Synthesis of Yttrium Complexes that Contain the $[NON]^{2-}$ Ligand, $[(t\text{-}Bu\text{-}d_6\text{-}N\text{-}o\text{-}C_6H_4)_2O]^{2-}$

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$Li_2[NON]$ ($[(t\text{-}Bu\text{-}d_6{-}N\text{-}o\text{-}C_6H_4)_2O]^{2-} = [NON]^{2-}$) reacts with YCl_3 in THF to give $[NON]YCl(THF)_2$, from which $[NON]Y[CH(SiMe_3)_2](THF)$ (**2a**) and $[NON]Y(CH_2SiMe_3)(THF)_2$ (**2b**) could be prepared straightforwardly. An X-ray structure of **2a** showed it to be a distorted five-coordinate species in which the nitrogen atoms of the $[NON]^{2-}$ ligand occupy (very approximately) apical sites in a trigonal bipyramid. Both **2a** and **2b** proved to be relatively unreactive toward molecular hydrogen or ethylene.

Introduction

In the past decade researchers have been searching for “single-site” group 4 metal olefin polymerization catalysts that do not contain one or more cyclopentadienyl rings.[1] “Noncyclopentadienyl” complexes that have catalytic potential include those that contain dialkoxide ligands,[2,3] diamido ligands,[4−26] or ligands that contain various combinations of nitrogen and oxygen atoms (quinolinato, benzamidinate, oxazoline, etc.).[27−34] Recent reports from our laboratory have described Ti and Zr complexes that contain the tridentate diamido/donor ligand $[(t\text{-}Bu\text{-}d_6{-}N\text{-}o\text{-}C_6H_4)_2O]^{2-}$ ($[NON]^{2-}$)[9,10] or Ti, Zr, and Hf complexes that contain the related ligand $[(ArylNCH_2CH_2)_2O]^{2-}$ ($[ArN_2O]^{2-}$ where Aryl = 2,6-$Me_2C_6H_3$ or 2,6-i-$Pr_2C_6H_3$).[14,15] In each system cationic zirconium monoalkyl complexes can be prepared from dialkyl precursors and shown to coordinate 1 equiv of a donor (e.g., a donor solvent) to give five-coordinate adducts. “$\{[NON]ZrMe(chlorobenzene)\}\{B(C_6F_5)_4\}$” is an especially interesting species in that it behaves as a catalyst for the living polymerization of 1-hexene at room temperature or below, in part as a consequence of loss of chlorobenzene to give a four-coordinate cation.[9,10] Therefore we became interested in the possibility of preparing a neutral group 3 metal $[NON]^{2-}$ complex that might be active for the polymerization of olefins. We were especially interested in yttrium, as “[NON]YR” and “$\{[NON]ZrR\}^+$” complexes would be isoelectronic. In this note we describe the synthesis of two yttrium monoalkyl complexes that contain the $[NON]^{2-}$ ligand and the X-ray structure of one of them.

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[1] For leading references see: (a) Martin, A.; Uhrhammer, R.; Gardner, T. G.; Jordan, R. F.; Rogers, R. D. *Organometallics* **1998**, *17*, 382. (b) Tjaden, E. B.; Swenson, D. C.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1995**, *14*, 371.

[2] van der Linden, A.; Schaverien, C. J.; Meijboom, N.; Ganter, C.; Orpen, A. G. *J. Am. Chem. Soc.* **1995**, *117*, 3008.

[3] Fokken, S.; Spaniol, T. P.; Kang, H.-C.; Massa, W.; Okuda, J. *Organometallics* **1996**, *15*, 5069.

[4] Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Organometallics* **1995**, *14*, 5478.

[5] Scollard, J. D.; McConville, D. H.; Payne, N. C.; Vittal, J. J. *Macromolecules* **1996**, *29*, 5241.

[6] Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008.

[7] Guérin, F.; McConville, D. H.; Vittal, J. J. *Organometallics* **1995**, *14*, 3154.

[8] Guérin, F.; McConville, D. H.; Vittal, J. J. *Orgaometallics* **1997**, *16*, 1491.

[9] Baumann, R.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 3830.

[10] Baumann, R.; Schrock, R. R. *J. Organomet. Chem.* **1998**, *557*, 69.

[11] Warren, T. H.; Schrock, R. R.; Davis, W. M. *Organometallics* **1996**, *15*, 562.

[12] Warren, T. H.; Schrock, R. R.; Davis, W. M. *Organometallics* **1998**, *17*, 308.

[13] Schattenmann, F.; Schrock, R. R.; Davis, W. M. *Organometallics* **1998**, *17*, 989.

[14] Schrock, R. R.; Schattenmann, F.; Aizenberg, M.; Davis, W. M. *Chem. Commun.* **1998**, 199.

[15] Aizenberg, M.; Turculet, L.; Davis, W. M.; Schattenmann, F.; Schrock, R. R. *Organometallics* **1998**, *17*, 4795.

[16] Clark, H. C. S.; Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B.; Wainwright, A. P. *J. Organomet. Chem.* **1995**, *501*, 333.

[17] Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B. *J. Chem. Soc., Dalton Trans.* **1995**, 25.

[18] Horton, A. D.; de With, J. *Chem. Commun.* **1996**, 1375.

[19] Horton, A. D.; de With, J.; van der Linden, A. J.; van de Weg, H. *Organometallics* **1996**, *15*, 2672.

[20] Canich, J. A. M.; Turner, H. W. Exxon, World Pat. Application 92/12 162, 1992.

[21] Aoyagi, K.; Gantzel, P. K.; Kalai, K.; Tilley, T. D. *Organometallics* **1996**, *15*, 923.

[22] Herrmann, W. A.; Denk, M.; Albach, R. W.; Behm, J.; Herdtweck, E. *Chem. Ber.* **1991**, *124*, 683.

[23] Male, N. A. H.; Thornton-Pett, M.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1997**, 2487.

[24] Friedrich, S.; Schubart, M.; Gade, L. H.; Scowen, I. J.; Edwards, A. J.; McPartlin, M. *Chem. Ber.-Rec.* **1997**, *130*, 1751.

[25] Tsuie, B.; Swenson, D. C.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1997**, *16*, 1392.

[26] Tinkler, S.; Deeth, R. J.; Duncalf, D. J.; McCamley, A. *Chem. Commun.* **1996**, 2623.

[27] Duchateau, R.; van Wee, C. T.; Meetsma, A.; van Duijnen, P. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2279.

[28] Bei, X.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 3282.

[29] Tsukahara, T.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 3303.

[30] Kim, I.; Nishihara, Y.; Jordan, R. F.; Rogers, R. D.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1997**, *16*, 3314.

[31] Duchateau, R.; Tuinstra, T.; Brussee, A. C.; Meetsma, A.; van Duijnen, P. T.; Teuben, J. H. *Organometallics* **1997**, *16*, 3511.

[32] Cozzi, P. G.; Floriani, C. *J. Chem. Soc., Perkin Trans.* **1995**, 2557.

[33] Cozzi, P. G.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1995**, *34*, 2921.

[34] Cozzi, P. G.; Gallo, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1995**, *14*, 4994.

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Results

Li_2[NON] reacts with an slight excess (10−15%) of YCl_3 in THF to give [NON]YCl$(THF)_2$ (**1**; eq 1) as a tan

$$\mathrm{Li_2[NON]} + 1.1\ \mathrm{YCl_3} \xrightarrow[75\%]{\mathrm{THF}} \underset{\mathbf{1}}{\mathrm{[NON]YCl(THF)_2}} \tag{1}$$

solid. Neither of the bound THF ligands could be removed upon heating **1** to 100 °C in vacuo (10^{-3} Torr, 14 h) or by refluxing a toluene solution of **1** for 1 day. NMR spectra of **1** are fully consistent with a molecule that has at least one plane of symmetry (equivalent THF ligands) on the NMR time scale, although they give no indication as to whether **1** contains the $[NON]^{2-}$ ligand in a *fac* or a *mer* arrangement about the metal.

Complex **1** reacts cleanly with LiCH$(SiMe_3)_2$ or $LiCH_2SiMe_3$ to give [NON]Y[CH$(SiMe_3)_2$](THF) (**2a**) or [NON]Y$(CH_2SiMe_3)(THF)_2$ (**2b**), respectively, in THF, diethyl ether, or toluene as the reaction solvent. We presume that compound **2a** binds only 1 equiv of THF for steric reasons. According to NMR spectra, **2a** and **2b** contain variable and nonstoichiometric amounts (0.1−1 equiv) of additional THF, ether, or toluene. On the basis of the structure of **2a** discussed below, where 0.5 equiv of toluene is found in the unit cell, most if not all of the “excess” solvent we believe is incorporated in the crystal lattice. Unfortunately, attempts to remove the solvent of crystallization in vacuo (10^{-3} Torr) led to appreciable decomposition, even within a few hours at room temperature for **2b**. Complex **2a** is more stable in vacuo than **2b**, but it decomposes appreciably within 12 h at room temperature or within 1−2 h at 80 °C. Therefore we were not been able to isolate pure complexes with a consistent known composition that were suitable for elemental analysis. Attempted high-resolution mass spectroscopy (EI) of **2a** and **2b** produced parent ions for the ligand only, consistent with the instability of these complexes in vacuo. Attempts to synthesize a THF-free form of **2a** by adding H_2[NON] to Y[CH$(SiMe_3)_2]_3$[35] in noncoordinating solvents led to pale orange solids that were sparingly soluble in toluene and that have not been identified.

Table 1. Crystallographic Data, Collection Parameters, and Refinement Parameters for [NON]Y[CH$(SiMe_3)_2$](THF)$(toluene)_{0.5}$

empirical formula	$C_{34.5}H_{57}N_2O_2Si_2Y$
fw	676.91
temp	183(2) K
wavelength	0.710 73
cryst system	monoclinic
space group	$P2_1/n$
unit cell dimens	$a = 9.242(8)$ Å $\alpha = 90°$ $b = 19.95(2)$ Å $\beta = 97.92(5)°$ $c = 20.140(14)$ Å $\gamma = 90°$
volume, Z	3678(5) Å^3, 4
density (calculated)	1.223 Mg/m^3
abs coeff	1.681 mm
F(000)	1444
cryst size	0.12 × 0.12 × 0.06 mm
θ range for data collection	1.44−20.00°
limiting indices	$-9 \le h \le 10, -22 \le k \le 20, -22 \le l \le 12$
no. of reflns collected	10 722
no. of ind reflns	3421 ($R_{int} = 0.1186$)
abs corr	semiempirical from ψ-scans
max. and min. transmission	0.4450 and 0.1731
refinement method	full-matrix least-squares on F^2
no. of data/restraints/param	3228/0/364
goodness-of-fit on F	1.070
final R indices [$I > 2\sigma(I)$]	R1 = 0.0892, wR2 = 0.2272
R indices (all data)	R1 = 0.1190, wR2 = 0.2630
extinction coeff	0.0015(8)
largest diff peak and hole	1.107 and −0.987 e Å^{-3}

Table 2. Bond Lengths (Å) and Angles (deg) for [NON]Y[CH$(SiMe_3)_2$](THF)$(toluene)_{0.5}$

Y−N(1)	2.294(9)	Y−N(2)	2.286(10)
Y−O(1)	2.337(8)	Y−O(2)	2.356(8)
Y−C(1)	2.422(11)		
N(1)−Y−N(2)	133.5(4)	N(2)−Y−C(1)	115.3(4)
N(1)−Y−O(1)	68.6(3)	O(1)−Y−O(2)	116.0(3)
N(1)−Y−O(2)	99.5(3)	O(1)−Y−C(1)	117.5(4)
N(1)−Y−C(1)	97.7(4)	O(2)−Y−C(1)	126.4(3)
N(2)−Y−O(1)	67.4(3)	C(2)−O(2)−Y	113.2(7)
N(2)−Y−O(2)	86.8(3)	C(5)−O(2)−Y	138.6(8)
Y−C(1)−Si(1)	123.4(6)	Si(1)−C(1)−Si(2)	116.1(6)
Y−C(1)−Si(2)	116.0(5)		
N(2)/Y/O(1)/N(2)[a]	165		
O(1)−Y−N(2)−C_{ipso}[a]	22		
O(1)−Y−N(1)−C_{ipso}[a]	19		

[a] Determined from a Chem 3D model.

An X-ray structure of **2a** showed it to be a distorted five-coordinate species in which the nitrogen atoms of the $[NON]^{2-}$ ligand occupy (very approximately) apical sites in a trigonal bipyramid (Tables 1 and 2; Figure 1). (The 0.5 equiv of toluene found in the structure is not near the metal; see Supporting Information.) The Y-ligand bond lengths are typical of those in related Y complexes.[27,31,36,37] All are approximately 0.1 Å or more longer than in [NON]ZrMe{MeB$(C_6F_5)_3$}[9] (the lengthened Zr−Me_{apical} bond being the exception), consistent with the larger radius of Y(III)[27,31,37,38] versus Zr(IV).[36] The amido nitrogen atoms are virtually planar (with sums of angle 358.8° and 358.3°), as expected, but the two oxygen donor atoms are also virtually planar (360.0° around O(2), 357.2° around O(1)). Both “planar” arrangements around oxygen could be said to be the result of sp^2 rehybridization of the oxygen. Therefore both O(1) and O(2) have a filled p orbital available for π bonding to Y. The “planar” form of the THF ligand and the orientation of the THF ligand are also the most sensible in terms of steric hindrance between the THF ligand and the two *tert*-butyl groups on the amido nitrogen atoms. The angles around the α carbon atom of the CH$(SiMe_3)_2$ ligand are large (with the sum being 355.5°), as has been found in other recently reported yttrium complexes that contain the CH$(SiMe_3)_2$ ligand.[27,31] Amido nitrogens N(1) and N(2) are bent away from the CH$(SiMe_3)_2$ ligand, as evidenced by the angle between the N(2)−Y−O(1) and N(1)−Y−O(1) planes of 165°. The ligand backbone is also twisted to a significant degree, as measured by the O(1)−Y−N(2)−C_{ipso} dihedral angle of 22° and O(1)−Y−N(1)−C_{ipso} dihedral angle of 19°. The “twisted” nature of the $[NON]^{2-}$ ligand backbone we believe results primarily from steric interaction between the two aryl protons on the ortho carbon atoms near the ether oxygen, but also in part as a consequence of the fact that the *o*-phenylene “arm” is planar and relatively inflexible. Some contribution to the twist also

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(35) Barker, G. K.; Lappert, M. F. *J. Organomet. Chem.* **1974**, *76*, C45.

(36) Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 283.

(37) Duchateau, R.; van Wee, C. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2291.

(38) Duchateau, R.; Meetsma, A.; Teuben, J. H. *Organometallics* **1996**, *15*, 1656.

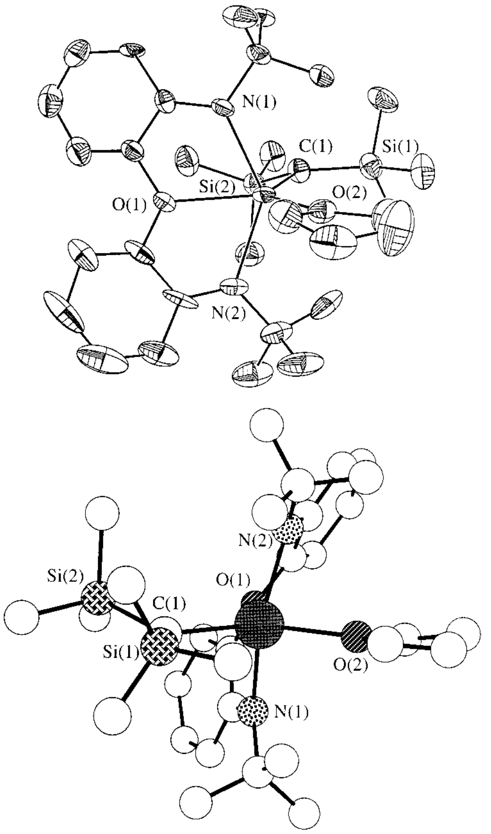


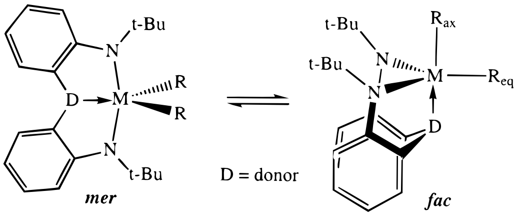
Figure 1. ORTEP view (top) and Chem 3D view (bottom) of the structure of **2a**.

might be a consequence of N(2) and N(1) bending away from the bulky alkyl ligand, as noted above. The three angles at the metal between the "equatorial" ligands (C(1), O(1), and O(2)) are approximately 120°, with their sum being 359.9°. The O(2)−Y−C(1) angle is the largest (126.4(3)°), possibly because the *tert*-butyl groups are oriented so that the plane of the nearest *o*-phenylene ring bisects one Me−C−Me angle, leaving the third methyl group pointing between and thereby driving apart O(2) and C(1).

Both **2a** and **2b** proved to be relatively unreactive toward molecular hydrogen or ethylene. Exposure of a toluene or benzene solution of **2a** or **2b** to 1 atm of molecular hydrogen for 1 week led only to slow decomposition, while **2a** and **2b** did not react with ethylene (1 atm) after 1 day, even upon heating the reaction to 70 °C.

Discussion

Five-coordinate d^0 complexes that contain diamido/ether ligands appear to be able to adopt either a *mer* structure or a *fac* structure (eq 2). The current hypothesis is that the *mer* structure is preferred for steric reasons up to the point where seric hindrance between the *tert*-butyl groups and the "equatorial" ligands (here two generic "R" groups) becomes significant. Much of this steric interaction is believed to be a consequence of the fact that two of the methyl groups in a given *tert*-butyl group lie on each side of the phenyl ring, leaving one methyl group to point roughly between the two R groups. When steric interaction between the amido nitrogen substituents and the R groups increases (e.g., as the size of R increases), the MR_2 unit rotates in the MR_2 plane and the N−M−N angle decreases from ~140° to ~115° to produce a *fac* structure. A "twisted" *fac* structure (with the *tert*-butyl groups twisted in one direction) is found in the solid state for both [NON]-$TiMe_2$ and [NON]ZrMe{MeB(C_6F_5)$_3$}.[9] However, in all known [NON]M(alkyl)$_2$ species (M = Ti or Zr) the two alkyl groups are equivalent on the NMR time scale down to −80 °C, presumably as a consequence of the ability of the *fac* and *mer* structures (in which inversion at the donor oxygen takes place) to interconvert rapidly. It is presumed that the donor atom does not dissociate from the metal because of the relatively rigid *o*-phenylene "arm" connecting it to the amido ligands. (In complexes that contain the [(ArylNCH$_2$CH$_2$)$_2$O]$^{2-}$ ligand (Aryl = 2,6-$Me_2C_6H_3$ or 2,6-i-$Pr_2C_6H_3$),[14,15] rotation about the O−C and C−C bonds in the CH_2CH_2 "arm" could *in theory* allow the donor to dissociate and turn away from the metal to give four-coordinate intermediates, although the likelihood of this actually being the case seems small.) The fact that the structure of **2a** is *mer*, while the structures of [NON]$TiMe_2$ and [NON]ZrMe{MeB(C_6F_5)$_3$}[9] are *fac*, we believe is a reflection of the relative size of the metals in the order Ti(IV) < Zr(IV) < Y(III);[36,39] for a large metal such as Y the steric interaction between the *tert*-butyl groups and the equatorial ligands (in this case CH(SiMe$_3$)$_2$ and THF) is not great enough to destabilize the *mer* structure. There is also evidence that the type of structure depends on the size of the R groups.[15] The stability of [NON]MR_2 complexes (where R is not methyl) is lowest for M = Ti, but even when M = Zr a limit in what is sterically possible apparently is reached when R = neopentyl, as the synthesis of [NON]Zr(CH$_2$CMe$_3$)$_2$ has not been successful.[40] Finally, the *mer* structure should be more tolerant of a small M or large R if the substituents on the amido nitrogens are smaller than *tert*-butyl. Indeed, all structures that have been obtained so far for Ti and Zr complexes that contain the related [(i-PrN-*o*-C_6H_4)$_2$O]$^{2-}$ ([i-PrNON]$^{2-}$) ligand are *mer*.[41]



(2)

We assume that [NON]YCl(THF)$_2$ and **2b** also contain the "pseudoplanar" *mer* version of the [NON]$^{2-}$ ligand with THF ligands bound trans to one another. This type of structure also is observed for {[(Me$_3$SiN-*o*-C_6H_4)$_2$O]-HfMe(THF)$_2$}{B(C_6F_5)$_4$}.[42] In fact so far all structurally characterized group 4 six-coordinate species have the *mer* arrangement of the ligand, even when the [NON]$^{2-}$ ligand is present, as in [NON]Zr(PMe$_3$)$_2$(CH$_2$CH$_2$).[40] The lack of reactivity of compounds **2a** and **2b** toward ethylene and molecular hydrogen can be ascribed to the relative difficulty of losing THF from the metal and

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(39) Evans, W. J. *Adv. Organomet. Chem.* **1985**, *24*, 131.

(40) Baumann, R. Schrock, R. R. Unpublished results.

(41) Baumann, R.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.*, submitted.

(42) Baumann, R. Ph.D. Thesis, Massachusetts Institute of Technology, 1998.

forming reactive pseudotetrahedral species. (The ability of THF to block reactions at "oxophilic" group 3 or 4 metal centers is well-known.) Whether the apparent decomposition of compounds **2** in vacuo can be ascribed to loss of THF and subsequent decomposition, perhaps by loss of a *tert*-butyl group from an amido nitrogen atom, is not known. It is also not known whether the decomposition observed upon treatment of compounds **2** with hydrogen is a consequence of formation and subsequent decomposition of hydride complexes, in contrast to the often facile formation of stable lanthanocene hydrides via similar hydrogenation routes and under similar conditions.[36,39]

We conclude that although yttrium alkyl complexes that contain the $[NON]^{2-}$ ligand can be synthesized readily, they appear to be relatively unreactive if THF is bound to the metal and unstable upon loss of THF from the metal. We also conclude that the relatively large size of Y(III) compared to Zr(IV) allows the $[NON]^{2-}$ ligand to adopt the *mer* structure in five-coordinate Y complexes. If reactive five-coordinate yttrium complexes, i.e., those in which THF is labile, or especially THF-free four-coordinate species, are to be synthesized, it will be necessary to design a diamido/donor ligand in which steric hindrance is also exerted by a substituent on the central donor. Efforts aimed in this direction currently are under way.

Experimental Section

General Considerations. All experiments were conducted under nitrogen in a Vacuum Atmospheres drybox, using standard Schlenk line techniques. Hydrogen and ethylene gases were deoxygenated and dried by passage through a zeolite-supported manganese oxide catalyst (BOC gases). Toluene, benzene, and hexamethyldisiloxane were distilled from sodium benzophenone under nitrogen. Pentane, diethyl ether, and tetrahydrofuran were dried and deoxygenated by first sparging with nitrogen and then passing through either (a) two large activated alumina columns (diethyl ether and tetrahydrofuran) or (b) one large activated alumina column and then one large column of activated Q5 (pentane).[43] All solvents were stored in the drybox over activated 4 Å sieves. Molecular sieves and Celite were activated for 24 h in vacuo (10^{-3} Torr) at 175 and 125 °C, respectively.

^1H and ^{13}C NMR spectra were recorded at room temperature. The reported δ values are referenced versus the residual solvent peak and are listed as parts per million downfield from tetramethylsilane. Routine coupling constants are not listed. For clarity in solvated complexes (0.1−0.5 equiv of solvent), the solvent resonances are not reported. NMR solvents were deoxygenated by sparging with nitrogen and dried over 4 Å sieves. Elemental analyses were performed by Microlytics of Deerfield, MA. As this analysis measures the number of moles of water produced, the %H for deuterium-containing compounds was calculated from the actual molecular weight assuming that all ^2H present was actually ^1H.

$Y[CH(TMS)_2]_3$,[35] $LiCH_2SiMe_3$,[44] $LiCH(SiMe_3)_2$,[45] and $H_2[NON]$[9] were prepared according to the literature procedures. Other reagents were purchased from commercial sources and used as received or dried/deoxygenated by standard techniques.

X-ray quality crystals of $[NON]Y[CH(TMS)_2](THF)(toluene)_{0.5}$ were grown by cooling a concentrated toluene solution. X-ray data were collected on a SMART/CCD diffractometer as described elsewhere.[46] Selected details of the structure are listed in Table 1. (See Supporting Information for full details.)

$[NON]YCl(THF)_2$ (1). Butyllithium (2.5 M in hexane, 6.2 mL, 16 mmol) was added to a −30 °C solution of $H_2[NON]$ (2.5 g, 7.7 mmol) in 30 mL of THF. The resulting orange solution was allowed to warm to room temperature for 1 h. The solution was cooled to −30 °C, and a small excess of solid YCl_3 (1.65 g, 8.5 mmol) was added in one portion. The reaction was warmed to room temperature, during which time most of the YCl_3 dissolved to give a cloudy orange-brown solution. After 14 h, the solvents were removed in vacuo and 15 mL of pentane was added. The solvents were again removed, and the sample was exposed to vacuum for 1 h. The product was extracted into diethyl ether (70 mL), and the extract was filtered through a bed of Celite and concentrated to about 15 mL, at which time crystallization/precipitation began. Pentane (10 mL) was added, and the suspension was cooled at −30 °C overnight. The tan solid was filtered and washed with 2 mL of cold diethyl ether and then twice with 5 mL of cold pentane. A second crop was isolated by concentration of the filtrate to about 8 mL, addition of 15 mL of pentane, and cooling to −30 °C overnight. The combined crops were dried in vacuo (30 mTorr) at 60 °C for 10 h. The product was extracted into toluene (10 mL), and the extract was filtered to remove some particulates. The solvents were removed in vacuo to yield a tan solid, which was thoroughly crushed and dried in vacuo overnight; yield 3.4 g (75%): ^1H NMR (C_6D_6) δ 7.23 (dd, 2), 6.99 (m, 4), 6.36 (td, 2), 3.76 (m, 8, THF), 1.68 (s, 6, $CCH_3(CD_3)_2$), 1.02 (s, 8, THF); ^{13}C NMR (C_6D_6) δ 148.26, 143.52, 125.21, 116.55, 114.64, 110.36, 71.62 (THF), 52.88, 31.09, 30.57 (m, $C(CH_3)_2(CD_3)$), 25.40 (THF). Anal. Calcd for $C_{28}H_{30}D_{12}ClN_2O_3Y$: C, 56.88; H, 7.17; N, 4.74. Found: C, 56.94; H, 6.64; N, 4.78.

$[NON]Y[CH(SiMe_3)_2](THF)$ (2a). Method A. Solid $LiCH(SiMe_3)_2$ (149 mg, 0.897 mmol) was added to a −30 °C solution of $[NON]YCl(THF)_2$ (530 mg, 0.897 mmol) in 8 mL of diethyl ether. The reaction was warmed to room temperature and stirred for 4 h as a white precipitate formed. The reaction was filtered through a bed of Celite and concentrated in vacuo to about 4 mL as crystallization began. After cooling the solution at −30 °C overnight, the crystals were collected by filtration, washed twice with 2 mL of cold diethyl ether, and dried in vacuo for 4 h. A second crop was obtained by concentrating the filtrate to 2 mL and cooling it to −30 °C overnight. The two crops were combined, thoroughly ground, and dried in vacuo overnight to give $[NON]Y[CH(SiMe_3)_2](THF)(ether)_x$ ($x = 1.0-1.2$) (450 mg, 70%) as an off-white powder.

Method B. To a −30 °C solution of $[NON]YCl(THF)_2$ (100 mg, 0.169 mmol) in 5 mL of toluene was added solid $LiCH(TMS)_2$ (28 mg, 0.169 mmol). The reaction was warmed to room temperature and stirred for 5 h as a white precipitate formed. The reaction was filtered through a bed of Celite and concentrated in vacuo to leave an oily residue, which was triturated with 5 mL of pentane. The suspension was cooled at −30 °C overnight, and the off-white solid was collected, washed once with 1 mL of cold pentane, and dried in vacuo for 4 h. A second crop was obtained by concentrating the filtrate to 1 mL and cooling at −30 °C overnight. The sample was dried in vacuo overnight to give $[NON]Y[CH(TMS)_2](THF)(toluene)_x$ ($x = 0.1-0.2$) (78 mg, 0.121 mmol, 72%) as an off-white powder.

Approximately 95% (by NMR) of the residual ether (method A) or toluene (method B) can be removed by repeatedly (two or three times) dissolving the sample in THF and removing the volatiles in vacuo. Subsequent drying of the sample in vacuo gives $[NON]Y[CH(TMS)_2](THF)_{1.2-1.5}(solvent)_x$ ($x < 0.1$).

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(43) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

(44) Tessier-Youngs, C.; Beachley, O. T. J. *Inorg. Synth.* **1986**, *24*, 95.

(45) Cowley, A. H.; Kemp, R. A. *Synth. React. Inorg. Met.-Org.* **1981**, *11*, 591.

(46) Rosenberger, C.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1997**, *36*, 123.

Unfortunately, the above procedure also leads to the formation of impurities (and slight decomposition), such that the isolated complex is estimated to be only ∼95−97% pure: ^{1}H NMR (C_6D_6) δ 7.31 (dd, 2), 6.99 (td, 2), 6.87 (dd, 2), 6.35 (td, 2), 3.38 (m, 4, THF), 1.45 (s, 6, $CC\mathit{H_3}(CD_3)_2$), 0.97 (s, 4, THF), 0.24 (s, 18, $Si(C\mathit{H}_3)_3$), −0.65 (d, 1, $J_{CY} = 1.8$ Hz, $C\mathit{H}(SiMe_3)_2$); ^{13}C NMR (C_6D_6) δ 147.86, 144.81, 126.03, 116.44, 116.29, 111.48, 70.29 (THF), 53.26, 37.88 (d, $J_{CY} = 35$ Hz, $\mathit{C}H(SiMe_3)_2$), 30.55, 29.95 (m, $C(CH_3)_2(\mathit{C}D_3)$), 25.40 (THF), 5.45 ($Si(\mathit{C}H_3)_3$).

[NON]Y(CH$_2$SiMe$_3$)(THF)$_2$ (2b). The synthesis was similar to that for [NON]Y[CH(TMS)$_2$](THF) (method B) except the final product was dried for only 30 min due to its instability in vacuo. Reaction of [NON]YCl(THF)$_2$ (100 mg, 0.169 mmol) with LiCH$_2$(TMS) gave 76 mg (70% yield) of [NON]Y(CH$_2$SiMe$_3$)(THF)$_2$(toluene)$_x$ ($x = 0.1-0.2$) as an off-white powder: ^{1}H NMR (C_6D_6) δ 7.11 (dd, 2), 6.96 (td, 2), 6.89 (dd, 2), 3.69 (br s, 8, THF), 1.61 (s, 6, $CC\mathit{H_3}(CD_3)_2$), 1.01 (br s, 8, THF), 0.39 (s, 9, $CH_2(Si(C\mathit{H}_3)_3)$), −0.58 (d, $J_{HY} = 2.7$ Hz, 2, $C\mathit{H}_2(Si(CH_3)_3)$; ^{13}C NMR ($C_6D_6$) δ 148.94, 143.61, 124.81, 116.69, 114.47, 110.08, 71.35 (THF), 53.42, 32.32 (d, $J_{CY} = 38$ Hz, $Y\mathit{C}H_2SiMe_3$), 31.34, 30.40 (m, $CCH_3(\mathit{C}D_3)_2$), 25.25 (THF), 5.35 ($Si(\mathit{C}H_3)_3$).

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Supporting Information Available: Summary of crystallographic data, collection, and refinement parameters for the X-ray structure of [NON]Y[CH(SiMe$_3$)$_2$](THF) (8 pages). Ordering information is given on any current masthead page.

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