly longer than in $(\eta^5\text{--}\eta^1\text{--C}_5\text{Me}_4\text{SiMe}_2\text{NCMe}_3)\text{YN}(\text{SiMe}_3)_2$.^[13c] In contrast to lanthanocene hydrides, **4** does not undergo H/D scrambling in deuterated solvents and is thermally stable in $[\text{D}_6]\text{benzene}$ at 50 °C for more than 24 hours.^[14]

α -Olefins such as 1-hexene or styrene react sluggishly with alkyl complexes **2** and **3a** (25 °C, $[\text{D}_6]\text{benzene}$, several days), whereas the hydrido complex **4** forms well-defined mono-insertion products. Ethene is readily polymerized by all complexes. Moreover, complexes **2**, **3a**, and **4** catalyze the polymerization of polar monomers, such as *tert*-butyl acrylate, and, in contrast to the lanthanocene hydrido and alkyl

Table 2. Polymerization of *tert*-butyl acrylate and acrylonitrile by **2**, **3a**, and **4** in toluene.

Cat.	<i>T</i> [°C]	<i>t</i> [h]	$[\text{M}_0]/[\text{cat.}]$	Yield [%]	$M_n \times 10^{-3}$ [g mol ⁻¹]	M_w/M_n	mm ^[c] [%]	mr ^[c] [%]	rr ^[c] [%]
<i>tert</i> -butyl acrylate									
2	25	2	95	85	25 ^[a]	1.56	21	50	29
2	–30	18	79	98	30 ^[a]	1.97	19	50	31
2	–30	18	201	90	38 ^[a]	1.61	25	49	26
2	–30	18	309	38	38 ^[a]	1.50	29	48	23
3a	–30	17	77	99	68 ^[a]	1.62	25	45	30
4	25	3	181	11	13 ^[a]	1.69	30	46	24
acrylonitrile									
2	25	16	328	24	3.3 ^[b]		27	41	32
2	–30	48	198	48	5.0 ^[b]		30	44	26
3a	–30	14	256	66	3.4 ^[b]		26	43	31
4	25	24	185	24	–		30	41	29

[a] By gel permeation chromatography in THF, universal calibration relative to polystyrene standard. [b] By ^1H NMR spectroscopic end-group analysis. [c] mm, mr, and rr are iso-, hetero-, and syndiotactic triads, respectively.

complexes, they catalyze the polymerization of acrylonitrile as well (Table 2).^[15] *tert*-Butyl acrylate is polymerized in the presence of either of the complexes **2**, **3**, or **4** at temperatures as low as –30 °C (i.e., well below the decomposition temperatures) to give poly(*tert*-butyl acrylate) in high yields and with molecular weights M_n greater than 20 000. Initiation is somewhat slower when the hydrido complex **4** is used. The molecular-weight distributions of the resulting polymers are in the range of 1.5–2.0,^[16] and the polymer microstructure as judged by ^{13}C NMR spectroscopy is predominantly atactic. An intense orange-red solution forms as soon as acrylonitrile is added to a solution of **2**, **3a**, or **4** in toluene ($\lambda_{\text{max}}(\epsilon) = 353 \text{ nm}$ (22 000) for **2** in the presence of one equivalent of acrylonitrile), followed by the precipitation of yellow, atactic poly(acrylonitrile). This unusual color is ascribed to an intermolecular charge transfer band between an f^0d^0 complex and an electron acceptor.^[17] Rapid chain propagation appears to be preceded by a slow initiation step in which the coordinated thf ligand at the yttrium center is substituted by the monomer to generate the active species, the keteneimino complex $[(\eta^5\text{--C}_5\text{Me}_4\text{SiMe}_2\text{X}')\text{Y}(\text{N}=\text{C}=\text{CHCH}_2\text{R})]$, by 1,4-insertion.^[18]

Experimental Section

2: To a solution of **1** (250 mg, 0.51 mmol), prepared from the reaction of $\text{YCl}_3(\text{thf})_{3.5}$ and $\text{LiCH}_2\text{SiMe}_3$, in pentane (10 mL) was added a solution of $(\text{C}_5\text{Me}_4\text{H})\text{SiMe}_2\text{NHCMc}_3^{[3b]}$ (128 mg, 0.51 mmol) in pentane (3 mL) at 0 °C. After the mixture was stirred at this temperature for 2 h, the solution was decanted and concentrated in vacuo. The crude product was recrystallized from pentane at –30 °C to give 233 mg (92 %) of **2** as colorless microcrystals. Complexes **3a–c** were prepared in a similar manner.

4: A solution of **2** (630 mg, 1.27 mmol) in pentane (10 mL) was loaded in a thick-walled 100-mL glass vessel. H_2 (4 atm) was charged at room temperature, and the reaction mixture was stirred vigorously. After 7 h of stirring, the solution above the white precipitate was decanted to provide 335 mg (64 %) of the colorless powder **4**.

Correct elemental analyses (C, H, N) were obtained for all compounds.

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- [11] a) Crystal size $0.70 \times 0.28 \times 0.15$ mm, monoclinic, space group $P2_1/n$ (no. 14), $Z = 4$; $a = 14.522(4)$, $b = 16.575(4)$, $c = 20.118(9)$ Å, $\beta = 110.65(3)^\circ$, $V = 4531(3)$ Å³, $\rho_{\text{calcd}} = 1.206$ g cm^{–3}, $T = 293(2)$ K, $3 < \theta < 23^\circ$, ($\lambda(\text{MoK}\alpha) = 0.71070$ Å, $\mu = 2.631$ mm^{–1}); of 12 823 reflections measured, 6266 were independent ($R_{\text{int}} = 0.1073$) and 3012 observed ($I > 2\sigma(I)$), Lorentz polarization and empirical absorption corrections (ψ scans), Patterson and Fourier syntheses (SHELXS-86 and SHELXL-93), 431 parameters, $R = 0.0509$, $wR_2 = 0.0933$, max./min. residual electron density $0.409/-0.384$ e Å^{–3}. b) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-410087. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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