Alkoxides as Ancillary Ligands in Organolanthanide Chemistry: Synthesis of, Reactivity of, and Olefin Polymerization by the μ-Hydride–μ-Alkyl Compounds $[Y(C_5Me_5)(OC_6H_3{}^tBu_2)]_2(\mu\text{-}H)(\mu\text{-alkyl})$

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Reaction of $Y(C_5Me_5)(OAr)_2$ (**2**; OAr = O-2,6-$C_6H_3{}^tBu_2$) with $MCH(SiMe_3)_2$ (M = Li, K) affords $Y(C_5Me_5)(OAr)\{CH(SiMe_3)_2\}$ (**3**), which on subsequent hydrogenation (20 bar, 25 °C) gives the μ-H dimer $[Y(C_5Me_5)(OAr)(\mu\text{-}H)]_2$ (**4**). Terminal olefins $H_2C{=}CHR$ (R = H, Me, Et, *n*-Bu) react regiospecifically and irreversibly with **4** to give the μ-*n*-alkyl species *trans*-$[Y(C_5Me_5)(OAr)]_2(\mu\text{-}H)(\mu\text{-}CH_2CH_2R)$ (R = H (**5**), Me (**6**), Et (**7**), *n*-Bu (**8**)), respectively. Reaction of $[Y(C_5Me_5)(OAr)(\mu\text{-}D)]_2$ (**4-D**) (prepared from **3** and D_2) with propene yields selectively only *trans*-$[Y(C_5Me_5)(OAr)]_2(\mu\text{-}D)(\mu\text{-}CH_2CHDMe)$ (**6-D**), confirming the nonreversibility of olefin insertion. Compounds **4**–**8** polymerize ethene and are single-component catalysts for the polymerization of α-olefins and nonconjugated dienes. Dissolution of **4** in neat 1-hexene (to give **8** in situ) results in slow polymerization to yield poly(1-hexene) with M_w = 15 700 and M_w/M_n = 1.67. **4** cyclopolymerizes neat 1,5-hexadiene to poly(methylene-1,3-cyclopentanediyl) rather than promotes cyclization to methylenecyclopentane. The μ-alkyls **5**-**8** show diastereotopic $\alpha\text{-}CH_2$ resonances, implying idealized C_2, rather than C_{2v} geometry, which indicates a mutually *trans* geometry for the attendant C_5Me_5 and OAr ligands. In **6**, exchange of the two diastereotopic $C_\alpha H_2$ hydrogens by inversion at $Y(\mu\text{-}C_\alpha)Y$ occurs with $\Delta G^\ddagger = 11.1 \pm 0.5$ kcal mol^{-1} (−25 °C), and *tert*-butyl group equilibation on the same phenoxide occurs with $\Delta G^\ddagger = 9.0 \pm 0.5$ kcal mol^{-1} (−93 °C). The terminal acetylene $HC{\equiv}CSiMe_3$ reacts with **4** to give the μ-acetylide $[Y(C_5Me_5)(OAr)]_2(\mu\text{-}H)(\mu\text{-}C{\equiv}CSiMe_3)$ (**9**). **9** reacts with excess $HC{\equiv}CSiMe_3$, only in the presence of THF, to give the monomeric acetylide $Y(C_5Me_5)(OAr)C{\equiv}CSiMe_3(THF)_2$ (**11**). The THF-free analog $Y(C_5Me_5)(OAr)C{\equiv}CSiMe_3$ (**10**) is prepared by reaction of **3** with excess $HC{\equiv}CSiMe_3$. Treatment of **2** with MeLi (1 equiv) affords the bis(μ-Me) species $[Y(C_5Me_5)(OAr)(\mu\text{-}Me)]_2$ (**12**), which is cleaved by THF, in contrast to the μ-H species **4**, to give $Y(C_5Me_5)(OAr)(Me)(THF)_2$ (**13**). Reaction of **2** with MeLi (1.6 equiv) gives the yttrium trimer $[Y(C_5Me_5)(\mu\text{-}Me)_2]_3$ (**14**). **14** undergoes metathesis with $LiOC_6H_3{}^tBu_2$ to give **12**. ^{89}Y NMR spectroscopy is a potentially useful diagnostic probe of ligand environment. The ^{89}Y NMR chemical shifts (all in C_6D_6) of $Y(OAr)_3$ (**1**), **2**, $Y(C_5Me_5)_2CH(SiMe_3)_2$, $Y\{CH(SiMe_3)_2\}_3$, and $Y(C_5Me_5)_2(OAr)$ have been determined. From these, group contributions to the ^{89}Y NMR chemical shift were calculated to be −100 ppm for C_5Me_5, +56 ppm for OAr, and +298 ppm for $CH(SiMe_3)_2$.

Introduction

The recent growth in organolanthanide chemistry has primarily focused on complexes stabilized by the bis(pentamethylcyclopentadienyl) ligand system. Pioneering work with methyl analogues $[M(C_5Me_5)_2Me]_2$ (M = Y, Lu)[1] demonstrated the potential for fascinating reactivity such as methane transmetalation, β-methyl elimination, and propene oligomerization. $[M(C_5Me_5)_2H]_2$ species (M = Sc,[2a] Y,[2b] La,[2c] Ce,[2d] Nd,[2c] Sm,[2c,e] Lu[2c,f]) have been shown to be extremely active for olefin hydrogenation[3a] and ethylene polymerization.[3b–e] Varying the cyclopentadienyl substituents or linking the cyclopentadienyl rings has led to α-olefin oligomerization,[4a] cyclization of α,ω-dienes,[4b]

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C–C σ-bond activation,[4c] hydroamination/cyclization of olefins,[4d] and isospecific α-olefin polymerization.[4e,f]

In extending our recent work on ligand variations in organolanthanide chemistry,[5] and their influence on fundamental reaction steps in modeling Ziegler–Natta polymerization systems, we have investigated the reactivity of the bridging hydride $[Y(C_5Me_5)(OAr)(\mu\text{-}H)]_2$ (4)[6] with α-olefins, particularly to compare the effect of the alkoxide groups on the reactivity with the corresponding bis(pentamethylcyclopentadienyl) systems.[1-3] From thermodynamic arguments, replacement of pentamethylcyclopentadienyl ligands by hard, electronegative ancillary ligands such as alkoxides would be expected[7] to suppress β-hydrogen elimination.

Elegant studies on dimeric $[\{(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NCMe_3)\}Sc(PMe_3)]_2(\mu\text{-}H)_2$[4a,b] and $\{R_2Si(C_5H_4)(C_5Me_4)M\}_2(\mu\text{-}H)_2$ (R = Me, Et; M = Y, Lu),[8] which display chemistry related to that described here, have recently been reported. It is also pertinent to note that polymetallic lanthanide (Y, Lu, La) chemistry[9] based on mixed cyclopentadienyl–alkoxide systems has been performed, primarily by reaction of $LnCl_3$ precursors with the relatively small akoxide NaO^tBu. Parts of the work reported here have been published in communication form.[6,10]

Results

Reaction of $Y(OAr)_3$ ($OAr = O\text{-}2,6\text{-}C_6H_3{}^tBu_2$) (1)[11] with KC_5Me_5 (1 equiv, toluene, 100 °C, 16 h) resulted in the formation of $Y(C_5Me_5)(OAr)_2$ (2) in 70–80% isolated yield. 2 is shown by x-ray studies[6] to be isostructural with its cerium congener.[12] 2 reacts cleanly with $KCH(SiMe_3)_2$ (1 equiv) in hexane, with loss of insoluble KOAr, enabling easy separation, to give the mixed alkyl–phenoxide complex $Y(C_5Me_5)(OAr)CH(SiMe_3)_2$ (3) in 70–80% isolated yield. Better yields are obtained by use of $KCH(SiMe_3)_2$ rather than $LiCH(SiMe_3)_2$ (40–50%). Although clean and selective monosubstitution of one alkoxide in 2 is observed with $MCH(SiMe_3)_2$ (M = Li, K) and LiMe (vide infra), the analogous alkyls $[Y(C_5Me_5)(OAr)(R)]_x$ (x = 1, 2) could not be prepared from 2 and RLi (1 equiv; R = Et, n-Bu, CH_2SiMe_3, CH_2CMe_3) by similar synthetic procedures. Decomposition of starting materials and formation of LiOAr was observed (R = Et, n-Bu, CH_2CMe_3). No reaction was observed between 2 and $LiCH_2SiMe_3$ in hexane. Additionally, although $Ln(C_5Me_5)(OAr)_2$ species (Ln = Y, La, Ce) are known,[13a] clean and selective monoalkylation (with $LiCH(SiMe_3)_2$) proved to be only possible[13b] for Ln = Y, which has thwarted attempts to extend this chemistry to La.

A technique[14] for the possible discrimination of the secondary interactions of the $CH(SiMe_3)_2$ group in 3 utilizes the coupling of two spin-active nuclei. This may have been a good method of determining the presence of an agostic β-Si–Me–Y interaction in 3. However, no coupling[15] to ^{89}Y was observed in the ^{29}Si NMR spectrum (C_7D_8, −80 °C), a sharp singlet at −12.2 ppm (fwhm = 12 Hz) being observed.

In contrast to the facile hydrogenation observed for the bis(pentamethylcyclopentadienyl) series $Ln(C_5Me_5)_2CH(SiMe_3)_2$,[2c,14b] hydrogenation of 3 is best performed in hexane under 10 bar of H_2, yielding $[Y(C_5Me_5)(OAr)(\mu\text{-}H)]_2$ (4) in 40–50% isolated yield (Scheme 1). At reaction times longer than 3 h significant quantities of 2 are formed. As both 3 and 4 are not susceptible to disproportionation, the origin of 2 in this reaction is unknown. It is possibly H_2 induced. The reaction was monitored in a high-pressure, sapphire 10-mm NMR tube[16a] (20 bar of H_2, 25 °C, C_6D_{12}). No intermediates were observed.[16b]

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(9) Pertinent examples were as follows. (a) $[(C_5H_5)_2Y(\mu\text{-}OMe)]_3(\mu_3\text{-}H)]^-$: Evans, W. J.; Sollberger, M. S.; Khan, S. I.; Bau, R. *J. Am. Chem. Soc.* **1988**, *110*, 439. (b) Preparation of $Y_3(\mu_3\text{-}O^tBu)(\mu_3\text{-}Cl)(\mu\text{-}O^tBu)_3(O^tBu)_4(THF)_2$ from YCl_3 and NaO^tBu and of $La_3(\mu_3\text{-}O^tBu)_2(\mu\text{-}O^tBu)_3(O^tBu)_4(THF)_2$ from $LaCl_3$ and NaO^tBu: Evans, W. J.; Sollberger, M. S.; Hanusa, T. P. *J. Am. Chem. Soc.* **1988**, *110*, 1841. (c) Reaction of $Y_3(O^tBu)_7Cl_2(THF)_2$[9b] with $AgBPh_4$: Evans, W. J.; Olofson, T. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 2308. (d) $Y_{14}(O^tBu)_{28}Cl_{10}(THF)_4$: Evans, W. J.; Sollberger, M. S. *Inorg. Chem.* **1988**, *27*, 4417.

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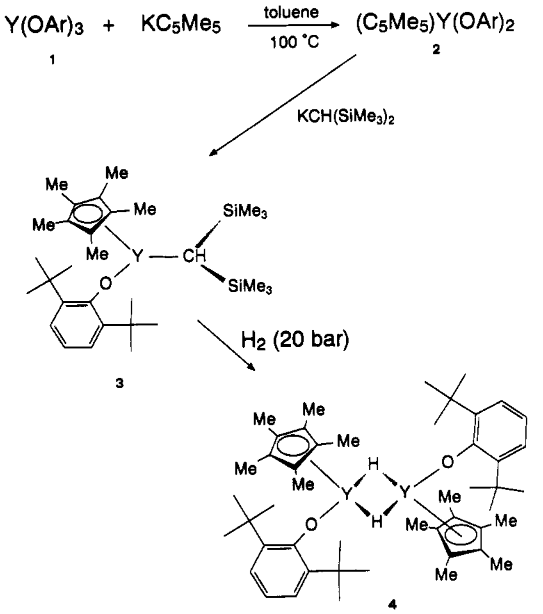
(13) The tendency for disproportionation in the synthesis of $Y(C_5Me_5)(OAr)_2$ (2) is much less than for its Ce or La counterparts[13a]. Unlike $Ln(C_5Me_5)\{CH(SiMe_3)_2\}_2$ (Ln = La,[13b] Ce[12]), putative $Y(C_5Me_5)\{CH(SiMe_3)_2\}_2$ cannot be prepared by reaction of 2 with $MCH(SiMe_3)_2$ (M = Li, K). No reaction occurs between 3 and $LiCH(SiMe_3)_2$, indicating that the remaining phenoxide is not susceptible to nucleophilic displacement. The La analogue of 3 $La(C_5Me_5)(OAr)CH(SiMe_3)_2$ could not be prepared, either by reaction of $La(C_5Me_5)\{CH(SiMe_3)_2\}_2$ with HOAr (1 equiv) or by reaction of $La(C_5Me_5)(OAr)_2$ with $LiCH(SiMe_3)_2$ (1 equiv). These differences (La vs Y) can only be due to the size of the metal. (a) Heeres, H. J.; Teuben, J. H. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 226. (b) Van der Heijden, H.; Schaverien, C. J.; Orpen, A. G. *Organometallics* **1989**, *8*, 255. (b) Although reaction of $(C_5Me_5)Ce(OAr)_2$ with $KCH(SiMe_3)_2$ has been reported[12] to give $(C_5Me_5)(OAr)CeCH(SiMe_3)_2$, it could not be obtained analytically pure.

(14) Although IR spectroscopy is often reported to be a reliable tool for studying agostic C–H···M interactions and diagnostic low-energy ν(C–H) stretching vibrations in the range 2700–2350 cm^{-1} have been observed[14a] for $(C_5Me_5)_2ScEt$,[2a] IR is not always particularly reliable in confirming the presence or absence of agostic interactions, these IR stretches being rather weak. For example, for $(C_5Me_5)_2LnCH(SiMe_3)_2$ (Ln = Y, Ce),[14b] $\{(Me_2SiC_5Me_4C_5H_4)\}LuCH(SiMe_3)_2$,[8] and $(C_5Me_5)_2Th(CH_2{}^tBu)_2$[14c] no such IR bands were found, although diffraction evidence confirmed their presence. Low-temperature ^{13}C NMR spectroscopy does provide evidence for α-C–H–Ln interactions (with typical $^1J(CH)$ values being in the range 85–100 Hz); however, only a very small reduction in the *time-averaged* $C\text{–}H_\gamma$ coupling constant should be expected, as a $CH(SiMe_3)_2$ group has 18 possible γ-hydrogens which could interact with the metal center. (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (b) den Haan, K. H.; de Boer, J. L.; Teuben, J. H.; Spek, A. L.; Kojic-Prodic, B.; Hays, G. R.; Huis, R. *Organometallics* **1986**, *5*, 1726. Heeres, H. J.; Renkema, J.; Booij, M.; Meetsma, A.; Teuben, J. H. *Organometallics* **1988**, *7*, 2495. (c) Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40.

(15) Both ^{89}Y and ^{29}Si have $I = {}^1/_2$. The lack of quadrupolar coupling results in sharp lines (in solution: ^{29}Si NMR, <10 Hz; ^{89}Y NMR, 2–10 Hz), enabling relatively small couplings to be observed. The magnitude of the possible coupling, however, was expected to be small, since direct through-bond $^2J_{YSi}$ couplings of only ca. 8 Hz have been observed in the ^{29}Si NMR spectra of yttrium siloxides (e.g. $Y(OSiPh_3)_3(THF)$): Coan, P. S.; Hubert-Pfalzgraf, L. G.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 1262.

Scheme 1



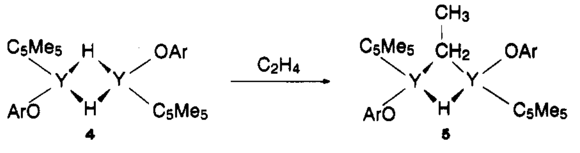
The chemical shift and Y–H coupling of the μ-H resonance (δ 5.64 ppm, J_{YH} = 35.2 Hz) are similar to those found in other bridging (yttrium) hydrides[17] and are consistent with a (time-averaged) symmetrical $Y(\mu\text{-}H)_2Y$ bridge. Low-temperature ^{1}H NMR (−90 °C, C_7D_8) studies provided no evidence for an asymmetric $Y(\mu\text{-}H)_2Y$ dimer, as observed[2b,18] for $[(C_5Me_5)_2YH]_2$. Only one isomer is observed, although NMR is insufficient to distinguish between mutually *cis* (idealized D_{2h}) or *trans* (idealized C_{2v}) phenoxide/C_5Me_5 ligands. However, subsequent reactivity studies (vide infra) indicate *trans* coordination. 4 is sparingly soluble in alkane solvents and quite soluble in aromatics. Addition of excess THF (10 equiv) to 4 in C_6D_6 does not result in cleavage of the μ-H dimer,[19] in contrast to the case for $[(C_5Me_5)_2YH]_2$.[2b] Hydrogenation of 3 (hexane, 20 bar of H_2) in the presence of THF (15 equiv) does not suppress (for an explanation, vide infra) bimolecular recombination of putative monomeric $Y(C_5Me_5)(OAr)(H)$, the adduct 4·4THF being the only observed product. Even performing the hydrogenation in THF (18 bar, 20 °C, 2 h, 100% conversion) also affords only 4·*n*THF.

There is no evidence for C_5Me_5 or phenoxide redistribution in this, or any subsequent, reactivity studies; compounds of the type $(C_5Me_5)_2Y(\mu\text{-}H)_2Y(OAr)_2$ or $(C_5Me_5)_2Y(\mu\text{-}H)(\mu\text{-alkyl})Y(OAr)_2$ have not been observed.

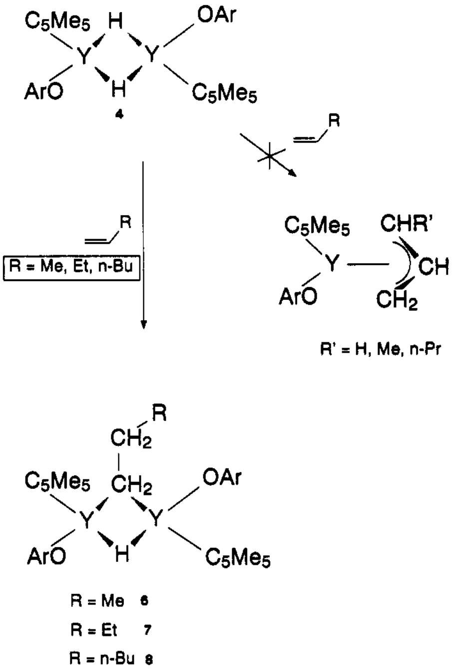
Synthesis of *trans*-$[Y(C_5Me_5)(OAr)]_2(\mu\text{-}H)(\mu\text{-}CH_2CH_2R)$. The reactivity of 4 with olefins and acetylenes was examined to determine the influence of replacing a C_5Me_5 ligand in $[(C_5Me_5)_2MH]_2$[2] with the electronically (and to a lesser extent, sterically) very different phenoxide ligand.

Reaction of 4 with C_2H_4 (1 bar, 25 °C) leads to the rapid formation of polyethene (mp 128 °C by differential scanning calorimetry). The μ-ethyl species *trans*-$[Y(C_5Me_5)(OAr)]_2(\mu\text{-}H)(\mu\text{-}CH_2Me)$ (5) can be isolated from the reaction by extraction with toluene. 5 is readily characterized by the diagnostic quartet (δ −0.08 ppm, $^3J_{HH}$ = 8 Hz) for the μ-CH_2Me protons. In the ^{1}H NMR spectra of 5-8 the μ-H resonance appears as a diagnostic triplet at δ 5.30–5.35 (J_{YH} = 39–41 Hz)[8,17] (Scheme 2).

Scheme 2



Scheme 3



4 reacts with excess propene (5 bar, 16 h, 25 °C, toluene) stoichiometrically to form cleanly and selectively the μ-propyl species *trans*-$[Y(C_5Me_5)(OAr)]_2(\mu\text{-}H)(\mu\text{-}CH_2CH_2Me)$ (6). In contrast to $[(C_5Me_5)_2YH]_2$, the allyl species $Y(C_5Me_5)(OAr)(\eta^3\text{-}CH_2CHCH_2)$ is not formed (Scheme 3).

The μ-propyl group in 6 displays resonances at δ 1.32 (t, 3H, 7.3 Hz, Me), 0.94 (br, 2H, $C_\beta H_2$), and 0.02 (t, 2H, 8.5 Hz, $C_\alpha H_2$). At −80 °C the $C_\alpha H_2$ resonance splits into two broad resonances at δ 0.76 and −0.70. In the ^{13}C NMR the μ-propyl group gives rise to resonances at δ 48.5 (tt, J_{CH} = 105 Hz, J_{YC} = 19.7 Hz, $C_\alpha H_2$), 23.4 (tt, J_{CH} = 123 Hz, $^2J_{YC}$ = 2.0 Hz, $C_\beta H_2$), and 21.0 (q, Me). At −60 °C (C_7D_8), the two $C_\alpha H_2$ coupling constants remain similar ($^1J_{CH}$ = 110 Hz), indicating similar C–H bond hybridization and not supporting the presence of agostic C_α–H–Y interactions (vide infra).

By similar methodology, the μ-*n*-butyl species *trans*-$[Y(C_5Me_5)(OAr)]_2(\mu\text{-}H)((\mu\text{-}CH_2CH_2CH_2Me)$ (7) was prepared by reaction of 4 with excess 1-butene. The μ-$C_\alpha H_2$ group resonates in the ^{1}H NMR at δ −0.05 (br t, $^3J_{HH}$ = 8 Hz) and at δ 45.55 (tt, J_{CH} = 105, $^1J_{YC}$ = 21 Hz) in the ^{13}C NMR.

To demonstrate that longer chain bridged alkyl species are not inherently unstable with respect to β-H elimination, the μ-*n*-hexyl species $[Y(C_5Me_5)(OAr)]_2(\mu\text{-}H)(\mu\text{-}CH_2CH_2CH_2CH_2CH_2Me)$ (8) was prepared straightforwardly by

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[16] (a) Roe, C. *J. Magn. Reson.* 1985, *63*, 388. (b) Low steady-state concentrations of intermediates, possibly $\{R_2Si(C_5H_4)(C_5Me_4)\}M(\mu\text{-}CH(SiMe_3)_2\}M(H)\{(C_5H_4)(C_5Me_4)SiR_2\}$, have been observed from hydrogenolysis of $\{R_2Si(C_5H_4)(C_5Me_4)\}MCH(SiMe_3)_2$.[8]

[17] den Haan, K. H.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* 1986, 682. Evans, W. J.; Solberger, M. S.; Khan, S. I.; Bau, R. *J. Am. Chem. Soc.* 1988, *110*, 439. Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* 1984, *106*, 1291.

[18] See footnote 12 in ref 1c. See however, the correction to ref 2b in: Booij, M.; Deelman, B.-J.; Duchateau, R.; Postma, D. S.; Meetsma, A.; Teuben, J. H. *Organometallics* 1993, *12*, 3531.

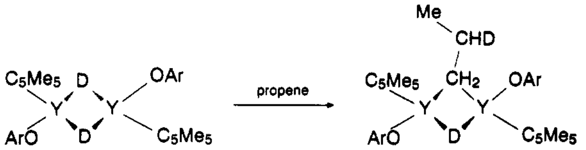
[19] Evans, W. J.; Drummond, D. K.; Hanusa, T. P.; Doedens, R. J. *Organometallics* 1987, *6*, 2279.

reaction of 4 with excess 1-hexene. In 8, μ-H resonates at δ 5.33 (t, J_{YH} = 40.2 Hz), with μ-$C_{\alpha}H_2$ at δ −0.08 (t, 7.3 Hz) in the ^{1}H NMR and with $C_{\alpha}H_2$ at δ 48.5 (t, $^1J_{YC}$ = 19 Hz) in the ^{13}C NMR spectrum. Interestingly, the $C_{\beta}H_2$ resonance at δ 32.4 is a doublet (d, $^2J_{YC}$ = 2.4 Hz). This may be indicative of a highly unsymmetrically bound μ-hexyl group due to the disparate steric requirements[20] of C_5Me_5 versus OAr and the *trans* geometry of the ancillary ligands in 8. Consequently, $C_{\beta}H_2$ interacts with one of the yttrium centers. A similar phenomenon was observed in the X-ray crystal structure of [{$Et_2Si(C_5H_4)(C_5Me_4)$}$Lu]_2$(μ-H)(μ-Et),[8] in which the two Lu–C_{α}–C_{β} angles were remarkably different (148 and 79°), and with the Et group orientationally disposed toward the less sterically demanding C_5H_4 ligand.

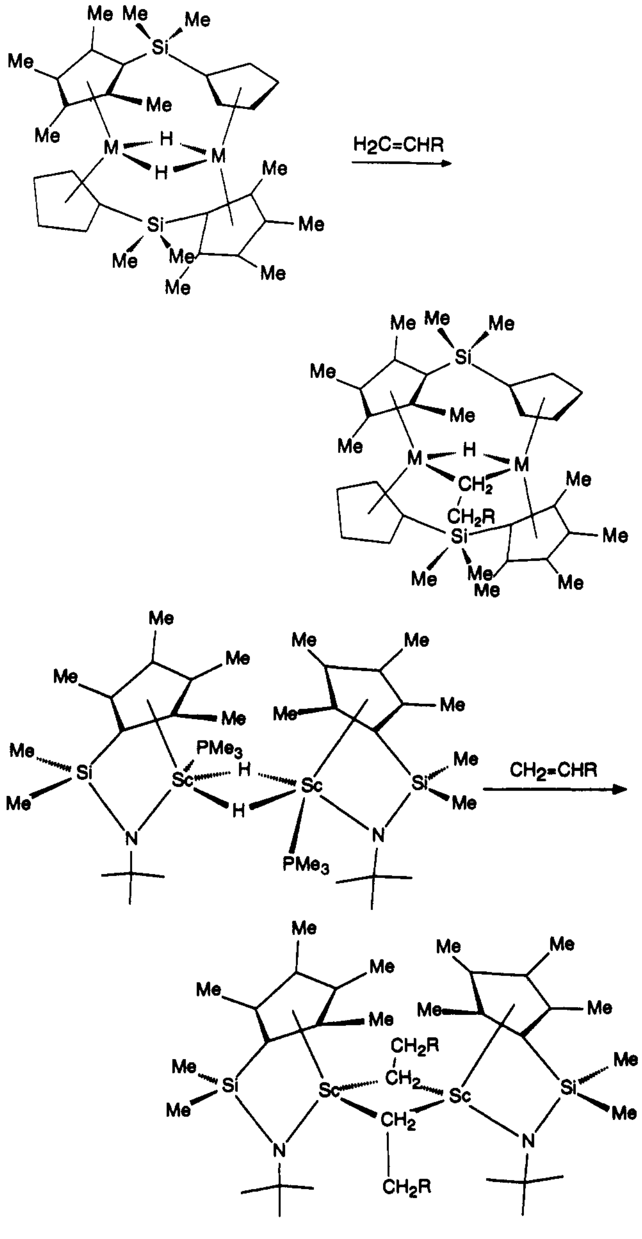
The magnitudes of J_{YC} and J_{CH} in 5-8 are characteristic of bent μ-alkyl groups.[8,21] For example, $[Y(C_5H_5)_2(\mu\text{-}Me)]_2$[22] has μ-Me at δ 23.0 (J_{YC} = 25.0 hz), and {$Et_2Si(C_5H_4)(C_5Me_4)Y$}$_2$(μ-H)(μ-CH_2CH_3)[8] has μ-$C_{\alpha}H_2$ at δ 28.1 ($^1J_{CH}$ = 107 Hz, $^1J_{YC}$ = 24 Hz). In contrast, the linear asymmetric methyl bridge in $Y(C_5Me_5)_2(\mu\text{-}Me)Y(C_5Me_5)_2Me$[21b] is coupled to just one yttrium and has a larger J_{CH} value, 120 Hz. The μ-alkyl group(s) in 5-8 and 11 (vide infra) presumably adopts a symmetric alkyl bridge, as found crystallographically in $[Y(C_5H_5)_2(\mu\text{-}Me)]_2$[22] and {$Et_2Si(C_5H_4)(C_5Me_4)Lu$}$_2$(μ-H)(μ-$CH_2CH_3$).[8] A μ-alkyl group containing an agostic C–H–Y interaction, as found for the μ-Me groups in $Os_3(CO)_{10}$(μ-H)(μ-Me)[23a-c] and cationic Fe_2[23d] and Ru_2[23e] complexes, is unlikely on structural[6,31] and NMR grounds. Since the triplet of triplets pattern for the C_{α} resonance in the ^{13}C NMR for 6 is temperature invariant (+25 to −80 °C), with its diastereotopic hydrogens retaining similar J_{CH} values, this suggests that there is no strong α-agostic interaction to electron-deficient yttrium.

Reaction of $[Y(C_5Me_5)(OAr)(\mu\text{-}D)]_2$ (**4-D**) (prepared from 3 and D_2) with propene yields only *trans*-$[Y(C_5Me_5)(OAr)]_2$(μ-D)(μ-CH_2CHDMe) (**6-D**) by ^{1}H and ^{13}C NMR (see Experimental Section), confirming the nonreversibility of olefinic insertion (Scheme 4).

Scheme 4



Scheme 5



As in the case of {$Et_2Si(C_5H_4)(C_5Me_4)M$}$_2$(μ-H)$_2$[8] (M = Y, Lu), but in contrast to the reactivity observed for the insertion of α-olefins into the related compound [{(η^5-C_5Me_4)$SiMe_2$(η^1-$NCMe_3$)}$Sc(PMe_3)]_2$(μ-H)$_2$[4a,b] to give the bis(μ-alkyl) species [{(η^5-C_5Me_4)$SiMe_2$(η^1-$NCMe_3$)}Sc(μ-CH_2CH_2R)]$_2$ (Scheme 5), we have observed only single-insertion μ-H, μ-alkyl products from α-olefin insertion into the Y–H bond of 4.

The C_5Me_5 ligands in 6 are magnetically equivalent at all accessible temperatures (^{1}H NMR, −85 to +25 °C). This is due to fast μ-propyl group rotation about the μ-H, μ-C_{α} axis on the NMR time scale in this temperature range. Rotation barriers about monomeric transition-metal–carbon σ-bonds are typically 3–10 kcal/mol,[24] dependent on the steric congestion provided by the ligands and alkyl group. Facile μ-alkyl rotation raises the idealized sym-

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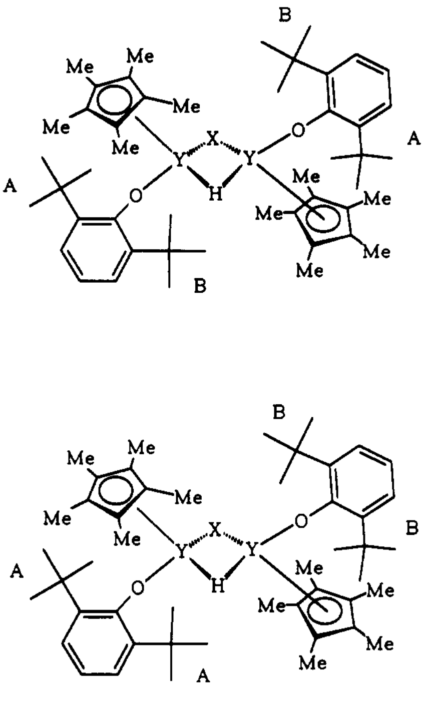
(20) Nb, Ta alkoxides: (a) Lubben, T. V.; Wolczanski, P. T.; Van Duyne, G. D. *Organometallics* 1985, *4*, 977. (b) LaPointe, R. E.; Wolczanski, P. T.; Van Duyne, G. D. *Organometallics* 1985, *4*, 1810. (c) LaPointe, R. E.; Wolczanski, P. T.; Mitchell, J. F. *J. Am. Chem. Soc.* 1986, *108*, 6382. (d) LaPointe, R. E.; Wolczanski, P. T. *J. Am. Chem. Soc.* 1986, *108*, 3535. The cone angle of silox (125°)[20a] is smaller than that of C_5H_5 (136°).[20e] (e) Tolman, C. A. *Chem. Rev.* 1977, *77*, 313 (but see discussion in ref 20a). Ti alkoxides: Latesky, S. L.; Keddington, J.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* 1985, *24*, 995. Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* 1991, *10*, 15 and references therein.

(21) (a) Olah, G. A.; Prakash, G. K. S.; Williams, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry*; Wiley: New York, 1987. (b) Busch, M. A.; Harlow, R.; Watson, P. L. *Inorg. Chim. Acta* 1987, *140*, 15. (c) Burns, C. J.; Andersen, R. A. *J. Am. Chem. Soc.* 1987, *109*, 5853. (d) Waymouth, R. M.; Santarsiero, B. D.; Grubbs, R. H. *J. Am. Chem. Soc.* 1984, *106*, 4050. Waymouth, R. M.; Santarsiero, B. D.; Coots, R. J.; Bronikowski, M. J.; Grubbs, R. H. *J. Am. Chem. Soc.* 1986, *108*, 1427.

(22) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* 1979, 54.

(23) (a) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* 1977, *99*, 5225. (b) Calvert, R. B.; Shapley, J. R.; Schultz, A. J.; Williams, J. M.; Suib, S. L.; Stucky, G. D. *J. Am. Chem. Soc.* 1978, *100*, 6240. (c) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* 1978, *100*, 7726. (d) Dawkins, G.; Green, M.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* 1982, 41. (e) Casey, C. P.; Fagan, P. J.; Miles, W. H. *J. Am. Chem. Soc.* 1982, *104*, 1134.

(24) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* 1975, *97*, 4292. Jordan, R. F.; Tsang, E.; Norton, J. R. *J. Organomet. Chem.* 1978, *149*, C53. McCormick, F. B.; Angelici, R. J.; Pickering, R. A.; Wagner, R. E.; Jacobsen, R. A. *Inorg. Chem.* 1981, *20*, 4108.



X = CH_2CH_2R or $CCSiMe_3$

Figure 1.

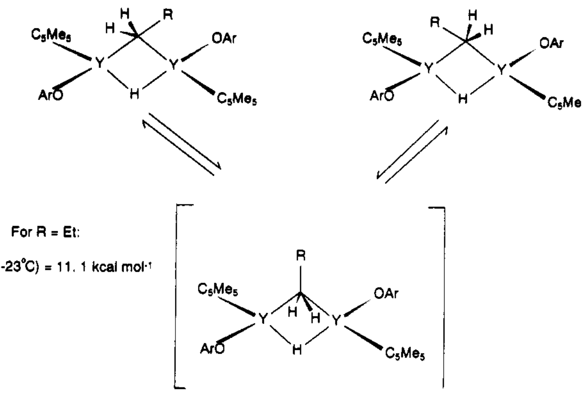
metry in 6 (and likewise in 5, 7, and 8 as well as the μ-acetylide 9 (vide infra)) from C_1 to C_2 (assuming M–O–C_{ipso} = 180°). The phenoxide ${}^tBu$ groups are, however, not equivalent, due to the absence of a plane of symmetry; hence, two sets of CMe_3 resonances are observed. Restricted rotation (assuming, as is probable, that inversion at the alkoxide oxygen is rapid) about the Y–OAr bond is sufficient to render the ${}^tBu$ groups on the *same* phenoxide ligand equivalent (i.e. Figure 1, upper molecule).

The phenoxide ${}^tBu$ groups display a temperature-dependent fluxionality. Activation parameters for *tert*-butyl group equilibration in 6 were calculated on the basis of coalescence (T_c = ca. 180 K, $\Delta\nu$ = 28 Hz, C_7D_8, 300 MHz) for a simple two-site exchange model. $\Delta G^{\ddagger}$(at ca. −93 °C) = 9.0 ± 0.5 kcal mol^{-1}.

The μ-alkyls 5-8 all show diastereotopic α-CH_2 resonances, confirming idealized molecular C_2 (rather than C_s imposed by a *cis* geometry) symmetry and indicating a mutually *trans* geometry for the C_5Me_5 and phenoxide ligands. Activation parameters for exchange of the two diasterotopic $C_{\alpha}H_2$ hydrogens in 6 were calculated on the basis of coalescence for a simple two-site exchange model; $\Delta G^{\ddagger}$(at −23 °C) = 11.1 ± 0.5 kcal mol^{-1}. This value is similar to that calculated for $\{Et_2Si(C_5H_4)(C_5Me_4)M\}_2(\mu$-$H)(\mu$-$CH_2CH_2R)$ (M = Y, Lu).[8] The equilibration of the diastereotopic $C_{\alpha}H_2$'s is not achieved by μ-propyl group rotation about the μ-H, μ-C_{α} vector, and hence another intramolecular mechanism, inversion at a planar μ-C_{α}, was invoked[8] (Scheme 6).

The geometrical consequences of μ-alkyl group inversion would seem to require a relatively obtuse M(μ-alkyl)M angle, with the bulky ML_n groups preferred to occupy the axial, rather than apical, positions. Electron-deficient main-group alkyls usually (but not always) bridge through bent rather than linear M–C–M bonds.[21] It is thus pertinent that M(μ-C_{α})M angles in crystallographically characterized μ-alkyl groups in dimeric d^0 and f-element species fall into two categories. $[M(C_5H_5)_2(\mu$-$Me)]_2$ (M = Y (87.7°), Yb (86.6°)),[22] $[Y(1,3$-$C_5H_3Me_2)_2(\mu$-$Me)]_2$ (86.6°),[19] $[\{(\eta^5$-$C_5Me_4)SiMe_2(\eta^1$-$NCMe_3)\}Sc]_2(\mu$-$CH_2CH_2Me)_2$ (angle not given),[4b] and $\{Et_2Si(C_5H_4)(C_5Me_4)Y\}_2(\mu$-$H)(\mu$-$CH_2CH_3)$ (84.7°)[8] possess highly bent geometries. In contrast, the dative asymmetric[21b] methyl bridges in $Lu(C_5Me_5)_2(\mu$-$Me)Lu(C_5Me_5)_2Me$ (170°)[1d] and $(C_5Me_5)_2Yb(\mu$-$Me)Be(C_5Me_5)$ (177°),[21c] as well as the symmetric[21b] methyl bridge in $\{(C_5H_5)_2Zr(OCCHCH_2CMe_3)\}_2(\mu$-$Me)(\mu$-$AlMe_2)$ (147°),[21d] are significantly closer to linear. Other mechanistic possibilities do not, however, appear feasible. For example, deinsertion, rotation of the coordinated olefin, and insertion would imply $C_{\beta}H_2$ also losing diastereotopicity. Furthermore, we have already demonstrated that β-H elimination from Y(μ-alkyl)(μ-H)Y is not facile. It is not mechanistically possible to differentiate between intramolecular inversion at planar C_{α} in the M(μ-alkyl)(μ-H)M moiety[8] and rapid (on the NMR time scale so that J_{YH} coupling, if present, is retained) μ-alkyl ⇄ terminal alkyl exchange with C_{α} inversion occurring in the M(μ-H)M(terminal alkyl) mode. Although this mechanism avoids invoking possibly unfavorable M(μ-C_{α})M geometries, it demands that inversion occurs at terminal M–CH_2R, thus invoking an extremely high-energy square-planar C_{α}. In this context, it is pertinent to note the mechanistic studies of Gladsyz[25] on stereospecific α-hydride abstraction in $(C_5H_5)Re(NO)(PPh_3)CH_2R$ and those by Davies[26] on stereocontrol by $(C_5H_5)Fe(CO)(PPh_3)$-CH_2R. These chiral auxiliaries confer diastereotopicity to the alkyl α-CH_2 protons. No evidence for equilibration of these protons has been reported. On this basis, metal-mediated inversion at terminal M–CH_2R can hence be effectively discounted as a possible equilibration mechanism in μ-alkyls 5-8.

Scheme 6



Bridged alkyl species 5-8 are stable to β-H elimination. Heating at 75 °C in C_6D_6 does not give 4 and free olefin, as anticipated, but instead yields $Y(C_5Me_5)(OAr)_2$ (in low yield) as the only identifiable yttrium-containing product. Under comparable conditions (80 °C, 16 h), only 5% of 4 decomposes to give $Y(C_5Me_5)(OAr)_2$.

In all reactions of 4 with terminal olefins there is no evidence for μ-isoalkyl species. The scope of the insertion process into Y–H in 4 and the steric influence of the ancillary ligands were explored. No reaction is observed between 4 and excess $PhCH{=}CH_2$ or $Me_3SiCH{=}CH_2$ (10

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(25) Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strause, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865. O'Conner, E. J.; Kobayashi, M.; Floss, H. G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 4837. Kiel, W. A.; Lin, G.-Y.; Bodner, G. S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 4958.

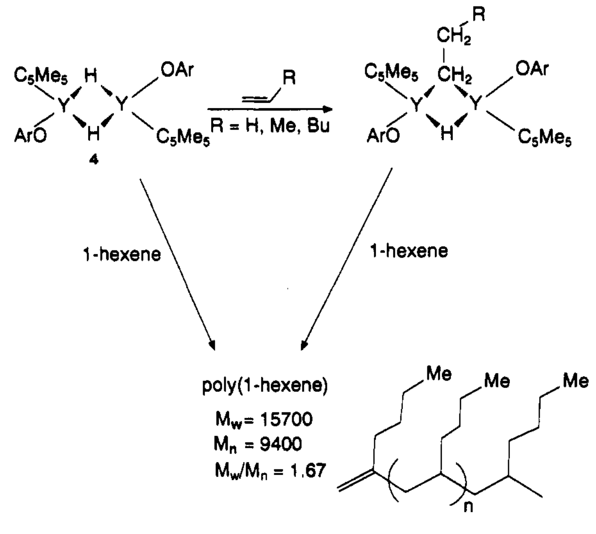
(26) Davies, S. G.; Dordor-Hedgecock, I. M.; Sutton, K. H.; Whittaker, M. *J. Am. Chem. Soc.* **1987**, *109*, 5711.

equiv, 25 °C, C_6D_6), demonstrating the steric demands of the ancillary ligand sphere. **4** is also recovered unchanged from dissolution in the substituted terminal olefin 2-methyl-1-butene (20 °C, 16 h); putative $(C_5Me_5)Y(OAr)CH_2CHMeEt$ or $[(C_5Me_5)Y(OAr)]_2(\mu\text{-}H)(\mu\text{-}CH_2CHMeEt)$ species are not formed. This indicates that secondary reactions in the polymerization of α-olefins do not occur. **4** does not react with an excess of the internal olefin *trans* 3-hexene (70 °C, C_6D_6, 16 h); insertion and/or isomerization to **8** do not occur, presumably due to unfavorable steric interactions of the internal olefin with Y–H.

***α*-Olefin and Diene Polymerization by $[Y(C_5Me_5)(OAr)]_2(\mu\text{-}H)(\mu\text{-alkyl})$.** The reaction of **4** with C_2H_4 to give **5** and polyethene (PE) has been described above. While polymerization proceeds, **4** is converted relatively slowly (from μ-H intensities of **4** and **5**; $\ll$1 bar C_2H_4, C_6D_6, 1 h) to **5**, which is itself only slowly consumed in the polymerization. This suggests that the rate of propagation is fast, relative to the rate of initiation (vide infra). The formation of PE was observed visibly, concomitant with the disappearance (^{1}H NMR) of dissolved C_2H_4. Only **5**, and no other μ-alkyl species, is observed (^{1}H NMR) during polymerization; the characteristic triplet ($^3J_{HH}$) of a $Y(\mu\text{-}CH_2CH_2R)Y$ ($R = (CH_2CH_2)_nCH_2Me$) propagating chain does not replace the distinct quartet of $Y(\mu\text{-}CH_2Me)Y$ in **5**, despite the (presumably) small free energy difference between the μ-*n*-ethyl (**5**), μ-*n*-butyl (**7**), μ-*n*-hexyl (**8**), etc. propagating chains. It should be noted, however, that a clear example of chain extension, i.e. $M(\mu\text{-}CH_2R)(\mu\text{-}H)M \rightarrow M(\mu\text{-}CH_2CH_2CH_2R)(\mu\text{-}H)M$, in these (or any other) systems has not been unequivocably identified. In a separate experiment,[27] **4** slowly polymerized ethene to give polyethene with M_w = 224 300 and broad polydispersity (M_w/M_n = 5.7).[28] In comparison, M_w/M_n for 1-hexene polymerization is <2 (vide infra). Significantly, **5** does not react at all with excess propene (5 bar, 25 °C). Oligomerization/polymerization was not observed, and neither was μ-Et/μ-*n*-Pr alkyl exchange.

4 reacts with excess propene under relatively forcing conditions (5 bar, 16 h, 25 °C) in toluene to give only **6**, there being no oligomers or polypropene formed. To determine whether this lack of α-olefin polymerization activity was a concentration phenomenon, **4** was dissolved in liquid 1-butene (–15 °C for 17 h). When this mixture was warmed to 20 °C for 1 h to allow 1-butene to evaporate, ^{1}H NMR analysis showed **7** as the major product.[30] No oligo-/polymerization occurred (under these conditions).[30] The presence of **7** indicates that the lack of polymerization activity is not decomposition related.

Scheme 7



Surprisingly, in contrast to the results above, dissolution of **4** in neat 1-hexene at 20 °C (hence giving **8** (and only **8**) in situ, vide supra, confirmed by NMR monitoring) results in slow polymerization to yield poly(1-hexene) with M_w = 15 700, M_n = 9400, and M_w/M_n = 1.67.[31] This molecular weight distribution (M_w/M_n) suggests that only one active catalyst species is present and that chain transfer occurs. This was confirmed by a labeling experiment (vide infra). (M_w/M_n = 1 is indicative of a living polymerization; M_w/M_n = 2 is indicative of a single active species but with chain transfer occurring.) Poly(1-hexene) is extremely soluble in hexane and is a viscous oil. Its molecular weight implies that ca. 150 units are built into each chain. Consistent with this, very weak signals, attributable to geminally disubstituted olefinic end groups, were observed by ^{1}H NMR spectroscopy at δ 4.95. This is consistent with chain propagation by 1,2-addition and termination by β-H elimination. The ^{13}C NMR ($CDCl_3$, 25 °C) of poly(1-hexene) is surprisingly simple with polymer [mmmm][32] (>85%) resonances being observed at δ 14.49 (Me), 23.6 (CH_2), 29.06 (CH_2), 34.7 (CH_2), 32.7 (CH), and 40.47 (br, CH_2).

In studies[4e] with a bridging cyclopentadienyl ligand substituted to favor the *rac* isomer, the isospecific α-olefin

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[27] In the drybox, 35 mg of **4** was dissolved in 10 mL of toluene in a glass liner, and this was placed in a small autoclave (volume ca. 30 mL). The liner was pressurized with C_2H_4 (5 bar, 15 min) and the autoclave returned to the drybox and vented. The polyethene was separated by centrifuging, washed with hexane, and dried to give 0.035 g of polyethene (M_w = 126 900, M_n = 11 800, M_w/M_n = 10.8). The colorless toluene solution containing **4** and/or **5** was added to another glass liner; this was placed in the autoclave and the autoclave repressurized with ethene (5 bar, 1 h). Similar workup as above gave 0.11 g of polyethene. This procedure was repeated once more to give polyethene (M_w = 224 300, M_n = 39 100, M_w/M_n = 5.7). The colorless toluene solution was then stripped. ^{1}H NMR analysis (C_6D_6) showed that all of **4** had been consumed. There was no indication of catalyst decomposition. Only **5** and a small quantity of an as yet unidentified dimeric yttrium hydride species with a characteristic ^{1}H NMR resonance at δ 4.79 (t, $^1J_{YH}$ = 43 Hz, μ-H) were observed.

[28] Note that rapid propagation relative to the rate of initiation cannot be used to explain a broad M_w/M_n value, since statistical analysis has shown, albeit for systems in which chain transfer is negligible, that even for $k_{propagation}/k_{initiation} = 10^6$, M_w/M_n is still <1.4: Gold, L. *J. Chem. Phys.* **1958**, *28*, 91. With slow initiation, a broader molecular weight distribution is to be expected, since molecules initiated early will cause a disproportionate degree of propagation, leading to high-molecular-weight products. Termination by β-H elimination and chain transfer will tend to exacerbate M_w/M_n broadening. The effect of (very slow) initiation on oligomer distribution was aptly depicted using $(C_5Me_5)_2ScR$ (R = Me, Et, *n*-Pr) for the low-temperature (–78 °C) living oligo/polymerization of ethylene at very low monomer conversion.[3d]

[29] The difficulties associated with propene polymerization at low pressures due to its high volatility and relatively low solubility at 25 °C have already been alluded to.[4a] Neat 1-hexene is ca. 10 M; however, the concentration of 5 bar of propene in toluene is ca. 2 M.

[30] In the drybox, 45 mg of **4** was dissolved in 1 mL of C_7D_8 in a Schlenk-type tube equipped with an external cooling jacket. This was removed from the drybox and cooled to –30 °C by passing cold ethanol through the cooling jacket, and ca. 10 mL of 1-butene was added by condensation. After 17 h at –15 °C, the cooling unit was switched off and the excess 1-butene allowed to evaporate slowly. After 1 h at 20 °C, the reaction vessel was briefly evacuated to remove any remaining 1-butene and returned to the drybox. ^{1}H NMR analysis showed only **7** and a small quantity of an as yet unidentified Y_2 species with μ-H at δ 5.13 ($^1J_{YH}$ = 40 Hz).

[31] The broader M_w/M_n value for ethylene polymerization can be attributed to heterogenization due to precipitation of long-chain Y-alkyl species from solution.

[32] The polyhexene is >85% tactic. We assume it to be isotactic, as stated, rather than syndiotactic. Definitive differentiation between isotactic and syndiotactic polyhexene by their ^{13}C NMR chemical shifts in the same solvent has, to our knowledge, not been performed. See, for example: Asakura, T.; Demura, M.; Nishiyama, Y. *Macromolecules* **1991**, *24*, 2334. See also the supplementary material of ref 4e.

polymerization catalyst [*rac*-$Me_2Si(2\text{-}SiMe_3\text{-}4\text{-}^tBuC_5H_2)Y(\mu\text{-}H)]_2$ has recently been reported. This gave highly isotactic poly(α-olefins), with moderate molecular weights. For example, for polypropene $M_w = 9700$, $M_w/M_n = 2.32$, and 97% mmmm isotactic pentad fraction and for polyhexene $M_w = 24\,000$ and $M_w/M_n = 1.75$.

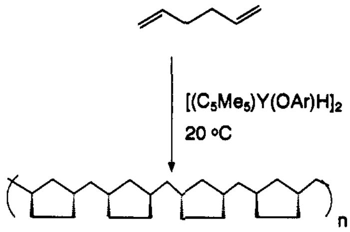
The μ-hydride dimer $[(C_5Me_4SiMe_2N^tBu)(PMe_3)Sc(\mu\text{-}H)]_2$[4a,b] containing the related cyclopentadienyl–amide ligand cleanly catalyzes the polymerization of α-olefins to relatively low molecular weight polymers, albeit rather slowly (*ca.* the same rate as with **4**). This reactivity is in contrast to that of $[\{Me_2Si(C_5H_3{}^tBu)_2\}ScH]_2$ or $\{Me_2Si(C_5Me_4)_2\}ScH(PMe_3)$, which catalytically dimerize α-olefins.[4b] As with **4**, it is difficult to assign this difference in reactivity to either steric or electronic effects. Clearly, chain termination (β-H elimination) and transfer is much more facile than in $[(C_5Me_4SiMe_2N^tBu)(PMe_3Sc(\mu\text{-}H)]_2$.[4a,b] The X-ray crystal structures of both $[(C_5Me_4SiMe_2N^tBu)(PMe_3)Sc(\mu\text{-}H)]_2$[4a,b] and the bis($\mu$-propyl) species $[(C_5Me_4SiMe_2N^tBu)(Sc(\mu\text{-}CH_2CH_2Me)]_2$[4b] have been determined.

The polymerization of 1-hexene by **4** and **8** is slow, due to the kinetically deactivated μ-H (and μ-alkyl), resulting in slow initiation. We therefore attempted to generate the putative monomeric terminal hydride $(C_5Me_5)Y(OAr)H$ in situ by hydrogenation of **3** in neat 1-hexene to circumvent problems associated with the kinetically deactivated μ-H. Thus, dissolution of **3** in neat 1-hexene under H_2[33] (3 bar, 25 °C) leads to virtually quantitative conversion to poly(hexene) with $M_w = 5500$, $M_n = 1570$, and $M_w/M_n = 3.49$. There is, however, no significant increase in rate from that obtained with **4**. No hexane (hydrogenation product) was observed (GLC). The lower M_w value and broader dispersity (in comparison with those for **4** (vide supra)) are ascribed to H_2 acting as a chain transfer agent and to slow in situ catalyst generation via $Y\text{–}CH(SiMe_3)_2$ bond hydrogenation (vide supra), respectively. The qualitatively similar rates between polymerization with **4** and in situ hydrogenation of **3** can be rationalized because bimolecular recombination of in situ generated "$Y(C_5Me_5)(OAr)H$" is not suppressed even in the presence of 15 equiv of THF. Only **4** is observed (cf. $Y(C_5Me_5)(OAr)Me(THF)_2$ (**13**), vide infra), demonstrating the strong propensity for Y–H stabilization through μ-H dimer formation.

Compounds **5-8** provide a unique opportunity to address the fundamental mechanistic question of the relative rates of olefin insertion into a metal–hydride bond (initiation), or a metal–alkyl bond (propagation), in the same well-defined single-component catalyst system. A prerequisite is that the two insertion pathways, into $Y(\mu\text{-}H)Y$ or into $Y(\mu\text{-alkyl})Y$, can be differentiated. This can be achieved by isotopic labeling. In $[Y(C_5Me_5)(OAr)]_2(\mu\text{-}D)(\mu\text{-}CH_2CHDMe)$ (**6-D**), the α-CH_2 ^1H NMR resonance is a distinctive *doublet* ($^3J_{HH}$) at δ –0.05, and the fate of μ-D (δ 5.3, t, $J_{YD} = 6$ Hz) can be determined by ^2D NMR spectroscopy. In addition, thermolysis of **6-D** (C_6D_6, 60 °C, 16 h) does not result in scrambling of the D label.

6-D reacts with neat 1-hexene to give poly(1-hexene). ^1H NMR spectroscopy indicates that the μ-CH_2CHDMe moiety is retained and that no μ-H "washes" into the μ-D site of **6-D**. However, ^2D NMR spectroscopy showed that, instead of μ-D being incorporated into the propagating alkyl chain, the μ-D resonance retains its intensity, indicating that very little **6-D** participates in the polymerization. It can be concluded that each "active" yttrium center produces ca. 20 polymer chains.[34,35] This is consistent with slow initiation, fast propagation, and chain transfer.

Scheme 8



The available evidence cannot rigorously exclude a rate-determining preequilibrium step, or prior reaction. It was therefore considered possible, despite only μ-hydrido μ-alkyl (**5-8**) species being observed, that preequilibrium dissociation to a low concentration of a catalytically active monomer (i.e. $Y(C_5ME_5)(OAr)X$ ($X = H$, CH_2R)) could be responsible for polymerization. However, the available evidence, i.e. irreversibility of propene insertion into $[Y(C_5Me_5)(OAr)(\mu\text{-}D)]_2$ (**4-D**), the lack of β-H elimination in isolated **5-8**, the propensity for Y–H stabilization by dimerization, and the lack of μ-Et/μ-*n*-Pr exchange on treatment of **5** with excess propene, suggests that this is highly unlikely. We can also effectively include a minor decomposition product being responsible. For example, although $[(C_5Me_5)_2MH]_2$ is an excellent ethylene polymerization and olefin hydrogenation catalyst,[2c] it reacts with α-olefins to form allylic organolanthanide products and olefinic dimers.

Dienes. The polymerization of (nonconjugated) dienes with **4** has also been investigated. **4** effects the catalytic cyclopolymerization[36] of 1,5-hexadiene (neat, 20 °C) to poly(methylene-1,3-cyclopentanediyl).[36,37] No clean (cyclopolymerization) reaction was observed with 1,6-heptadiene. Cyclopolymerization rather than cyclization indicates that further 1,5-hexadiene insertion into an [Y-CH_2-cyclopentane] intermediate is favored over β-H elimination (Scheme 8). This differentiating step between cyclopolymerization (formation of poly(methylene-1,3-cyclopentanediyl)) and β-H elimination (cyclization to

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(33) A "blank" experiment showed that **3** does not react with neat 1-hexene (days, 25 °C).

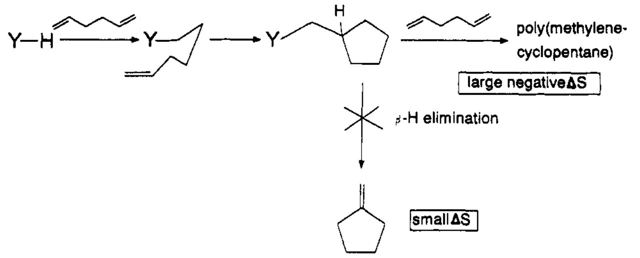
(34) **4** (20 mg, 12 μmol) affords ca. 200 mg (=20 μmol) of polyhexene (M_r ca. 10 000 from GPC) = 20 μmol. Assuming a (conservative) NMR detection limit of 5% (or better), this gives an upper limit for the number of active sites. Because of the ca. 1:1 mol:mol ratio of **4**:polyhexene, this infers that each active site affords >20 polymer chains.

(35) Note that the creation of only a small percentage of active sites has no influence on the living, or other, nature of the catalysis. Many examples of living polymerization, and hence M_w/M_n = ca. 1.05–1.2, are known where only a few percent of the added (pre)catalyst is active, e.g. propene polymerization by $V^{3+}/AlEt_2Cl$[35a] and the ROMP[35b,c] of cyclic olefins. (a) Doi, Y.; Ueki, S.; Keii, T. *Macromolecules* **1979**, *12*, 814. (b) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 3974. (c) Wu, Z.; Wheeler, D. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 146. Here, in the absence of PMe_3, the rate of propagation was much faster than the rate of initiation and chain termination resulted in broad polydispersity polymers using $W({=}CH^tBu)({=}NC_6H_3{}^iPr_2)(O^tBu)_2$ as catalyst.

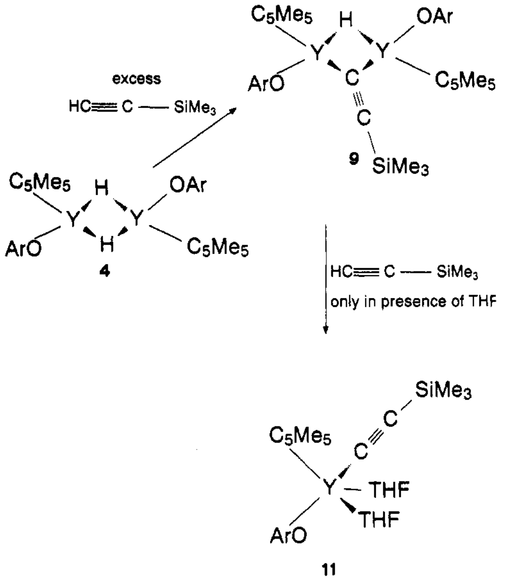
(36) (a) Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 6270. (b) Resconi, L.; Waymouth, R. M. *J. Am. Chem. Soc.* **1990**, *112*, 4953. (c) Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 91.

(37) **4** (30 mg, 35 μmol) was dissolved in 4 mL (2.77 g) of 1,5-hexadiene. After 20 h at 20 °C a copious white precipitate had formed. Excess 1,5-hexadiene was removed under vacuum, and after washing with hexane 2.6 g of poly(methylene-1,3-cyclopentanediyl) was isolated. ^{13}C NMR analysis and assignments agree with and were based on those in the literature.[36]

Scheme 9



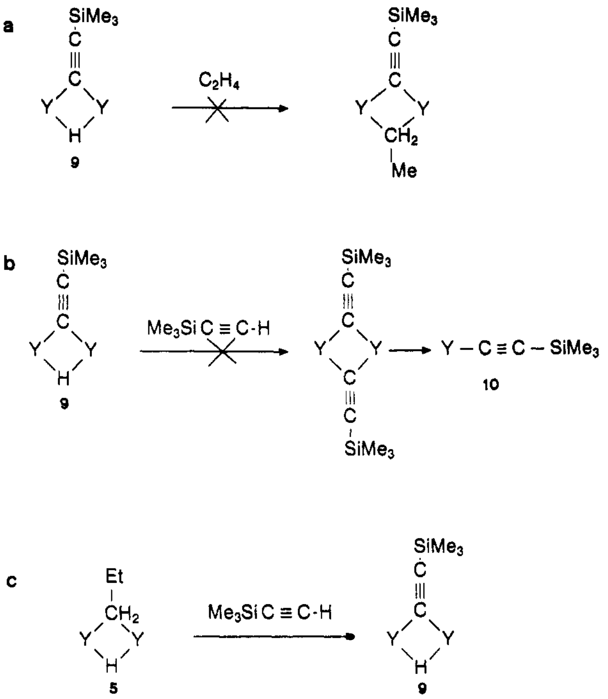
Scheme 10



methylenecyclopentane) is likely to be characterised by a large, negative ΔS and a small ΔS, respectively. These competitive pathways would thus be temperature dependent, with polymerization being favored at lower temperatures (Scheme 9). So far, we have not investigated this temperature-dependent competition. That a fine balance between cyclopolymerization and cyclization exists is demonstrated in that related $[Me_2Si(C_5H_3{}^tBu)_2ScH]_2$ and $Me_2Si(C_5Me_4)_2ScH(PMe_3)$[4b] catalytically cyclize a range of α,ω-dienes to methylenecycloalkanes.

^{13}C NMR analysis ($C_2D_2Cl_4$, 80 °C) shows a slight selectivity[36b] (at this polymerization temperature) towards *trans* five-membered rings (*trans*:*cis* ratio 1.0:0.8). Thermal gravimetric analysis shows that this semicrystalline polymer is quite thermally stable, showing only a gradual weight loss of ca. 1% up to 350 °C, with complete and clean decomposition (no residue) occurring at 435 °C. By DSC its melting point and onset of crystallization out the melt are reversible and constant and occur at 115 and 92 °C, respectively. Measured heat flows were also reproducible, indicating a stable polymer, and are 16.7 J g^{-1} for melting and 10.4 J g^{-1} for crystallization from the melt. A T_g value was not found (temperature range 20 °C to T_m).

Scheme 11



Reaction with Terminal Acetylenes. A different reaction pathway is observed between 4 and the terminal acetylene $Me_3SiC{\equiv}CH$. Instead of insertion into an Y—H bond, protonolysis occurs with loss of H_2 (^1H NMR) to give the μ-acetylide $[Y(C_5Me_5)(OAr)]_2(\mu\text{-}H)(\mu\text{-}C{\equiv}CSiMe_3)$ (**9**) (Scheme 10). Acetylide bridges are common structural types in organolanthanide chemistry.[38] The μ-acetylide carbons resonate at δ 165.7 (t, $^1J_{YC}$ = 25.0 Hz, μ-C_α) and 136.1 (t, $^2J_{YC}$ = 2.7 Hz, C_β). Although the geometry of **9** (C_5Me_5 *trans* or *cis* to each other in the dimer) cannot be determined by NMR spectroscopy, we assume the C_5Me_5 ligands to be mutually *trans* (idealized C_2 symmetry instead of C_s for *cis*) as in **5**-**8**. In **9**, which possesses symmetrical μ-acetylide and μ-H bridges (giving idealized C_2 molecular symmetry), two ^tBu resonances are observed in the ^{13}C NMR spectrum (see Experimental Section). As in **5**-**8**, asymmetry is caused by the second bridging group X (X $\neq$ H) in $Y(\mu\text{-}H)(\mu\text{-}X)Y$.

In compounds **5**-**9**, the second μ-H is significantly kinetically deactivated. For example, ethylene (10 bar, 25 °C) does not insert into the μ-H group of **9** (Scheme 11a).

9 also does not react with excess $Me_3SiC{\equiv}CH$ (5 equiv, 25 °C, 16 h), although $Y(C_5Me_5)(OAr)C{\equiv}CSiMe_3$ (**10**) can be prepared directly from $Y(C_5Me_5)(OAr)CH(SiMe_3)_2$ (**3**) and $HC{\equiv}CSiMe_3$ (Scheme 11b). **6** reacts with $Me_3SiC{\equiv}CH$, not to give putative $[Y(C_5Me_5)(OAr)]_2(\mu\text{-}CH_2CH_2Me)(\mu\text{-}C{\equiv}CSiMe_3)$ but to give **9**, the more basic μ-alkyl clearly being more susceptible to protonolysis than μ-H (Scheme 11c). **9** reacts with excess $Me_3SiC{\equiv}CH$, *only* in the presence of THF, to give the monomeric terminal acetylide $Y(C_5Me_5)(OAr)(C{\equiv}CSiMe_3)(THF)_2$ (**11**) (see Scheme 10).

To probe possible fragment redistribution and association of **4**, $Y(C_5Me_5)(OAr)C{\equiv}CSiMe_3$ (**10**) was considered to be a possible trap, giving **9** on trapping putative $Y(C_5Me_5)(OAr)H$ (but see attempted trapping with THF, vide supra). No reaction between the μ-H complex **4** and **10** (2 equiv) was observed at 60 °C.

Catalytic dimerization of terminal acetylenes to $H_2C{=}C(R)C{\equiv}CR$ by $M(C_5Me_5)_2CH(SiMe_3)_2$ (M = Y,[2b,39] La,[39] Ce[39]) (thus giving $M(C_5Me_5)_2C{\equiv}CR$ in situ) has been reported. **10** reacts slowly (weeks, 20 °C) with neat $Me_3SiC{\equiv}CH$ to give selectively only the head-to-head enyne

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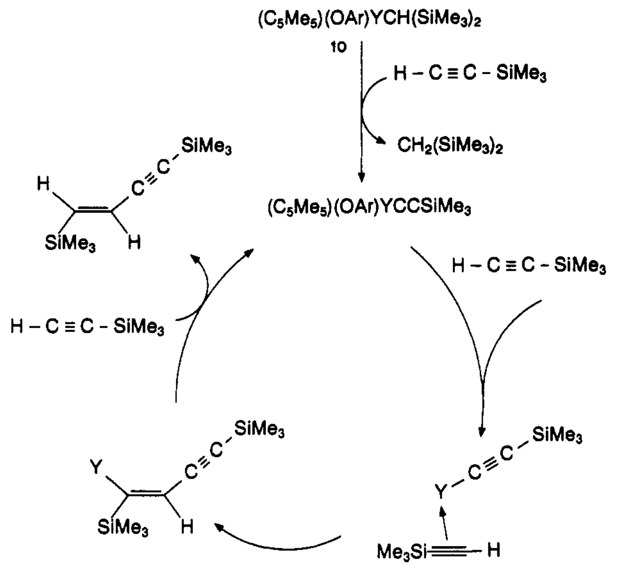
(38) Atwood, J. L.; Bloom, I.; Hunter, W. E.; Evans, W. J. *Organometallics* **1983**, *2*, 709 and references therein.

(39) Heeres, H. J.; Teuben, J. H. *Organometallics* **1991**, *10*, 1980. Heeres, H. J. Ph.D. Thesis, University of Groningen, Groningen, The Netherlands, 1990.

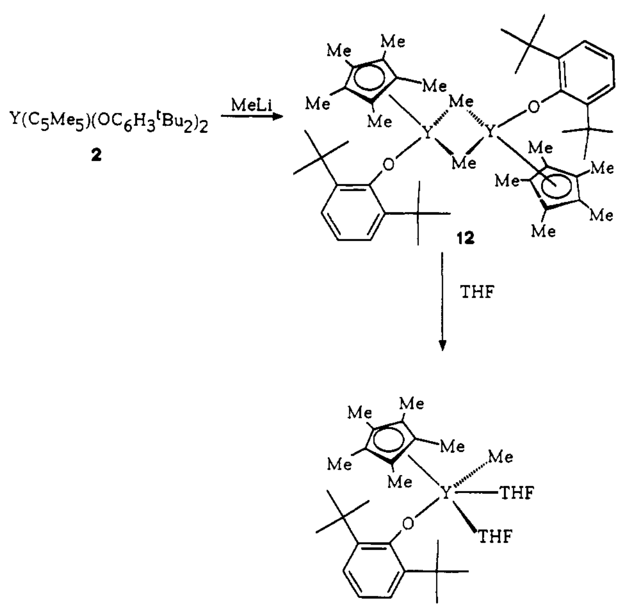
Scheme 12



trans-$Me_3SiCH{=}CHC{\equiv}CSiMe_3$ (Scheme 12). The absence of higher oligomers is ascribed to favorable C—H bond activation of RC≡CH, compared to its insertion into the Y—C σ-bond in the intermediate $(C_5Me_5)(OAr)Y{-}C(SiMe_3){=}CHC{\equiv}CSiMe_3$. For both steric and electronic reasons the small yttrium center favors this termination step rather than insertion. Interestingly, $(C_5Me_5)_2YCH(SiMe_3)_2$ as (pre)catalyst afforded[39] a mixture of the head-to-head (*trans*-$Me_3SiCH{=}CHC{\equiv}CSiMe_3$) and head-to-tail ($H_2C{=}C(SiMe_3)C{\equiv}CSiMe_3$) enyne dimers. This suggests that steric control plays less of a role here (steric repulsions between the alkyne substituent and ancillary ligands on yttrium would be minimized by head-to-tail insertion). A 2,1-insertion mode would be favored by OAr, presenting less steric hindrance than C_5Me_5. The 2,1-insertion mode of $HC{\equiv}CSiMe_3$ is electronically favored, as expected for the mode of polarization of its π^* orbital.[40]

Methyl Species. The α-olefin polymerization activity of the related compounds $[\{(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NCMe_3)\}Sc(PMe_3)]_2(\mu\text{-}H)_2$ and $[\{(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NCMe_3)\}Sc]_2(\mu\text{-}CH_2CH_2Me)_2$ has been recently reported.[4a,b] Synthesis of the model compounds $[Y(C_5R_5)_2(\mu\text{-}R')]_2$ (C_5R_5 = C_5H_5, C_5H_4Me, $C_5H_4SiMe_3$; R′ = Me, *n*-Bu)[3b,22] was taken as evidence to support polymerization via a $Y(\mu\text{-}R')_2Y$ intermediate. To determine if this was a possibility here, the bis μ-Me species $[Y(C_5Me_5)(OAr)(\mu\text{-}Me)]_2$ (**12**) was prepared from $Y(C_5Me_5)(OAr)_2$ and MeLi (1 equiv) (Scheme 13). This provides an opportunity to compare the reactivity of μ-H (in **4**) and μ-Me (in **12**) in a system possessing otherwise identical ligand environments. The μ-Me group in **12** resonates in the ^{1}H NMR at δ −0.08 (t, J_{YH} = 3.8 Hz) and at δ 30.92 (qt, J_{CH} = 104 Hz, J_{YC} = 28 Hz) in the ^{13}C NMR. These data are in agreement with those found for **6** and other symmetrically bridging μ-Me groups[3b,7,19,21] (vide supra) (Scheme 8). **12** slowly polymerizes ethylene and does not react with excess propene (ca. 10 equiv, 25 °C, days). A similar lack of reactivity for $[Sc(C_5Me_5)(O\text{-}3,5\text{-}C_6H_3{}^tBu_2)Me]_2$[41] was attributed to the presence of robust, apparently bridging phenoxides. In

Scheme 13



13

12, it is the *influence* of the terminal phenoxides that results in a kinetically deactivated μ-Me group. In marked contrast to the μ-H species **4** (vide supra) and $[Sc(C_5Me_5)(O\text{-}3,5\text{-}C_6H_3{}^tBu_2)Me]_2$,[41] μ-Me compound **12** is cleaved instantly with THF (4 equiv) to quantitatively afford $Y(C_5Me_5)(OAr)Me(THF)_2$ (**13**). The terminal methyl group resonates at δ 22.8 (dq, J_{YC} = 60 Hz, J_{CH} = 108 Hz). This chemical shift, J_{YC}, and J_{CH} are virtually identical with those for $Y(C_5Me_5)_2Me(THF)$,[42] suggesting that such parameters are not necessarily good indicators of metal environment.

In contrast to the synthesis of **12**, addition of 1.6 equiv of MeLi to ~**2** in hexane leads to substitution of *both* phenoxides and affords a white crystalline powder, whose ^{1}H NMR and elemental analysis (see Experimental Section) suggests the stoichiometry "$Y(C_5Me_5)Me_2$". The ^{1}H NMR spectrum (25 °C, C_6D_6) shows C_5Me_5 at δ 2.00. The yttrium-bound methyl groups are all equivalent (δ −0.40, *quartet*, $^2J_{YH}$ = 1.5 Hz). The ^{1}H NMR spectrum is temperature-independent (+25 to −80 °C, C_7D_8), the highly fluxional methyl groups all experiencing (time-averaged) coupling to a Y_3 framework. These data are suggestive of $[Y(C_5Me_5)Me_2]_3$ (**14**) (Scheme 14).

A related species, oligomeric $[(C_5Me_5)ScMe_2]_x$, has recently been reported.[41] **14** can also be synthesized by reaction of **12** with MeLi (1 equiv) in hexane. **14** reacts, however, with $LiOAr{\cdot}OEt_2$ in solvents in which they both dissolve (e.g. toluene),[43] to re-form **12** (and presumably MeLi). An analogous metathesis reaction has been observed between $(C_5Me_5)_2CeCH(SiMe_3)_2$ and LiCl.[2d]

Discussion

^{89}Y NMR Spectroscopy. The synthesis of a range of related pseudo-three-coordinate, highly soluble organoyt-

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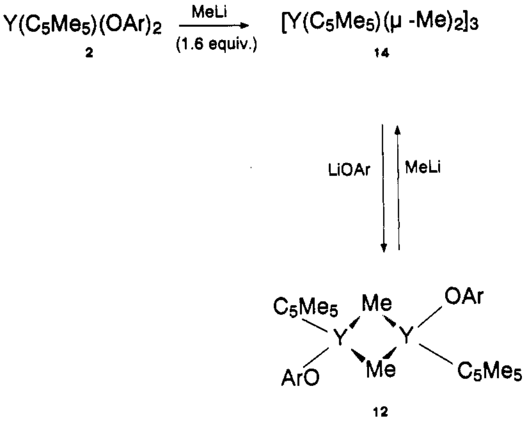
(40) Stockis, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2952.

(41) Piers, W. E.; Bunel, E. E.; Bercaw, J. E. *J. Organomet. Chem.* **1991**, *407*, 51. The spectroscopic data do not necessarily support the formulation $[(C_5Me_5)Sc(\mu\text{-}O\text{-}3,5\text{-}C_6H_3{}^tBu_2)(Me)]_2$, rather than the, in our opinion by analogy with **12**, more probable $[(C_5Me_5)Sc(O\text{-}3,5\text{-}C_6H_3{}^tBu_2)(\mu\text{-}Me)]_2$.

(42) den Haan, K. H.; Wielstra, Y.; Eshuis, J. J. W.; Teuben, J. H. *J. Organomet. Chem.* **1987**, *323*, 181.

(43) For this reason, **14** has to be separated from $LiOAr{\cdot}OEt_2$ by washing with benzene rather than toluene (see Experimental Section).

Scheme 14



trium compounds allowed the use of ^{89}Y NMR spectroscopy as a direct spectroscopic tool to probe the influence of the fundamentally important ligands C_5Me_5, alkoxide, and $CH(SiMe_3)_2$ on the shielding at the metal center. The nuclear properties[44a] of ^{89}Y (100% abundance, $I = 1/2$, and narrow line widths) partially offset its low sensitivity, long T_1's, and small and negative magnetic moment (magnetogyric ratio −0.1373, at 300 MHz for ^{1}H; ^{89}Y resonates at 14.697 MHz).

A few nonaqueous ^{89}Y NMR studies have been performed;[15,45] however, most studies have been confined to aqueous systems.[44] Our choice of suitable, related yttrium compounds was limited by our imposed prerequisite that they be sufficiently soluble in innocuous aromatic NMR solvents.[46] The ^{89}Y NMR spectra of compounds **1**, **2**, $Y(C_5Me_5)_2CH(SiMe_3)_2$, $Y\{CH(SiMe_3)_2\}_3$, and $Y(C_5Me_5)_2(OAr)$ were determined. These are listed in Table 1 together with the ^{89}Y NMR chemical shifts of the other three-coordinate (Lewis base free) yttrium species reported in the literature.

Table 1

compd	^{89}Y NMR chem shift[a] (ppm)	ref
$Y\{CH(SiMe_3)_2\}_3$	895.0[b]	this work
$Y(OAr)_3$ (**1**)	168.4	this work
$Y(C_5Me_5)_2CH(SiMe_3)_2$	78.9	this work
$Y(C_5Me_5)(OAr)_2$ (**2**)	21.0	this work
$Y(C_5Me_5)_2(OAr)$	−129.3	this work
$Y(C_5Me_5)(OAr)CH(SiMe_3)_2$ (**3**)	ns[c]	this work
$Y\{N(SiMe_3)_2\}_3$	570.0[d]	15
$Y(O\text{-}2,6\text{-}{}^tBu_2C_6H_2\text{-}4\text{-}Me)_3$	170.8[d]	15
$Y(OCMe_2{}^iPr)_3$	36.8[e]	45e
$Y(OCMeEt^iPr)_3$	45.6[e]	45e
$Y(OCEt_3)_3$	47.8[b]	45e

[a] In C_6D_6, peak widths fwhm = 2–10 Hz at 25 °C. [b] In $C_6D_5CD_3$ at 25 °C. [c] No signal observable. [d] In $CDCl_3$ at 23 °C. [e] In $C_6D_5CD_3$ at 37 °C.

Table 2. Group Contributions to ^{89}Y NMR Chemical Shift

group	contribn (ppm)
C_5Me_5	−100
$OCMe_2{}^iPr$	+12
$OCMeEt^iPr$	+15
$OCEt_3$	+16
OAr	+56
$O\text{-}2,6\text{-}{}^tBu_2C_6H_2\text{-}4\text{-}Me$	+57
$N(SiMe_3)_2$	+190
$CH(SiMe_3)_2$	+298

From Table 1 it can be seen that the ^{89}Y NMR resonance shifts to progressively higher field as σ-donating alkyl groups are sequentially subtituted by groups of increased electronegativity and π-donating ability. This trend can be correlated with increased ^{89}Y nuclear shielding. From the ^{89}Y NMR chemical shifts, group contributions to the ^{89}Y NMR chemical shift were calculated[47] (Table 2). The group contributions for C_5Me_5, OAr, and $CH(SiMe_3)_2$ display good additivity and internal consistency. There is a clear trend in decreasing electron donation to the yttrium center from the good σ-donor C_5Me_5 (−100 ppm) > alkoxides (ca. 15 ppm) > aryloxides (ca. 56 ppm) > amides (190 ppm)[15] > alkyls (300 ppm). Note that as the ^{89}Y NMR chemical shifts were measured with aqueous YCl_3 as reference at δ 0.0 ppm, these group contributions are relative to Cl at 0 ppm.[44] The correlation of metal electrophilicity with shielding and chemical shift is, admittedly, at best rather tenuous.[49] Although the diagnostic and predictive value of group contributions is now well established in ^{31}P NMR spectroscopy for substituted phosphines, the paucity of strictly comparable ^{89}Y NMR data makes the predictive value somewhat premature.[6,15,45] Although no quantitative significance should be attributed to these calculated group contributions, some qualitative states can be made. In terms of the known electron-donating ability (σ and π) of such ligands, this order fits with expectations. Correlation of the group contributions with the electrophilicity of the yttrium center are in good agreement with the observed[7e] effects of such ancillary ligands. Such correlations are, however, not valid for yttrium complexes of differing coordination number, as Lewis base adducts can result in both increased shielding[15] and deshielding[45e] of the yttrium nucleus. The order of group contributions alkoxides > amides > alkyls is in line with the experimentally determined BDE's. These have been shown to increase with the electronegativity of the coordinating atom with $E(M\text{-}OR) > E(M\text{-}NR_2) > E(M\text{-}CR_3)$.[7h,50] For example, in $(C_5Me_5)_2NdX$ the experimentally determined Nd–X

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(44) Harris, R. K.; Mann, B. E. In *NMR and the Periodic Table*; Academic Press: New York, 1978; p 199. Kidd, R. G. *Annu. Rep. NMR Spectrosc.* **1980**, *10A*, 1. Levy, G. C.; Rinaldi, P. L.; Bailey, J. T. *J. Magn. Reson.* **1980**, *40*, 167. Adam, R. M.; Fazakerley, G. V.; Reid, D. G. *J. Magn. Reson.* **1979**, *33*, 655. Kronenbitter, J.; Schwenk, A. *Z. Phys. A* **1977**, *280*, 117. Kronenbitter, J.; Schwenk, A. *J. Magn. Reson.* **1977**, *25*, 147. Rehder, D. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; p 482, and references therein.

(45) (a) Evans, W. J.; Meadows, J. H.; Kostka, A. G.; Closs, G. L. *Organometallics* **1985**, *4*, 324. (b) Reger, D. L.; Lindeman, J. A.; Lebioda, L. *Inorg. Chem.* **1988**, *27*, 1890. (c) Reger, D. L.; Lindeman, J. A.; Lebioda, L. *Inorg. Chem.* **1988**, *27*, 3923. (d) Fryzuk, M. D.; Haddad, T. S. *J. Am. Chem. Soc.* **1988**, *110*, 8263. (e) Bradley, D. C.; Chudzynska, H.; Hursthouse, M. B.; Motevalli, M. *Polyhedron* **1991**, *10*, 1049. (f) Poncelet, O.; Sartain, W. J.; Hubert-Pfalzgraf, L. G.; Folting, K.; Caulton, K. G. *Inorg. Chem.* **1989**, *28*, 263. (g) Solid-state CPMAS ^{89}Y NMR spectroscopy on organoyttrium complexes has recently been reported: Wu, J.; Boyle, T. J.; Shreeve, J. L.; Ziller, J. W.; Evans, W. J. *Inorg. Chem.* **1993**, *32*, 1130.

(46) Due to the oxophilicity of such organoyttrium species, and their strong tendency to form adducts with or react with THF, this was deemed an inappropriate solvent in which to study ancillary ligand contributions to the ^{89}Y chemical shift.

(47) For C_5Me_5 the range (−91 to −110 ppm) was calibrated using the phenoxide and alkyl contributions in $Y(OAr)_3$ and $Y\{CH(SiMe_3)_2\}_3$, respectively, as the basis set.

(48) The molecular structure of $(C_5H_5)_2Ti(OEt)Cl$ was used to argue that OEt is a better π-donor than Cl: Huffman, J. C.; Moloy, K, G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009.

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BDE's are as follows (kcal mol^{-1}): are X = O^tBu, 82.2; X = NMe_2, 47.4; X = $CH(SiMe_3)_2$, 47.5.[7a] The BDE's for the Sm analogues are almost identical.[7c]

Similar trends in chemical shift have been observed by Maatta[51] in a study of the ^{51}V NMR chemical shifts of the series of complexes $V(Ntolyl)X_3$. For example, in the series $V(Ntolyl)(CH_2SiMe_3)_3$, $V(Ntolyl)Cl_3$, $V(Ntolyl)(OC_6H_3Me_2)_3$, and $V(Ntolyl)(O^tBu)_3$ the ^{51}V NMR chemical shifts were reported[51] to be δ 1048, 305, −428, and −654 ppm, respectively. In an at least superficially related series of compounds, the substituent effect on the ^{11}B NMR resonance for three-coordinate, trigonal, diamagnetic boron compounds has been studied.[49]

Thermodynamic Effects of C_5R_5 versus Alkoxides. Although this order of M–X BDE's for electrophilic d^0 and f^0 metals has been well established,[7a,g] these results have been largely derived from thermochemical measurements on $(C_5Me_5)_2LnX$. To establish a correlation with our group contributions, we wish to compare the influence of the different ancillary ligands X on a constant M–Y in $L_2M(X)(Y)$. To date, very few such experiments have been performed.[7b,g,52] Hydrogenolysis of $Th(C_5Me_5)_2(Me)(OCH^tBu_2)$ has been shown to be 4000 times slower[7e] than for $Th(C_5Me_5)_2Me_2$. This was ascribed to a decrease in electrophilicity (relative to a methyl group) of thorium arising from alkoxide π-donation. In addition, the bond dissociation energy (BDE) of Th–R is, in general, 2–4 kcal mol^{-1} greater for the series $(C_5Me_5)_2ThR(OR')$ than for $(C_5Me_5)_2ThR_2$,[7b] D(Th–Et) for $(C_5Me_5)_2Th(O^tBu)Et$, $(C_5Me_5)_2ThEt_2$, and $(C_5Me_5)_2Th(Cl)Et$[7b] being 76.3, 73.5, and 72.2 kcal mol^{-1}, respectively. Clearly, the influence on D(Th–Et) by the different ancillary ligands is relatively small, varying by just 4.1 kcal mol^{-1}. Enhancement of Zr–H by alkoxide ligation was also observed[7g] in $(C_5Me_5)_2ZrH(X)$ (X = O^Bu, D(Zr–H) = 83.2; X = Ph, D(Zr–H) = 78.7; X = H, D(Zr–H) = 74.4 kcal mol^{-1}). The influence due to ancillary ligands on D(Zr–Me) was generally smaller.[7g] The strengthening of D(M–R) by alkoxide ligands was attributed[5f] to stabilization of M–R in the reductive homolytic bond dissociation process $L_nM{-}R(g) \rightarrow L_nM(g) + R^\bullet(g)$, rendering it more endothermic.

Much recent research in Nb, Ta, and Ti chemistry[20] has investigated the use of alkoxides as alternatives to the ubiquitous cyclopentadienyl ligand. The difference in steric hindrance between C_5Me_5 and OAr is difficult to quantify.[20a,e] C_5Me_5 clearly exerts a conical steric influence, whereas that for OAr is wedge-shaped. Nevertheless, similar series, $(C_5Me_5)_2YX$ versus $(C_5Me_5)Y(OAr)X$, have proven accessible.

The electronic properties of a hard electronegative alkoxide ligand are dissimilar to those of the good σ-donor pentamethylcyclopentadienyl ligands. In a study of electronegativity differences of metal fragments and the influence on M–C versus M–H bond strengths, it was proposed that the effective electronegativity of the metal center in C_5Me_5 early-transition-metal complexes is actually quite high.[53] The C_5Me_5 ligand is a good donor and is quite electronegative, the electron affinities of the cyclopentadienyl radical and $Cl^\bullet$ being similar, and hence the Sc–C_5Me_5 bond, like Sc–Cl, is expected to be very polar. A considerable degree of oxygen pπ to metal dπ bonding occurs at these electron-deficient d^0 metal centers, and, in the extreme case, an aryloxide may donate six electrons (but usually four electrons) to the metal, providing that the metal has available orbitals of the correct symmetry. This is reflected in fairly linear M–O–C angles and strong M–O bonds (cf. $(C_5Me_5)_2NdO^tBu$, 82.4 kcal mol^{-1};[7c] $(C_5Me_5)_2SmOCH^tBu_2$, 81.3 kcal mol^{-1};[7c] $(C_5H_5)Zr(OCH_2CF_3)_2$, 103.2 kcal mol^{-1};[7g] $(C_5H_5)Th(O^tBu)_2$, 124 kcal mol^{-1} [7f]). These large D(M–O) values are typical of such electropositive metals.[52] However, in absolute terms, in comparison to the inherent electronegativity of the alkoxide oxygen, alkoxide π-donation, although undoubtedly present,[7e,54] is likely to be a secondary effect and may not be especially significant in comparing relative electronic effects on the metal of the strong σ-donor C_5Me_5 versus alkoxide ligands (vide infra).[7b,e,54]

Although this may seem counterintuitive, recent studies on Al and Ga alkoxides do not support significant π-bonding.[55a] Evidence against Ti–N π-bonding in the formally 15-electron titanium amides $Ti(C_5Me_5)_2(NMePh)$ has been reported,[55b] although here the requisite orientation of the imido group is restricted due to steric interactions between the C_5Me_5 ligands and the bulky NMePh group. The influence of alkoxides as ancillary ligands on the propensity for olefin insertion and hydrogenolysis in f-element chemistry has been addressed thermochemically[7] as well as theoretically.[56]

Influence of Alkoxide Ancillary Ligands on *D*(M–C) and *D*(M–H). The relative thermodynamics of Ln–C versus Ln–H bond dissociation energies[7] suggests that chain termination (β-hydrogen elimination, chain transfer) reactions should be further inhibited or slow, in comparison with the rate of propagation, by replacement of C_5Me_5 by hard, electronegative ancillary ligands such as alkoxides. In addition, the relative inability of hydrides to disperse negative charge, the electropositivity of the proximate lanthanide or related metal center (M–H bond polarization), means that hydrides in these systems are constrained to a bridging mode. The hydride is constrained to bridge two yttrium centers in 4 because of the additional electropositivity of yttrium induced by the hard, electronegative ancillary alkoxide ligands (compared with its C_5Me_5 counterpart[7]). This enables μ-H to disperse its additional negative charge resulting from Y–H bond polarization. Similar trends have been observed in organoboron and aluminum main-group chemistry.[57] Trends in M–C versus M–H BDE's for d^0 and f^0 species can be ascribed to electronegativity differences[53] and (lack of) orbital repulsion,[7h] as well as π-bonding effects.

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Conclusions

In a comparison of $(C_5Me_5)(OAr)Y$ with $(C_5Me_5)_2Y$ and $(C_5H_5)_2Y$ coordination spheres, ^{89}Y NMR spectroscopy has been used as a direct spectroscopic probe to afford a semiquantitative indication of the relative effects of C_5Me_5 vs OAr ligands. Group contributions to the ^{89}Y NMR chemical shift were calculated to be −100 ppm for C_5Me_5, 56 ppm for OAr, and 298 ppm for $CH(SiMe_3)_2$.

Ethene polymerization with $[Y(C_5Me_5)(OAr)]_2(\mu\text{-}H)(\mu\text{-}CH_2Me)$ (**5**) and 1-hexene polymerization with $[Y(C_5Me_5)(OAr)]_2(\mu\text{-}D)(\mu\text{-}CH_2CHDMe)$ (**6-D**) indicate that polymerization is characterized by slow initiation and relatively fast propagation. The homogeneous, single-component α-olefin catalysts **4**, **6**, and **8** and nonconjugated diene polymerization catalyst **4** afford low-polydispersity poly(1-hexene) and poly(methylene-1,3-cyclopentanediyl). Significantly, no solvent is necessary; the catalysis can be performed conveniently in the neat olefin. Peculiarly, neither propene nor 1-butene could be polymerized by $[Y(C_5Me_5)(OAr)]_2(\mu\text{-}H)(\mu\text{-alkyl})$ (**5**-**8**). The reason for this difference in reactivity is unclear.

In contrast with the reactivity observed with $(C_5Me_5)_2Ln$ species, regioselective and irreversible α-olefin insertion into $Y(\mu\text{-}H)_2Y$ (**4**) affords dimeric *trans*-$Y(\mu\text{-alkyl})(\mu\text{-}H)Y$- (**5**-**8**) species. The phenoxides also stabilize the bridging alkyl groups in **5**-**8** toward β-H elimination. On purely steric considerations, the chemistry of $[Y(C_5Me_5)(OAr)]_2(\mu\text{-}X)(\mu\text{-}Y)$ (X = H; Y = alkyl; X = Y = H, Me) would be expected to be similar to the chemistry $(C_5Me_5)_2Y$, rather than that of its $(C_5H_5)_2Y$ analogue. However, reactivity is hampered by the kinetic inhibition of preequilibrium dissociation to kinetically more reactive monomeric species, not because of the limited steric hindrance afforded by the $(C_5Me_5)Y(OAr)$ coordination sphere but due to the additional electropositivity afforded by the alkoxides, thus necessitating dimeric stabilization of the basic hydride and alkyl groups. In contrast to $(C_5Me_5)_2Ln$ species we have not observed C–H σ-bond activation. The chemistry described here parallels more closely that of $[(C_5H_5)_2YMe]_2$[22] than that of $(C_5Me_5)_2Y(\mu\text{-}Me)YMe(C_5Me_5)_2$.[1]

Experimental Section

All experiments were performed under an argon atmosphere using Schlenk type glassware or in a Braun single-station drybox equipped with a −40 °C refrigerator under a nitrogen atmosphere. Elemental analyses were performed at Analytische Laboratorien, Elbach, West Germany. ^1H NMR spectra were recorded on Varian XL 200-MHz, Varian VXR 300-MHz, or Bruker 500-MHz spectrometers. ^{13}C, ^{29}Si, and ^{89}Y NMR spectra were performed on the VXR-300. Chemical shifts are reported in parts per million and referenced to the residual protons in deuterated solvents (for ^1H NMR). Coupling constants are reported in hertz. Coupling constants (J_{CH}) were obtained from gated (^1H NOE enhanced) spectra. Deuterated solvents were dried over 4-Å molecular sieves. Obvious multiplicities and routine coupling constants in the coupled ^{13}C NMR spectra are usually not given. Solvents were PA grade. Ether, hexane, and toluene were dried initially over sodium wire, and THF was dried over solid KOH; these were then distilled from the appropriate drying reagent (sodium benzophenone ketyl for ether and THF, sodium for hexane and toluene) under argon prior to use. $KCH(SiMe_3)_2$ was prepared from $LiCH(SiMe_3)_2$ by our published method.[58] $Y(OAr)_3$ (**1**)[11] was prepared from $Y\{N(SiMe_3)_2\}_3$.[59] 1-Hexene, 1,5-hexadiene, styrene, 2-methyl-1-butene, and (trimethylsilyl)acetylene were purchased from Aldrich and dried over 4-Å molecular sieves before use. Molecular weights and molecular weight distributions of poly(hexene) were measured using cyclohexane as eluent on a Waters 150 gel permeation chromatograph at KSLA. A poly(isoprene) standard was used as reference. GPC analysis of polyethene and poly(methylene-1,3-cyclopentanediyl) were performed at Laborataire des Hauts Polymerés, Catholic University of Louvain, Louvain de Neuve, Belgium, on a Waters 150C chromatograph in 1,2,4-trichlorobenzene at 135 °C. Some samples were apparently insufficiently soluble in 1,2,4-trichlorobenzene for GPC analysis. We suspect that this may be due to cross-linking caused by attempted polymer dissolution in $1,2,4\text{-}C_6H_3Cl_3$ at 160 °C under air. Thermal gravimetric analysis was performed on a Perkin-Elmer 7 series thermal analysis system at a temperature gradient of 10 °C min^{-1}.

Despite promising visual inspection of a number of crystals of compounds **4**, **5**, **8**, and **9**, analysis on the diffractometer revealed that none were suitable for single-crystal X-ray diffraction purposes.[60]

^{89}Y NMR Spectra. ^{89}Y NMR spectra were measured on a Varian VXR-300 at a transmitter frequency of 14.697 MHz using 10-mm tubes with a microcell insert. The yttrium compound (200–250 mg) was dissolved in approximately 0.8 mL of C_6D_6 giving ca. 0.3–0.4 M solutions. Because of the negative NOE effect of ^{89}Y the decoupler was not used. Assuming relaxation by a dipolar relaxation to ^1H, a theoretical maximum signal enhancement by an NOE of −9.17 is possible. Because of the long relaxation times of ^{89}Y, relaxation delays were typically 50 s. Shifts are with respect to 2 M YCl_3 in D_2O. A total of 200–1000 transients were accumulated. Negative shifts infer a more shielded environment than the reference, and so resonance occurs at higher field. Variation of the transmitter offset confirmed that the reported chemical shifts do not arise from foldovers. No ^{89}Y resonance could be observed for **3**, despite repeated attempts and changes in the transmitter offset. No variable-temperature experiments were, however, attempted.

KC_5Me_5. A suspension of 3.8 g (95 mmol) of KH (prewashed with hexane) and 13.0 g (95.5 mmol) of C_5Me_5H was stirred in 200 mL of THF at 80 °C for 4 h. The resulting white suspension was cooled and $KC_5Me_5{\cdot}THF$ isolated by filtration. This was washed with 2 × 100 mL of hexane and dried to give 21 g of $KC_5Me_5{\cdot}THF$. This was heated at 60 °C under vacuum until all coordinated THF had been removed (ca. 24 h was found to be necessary by periodic ^1H NMR monitoring) to afford 14 g of THF-free KC_5Me_5, yield 85%.

$Y(C_5Me_5)(OAr)_2$ (2). $Y(OAr)_3$ (**1**; 4.16 g, 5.91 mmol) and 1.03 g (5.91 mmol) of KC_5Me_5 were heated in 80 mL of toluene at 100 °C for 16 h. After the mixture was cooled, and toluene was removed under vacuum, the residue was extracted with 2 × 50 mL of hexane and the extracts were filtered and concentrated under vacuum to give 2.76 g of $Y(C_5Me_5)(OAr)_2$, yield 74%. The use of KC_5Me_5 gives higher yields than LiC_5Me_5, and the reaction proceeds more readily to completion. ^1H NMR (C_6D_6, 25 °C): δ 7.25 (d, 2H, H_m), 6.85 (t, 1H, H_p), 1.86 (s, 15H, C_5Me_5), 1.53 (s, 36H, CMe_3). ^{13}C NMR (C_6D_6, 25 °C): δ 160.6 (s, C_{ipso}), 136.4 (s, C_o), 125.5 (d, C_m), 121.4 (s, C_5Me_5), 117.4 (d, C_p), 35.2 (s, CMe_3), 32.5 (q, CMe_3), 11.6 (q, C_5Me_5). Anal. Calcd for $C_{38}H_{57}O_2Y$: C, 71.90; H, 9.05. Found: C, 71.80; H, 9.01.

$Y(C_5Me_5)(OAr)CH(SiMe_3)_2$ (3). $KCH(SiMe_3)_2$[48] (0.85 g, 4.26 mmol) was added as a solid to 2.7 g (4.26 mmol) of **2** dissolved in 80 mL of hexane at 25 °C. The resulting white suspension was stirred for 24 h at 25 °C, the solution was filtered, and the hexane was removed under vacuum. ^1H NMR showed that some **2** remained; hence, an additional 0.4 g of $KCH(SiMe_3)_2$ was added. After it was stirred for a further 24 h, the solution was centrifuged and extracted with 2 × 50 mL hexane, and the hexane extracts were concentrated under vacuum. Crystallization at −40 °C from 30 mL of hexane afforded 1.8 g of **3** as a white crystalline solid,

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yield 72%. It is extremely soluble in hexane. use of $LiCH(SiMe_3)_2$ gives an inferior yield (ca. 40%). ^1H NMR (C_6D_6, 25 °C): δ 7.25 (d, 2H, H_m), 6.85 (t, 1H, H_p), 1.91 (s, 15H, $C_5\mathit{Me}_5$), 1.48 (s, 18H, $C\mathit{Me}_3$), 0.26 (s, 18H, $Si\mathit{Me}_3$), −0.39 (d, 1H, $C\mathit{H}(SiMe_3)_2$). ^{13}C NMR (C_7D_8, −80 °C): δ 158.0 (s, C_{ipso}), 134.7 (s, C_o), 124.7 (d, C_m), 118.7 (s, C_5Me_5), 116.4 (d, C_p), 33.8 (s, $\mathit{C}Me_3$), 32.0 (d, $^1J_{YC}$ = 33 Hz), 30.9 (q, $C\mathit{Me}_3$), 10.4 (q, $C_5\mathit{Me}_5$), 2.7 (q, $Si\mathit{Me}_3$). ^{29}Si NMR (C_7D_8, −80 °C): δ −12.2 (s, $SiMe_3$, fwhm = 12 Hz). Anal. Calcd for $C_{31}H_{55}OSi_2Y$: C, 63.23; H, 9.41; Y, 15.10. Found: C, 63.06; H, 9.23; Y, 15.35.

[Y(C₅Me₅)(OAr)(μ-H)]₂ (4). $Y(C_5Me_5)(OAr)CH(SiMe_3)_2$ (3; 492 mg) was dissolved in ca. 15 mL of hexane in a 25-mL autoclave equipped with a removable glass liner, which was pressurized with 18 bar H_2. The mixture was stirred for 3 h at 25 °C. The autoclave was brought back into the drybox, the H_2 vented, and the hexane solution decanted from the crystalline white precipitate. 4 was washed with 2 × 2 mL of hexane, and the supernatant liquor and hexane washings were concentrated in vacuo to ca. 5 mL. Crystallization at −40 °C gave another 52 mg of 4, total isolated yield 60–70%. ^1H NMR (C_6D_6, 25 °C): δ 7.29 (d, 4H, H_m), 6.86 (t, 2H, H_p), 5.64 (t, 2H, J_{YH} = 35.2 Hz, $Y\mathit{H}$), 2.02 (s, 30H, $C_5\mathit{Me}_5$), 1.57 (s, 36H, $C\mathit{Me}_3$). Anal. Calcd for $C_{24}H_{37}OY$: C, 66.97; H, 8.66; Y, 20.65. Found: C, 66.90; H, 8.42; Y, 20.83.

Another product, of apparent stoichiometry $[Y(C_5Me_5)(OAr)]_2(\mu\text{-}H)_4$, is occasionally formed. The four (from integration) bridging hydrides are chemically equivalent at δ 4.25 (br t, 4H, J_{YH} = 26 Hz), with CMe_3 at δ 1.35. The identity of this species is, as yet, unknown. ^1H NMR (C_6D_6, 25 °C): δ 7.05 (d, 4H, H_m), 6.4 (t, 2H, H_p), 4.25 (br t, 4H, J_{YH} = 26 Hz, $Y(\mu\text{-}\mathit{H})Y$), 2.23 (s, 30H, $C_5\mathit{Me}_5$), 1.35 (s, 36H, $C\mathit{Me}_3$).

[Y(C₅Me₅)(OAr)]₂(μ-H)(μ-CH₂Me) (5). In the drybox, 0.08 g (93 μmol) of $[Y(C_5Me_5)(OAr)(\mu\text{-}H)]_2$ (4) was dissolved in 10 mL of hexane/toluene in a 50-mL Schlenk tube. C_2H_4 was added through a septum cap. Polyethene (PE) forms immediately as a white precipitate. After 5 min the solvent was removed in vacuo and 5 was separated from PE by extraction with toluene and crystallized from toluene/hexane by layered diffusion at −40 °C. ^1H NMR (C_6D_6, 25 °C): δ 7.35 (br "t", 4H, H_m), 6.85 (t, 2H, H_p), 5.35 (t, 1H, J_{YH} = 41.2 Hz, μH), 1.97 (s, 30H, $C_5\mathit{Me}_5$), 1.68 (br s, 18H, $C\mathit{Me}_3$), 1.54 (br s, 18H, $C\mathit{Me}_3$), 1.23 (t, 3H, 8.3 Hz, Me), −0.08 (q, 2H, 8.3 Hz, $C_\alpha\mathit{H}_2$). ^{13}C NMR (C_6D_6, 25 °C): δ 160.82 ("d", J_{YC} = 2.3 Hz, C_{ipso}), 137.8 and 136.7 (s, C_o), 125.8 and 125.0 (d, C_m), 120.23 (s, C_5Me_5), 117.9 (d, C_p), 35.4 and 33.9 (s, $\mathit{C}Me_3$), 31.8 (q, $C\mathit{Me}_3$), 23.0 (q, Me), 12.0 (q, $C_5\mathit{Me}_5$), μ-$\mathit{C}H_2$ not found. Anal. Calcd for $C_{50}H_{78}O_2Y_2$: C, 67.55; H, 8.84. Found: C, 67.29; H, 8.73.

[Y(C₅Me₅)(OAr)]₂(μ-H)(μ-CH₂CH₂Me) (6). $[Y(C_5Me_5)(OAr)(\mu\text{-}H)]_2$ (4; 200 mg) was dissolved in 15 mL of hexane in the glass liner of a small (total volume ca. 25 mL) autoclave. Propene (10 bar initial pressure) propene was added and the colorless solution allowed to stand for 16 h. (Little reaction occurs after 2 h at 5 bar.) The autoclave was returned to the drybox, the pressure released, and the autoclave opened. No propene oligomers or polypropene was observed. 6 can be crystallized from hexane at −40 °C to give a white crystalline solid. ^1H NMR (C_6D_6, 25 °C): δ 7.35 (br "t", 4H, H_m), 6.85 (t, 2H, H_p), 5.30 (t, 1H, J_{YH} = 39.5 Hz, μ-H), 1.97 (s, 30H, $C_5\mathit{Me}_5$), 1.65 (br s, 18H, $C\mathit{Me}_3$), 1.56 (br s, 18H, $C\mathit{Me}_3$), 1.32 (t, 3H, 7.3 Hz, Me), 0.94 (br, 2H, $C_\beta\mathit{H}_2$), 0.02 (t, 2H, 8.5 Hz, $C_\alpha H_2$). ^{13}C NMR (C_6D_6, 10 °C): δ 160.5 (virtual t, J_{YC} = 2.3 Hz, C_{ipso}), 137.6 and 136.1 (s, C_o), 127.4 (d, 154 Hz, C_m), 125.0 (d, 158 Hz, C_m), 119.9 (s, C_5Me_5), 117.8 (d, C_p), 48.5 (tt, J_{CH} = 105 Hz, J_{YC} = 19.7 Hz, $\mathit{C}_\alpha H_2$), 35.6 and 35.3 (s, $\mathit{C}Me_3$), 33.9 and 31.5 (q, $C\mathit{Me}_3$), 23.4 (tt, J_{CH} = 123 Hz, $^2J_{YC}$ = 2.0 Hz, $\mathit{C}_\beta H_2$), 21.0 (q, Me), 11.9 (q, $C_5\mathit{Me}_5$). Anal. Calcd for $C_{51}H_{80}O_2Y_2$: C, 67.84; H, 8.93. Found: C, 67.46; H, 8.78. The frequency differences between the phenoxide $C\mathit{Me}_3$ resonances in the ^1H NMR spectrum are 28 Hz at 298 K, 24 Hz at 243 K, 23 Hz at 238 K, 16.3 Hz at 213 K, and 9.6 Hz at 193 K.

[Y(C₅Me₅)(OAr)]₂(μ-D)(μ-CH₂CHDMe) (6-D). This was prepared analogously to 6. ^1H NMR (C_6D_6, 25 °C): δ 7.35 (br "t", 4H, H_m), 6.85 (t, 2H, H_p), 1.96 (s, 30H, $C_5\mathit{Me}_5$), 1.63 (br s, 18H, $C\mathit{Me}_3$), 1.54 (br s, 18H, $C\mathit{Me}_3$), 1.32 (d, 3H, 7.3 Hz, Me), 0.94 (br, 1H, $C_\beta\mathit{H}D$), 0.02 (d, 2H, 8.9 Hz, $C_\alpha\mathit{H}_2$). ^{13}C NMR (C_6D_6, 25 °C): C_5Me_5 and phenoxide resonances same as for 6. Pertinent resonances (δ) are 49.0 (t, J_{YC} = 19.8 Hz, $\mathit{C}_\alpha H_2$), 23.4 (br, fwhm = 50 Hz, $\mathit{C}_\beta HD$), and 21.0 (s, Me).

[Y(C₅Me₅)(OAr)]₂(μ-H)(μ-CH₂CH₂CH₂Me) (7). $[Y(C_5Me_5)(OAr)(\mu\text{-}H)]_2$ (4; 100 mg) was suspended in 3 mL of C_6D_6 in the glass liner of a small (total volume ca. 25 mL) autoclave. 1-Butene (1.5 bar) was added. After 16 h at 25 °C, the autoclave was returned to the drybox, the pressure released, and the autoclave opened. A clear colorless solution was observed. No butene oligomers or polybutene was observed by ^1H NMR inspection of the reaction solution. The C_6D_6 was removed in vacuo and the resulting white powder crystallized from ca. 3 mL of hexane at −40 °C to give 7 as a white crystalline solid. ^1H NMR (C_6D_6, 20 °C): δ 7.35 (br, 4H, H_m), 6.85 (t, 2H, H_p), 5.27 (t, 1H, J_{YH} = 40 Hz, μ-H), 1.96 (s, 30H, $C_5\mathit{Me}_5$), 1.63 (br s, 18H, $C\mathit{Me}_3$), 1.55 (br s, 18H, $C\mathit{Me}_3$), 1.2 (t, 3H, 7.3 Hz, Me), 0.94 (br, 2H, $C_\beta\mathit{H}_2$), −0.05 (br t, 2H, 8 Hz, $C_\alpha\mathit{H}_2$), other $C\mathit{H}_2$ groups not unambiguously located. ^{13}C NMR (C_6D_6, 20 °C): δ 160.63 (C_{ipso}), 137.7 and 136.2 (s, C_o), 127.5 (d, C_m), 125.0 (d, C_m), 119.9 (s, C_5Me_5), 117.8 (d, C_p), 45.55 (tt, J_{CH} = 105, J_{YC} = 21 Hz, $\mathit{C}_\alpha H_2$), 35.6 and 35.4 ($\mathit{C}Me_3$), 34.0 and 31.8 (q, $C\mathit{Me}_3$), 30.2 (t, CH_2), 14.2 (q, Me), 11.9 (q, $C_5\mathit{Me}_5$).

[Y(C₅Me₅)(OAr)]₂(μ-H)(μ-CH₂CH₂CH₂CH₂CH₂Me) (8). Excess 1-hexene (ca. 100 μL) was added to a suspension of 100 mg of $[Y(C_5Me_5)(OAr)(\mu\text{-}H)]_2$ (4) in 3 mL of C_6D_6. The colorless suspension was allowed to stand for 16 h and became a light yellow solution. Compound 8 is very soluble in hexane and was crystallized from a minimum of hexane at −40 °C. ^1H NMR (C_6D_6, 25 °C): δ 7.35 (br "t", 4H, H_m), 6.85 (t, 2H, H_p), 5.33 (t, 1H, J_{YH} = 40.2 Hz, μ-H), 2.005 (s, 30H, $C_5\mathit{Me}_5$), 1.67 (br s, 18H, $C\mathit{Me}_3$), 1.60 (br s, 18H, $C\mathit{Me}_3$), 1.5–1.3 (br, CH_2's), 1.02 (t, 3H, 7.5 Hz, Me), −0.08 (t, 2H, 7.3 Hz, $C_\alpha H_2$). ^{13}C NMR (C_6D_6, 25 °C): δ 160.52 (virtual t, J_{YC} = 2.3 Hz, C_{ipso}), 137.6 and 136.1 (s, C_o), 127.4 and 125.0 (d, C_m), 119.9 (s, C_5Me_5), 117.8 (d, C_p), 48.5 (t, J_{YC} = 19 Hz, $\mathit{C}_\alpha H_2$), 35.6 (s, $\mathit{C}Me_3$), 35.3 (s, $\mathit{C}Me_3$), 33.9 (s, $C\mathit{Me}_3$), 32.4 (d, J_{YC} = 2.4 Hz), 31.5 (s, $C\mathit{Me}_3$), 23.3 (s), 21.0 (s), 11.9 (s, $C_5\mathit{Me}_5$), the other *n*-hexyl resonances were not unequivocably located. Anal. Calcd for $C_{54}H_{86}O_2Y_2$: C, 68.63; H, 9.17. Found: C, 68.53; H, 9.27.

[Y(C₅Me₅)(OAr)]₂(μ-H)(μ-C≡CSiMe₃) (9). Excess $HC{\equiv}CSiMe_3$ was added to 4 in C_6D_6 at 25 °C, giving 9. The reaction is complete after 20 min. 9 does not react with excess $HC{\equiv}CSiMe_3$. Crystallization is from toluene/hexane. ^1H NMR (C_6D_6, 25 °C): δ 7.34 ("t", 4H, H_m), 6.88 (t, 2H, H_p), 5.09 (t, 1H, J_{YH} = 37 Hz, μ-H), 2.03 (s, 30H, $C_5\mathit{Me}_5$), 1.65 (s, 36H, $C\mathit{Me}_3$), 0.24 (s, 9H, $SiMe_3$). ^{13}C NMR (C_6D_6, 10 °C): δ 165.7 (t, J_{YC} = 25.0 Hz, μ-C_α), 160.52 (virtual t, J_{YC} = 2.5 Hz, C_{ipso}), 137.5 and 136.6 (s, C_o), 136.1 (t, J_{YC} = 2.7 Hz, C_β), 126.6 and 124.9 (d, C_m), 121.2 (s, C_5Me_5), 117.7 (d, C_p), 35.5 and 34.8 (s, $\mathit{C}Me_3$), 32.9 and 32.8 (q, $C\mathit{Me}_3$), 12.1 (q, $C_5\mathit{Me}_5$), 0.6 (q, $Si\mathit{Me}_3$). Anal. Calcd for $C_{53}H_{82}O_2SiY_2$: C, 66.51; H, 8.64. Found: C, 66.34; H, 8.50.

Y(C₅Me₅)(OAr)(C≡CSiMe₃) (10). Excess (0.2 mL) $HC{\equiv}CSiMe_3$ was added to 200 mg of 3 in 5 mL of toluene at 25 °C. This mixture was allowed to stand for 16 h, during which time a light yellow precipitate slowly formed. The supernatant liquor was pipetted off and the light yellow powder washed with 3 × 2 mL hexane. ^1H NMR (C_6D_6, 25 °C): δ 7.35 (d, 2H, H_m), 6.85 (t, 1H, H_p), 2.04 (s, 15H, $C_5\mathit{Me}_5$), 1.69 (s, 18H, $C\mathit{Me}_3$), 0.32 (s, 9H, $SiMe_3$). Anal. Calcd for $C_{29}H_{45}OSiY$: C, 66.14; H, 8.61. Found: C, 65.85; H, 8.34.

Y(C₅Me₅)(OAr)(C≡CSiMe₃)(THF)₂ (11). Excess (70 μL) $HC{\equiv}CSiMe_3$ was added to 70 mg (0.08 mmol) of 4 in C_6D_6 at 25 °C, giving 10 (as above). After 30 min, THF was added to yield 11. Crystallization from 5 mL of hexane at −40 °C gave 11 as large white crystals. ^1H NMR (C_6D_6, 25 °C): δ 7.35 (d, 2H, H_m), 6.85 (t, 1H, H_p), 3.73 (m, 8H, THF), 2.14 (s, 15H, $C_5\mathit{Me}_5$), 1.61 (s, 18H, $C\mathit{Me}_3$), 1.28 (m, 8H, THF), 0.37 (s, 9H, $SiMe_3$). Anal. Calcd for $C_{37}H_{61}O_3SiY$: C, 66.24; H, 9.17. Found: C, 65.99; H, 9.02.

[Y(C₅Me₅)(OAr)(μ-Me)]₂ (12). Compound 2 (1.00 g, 1.6 mmol) was dissolved in 40 mL of hexane and cooled to −40 °C.

MeLi (1.0 mL, 1.6 M in hexane, 1 equiv) was added and the colorless solution warmed to 20 °C to afford a white precipitate. After 1 h, all solvents were removed under vacuum (both the white precipitate and the hexane-soluble species are a mixture of $LiOAr{\cdot}OEt_2$ and 12). This residue was washed with 4 × 1 mL of C_6H_6 to separate $LiOC_6H_3{}^tBu_2{\cdot}OEt_2$ and leave behind sparingly soluble 12. (Attempted separation with toluene is ineffective. 12 is sparingly soluble in benzene but too soluble in toluene for efficient separation from $LiOAr{\cdot}OEt_2$.) 12 can be recrystallized from toluene/hexane; yield 0.35 g (50%). ^1H NMR (C_6D_6, 25 °C): δ 7.35 (d, 2H, H_m), 6.85 (t, 1H, H_p), 1.90 (s, 15H, $C35\mathit{Me}_5$), 1.55 (s, 18H, $C\mathit{Me}_3$), −0.076 (t, 3H, J_{YH} = 3.8 Hz, μ-*Me*). ^{13}C NMR (C_6D_6/CD_2Cl_2, 25 °C): δ 162.2 (s, C_{ipso}), 137.8 (s, C_o), 125.9 (d, 160 Hz, C_m), 121.1 (s, C_5Me_5), 117.6 (d, 158 Hz, C_p), 35.9 (s, $\mathit{C}Me_3$), 33.0 (q, $C\mathit{Me}_3$), 30.92 (qt, J_{CH} = 104 Hz, J_{YC} = 28 Hz, μ-*Me*), 12.4 (q, $C_5\mathit{Me}_5$). Anal. Calcd for $C_{50}H_{78}O_2Y_2$: C, 67.55; H, 8.84; Y, 20.00. Found: C, 67.28; H, 8.65; Y, 19.85.

$Y(C_5Me_5)(OAr)Me(THF)_2$ (13). 12 (0.100 g, 0.113 mmol) was suspended in 3 mL of C_6D_6. THF (50 μL, 0.614 mmol, 5.4 equiv) was added at 25 °C, whereupon the suspension dissolved rapidly (seconds). After 10 min, ^1H NMR analysis showed complete and quantitative conversion to 13. Recrystallization gives analytically pure 13. ^1H NMR (C_6D_6, 25 °C): δ 7.35 (d, 2H, H_m), 6.85 (t, 1H, H_p), 3.55 (m, 8H, THF), 2.02 (s, 15H, $C_5\mathit{Me}_5$), 1.54 (s, 18H, $C\mathit{Me}_3$), 1.24 (m, 8H, THF), −0.33 (d, 3H, J_{YH} = 2.3 Hz, Me). ^{13}C NMR (C_6D_6, 25 °C): δ 162.9 (d, J_{YC} = 5.0 Hz, C_{ipso}), 137.8 (s, C_o), 125.0 (d, 153 Hz, C_m), 118.0 (s, C_5Me_5), 116.5 (d, 158 Hz, C_p), 70.4 (t, 151 Hz, THF), 35.0 (s, $\mathit{C}Me_3$), 31.5 (q, $C\mathit{Me}_3$), 25.2 (t, 131 Hz, THF), 22.8 (dq, J_{YC} = 60 Hz, J_{CH} = 108 Hz, *Me*), 11.6 (q, $C_5\mathit{Me}_5$). Anal. Calcd for $C_{33}H_{55}O_3Y$: C, 67.33; H, 9.42. Found: C, 67.07; H, 9.01.

$[Y(C_5Me_5)(\mu\text{-}Me)_2]_3$ (14). 2 (270 mg, 0.46 mmol) was dissolved in 60 mL of hexane, and the solution was cooled to −40 °C. MeLi (0.46 mL of a 1.6 M solutionu, 1.6 equiv) was added by syringe. The solution was warmed to 25 °C, and after 1 h the hexane was removed under vacuum. ^1H NMR analysis of the resulting white solid shows only 14 (no 12 was formed) and $LiOAr{\cdot}OEt_2$. This was washed with 3 mL of C_6H_6 to remove $LiOAr{\cdot}OEt_2$ and give 14 as a white powder. Addition of 2 equiv of MeLi leads only to decomposition, and $LiOAr{\cdot}OEt_2$. 14 reacts with $LiOAr{\cdot}OEt_2$ to re-form 12 (and presumably MeLi). Thus, rapid manipulation of 14 in solvents in which both 14 and $LiOAr{\cdot}OEt_2$ dissolve, such as benzene or toluene, is recommended. ^1H NMR (C_6D_6, 25 °C): δ 2.00 (s, 15H, $C_5\mathit{Me}_5$), −0.403 (q, 6H, $^2J_{YH}$ = 1.5 Hz, μ-*Me*). 14 proved to be insufficiently soluble (in C_7D_8 or $C_2D_2Cl_4$, 25 °C) to obtain a reliable ^{13}C NMR spectrum, especially with respect to the *Me* resonance. Anal. Calcd for $C_{36}H_{63}Y_3$: C, 56.70; H, 8.33; Y, 34.97. Found: C, 56.42; H, 8.12; Y, 34.65.

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