Ethylene Polymerization with Hydridotris(pyrazolyl)boratoniobium Complexes as Precursors

Joëlle Jaffart, Céline Nayral, Robert Choukroun, René Mathieu, and Michel Etienne*

Laboratoire de Chimie de Coordination, UPR CNRS 8241,
205 Route de Narbonne, F-31077 Toulouse Cedex 4, France
E-mail: etienne@lcc-toulouse.fr

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Substituted hydridotris(pyrazolyl)borato (Tp′) niobium complexes of the type [Tp′$NbMe_2$(PhC≡CMe)] polymerize ethylene (under 1 atm, at room temp. and in toluene) when treated with an equimolar amount of $B(C_6F_5)_3$. A clear relationship is observed between the stereoelectronic nature of the complex and catalytic activity. This is discussed on the basis of electrochemical data for the dichloro complexes [Tp′$NbCl_2$(PhC≡CMe)], and the rates of alkyl migration in [Tp′Nb(Cl)(R)(PhC≡CMe)] (R = CH_2Me, CH_2SiMe_3). For a given electron density at the metal, the bulky $Tp^{Me2,4\text{-}Cl}$ yields a catalyst which is more than 6 times as active as the unsubstituted Tp based catalyst.

Several attempts have recently been made, with related group 5 metal complexes, to mimic the outstanding activity in the polymerization of olefins of group 4 metal molecular complexes[1]. It is also hoped that the group 5 catalysts would be more tolerant to functionalized monomers, a highly desirable property if co-polymers are targeted. Most of the approaches have relied on an isoelectronic comparison with the 14-electron metallocene alkyl cations $[Cp_2MR]^+$, known to be the active species in group 4 catalysis[1]. As far as we are aware, a true Nb- or Ta-based catalyst, akin to $[Cp_2MR]^+$, has not so far been isolated, so we will base this discussion on its precursor. The combination [Cp′M(diene)X_2]/MAO (MAO = methylaluminoxane) gives polyethylene (PE) with a maximum activity of 39 (kg of PE) (mol of catalyst)$^{-1}$ h^{-1}. Interestingly the PE has a very narrow polydispersity (1.05)[2]. Based on the isolobal analogy, developed by Gibson and co-workers, between the bent metallocene Cp_2Zr and the imido CpNb(=NR) moieties[3], several systems have been explored. However, their activity is highly dependant on the substituents bound either to the metal or to the imido nitrogen, as well as on the activation mode[4]. The highest reported activity is 61 kg mol^{-1} h^{-1} for the [Cp*Ta(=N−SitBu$_3$)(η^1-allyl)(η^3-allyl)]/MAO system[4a], whereas some other imido complexes are, at best, only marginally active[4c]. The borollide−Cp ligand set leads to a deceptively low activity (2 kg mol^{-1} h^{-1} for [Cp*(η^5-$C_4H_4BNR_2$)$TaCl_2$/MAO)][5]. Imidovanadium complexes [LV(=NR)Cl_2] [L = Cp, Tp′ (Tp′ = a substituted hydridotris(pyrazolyl)borate)] generate active systems[4c][6], particularly with respect to propene polymerization.

Given the similarity between imido and (4e)-alkyne ligands[7] and between Cp and Tp′ ligands[8], we describe here preliminary results: (i) showing that complexes of the type [Tp′$NbMe_2$(alkyne)] do polymerize ethylene when properly activated; (ii) providing a basis for a stereoelectronic/activity relationship in this series of complexes, which has not been previously made for the group 5 metal catalysts. Related studies have been reported for Tp′-supported yttrium catalysts[9].

In Table 1, we summarize the data for ethylene polymerization by the system [Tp′$NbMe_2$(PhC≡CMe)]/$B(C_6F_5)_3$ (Tp′ = Tp, Tp^{Me2}, $Tp^{Me2,4\text{-}Cl}$, see Scheme 1)[10], electrochemical behaviour for the first monoelectronic reduction of the parent dichloro complexes [Tp′$NbCl_2$(PhC≡CMe)], and first-order rate constants k for alkyl migration to the alkyne in [Tp′Nb(Cl)(CH_2SiMe_3)(PhC≡CMe)] and [Tp′Nb(Cl)(CH_2Me)(PhC≡CMe)] (a reaction which ultimately yields [Tp′Nb(Cl)(Me)(PhC≡CCH_2SiMe_3)] and [Tp′Nb(Cl)(Me)(PhC≡CCH_2Me)] respectively, as shown elsewhere[11]). Several of these compounds are new and their syntheses and full characterization may be found in the Experimental Section.

Table 1. Ethylene polymerization activity for [Tp′$NbMe_2$(PhC≡CMe)]/$B(C_6F_5)_3$, electrochemical data for [Tp′$NbCl_2$(PhC≡CMe)] and first-order rate constants k for alkyl migration to the alkyne in [Tp′Nb(Cl)(R)(PhC≡CMe)], as a function of Tp′

Tp′	Activity[a]	$E_{1/2}$ (ΔE_p, i_a/i_c)[b]	$k \times 10^5$ [c]	$k \times 10^5$ [d]
Tp^{Me2}	100	−1.18 (0.15, 0.9)[e]	2.3[f]	3.0[f]
$Tp^{Me2,\ 4\text{-}Cl}$	130	−0.97 (0.10, 0.9)	2.2	4.75
Tp	20	−0.93 (0.25, 0.5)[e]	3.5	–

[a] Average of at least 3 runs, kg of PE (mol of catalyst)$^{-1}$ h^{-1}. – [b] V vs SCE. – [c] s^{-1}, R = CH_2SiMe_3. – [d] s^{-1}, R = CH_2Me. – [e] From ref.[10]. – [f] From ref.[11].

The first observation is that the dimethyl complexes [Tp′$NbMe_2$(PhC≡CMe)] do polymerize ethylene when activated by the methyl abstracting agent $B(C_6F_5)_3$ in a tolu-

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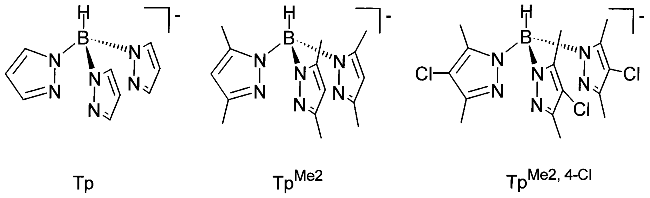
Scheme 1



ene solution[12], with the activities being higher than those observed for previously described systems based on heavier group 5 metal complexes. When red-purple [$Tp^{Me2}NbCl_2(PhC{\equiv}CMe)$] is treated with 500 equiv. of MAO in toluene, a light yellow solution is obtained which fails to polymerize ethylene. The choice of the activator is critical in other group 5 systems[4a]. We have also verified (^{1}H NMR) that toluene solutions of yellow [$Tp^{Me2}NbMe_2(PhC{\equiv}CMe)$] do not react with ethylene (1 atm).

The second observation is that the activity is notably dependent on the nature of Tp′. Bulky Tp^{Me2} and $Tp^{Me2,4\text{-}Cl}$ lead to a much higher catalytic activity than the less sterically demanding, unsubstituted Tp. Increased electrophilicity, as probed by comparison of the reduction potential $E_{1/2}$ for the parent dichloro Tp^{Me2} and $Tp^{Me2,4\text{-}Cl}$ complexes, only slightly increases the catalytic activity. By way of contrast, steric protection is mandatory: Tp and $Tp^{Me2,4\text{-}Cl}$ offer virtually the same electron density at the metal (cf. $E_{1/2}$), but catalytic production is dramatically favored by the bulky ligand[13]. We propose that these effects result from a steric shielding of the metal center by Tp^{Me2} and $Tp^{Me2,4\text{-}Cl}$ which prevents decomposition of the catalytic species via some kind of association. Several decomposition processes of the group 4 catalysts involve the formation of dinuclear species[1].

Parallel experiments lend further support to this view. We have previously studied in detail the mechanism of alkyl exchange in [$Tp^{Me2}Nb(Cl)(R)(PhC{\equiv}CMe)$] that leads to [$Tp^{Me2}Nb(Cl)(Me)(PhC{\equiv}CR)$] via the rate determining step of migratory insertion of R on to the alkyne[11]. The disappearance of [$Tp^{Me2}Nb(Cl)(R)(PhC{\equiv}CMe)$] at 343 K occurs with first-order rate constants of $2.3 \cdot 10^{-5}$ s^{-1} and $3.0 \cdot 10^{-5}$ s^{-1} for R = CH_2SiMe_3 and CH_2Me, respectively[11]. The corresponding Tp and $Tp^{Me2,4\text{-}Cl}$ complexes have thus been synthesized and their thermolysis studied by ^{1}H NMR in [D_6]benzene at 343 K. The experimental first-order rate constants k provided in Table 1 indicate that, again, the steric bulk of the Tp′ ligand largely governs the stability of the complexes and the alkyl group migration on to the alkyne. On one hand, for similar electron density at the metal, the rate constant for alkyl migration is significantly higher when a less sterically demanding ligand is used (cf. rate and electrochemical data for Tp and $Tp^{Me2,4\text{-}Cl}$). On the other hand, ligands of similar size such as Tp^{Me2} and $Tp^{Me2,4\text{-}Cl}$ which significantly differ in their electron-donating ability provide a similar barrier to alkyl migration as soon as the migrating R becomes too bulky. When R = CH_2Me, the migration is slightly faster for $Tp^{Me2,4\text{-}Cl}$ as expected, whereas there is no difference for the bulkier R = CH_2SiMe_3. In addition, the rearrangement of [$TpNb(Cl)(CH_2SiMe_3)(PhC{\equiv}CMe)$], although faster, is accompanied by important decomposition while putative [$TpNb(Cl)(CH_2Me)(PhC{\equiv}CMe)$] decomposes during its attempted synthesis. In the same vein, the chemical and electrochemical reversibilities of the first one-electron reduction of the parent dichloro complexes are low for Tp only. These observations may be ascribed to steric protection of the metal by the bulkier Tp′.

Assuming that these alkyl to alkyne migrations mimic with sufficient reliability the migration of a growing alkyl chain to a coordinated ethylene at least with respect to steric interactions, we conclude that a more active catalyst is obtained when an efficient protection of the metal is realized at the expense of faster intramolecular migration of alkyl chains. Since ethylene coordination is expected to be easier for the less bulky Tp, the central role played by the size of Tp′ is to be emphasized.

Hydridotris(pyrazolyl)borato group 5 complexes can indeed be used as ethylene polymerization catalysts. Such ligands provide a high degree of steric control which prevents catalyst decomposition, a major feature of the polymerizations reported herein. Up to now, attempts at observing putative naked or base-stabilized alkyl cations such as [$Tp'NbMe(PhC{\equiv}CMe)$]$^+$ or [$Tp'NbMe(PhC{\equiv}CMe)(L)$]$^+$ have failed. Further studies aimed at improving the activity of ethylene polymerization and studying α-olefins are in progress.

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Experimental Section

General: All experiments were carried out under a dry dinitrogen atmosphere using either Schlenck tube or glove box techniques. THF was obtained after refluxing a purple solution of Na/benzophenone under dinitrogen. Toluene, *n*-hexane, and pentane were dried by refluxing over CaH_2 under dinitrogen. Toluene used for the polymerization reactions was treated with concentrated sulfuric acid, washed three times with water, stored over $CaCl_2$, then further dried by refluxing over CaH_2 under dinitrogen before use. [D_6]Benzene (used unless otherwise stated) and $CDCl_3$ were dried over molecular sieves and stored under dinitrogen. − ^{1}H and ^{13}C NMR (only pertinent $^1J_{CH}$ are quoted): Bruker AC 200 (200, 50 MHz resp) and AM 250 (250, 62.9 MHz resp). − Elemental analyses: Perkin Elmer 2400 Series II. DTA: Sétaram 92−16.18. − Cyclic voltammetry data (home-made potentiostat interfaced with a PC-computer, scan rate 100 mV s^{-1}): Pt disk (1 mm) working electrode, THF solution, 0.1 M Bu_4NBF_4 as supporting electrolyte, Pt wire as auxiliary electrode, SCE as reference electrode.

The new compounds [$Tp^{Me2,4\text{-}Cl}NbCl_2(PhC{\equiv}CMe)$], [$Tp^{Me2,4\text{-}Cl}NbMe_2(PhC{\equiv}CMe)$], [$Tp^{Me2,4\text{-}Cl}Nb(Cl)(CH_2Me)(PhC{\equiv}CMe)$], [$Tp^{Me2,4\text{-}Cl}Nb(Cl)(CH_2SiMe_3)(PhC{\equiv}CMe)$], [$TpNb(Cl)(CH_2SiMe_3)(PhC{\equiv}CMe)$] have been obtained following published procedures established for related Tp and Tp^{Me2} complexes[10][11]. Yields and full characterization of these new compounds are provided below. Tp^{Me2} and $Tp^{Me2,4\text{-}Cl}$ complexes exist as a mixture of discrete alkyne rotamers[10][11]. Some NMR resonances of the minor isomer may be obscured.

[TpNbMe$_2$(PhC≡CMe)] could not be obtained cleanly from [TpNbCl$_2$(PhC≡CMe)] and 2 equiv. of LiMe. Its synthesis from MeMgCl is described below. B(C$_6$F$_5$)$_3$ (ref.[14]) was sublimed in vacuo before use. Kinetic data on the rearrangement of [Tp′Nb(Cl)(R)(PhC≡CMe)] were obtained from [D$_6$]benzene solutions at 343 K as previously reported[11].

[Tp$^{Me2,4-Cl}$NbCl$_2$(PhC≡CMe)]: Yield 59%. – $C_{24}H_{27}BCl_5N_6Nb$ calcd: C 42.4, H 4.0, N 12.35; found: C 42.3, H 4.0, N 12.20. – ^{1}H NMR: Major isomer δ = 6.90–6.60 (m, 5 H, *Ph*C≡CMe), 3.84 (s, 3 H, PhC≡C*Me*), 2.94, 1.97 (s, 3 H each, Tp$^{Me2,4-Cl}$*Me*), 1.85, 1.79 (s, 6 H each, Tp$^{Me2,4-Cl}$*Me*). Minor isomer: δ = 8.3 (d, 2 H, *o-Ph*C≡CMe), 7.38 (t, 2 H, *m-Ph*C≡CMe), 2.97 (s, 3 H, PhC≡C*Me*), 2.21, 1.95 (s, 3 H each, Tp$^{Me2,4-Cl}$*Me*), 1.94, 1.81 (s, 6H each, Tp$^{Me2,4-Cl}$*Me*). – ^{13}C{^{1}H} NMR (CDCl$_3$): Major isomer: δ = 267.1, 221.4 (Ph*C*≡*C*Me), 150.3, 148.7, 141.4, 141.2 (Tp$^{Me2,4-Cl}$*C*Me), 136.9 (*ipsoPh*), 129.7, 128.9, 128.8 (*Ph*), 111.1 (Tp$^{Me2,4-Cl}$*C*Cl), 25.1 (PhC≡C*Me*), 13.4, 13.1, 11.2, 11.0 (Tp$^{Me2,4-Cl}$*Me*). Minor isomer: δ = 249.7, 234.5 (Ph*C*≡*C*Me), 136.2 (*ipsoPh*), 132.4, 131.1, 130.3 (*Ph*), 111.1 (Tp$^{Me2,4-Cl}$*C*Cl), 23.8 (PhC≡C*Me*), 13.6, 13.5, 10.8 (Tp$^{Me2,4-Cl}$*Me*).

[Tp$^{Me2,4-Cl}$NbMe$_2$(PhC≡CMe)]: Yield 50%. – $C_{26}H_{33}BCl_3N_6Nb$ calcd: C 48.8, H 5.2, N 13.1; found: C 49.1, H 5.2, N 12.9. – ^{1}H NMR: Major isomer δ = 7.10–6.90 (m, 5 H, *Ph*C≡CMe), 3.50 (s, 3 H, PhC≡C*Me*), 2.47, 2.12 (s, 3 H each, Tp$^{Me2,4-Cl}$*Me*), 1.97, 1.69 (s, 6 H each, Tp$^{Me2,4-Cl}$*Me*), 1.02 (s, 6 H, Nb*Me*). Minor isomer: δ = 7.93 (d, 2 H, *o-Ph*C≡CMe), 6.90 (t, 2 H, *m-Ph*C≡CMe), 2.52 (s, 3 H, PhC≡C*Me*), 2.09 (s, 3 H, Tp$^{Me2,4-Cl}$*Me*), 1.93, 1.89 (s, 6H each, Tp$^{Me2,4-Cl}$*Me*), 1.14 (s, 6 H, Nb*Me*). – ^{13}C NMR: Major isomer: δ = 250.1, 223.9 (Ph*C*≡*C*Me), 148.4, 148.2, 141.1, 141.0 (Tp$^{Me2,4-Cl}$*C*Me), 139.2 (*ipsoPh*), 130.0, 129.0, 128.9 (*Ph*), 110.9, 110.1 (Tp$^{Me2,4-Cl}$*C*Cl), 55.4 (q, J_{CH} = 120 Hz, Nb*Me*), 22.8 (PhC≡C*Me*), 14.3, 12.9, 12.8, 10.9 (Tp$^{Me2,4-Cl}$*Me*). Minor isomer: δ = 238.2, 235.8 (Ph*C*≡*C*Me), 56.4 (q, J_{CH} = 120 Hz, Nb*Me*), 23.2 (PhC≡C*Me*), 13.2, 13.1, 12.7, 10.7 (Tp$^{Me2,4-Cl}$*Me*).

[Tp$^{Me2,4-Cl}$Nb(Cl)(CH$_2$Me)(PhC≡CMe)]: Yield 45%. – $C_{26}H_{32}BCl_4N_6Nb$ calcd: C 46.3, H 4.8, N 12.5; found: C 46.8, H 5.2, N 12.2. – ^{1}H NMR: Major isomer δ = 7.30–6.80 (m, 5 H, *Ph*C≡CMe), 3.70 (dq, *J* = 12.8, 7.7 Hz, 1 H, NbC*H$_2$*Me), 3.54 (s, 3 H, PhC≡C*Me*), 2.75, 2.06, 1.96, 1.93, 1.87, 1.56 (s, 3 H each, Tp$^{Me2,4-Cl}$*Me*), 1.00 (dd, *J* = 7.7, 6.2 Hz, NbCH$_2$*Me*), 0.20 (dq, *J* = 12.8, 6.2 Hz, 1 H, NbC*H$_2$*Me). Minor isomer: δ = 8.10 (d, 2 H, *o-Ph*C≡CMe), 7.40 (t, 2 H, *m-Ph*C≡CMe), 3.90 (dq, *J* = 12.8, 7.7 Hz, 1 H, NbC*H$_2$*Me), 2.79 (s, 3 H, PhC≡C*Me*), 2.30, 2.08, 2.02, 1.90, 1.89, 1.74 (s, 3 H each, Tp$^{Me2,4-Cl}$*Me*), 0.97 (dd, *J* = 7.7, 6.2 Hz, NbCH$_2$*Me*), 0.30 (m, 1 H, NbC*H$_2$*Me). – ^{13}C NMR: Major isomer: δ = 249.6, 216.5 (Ph*C*≡*C*Me), 150.3, 149.6, 147.4, 141.6, 141.3, 141.0 (Tp$^{Me2,4-Cl}$*C*Me), 138.5 (*ipsoPh*), 131.9, 129.8, 129.0 (*Ph*), 111.0, 110.6, 110.4 (Tp$^{Me2,4-Cl}$*C*Cl), 88.4 (dd, J_{CH} = 105, 126 Hz, Nb*C*H$_2$Me), 23.1 (PhC≡C*Me*), 13.2, 13.1, 12.2, 11.1, 10.9, 10.8, 10.7 (Tp$^{Me2,4-Cl}$*Me* and CH$_2$*Me*). Minor isomer: δ = 235.8, 227.8 (Ph*C*≡*C*Me), 149.5, 149.2, 146.1, 141.4, 141.3, 140.9 (Tp$^{Me2,4-Cl}$*C*Me), 91.2 (dd, J_{CH} = 105, 126 Hz, Nb*C*H$_2$Me), 23.0 (PhC≡C*Me*), 13.4, 11.9, 10.5 (Tp$^{Me2,4-Cl}$*Me* and CH$_2$*Me*).

[Tp$^{Me2,4-Cl}$Nb(Cl)(CH$_2$SiMe$_3$)(PhC≡CMe)]: Yield 34%. – $C_{28}H_{38}BCl_4N_6NbSi$ calcd: C 45.9, H 5.2, N 11.5; found: C 46.5, H 5.5, N 10.8. – ^{1}H NMR: Major isomer δ = 7.00–6.80 (m, 5 H, *Ph*C≡CMe), 3.65 (s, 3 H, PhC≡C*Me*), 3.06 (d, *J* = 12.4 Hz, 1 H, NbC*H$_2$*SiMe$_3$), 2.82, 2.09, 2.06, 1.91, 1.73, 1.65 (s, 3 H each, Tp$^{Me2,4-Cl}$*Me*), 0.27 (d, *J* = 12.4 Hz, 1 H, NbC*H$_2$*SiMe$_3$), –0.17 (s, 9 H, Si*Me$_3$*). Minor isomer: δ = 8.14 (d, 2 H, *o-Ph*C≡CMe), 7.40 (t, 2 H, *m-Ph*C≡CMe), 3.45 (d, *J* = 11.8 Hz, 1 H, NbC*H$_2$*SiMe$_3$), 2.87 (s, 3 H, PhC≡C*Me*), 2.30, 2.09, 2.02, 1.98, 1.85 (s, 3 H each, Tp$^{Me2,4-Cl}$*Me*), 0.37 (d, *J* = 11.8 Hz, 1 H, NbC*H$_2$*SiMe$_3$), –0.44 (s, 9 H, Si*Me$_3$*). – ^{13}C NMR: Major isomer: δ = 251.5, 221.4 (Ph*C*≡*C*Me), 149.7, 149.6, 148.2, 141.2, 138.2 (Tp$^{Me2,4-Cl}$*C*Me), 138.3 (*ipsoPh*), 129.8, 129.6, 128.9 (*Ph*), 111.4, 110.9, 110.5 (Tp$^{Me2,4-Cl}$*C*Cl), 81.5 (dd, J_{CH} = 106, 124 Hz, Nb*C*H$_2$SiMe$_3$), 24.0 (PhC≡C*Me*), 14.5, 14.0, 12.9, 11.0, 10.7, 10.6 (Tp$^{Me2,4-Cl}$*Me*), 2.3 (Si*Me*).

[TpNbMe$_2$(PhC≡CMe)]: 0.7 ml of a 3.0 M THF solution of MeMgCl was added dropwise to a stirred cooled (0°C) toluene solution (50 ml) of [TpNbCl$_2$(PhC≡CMe)] (0.49 g, 1.0 mmol). Stirring was continued at 0°C for 4 h as the colour of the solution turned from red-purple to yellow greenish. The solution was then pumped to dryness. Extraction with pentane (30 ml), and filtration through a Celite pad, followed by several washings, afforded a yellow solution which was then evaporated to dryness. Crystallization from pure pentane afforded yellow crystals of the title compound (0.20 g, 0.44 mmol, 44%). The yield is limited by the high solubility of the compound. –$C_{20}H_{25}BN_6Nb$ calcd: C 53.1, H 5.5, N 18.6; found: C 53.1, H 4.9, N 18.3. – ^{1}H NMR: δ = 7.98, 7.45 (br s, 1 H each, Tp-3-C*H* and Tp-5-C*H*), 7.40–7.10 (m, 5 H, *Ph*C≡CMe), 7.45, 6.92 (br s, 2 H each, Tp-3-C*H* and Tp-5-C*H*), 6.06 (br s, 1 H, Tp-4-C*H*), 5.69 (br s, 2 H, Tp-4-C*H*), 3.28 (s, 3 H, PhC≡C*Me*), 1.14 (s, 6 H, Nb*Me*). – ^{13}C NMR: δ = 242.0, 227.7 (Ph*C*≡*C*Me), 143.3, 142.4, 135.0, 134.4 (br, Tp-3-*C*H and Tp-5-*C*H), 139.3 (*ipsoPh*), 130.7, 128.8, 128.4 (*Ph*), 105.7, 104.9 (br, Tp-4-*C*H), 55.0 (q, J_{CH} = 118 Hz, Nb*Me*), 22.0 (PhC≡C*Me*).

[TpNb(Cl)(CH$_2$SiMe$_3$)(PhC≡CMe)]: Yield 88%. – $C_{22}H_{29}BClN_6NbS$ calcd: C 48.5, H 5.4, N 15.4; found: C 48.9, H 5.0, N 15.1. – ^{1}H NMR: δ = 8.40, 7.42, 7.31, 7.00, 6.93 (d, *J* = 2.2 Hz, 1 H each, Tp-3-C*H* and Tp-5-C*H*), 7.30–7.00 (m, 5 H, *Ph*C≡CMe), 5.99, 5.71, 5.50 (t, *J* = 2.2 Hz, 1 H each, Tp-4-C*H*), 3.34 (s, 3 H, PhC≡C*Me*), 1.93 (s, 2 H, NbC*H$_2$*SiMe$_3$), –0.09 (s, 9 H, Si*Me$_3$*). – ^{13}C NMR: δ = 242.8, 225.9 (Ph*C*≡*C*Me), 144.7, 144.5, 144.0, 135.0, 134.9, 134.4 (Tp-3-*C*H and Tp-5-*C*H), 138.0 (*ipsoPh*), 131.1, 129.2, 128.7 (*Ph*), 105.8, 106.3 (Tp-4-*C*H), 83.1 (t, J_{CH} = 108 Hz, Nb*C*H$_2$SiMe$_3$), 23.3 (PhC≡C*Me*).

Typical Ethylene Polymerization Run: In the glove box [Tp$^{Me2,4-Cl}$NbMe$_2$(PhC≡CMe)] (12.8 mg, 0.02 mmol), a magnetic stir bar and purified toluene (5 ml) were introduced in a Fischer-Porter bottle equiped with a side arm. To this side arm was attached (Teflon joint, screw connection, Teflon stopcock) a glass vessel containing B(C$_6$F$_5$)$_3$ (10.4 mg, 0.02 mmol) dissolved in toluene (5 ml). The apparatus was removed from the glove box, and attached to a double manifold vacuum line connected to an ethylene tank through molecular sieves and CuO purifying devices. The main Fischer-Porter volume, containing the vigorously stirred (500 rpm) yellow solution of the niobium complex, was saturated with ethylene under 1 atm. No reaction occured at that stage. The Teflon stopcock of the side arm was opened to allow instantaneous mixing of the co-catalyst, then closed again. A chronometer was started. Virtually instantaneous precipitation of a whitish powder commenced together with temp. increase. Methanol (10 ml) containing a few drops of an aqueous HCl solution was introduced through the side arm after 5 min to quench the polymerization reaction. The precipitate was collected on a frit in air, washed several times with methanol and then diethyl ether, and dried to a constant weight in an oven (75°C). 0.212 mg of a white solid, corresponding to a catalytic activity of 125 kg mol^{-1} h^{-1}, were obtained. – $(C_2H_4)_n$ calcd: C 85.6, H 14.4, N 0.0; found: C 85.6, H 15.2, N 0.0. – DTA: m.p. 133.5°C.

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