Highly electron deficient Group 3 organometallic complexes based on the 1,4,7-trimethyl-1,4,7-triazacyclononane ligand system

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Abstract

Reaction of the neutral ligand 1,4,7-trimethyl-1,4,7-triazacyclononane (Cn) with $MCl_3(THF)_3$ (M = Sc, Y) in acetonitrile affords the novel trihalide complexes $CnMCl_3$. The crystal structure of $CnScCl_3$ has been determined: $(CH_3)_3N_3(C_2H_4)_3ScCl_3$; monoclinic, $a = 12.477(3)$, $b = 7.462(2)$, $c = 15.984(4) Å$, $\beta = 90.45(3)°$; $P2_1/c$, $Z = 4$. Subsequent alkylation with $LiCH_3$ in THF gives the corresponding trimethyl species $CnM(CH_3)_3$ cleanly. Reactivity studies reveal that the metal carbon bonds of these highly coordinatively unsaturated 12 e⁻, d⁰ complexes are remarkably unreactive toward insertion chemistry with typical unsaturated substrates such as alkenes and alkynes. 2-Butyne does, however, react with $CnY(CH_3)_3$ by C–H activation to give a compound that is characterized as a major allenyl isomer, $Cn(CH_3)_2Y(\eta^1\text{-}C(CH_3)CCH_2)$, in equilibrium with a minor propargyl isomer, $Cn(CH_3)_2Y(\eta^1\text{-}CH_2CC(CH_3))$. In general, $CnSc(CH_3)_3$ is observed to be significantly more stable, and also less reactive, than $CnY(CH_3)_3$. $CnSc(CH_3)_3$ can, however, be activated by reaction with either $B(C_6F_5)_3$ or $[H(CH_3)_2NPh]^+[B(C_6F_5)_4]^-$ to give complexes which exhibit olefin polymerization chemistry.

Keywords: Scandium; Yttrium; Macrocyclic amine ligands; Methyl; Polymerization; Olefins

1. Introduction

While the organometallic chemistry of the early transition metals has traditionally been dominated by systems which incorporate cyclopentadienyl (Cp) and substituted Cp ancillary ligands, there has recently been a renewed interest in the use of new ligands and ligand combinations in early transition metal organometallic systems. One aspect of these studies has involved ligands which are isoelectronic with cyclopentadienyls, but which have different valency requirements. For example, metal complexes possessing one cyclopentadienyl ligand Cp⁻ and one dianionic analog (for recent examples with leading references see Ref. [1]) such as dicarbollide $[\eta^5\text{-}C_2B_9H_{11}]^{2-}$ or aminoborollide $\{\eta^5\text{-}C_4H_4BN(CHMe_2)_2\}^{2-}$ afford systems which, relative to the parent metallocene, carry an additional net negative charge. Several research groups have prepared out-of-plane $(N_4\text{-macrocycle})MX_2$ (M = Ti(IV), Zr(IV), Hf(IV)) complexes, where $(N_4\text{-macrocycle})$ represents a dianionic, 14- or 16-membered tetraaza macrocycle or porphyrin (see for example Ref. [2]). As noted by Tjaden and Jordan [3], systematic investigation of an appropriate set of complexes with these types of ligand combination might help clarify the relationship of net charge to the observed reactivity within an isoelectronic series.

Similarly, formal substitution of Cp⁻ with a suitable neutral ligand would lead to isoelectronic metal complexes which possess an additional positive charge. While the inorganic and bioinorganic coordination chemistry of azamacrocycles and other neutral polyamines and polyethers have been developed extensively [4], and these types of ligand have been shown to coordinate quite strongly to a broad range of transition metals, their use as ancillary ligands in organometallic systems, [1] especially for early transition-metals, remains virtually unexplored. [2] Accordingly, we have undertaken a study of the chemistry of scandium and yttrium

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[1] For a recent review of nitrogen donors in organometallic chemistry see Ref. [5].
[2] A Ti(0) tricarbonyl species has been reported, see Ref. [6].

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in the coordination sphere of the neutral ligand, 1,4,7-trimethyl-1,4,7-triazacyclononane (Cn). [3]
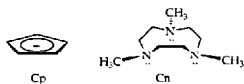

Flood and coworkers have found that the azamacrocyclic complex CnRhCl₃ can be converted cleanly to the trimethyl species CnRh(CH₃)₃ (1) [7]. For example, rhodium dimethyl and monomethyl cations derived from 1 are quite robust and exhibit interesting and unusual reactivity compared with the closely related cyclopentadienyl–rhodium systems. Köhn and Kociok-Köhn have also recently begun to study the organometallic chemistry of iron and chromium derivatives of triazacyclohexane–metal complexes [8].

We report herein the synthesis, structural characterization and some preliminary reactivity studies of trivalent compounds having the Cn-supported Group 3 transition metal fragment, [CnM] (M = Sc,Y). As in the case of Flood's rhodium system, 1, use of the Cn ligand affords a new class of scandium- and yttrium-alkyl compounds whose reactivity patterns differ markedly from those of the previously studied metallocene-derived systems [9].

2. Results and discussion

2.1. Synthesis and characterization of CnMCl₃ (2) and CnM(CH₃)₃ (3)

The syntheses of trichlorides CnMCl₃ (2) (2a, M = Sc; 2b, M = Y) are readily accomplished by allowing the corresponding tetrahydrofuran adducts, (THF)ₓScCl₃, and (THF)₃.₅YCl₃, to react with the Cn ligand in acetonitrile (Eq. (1)).
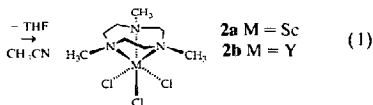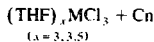
(THF)ₓMCl₃ + Cn

(x = 3,3.5)

Initial synthetic approaches to 2 were directed toward noncoordinating solvent systems in order to minimize competition with Cn ligand coordination; however, we have found that the relatively strongly coordinating acetonitrile is critical to obtaining high yields in these reactions. Both reactants are highly soluble whereas the product is not. Apparently, the tridentate Cn ligand competes quite effectively with both THF and acetonitrile for metal binding. (In a related reaction, Wieghart and coworkers [10] have observed that the cyclic triamine 1,4,7-triisopropyl-1,4,7-triazacyclononane (tiptacn) reacts with Ti(CH₃CN)₃Cl₃ in acetonitrile solution to give (tiptacn)TiCl₃.)

Both complexes have been characterized by NMR and elemental analysis. The scandium complex 2a is moderately air stable and a suitable crystal grown from acetonitrile has been characterized by X-ray diffraction (Table 1, Fig. 1). As expected, the ligand is facially coordinated, and the complex has a slightly distorted octahedral geometry.

Attempts to prepare cyclopentadienyl derivatives, e.g. (η⁵-C₅H₅)CnMCl₂, by reaction of 2 with cyclopentadienyl anion under a variety of conditions have been unsuccessful. In contrast, methylation of 2 proceeds quickly and cleanly in THF under ambient conditions to afford the trimethyl complexes CnM(CH₃)₃ (3) (3a, M = Sc; 3b, M = Y) in good yield (Eq. (2)).

CnMCl₃ + 3LiCH₃
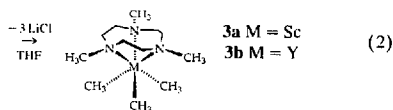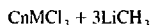
On the basis of the crystal structure of 2a, we presume that the complexes 3 are octahedral, although it has also been proposed that such d⁰ transition metal systems could exhibit trigonal prismatic ground state geometries [11]. In an effort to clarify this situation, we have attempted repeatedly to grow crystals of complexes 3. Indeed, when saturated solutions of 3a in

Table 1
Crystallographic data for CnScCl₃ (2a)

| (CH₃)₃N₃(C₂H₄)₃ScCl₃	Formula weight 322.60
a = 12.477(3) Å	Space group #14, $P2_1/c$
b = 7.462(2) Å	T = 25 °C
c = 15.984(4) Å	λ = 0.71073 Å
β = 90.45(3)°	ρ_{calc} = 1.44 g cm⁻¹
V = 1488.1(7) Å³	μ = 10.19 cm⁻¹
Z = 4	μr_{max} = 0.23 cm⁻¹
	R(Fₒ) = 0.069
	$R_w(F_o^2)$ = 0.018

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[3] Although there are several common acronyms for the azamacrocycle 1,4,7-trimethyl-1,4,7-triazacyclononane we have chosen to use "Cn" in deference to the proposal of Flood and coworkers [7] who have recently pioneered its use in organometallic systems.
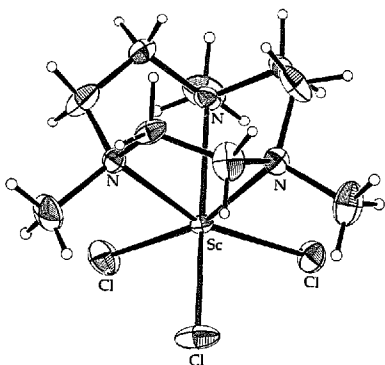
Fig. 1. ORTEP drawing of the structure of CnScCl₃ (2a), 30% ellipsoid.

aromatic solvents are allowed to cool slowly, large, clear colorless crystals are reproducibly formed. Unfortunately, these crystals rapidly lose integrity by an apparent loss of co-crystallized solvent, and thus far we have been unable to find suitable conditions for isolation of crystals sufficiently stable for X-ray structural analysis.

2.2. Reactivity studies of 3

Investigations of the reactivity of **3a** reveal that the scandium–methyl bonds in this highly coordinatively unsaturated $12 e^-$ complex are surprisingly unreactive toward typical unsaturated organic substrates such as olefins, acetylenes, or even acetonitrile. In fact, **3a** reacts with H_2 only under forcing conditions (4 atm, 80 °C, several days) to afford a product which appears (by ${}^1H$ NMR) to be the trihydride $CnScH_3$. Unfortunately, this assignment is somewhat tentative because the large quadrupole moment for ${}^{45}Sc$ (100% abundant, $I = 7/2$) normally precludes the observation of Sc–H resonances. (An alternative interpretation is that the product is actually the perdeuteriotriphenyl complex, $CnSc(C_6D_5)_3$, arising from σ bond metathesis of solvent (benzene-d_6) with transient, highly reactive Sc–H bonds. HD (the expected coproduct), however, is not observed in the sealed NMR tube.)

We have found that the yttrium complex, **3b**, is somewhat more reactive than the scandium analog, but yields products that are also significantly less stable. Thus, whereas **3a** requires forcing conditions to effect reaction with dihydrogen, **3b** reacts quite rapidly at room temperature. Unfortunately, the products are not the expected methane and $CnYH_3$, but rather the components of a subsequent (or concurrent) decomposition
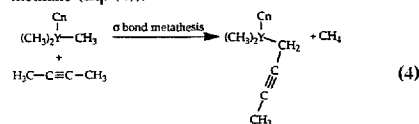
to give methane, free Cn ligand (${}^1H$ NMR), and a gray precipitate which is presumed to be amorphous YH_3 (Eq. (3)).

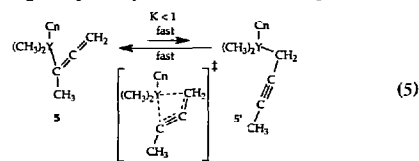$$CnYMe_3 + 3H_2 \rightarrow Cn + 3CH_4 + [YH_3] \, (ppt) \qquad (3)$$

As expected, upon exposure to air the yttrium complex, **3b**, decomposes rapidly. Remarkably, when **3a** is treated analogously, the Cn ligand is not demetallated from the scandium center. When air is bubbled through a benzene-d_6 solution of **3a** in an NMR tube, the solution takes on a slight cloudiness; however, free Cn ligand is not observed; **3a** is still present (${}^1H$ NMR). The material constituting the cloudiness has not been identified.

2.3. Reaction of 3b with 2-butyne

As might be anticipated from its generally low reactivity as described above, **3b** is completely inert toward olefinic substrates. However, 2-butyne does react slowly at room temperature. Again unexpectedly, the product (**5**) appears to arise from C–H activation rather than insertion. A straightforward σ bond metathesis reaction [12] of **3b** with a C–H bond of 2-butyne would yield the propargyl complex, $Cn(CH_3)_2Y–CH_2C\equiv CH_3$, and methane (Eq. (4)).

$$\begin{array}{c} \overset{Cn}{\underset{|}{(CH_3)_2Y{-}CH_3}} \\ + \\ H_3C{-}C{\equiv}C{-}CH_3 \end{array} \xrightarrow{\text{σ bond metathesis}} \begin{array}{c} \overset{Cn}{\underset{|}{(CH_3)_2Y{\diagdown}CH_2}} \\ \underset{|}{\overset{|}{\underset{C}{\overset{|||}{C}}}} \\ CH_3 \end{array} + CH_4 \qquad (4)$$

Although the spectroscopic data are not fully in accord with any individual structure, they do indicate that **5** is not simply the propargyl compound indicated in Eq. (4). Indeed, NMR studies of this product lead us to assign its solution structure as one consisting of a major η^1-allenyl form along with a minor η^1-propargyl isomer in rapid equilibrium (Eq. (5)). (The fluxional process for **5** must also effectively make three-fold equivalent the Cn ligand on the ${}^{13}C$ and ${}^1H$ NMR time scales, since the highest symmetry for static **5** and **5'** is C_S.)

$$\begin{array}{c} \overset{Cn}{\underset{|}{(CH_3)_2Y}}{\diagdown}{\overset{CH_2}{\underset{C}{\parallel}}} \\ \underset{|}{\overset{}{C}} \\ CH_3 \end{array} \underset{\text{fast}}{\overset{K < 1}{\underset{\text{fast}}{\rightleftharpoons}}} \left[\begin{array}{c} \overset{Cn}{\underset{|}{(CH_3)_2Y}}{\cdots}CH_2 \\ \underset{}{\overset{}{\underset{C}{\parallel}}} \\ C \\ CH_3 \end{array} \right]^{\ddagger} \begin{array}{c} \overset{Cn}{\underset{|}{(CH_3)_2Y}}{\diagdown}CH_2 \\ \underset{|}{\overset{|||}{C}} \\ \underset{|}{C} \\ CH_3 \end{array} \qquad (5)$$

5   **5'**

Perhaps most telling is the anomalous low field chemical shift observed for the methylene ${}^1H$ NMR resonance (δ 3.87), along with an absence of the two-bond cou-

pling to yttrium ($^2J^{av}_{YH}$ expected to be 1–3 Hz) that would be expected if the product were the propargyl isomer. The ^{13}C NMR data are in accord with a predominance of the allenyl isomer, particularly on the basis of the significantly low field chemical shift of the central sp-hybridized [YC(CH$_3$)CCH$_2$] carbon (δ 169.15). (The chemical shifts for the central carbon in free allenes are around 200 ppm, whereas those for acetylenic carbons are about 70 ppm.) That the product is only the η^1-allenyl isomer is inconsistent with the NMR data, however. The allenyl carbon attached to yttrium exhibits a broad ^{13}C resonance, [4] and variable-temperature ^{1}H NMR experiments, while always carried out under conditions in which the two compounds are in fast exchange, show a strong correlation between temperature and chemical shift, particularly for the methylene resonance of the allenyl moiety, which moves from δ 4.55 at 180 K to δ 3.45 at 340 K. This behavior is consistent with the proposed rapid η^1-allenyl to η^1-propargyl fluxional behavior, since the temperature-dependent shift for methylene hydrogens is in the correct direction for a minor isomer possessing a large downfield shift vs. the major one. In considering the structural model for **5**, we note that Casey and Yi have characterized a rhenium–propargyl complex [13] for which the ground state resonance forms are, in the limit of no π-bond coordination, the two different isomers proposed in our case. Additionally, the ground state of the rhenium complex provides an attractive model of the transition state for the isomerization of the yttrium complex. (The stronger Y–C bond presumably provides the driving force towards the allenyl isomer, but sterics and other subtle factors that may also be causal cannot easily be dismissed.)

The kinetic deuterium isotope effect accompanying formation of **5** was examined by following the reaction of CH$_3$C≡CCD$_3$ with **3b** The value is very large, i.e. $k_{CH_3}/k_{CD_3} = 17$ at 25 °C, compared with the magnitude of the kinetic deuterium isotope effect for σ bond metathesis of Cp$_2^*$Sc–CH$_3$ with C$_6$L$_6$ (L = H, D): $k_H/k_D = 2.8(2)$ at 80 °C [12]. A very large effect has been observed for methane elimination from a tantalum–amido complex, $k_H/k_D = 9.7$ at 25 °C [14]. Such large values are suggestive of tunneling in the rate determining step. As shown in Scheme 1, a possible mechanism for the reaction would involve weak, reversible coordination of 2-butyne to **3b**, followed by methane elimination. This reaction is apparently not general for other methyl acetylenes; in contrast to 2-butyne, even 2-pentyne fails to react cleanly with **3b**. Presumably the required acetylene coordination is too disfavored for even modestly more bulky substrates.

[4] Unexplained for this resonance is the lack of ^{89}Y–^{13}C coupling expected to be 40 to 50 Hz.
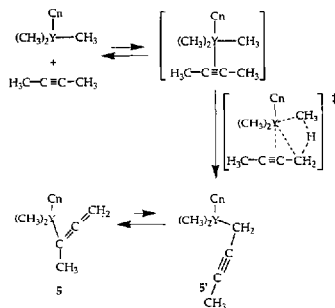
Scheme 1.

2.4. Activation of 3a with [HN((CH$_3$)$_2$)Ph]$^+$-[B(C$_6$F$_5$)$_4$]$^-$ and B(C$_6$F$_5$)$_3$

The reactivity patterns observed for the trimethyl complexes **3** suggested that protonolysis of one methyl group to give the corresponding dimethyl cation [CnM(CH$_3$)$_2$]$^+$ might be accomplished [15]; for a recent example with leading references see Ref. [16]. We were initially hesitant to pursue these reactions, since we expected that the resultant 10 e$^-$ cations would be quite unstable based on their extremely low formal electron count. In fact, reaction of the yttrium complex, **3b**, with N,N-dimethylanilinium perfluorotetraphenylborate results in rapid decomposition accompanied by methane loss and demetallation of the Cn ligand. In contrast, the analogous reaction with **3a** in THF leads to formation of methane and (free) dimethylaniline with no evidence of demetallation of the Cn ligand. Although NMR spectra of the resultant product(s) are quite complex, addition of ethylene to a THF solution of the product, possibly [CnSc(CH$_3$)$_2$·(THF)$_n$]$^+$[B(C$_6$F$_5$)$_4$]$^-$, results in slow formation of a polyethylene precipitate.

The analogous reaction of **3a** with anilinium perfluorotetraphenylborate in benzene-d_6 results in methane evolution and separation of a dense orange-red oil. The ^{1}H NMR spectrum of this heterogeneous reaction mixture shows a sharp set of signals due to N,N-dimethylaniline and a small amount of residual methane, as well as very broad signals centered around δ 2 ppm and −0.5 ppm, which are assigned to the Cn and Sc–CH$_3$ moieties of the expected product, [CnSc(CH$_3$)$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$. The two fractions were easily separated by decanting residual liquid (solvent and N,N-dimethylaniline) away from the oily product. Addition of THF-d_8 to the residual oil results in dissolution, giving a colorless solution which has essentially the same spectral features as the THF-d_8 reaction product described above (with the exception of missing

methane and dimethylaniline resonances). Addition of neat 1-pentene to a sample of the red oil results in moderately fast formation of a highly viscous solution of oligo(1-pentene) after about 2 h at room temperature. GPC analysis of the crude polymer so obtained reveals a low polydispersity (PDI = 1.32), but a rather low molecular weight ($M_w = 4000$).

The ability of perfluoro-triphenylborane to activate Group IV metal–alkyl systems via a μ-methyl complex has also been observed [17]; for a recent example with leading references see Ref. [18]. We hoped that this relatively milder form of activation might generate a more easily characterized species pertinent to the olefin polymerization reactions with the cationic systems. Indeed, when 3a and $B(C_6F_5)_3$ are allowed to react in an NMR tube in THF-d_8, a subsequent ^{1}H NMR spectrum, though broad, could be taken as consistent with formation of $CnSc(CH_3)_2(\mu-CH_3)B(C_6F_5)_3$. As in the case for the cationic species above, the THF solution obtained proves competent for ethylene polymerization at modest temperatures (80 °C); however, it does not react with propene even after several days at 80 °C.

Treatment of 3a with $B(C_6F_5)_3$ in benzene results in formation of an insoluble red oil. Room temperature polymerization of 1-pentene with this red oil results in crude oligo(1-pentene) which, quite remarkably, has exactly the same properties as that obtained from the anilinium perfluorotetraphenylborate activation route: $M_w = 4000$, PDI = 1.32 (vide supra).

3. Conclusions

The syntheses of Cn complexes of scandium and yttrium $CnMCl_3$ (2) (2a, M = Sc; 2b, M = Y) and the corresponding trimethyl species $CnM(CH_3)_3$ (3) (3a, M = Sc; 3b, M = Y) are readily accomplished in high yield. These formally 12 e$^-$, d^0 compounds comprise a new class of highly electron deficient Group III metal complexes, and offer the opportunity to examine the differences in the chemistry of the Group III metals in facial octahedral coordination geometries for comparison with the better studied bent-metallocene systems.

In contrast to the scandium complex 3a and Flood's rhodium complex, $CnRh(CH_3)_3$, it is apparent that the Cn ligand does not provide a sufficiently stable coordination environment for significant organometallic chemistry at yttrium. It is likely that the large size of Y^{3+} (1.04 Å) is less compatible with the bite size of the Cn ligand, resulting in weaker binding relative to the smaller metals Sc^{3+} (0.89 Å) and Rh^{3+} (0.81 Å).

Although the present studies are only preliminary, the initial findings appear to indicate some similarities in reactivity for 3a to that for isoelectronic Group IV monocyclopentadienyl trimethyl complexes $CpM(CH_3)_3$ (4) (M = Ti, Zr, Hf) which are of current interest as

catalyst precursors for α-olefin polymerization and syndiotactic polystyrene production; for recent examples see Ref. [19]. Both classes of compounds require activators to promote olefin polymerizations.

4. Experimental section

All air- and/or moisture-sensitive compounds were manipulated using standard high vacuum line, Schlenk, or cannula techniques, or in a dry box under a nitrogen atmosphere, as described previously [20]. Argon and hydrogen gases were purified and dried by passage over columns of MnO on vermiculite and activated molecular sieves. Solvents were stored under vacuum over titanocene [21] or sodium benzophenone ketyl. 1,4,7-Trimethyl-1,4,7-triazacyclononane was either purchased (Aldrich) and used as-received, or synthesized by the method of Flood and coworkers [7]. $B(C_6F_5)_3$ was synthesized and provided by Dr. Robert E. Blake, Jr. A generous loan of N,N-dimethylanilinium perfluorotetraphenylborate by Dr. Howard Turner (Exxon Chemical) is gratefully acknowledged.

Unless otherwise specified, all NMR spectra were recorded at ambient temperature on a Bruker AM500 (500.13 MHz for ^{1}H; 125.76 MHz for ^{13}C) spectrometer. GPC and differential scanning calorimetry (DSC) analyses of polymer samples were carried out in the laboratories of Professor Robert H. Grubbs with the help of Dr. Geoffrey W. Coates and Amy Pangborn. Many of the reactions were carried out in sealed NMR tubes. The tubes were fitted with a 180°, concentric, Teflon needle-valve which was fused directly on to the tube (which was purchased from J. Young [5]); this could be attached to the high vacuum line by a simple adapter tube. These assemblies allow convenient loading of solids in the glove-box as well as a reversible vacuum tight seal which allows facile manipulations of volatiles into and out of the tube assembly. In a typical experiment, the NMR tube was loaded with 10–30 mg (ca. 0.03–0.1 mmol) of the desired reactants.

4.1. CnYCl₃

In the glove box a 50 ml Kjeldahl flask was charged with $YCl_3(THF)_3$ (5.0 g, 12.15 mmol, 1 equivalent). The solid was dissolved, with stirring, in a minimum amount of acetonitrile (ca. 40–50 ml). To this solution was added the Cn ligand (2.5 g, 14.57 mmol, 1.2 equivalents), dropwise with a pipette. During the addition a yellow precipitate began to form, and this increased over a period of a few minutes after the addition. The

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flask was attached to a medium-sized swivel frit assembly, taken onto the vacuum line, filtered, and dried in vacuo. Yield 3.41 g (77%) of CnYCl$_3$ as a free flowing, yellow, microcrystalline powder. Analysis calculated for C$_9$H$_{21}$Cl$_3$N$_3$Y: C, 29.49%; H, 5.79%; N, 11.46%; found (two runs with oxidant): C, 30.02%, 29.84%; H, 5.81%, 5.78; N, 11.11%, 11.43%. ^{1}H NMR (CD$_3$CN): δ 3.097 (m, 6H, CH$_2$), 2.890 (m, 6H, CH$_2$), 2.807 (s, 9H, CH$_3$). {^{1}H}^{13}C NMR (THF-d_8): δ 56.99 (CH$_2$), 49.68 (CH$_3$).

4.2. CnScCl$_3$

An analogous procedure to that employed above for CnYCl$_3$ gave CnScCl$_3$ as a white powder in 59% yield. Analysis calculated for C$_9$H$_{21}$Cl$_3$N$_3$Sc: C, 33.50%; H, 6.57%; N, 13.02%; found (three runs): C, 32.85%, 33.19%, 32.96%; H, 6.43%, 6.50%, 6.44%; N, 12.74%, 12.96%, 12.86%. ^{1}H NMR (CD$_3$CN): δ 3.212 (m, 6H, CH$_2$), 2.911 (m, 6H, CH$_2$), 2.870 (s, 9H, CH$_3$). {^{1}H}^{13}C NMR (CD$_3$CN): δ 56.48 (CH$_2$), 50.87 (CH$_3$).

4.3. CnSc(CH$_3$)$_3$

A medium-sized swivel frit assembly was charged with CnScCl$_3$ (1.000 g, 3.100 mmol, 1 equivalent) and halide-free LiCH$_3$ (204.4 mg, 9.300 mmol, 3 equivalents). On the vacuum line, ca. 75 ml of THF was condensed onto the solids and the reaction mixture was warmed to room temperature. The milky white suspension was stirred for about 6 h after which the solvent was removed in vacuo leaving an off-white solid residue. Toluene (ca. 100 ml) was condensed in and the resulting light yellow mixture was warmed slightly (ca. 40 °C) and filtered to remove LiCl. The filtrate was washed once with fresh solvent and the supernatant solution was concentrated to ca. 10 ml giving an orange precipitate. An equal volume of petroleum ether was condensed into the solution to precipitate more of the product, which was collected by filtration and dried in vacuo. Yield 551.2 mg (68%) of CnSc(CH$_3$)$_3$ as a light orange powder. Analysis calculated for C$_{12}$H$_{30}$N$_3$Sc: C, 55.13%; H, 11.59%; N, 16.08%; found (two runs): C, 54.67%, 54.43%; H, 10.94%, 11.02%; N, 15.59%, 15.89%. ^{1}H NMR (THF-d_8): δ 2.984 (m, 6H, CH$_2$), 2.780 (m, 6H, CH$_2$), 2.650 (s, 9H, N–CH$_3$), −0.643 (s br, 9H, Sc–CH$_3$). {^{1}H}^{13}C NMR (THF-d_8): δ 55.97 (CH$_2$), 48.97 (N–CH$_3$); Sc–CH$_3$ not detected.

4.4. CnY(CH$_3$)$_3$

Starting with CnYCl$_3$, an analogous procedure to that employed above for CnSc(CH$_3$)$_3$ gave CnY(CH$_3$)$_3$ as a light yellow powder in 78% yield. Analysis calculated for C$_{12}$H$_{30}$N$_3$Y: C, 47.20%; H, 9.92%; N, 13.76%; found (two runs): C, 46.75%, 47.18%; H, 9.38%, 9.43%;

N, 13.76%, 13.81%. ^{1}H NMR (C$_6$D$_6$): δ 2.266 (m, 6H, CH$_2$), 1.723 (m, 6H, CH$_2$), 2.394 (s, 9H, N–CH$_3$), −0.220 (d, $^2J_{Y-H} = 1.55$ Hz, 9H, Y–CH$_3$). {^{1}H}^{13}C NMR (benzene-d_6): δ 54.57 (CH$_2$), 47.13 (CH$_3$), 21.3 (d, $^1J_{Y-C} = 44.59$ Hz, Y–CH$_3$).

4.5. Reaction of CnY(CH$_3$)$_3$ with 2-butyne

Typical reactions were carried out in NMR tubes as described above using toluene-d_8 as solvent.
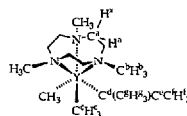
^{13}C NMR (125 MHz, room temperature, benzene-d_6): C^a δ 54.90, 6C, triplet ($^1J_{CH} = 135$ Hz); C^b δ 47.67, 3C, quartet ($^1J_{CH} = 141$ Hz); C^c δ 19.90, 2C, quartet of doublets ($^1J_{CH} = 104$ Hz, $^3J''_{YH} = 46$ Hz); C^d δ 109.91, 1C, broad; C^e δ 169.15, 1C, singlet; C^f δ 55.47, 1C, triplet ($^1J_{CH} = 159$ Hz); C^g δ 13.44, 1C, quartet ($^1J_{CH} = 127$ Hz). ^{1}H NMR (500 MHz, room temperature, benzene-d_6): H^a, H$^{a'}$ δ 2.34, 6H, broad; H^x, H$^{x'}$ δ 1.71, 6H, broad; H^b δ 2.39, 9H, broad; H^c δ −0.37, 6H, doublet ($^2J''_{YH} = 1.5$ Hz); H^f δ 3.87, 2H, quartet ($^5J_{HH} = 2.7$ Hz); H^g δ 2.11, 3H, triplet ($^5J_{HH} = 2.7$ Hz). CH$_3$C≡CCD$_3$ had been previously synthesized in our laboratory by Dr. W.D. Cotter [22]. 2-Butyne-d_6 was purchased (Fluka) and purified by drying over activated 3A molecular sieves followed by low temperature vacuum distillation prior to use. The isotope effect was determined by relative integration of the appropriate product resonances in the ^{1}H NMR spectra.

4.6. Reaction of CnSc(CH$_3$)$_3$ with [H(CH$_3$)$_2$NPh]-[B(C$_6$F$_5$)$_4$] in benzene-d_6

In a typical reaction, CnSc(CH$_3$)$_3$ (10 mg, 0.0383 mmol, 1 equivalent) and [H(CH$_3$)$_2$NPh]$^+$[B(C$_6$F$_5$)$_4$] (30.7 mg, 0.0383 mmol, 1 equivalent) were loaded into an NMR tube in the glove box as described above. Addition (in the glove box, by pipette) of benzene-d_6 solvent resulted in gas (CH$_4$) evolution and gave, eventually, a dense orange-red oil. The two fractions were easily separable by simply decanting the residual liquid (solvent and N,N-dimethlyaniline) away from the oily product. The ^{1}H NMR spectrum of the mixture before decanting shows a sharp set of signals which have been assigned to N,N-dimethlyaniline and a small amount of residual methane,

as well as very broad signals centered around 62 ppm and −0.5 ppm.

4.7. Polymerization of 1-pentene using product red oil of previous reaction

A preparation of 'decanted' red oil was carried out as above, but in a 200 ml thick-walled glass reaction vessel rather than an NMR tube. The thick-walled glass reaction vessel was taken onto the vacuum line and 1-pentene (25 ml) was condensed into the reactor at −78 °C. Although the oil did not seem to dissolve to any appreciable extent, after about 2 h polymer formation was evident as the solution had become quite thick and viscous. The reaction mixture was opened to air, and the crude polymer–pentene mixture was analyzed by GPC in CH_2Cl_2 against a polystyrene calibration: $M_n = 2800$, $M_w = 3700$; PDI = 1.32.

4.8. Reaction of CnSc(CH₃)₃ with [H(CH₃)₂NPh]-[B(C₆F₅)₄] in THF-d₈ and subsequent polymerization of ethylene

CnSc(CH₃)₃ (10 mg, 0.0383 mmol, 1 equivalent) and [H(CH₃)₂NPh][B(C₆F₅)₄] (30.7 mg, 0.0383 mmol, 1 equivalent) were loaded into an NMR tube in the glove box. On the vacuum line, condensation of THF-d₈ into the assembly at −78 °C resulted in vigorous gas (methane) evolution, which persisted for ca. 15 min. The tube was allowed to warm to room temperature. A subsequent NMR spectrum revealed, as above, sharp resonances for N,N-dimethylaniline and methane. Broad resonances were also apparent in the region for Cn coordinated to scandium; however, the expected Sc–CH₃ resonances were apparently completely coalesced into the baseline. The tube was returned to the vacuum line, and ethylene (0.2 ml) was condensed into the reaction mixture at −198 °C. **(CAUTION! This may result in extremely high pressure and should be carried out with great care behind an adequate blast shield.)** ¹H NMR spectra indicated no significant changes over the next few hours. The tube was placed in an 80 °C oil bath overnight. Inspection of the tube the next day revealed a white polymeric precipitate.

4.9. Reaction of CnSc(CH₃)₃ with B(C₆F₅)3 in THF-d₈ and subsequent polymerization of ethylene

In the glove box, a J. Young NMR tube was charged with CnSc(CH₃)₃ (10 mg, 0.0383 mmol, 1 equivalent) and B(C₆F₅)₃ (19.5 mg, 0.0383 mmol, 1 equivalent). On the vacuum line, THF-d₈ (1 ml) was condensed onto the solids. The ¹H NMR spectrum at room temperature consisted of broad resonances between δ 2.3 and 3.3, attributable to the Cn hydrogens, a broad singlet at δ 0.50 due to [Sc(μ-CH₃)B] and a sharp singlet at

δ 0.66 due to Sc(CH₃)₂. **CAUTION! The following procedure may result in extremely high pressure and should be carried out with great care behind an adequate blast shield.** The tube was returned to the vacuum line and ethylene (0.4 ml) was condensed into the reaction mixture at −198 °C. The tube was allowed to warm to room temperature (ca. 1 h) behind a blast shield in a fume hood and was then carefully moved to an 80 °C oil bath overnight. Inspection of the tube the next day revealed a white polymeric precipitate which was isolated by extraction/precipitation from hot toluene. A melting point of 117 °C was determined for this polymer by DSC.

4.10. Reaction of CnSc(CH₃)₃ with B(C₆F₅)3 in benzene-d₆

CnSc(CH₃)₃ (10 mg, 0.0383 mmol, 1 equivalent) and B(C₆F₅)₃ (19.5 mg, 0.0383 mmol, 1 equivalent) and benzene-d₆ (ca. 1 ml) were sequentially loaded into an NMR tube in the glove box. Upon stirring, an initially clear oily film was observed clinging to the walls of the tube. The oil slowly darkened to an orange-red color over about 30 min. The NMR spectrum of this mixture was very broad and not easily interpretable. The tube was taken back into the box and the solvent decanted into a fresh NMR tube; the spectrum obtained from this tube indicated only the presence of residual protons from the benzene-d₆ solvent. To the tube containing the oil was added chlorobenzene-d₅, which took on a light red color indicating partial solubility of the still largely undissolved oil; the broad NMR spectrum obtained from this tube could not be unambiguously assigned, but contained peaks in the spectral regions expected for Cn–Sc, Sc–CH₃, and Sc(μ-CH₃)B (vide supra). The solvent was removed in vacuo and the red oil obtained was used in the following reaction.

4.11. Polymerization of 1-pentene using product red oil of previous reaction

1-Pentene was condensed onto the red oil in the tube obtained from the previous procedure. The assembly was stirred by slow rotation overnight. The next day, polymer formation was evident as the solution had become quite thick and viscous. ¹³C NMR analysis revealed that the tube contained mostly poly(pentene) and a relatively smaller amount of unreacted monomer. The tube was opened to air, and the crude polymer–pentene mixture was analyzed by GPC in CH_2Cl_2 against a polystyrene calibration: $M_n = 2782$, $M_w = 3665$, PDI = 1.32.

4.12. Crystal structure determination for CnScCl₃

A suitable clear, colorless crystal of approximate dimensions $0.18 \times 0.24 \times 0.34 \, mm^3$ was selected from

a batch grown by slow evaporation in air of an aceto-nitrile solution of CnScCl$_3$ in a loosely capped small vial. The crystal was optically centered on an Enraf Nonius CAD 4 diffractometer equipped with an Mo Kα source, operating in omega scan mode. 25 well-dispersed reflections in the range of θ between 12 and 13° were used for determining the unit cell parameters. No absorption correction was applied to the data. Data were collected for h, k, and l within the limits 0 to 14, −8 to 8, and −19 to 19 respectively. Four intensity check reflections were used to monitor crystal decay. An approximately linear increase of 3% was observed over 49.56 h. The total number of reflections measured was 5625. The total number of independent measurements was 2603. Only 2370 of the reflections were used for solution and refinement (vide infra). Patterson methods were used to determine the positions of scandium atom and one of the chlorine atoms. Subsequent structure factor–Fourier analysis revealed the remaining heavy atom positions. All non-hydrogen atoms were refined anisotropically using full matrix least squares on F_{obs}^2, $w = 1/\sigma^2(F_{obs}^2)$. The hydrogen atoms were positioned by calculation in their idealized staggered geometry at a distance of 0.95 Å from their respective carbon atoms and were included in the structure factor calculations but their parameters were not refined. The final R was 0.077 on F for 2249 reflections with $F_{obs}^2 > 0$ and 0.069 on F for 1969 reflections with $F_{obs}^2 > 3\sigma(F_{obs}^2)$. wR on F^2 for all 2370 reflections used was 0.018. The maximum and minimum heights in the final difference Fourier were 1.07 and −0.60 e Å^{-3} respectively. A secondary extinction parameter [23] of $1.72(19) \times 10^{-6}$ was used. Atomic scattering factors were taken from Cromer and Waber [24]. Programs used were the CRYM crystallographic computing system [25], MULTAN88 [26], and ORTEP [27]. *Note*: The crystal used was a twin, with a minor component about 10% that of the major one. The two sets of reflections overlapped, however, as shown by scan profiles on selected reflections. Of the 2603 total independent reflections, 232 that were seriously affected by this overlap, and one with a bad background correction, were eventually deleted. The data, unfortunately, are still contaminated, as shown by the high value for the goodness of fit and by the observation that of the 47 reflections with the largest values of $w(F_{obs} - F_{calc})$, 34 are positive — well over half. While more peaks could have been removed, a point of diminishing returns had been reached: the largest $w(\delta F)$ values are now negative, and the largest δF values are about six electrons (one, the 600, is 8.98 electrons). The details of the thermal motions are probably affected by this, as are the noise peaks in the difference map, but the molecular geometry is correct within the reported esd values.

5. Supplementary material available

Details of the X-ray crystal structure determination for **2a**. ^{1}H NMR spectra for **3a**, **3b**, and the products of reaction of **3a** with [HNMe$_2$Ph]$^+$[B(C$_6$F$_5$)$_4$]$^-$.

Acknowledgements

References

[1] (a) D.J. Crowther, N.C. Baenziger and R.F. Jordan, *J. Am. Chem. Soc.*, *113* (1991) 1455. (b) R. Uhrhammer, D.J. Crowther, D.J. Olson, D.C. Swenson and R.F. Jordan, *Organometallics*, *11* (1992) 3098. (c) D.J. Crowther, S.L. Borkowsky, D.C. Swenson, T.Y. Meyer and R.F. Jordan, *Organometallics*, *12* (1993) 2897. (d) R. Uhrhammer, Y.X. Su, D.C. Swenson and R.F. Jordan, *Inorg. Chem.*, *33* (1994) 4398. (e) C. Kreuder, R.F. Jordan and H.M. Zhang, *Organometallics*, *14* (1995) 2993. (f) D.E. Bowen, R.F. Jordan and R.D. Rogers, *Organometallics*, *14* (1995) 3630. (g) D.J. Crowther, D.C. Swenson and R.F. Jordan, *J. Am. Chem. Soc.*, *117* (1995) 10403. (h) R.W. Quan, G.C. Bazan, A.F. Kiely, W.P. Schaefer and J.E. Bercaw, *J. Am Chem. Soc.*, *116* (1994) 4489. (i) G.C. Bazan, S.J. Donnelly and G. Rodriguez, *J. Am Chem. Soc.*, *117* (1995) 2671. (j) G.C. Bazan, W.P. Schaefer and J.E. Bercaw, *Organometallics*, *12* (1993) 2126. (k) A. Pastor, A.K. Kiely, L.M. Henling, M.W. Day and J.E. Bercaw, submitted to *J. Organomet. Chem.*
[2] (a) H. Brand and J. Arnold, *J. Am. Chem. Soc.*, *114* (1992) 2266. (b) H. Brand and J. Arnold, *Organometallics*, *13* (1994) 4469. (c) H. Ryu, D. Whang, J. Kim, W. Yeo and Y. Do, *J. Chem. Soc. Dalton Trans.*, (1993) 205. (d) C. Yang and V.L. Goedken, *J. Chem. Soc. Chem. Commun.*, (1986) 11101. (e) L. Giannini, E. Solari, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Angew. Chem. Int. Ed. Engl.*, *33* (1994) 2204. (f) C. Floriani, S. Ciurli, A. Chiesi-Villa and L. Giannini, *Angew. Chem. Int. Ed. Engl.*, *26* (1987) 70. (g) R. Uhrhammer, D.G. Black, T.G. Gardner, J.D. Olsen and R.F. Jordan, *J. Am. Chem. Soc.*, *115* (1993) 8493. (h) E.B. Tjaden, D.C. Swenson, R.F. Jordan and J.L. Petersen, *Organometallics*, *14* (1995) 371. (i) D.G. Black, D.C. Swenson, R.F. Jordan and R.D. Rogers, *Organometallics*, *14* (1995) 3539.
[3] E.B. Tjaden and R.F. Jordan, *St. Surf. Sci.*, *89* (1994) 271.
[4] (a) P. Chaudhuri and K. Wieghart, *Prog. Inorg. Chem.*, *35* (1987) 329 and references cited therein.
[5] A. Togni and L.M. Venanzi, *Angew. Chem. Int. Ed. Engl.*, *33* (1994) 497.
[6] J.E. Ellis, A.J. DiMaio, A.L. Rheingold and B.S. Haggerty, *J. Am Chem. Soc.*, *114* (1992) 10676.
[7] (a) L. Wang and T.C. Flood, *J. Am Chem. Soc.*, *114* (1992) 3169. (b) L. Wang, R.S. Lu, R. Bau and T.C. Flood, *J. Am Chem. Soc.*, *115* (1993) 6999.
[8] R.D. Köhn and G. Kociok-Köhn, *Angew. Chem. Int. Ed. Engl.*, *33* (1994) 1877.

[9] (a) F.T. Edelmann, in F.W. Abel, F.G.A. Stone and G. Wilkinson (eds.), *Comprehensive Organometallic Chemistry II*, Vol. 4, Pergamon, Tarrytown, NY, 1995. (b) M.E. Thompson and J.E. Bercaw, *Pure Appl. Chem.*, 56 (1984) 1. (c) J.E. Bercaw, *Pure Appl. Chem.*, 62 (1990) 1151 and references cited therein. (d) W.E. Piers, P.J. Shapiro, E.E. Bunel and J.E. Bercaw, *Synlett.*, 2 (1990) 74 and references cited therein. (e) E. Bunel, B.J. Burger and J.E. Bercaw, *J. Am. Chem. Soc.*, 110 (1988) 976.

[10] P. Jeske, K. Wieghart and B. Nuber, *Inorg. Chem.*, 33 (1994) 47.

[11] A. Haaland et al., *J. Am Chem. Soc.*, 112 (1991) 4547.

[12] M.E. Thompson, S.M. Baxter, A.R. Bulls, B.J. Burger, M.C. Nolan, B.D. Santarsiero, W.P. Schaefer and J.E. Bercaw, *J. Am. Chem. Soc.*, 109 (1987) 203.

[13] C.P. Casey and C.S. Yi, *J. Am. Chem. Soc.*, 114 (1992) 6597.

[14] (a) L. Melander and W.H. Saunders, *Reaction Rates of Isotopic Molecules*, Robert E. Krieger, Malabar, FL, 1987, p. 140. (b) J.M. Mayer, C.J. Curtis and J.E. Bercaw, *J. Am Chem. Soc.*, 105 (1983) 2651.

[15] G.G. Hlatky, H.W. Turner and R.R. Eckman, *J. Am Chem. Soc.*, 111 (1989) 2728.

[16] C. Pellecchia, A. Immirzi, A. Grassi and A. Zambelli, *Organometallics*, 12 (1993) 4473.

[17] X. Yang, C.L. Stern and T.J. Marks, *J. Am Chem. Soc.*, 113 (1991) 3623.

[18] M. Bochmann, S.J. Lancaster, M.B. Hursthouse and K.M.A. Malik, *Organometallics*, 13 (1994) 2235.

[19] (a) P. Longo, A. Proto and L. Oliva, *Macromol. Rapid Commun.*, 15 (1994) 151 and references cited therein. (b) R. Quyoum, Q. Wang, M.-J. Tudoret, M.C. Baird and D.J. Gillis, *J. Am Chem. Soc.*, 116 (1994) 6435. (c) D.J. Gillis, M.-J. Tudoret, R. Quyoum, J.R. Irving and M.C. Baird, *Abstr. Pap. ACS, 203* (1993) 37-INORG. (d) C. Pellicchia, P. Longo, A. Proto and A. Zambelli, *Makromol. Chem. Rapid Commun.*, 13 (1992) 265.

[20] B.J. Burger and J.E. Bercaw, in A.L. Wayda and M.Y. Darensbourg (eds.), *Experimental Organometallic Chemistry*, ACS Symposium Series 357, American Chemical Society, Washington, DC, 1987.

[21] R.H. Marvich and H.H. Brintzinger, *J. Am. Chem. Soc.*, 93 (1971) 2046.

[22] W.D. Cotter and J.E. Bercaw, *J. Organomet. Chem.*, 417 (1991) C1.

[23] A.C. Larson, *Acta Crystallogr.*, 23 (1964) 644.

[24] D.T. Cromer and J.T. Waber, *International Tables For X-Ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, 1974, pp. 99–101.

[25] D.J. Duchamp, *Am. Crystallogr. Assoc. Meet., Bozeman, MT, 1964*, Paper B14, p. 29.

[26] T. Debaerdemaeker, G. Germain, P. Main, L.S. Refaat, C. Tate and M. Woolfson, MULTAN 88. *Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data*, 1988, Universities of York (UK) and Louvain (Belgium).

[27] C.K. Johnson, ORTEP II, *Rep. ORNL-3794*, 1976 (Oak Ridge National Laboratory, Oak Ridge, TN, USA).