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Elusive Niobium Alkyl Cations Related to Ethylene Polymerization

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Summary: Elusive cationic methyl complexes of niobium, [$Tp^{Me2}NbMe(L)(MeC\equiv CMe)$][$BAr_{f4}$] (L = OEt_2, PMe_2Ph, PEt_3), that model the active species in alkene polymerization by group 5 metals have been prepared. The X-ray crystal structure of the diethyl ether adduct has been obtained.

The generation, identification, and isolation of d^0 alkyl cations of the group 4 metals has confirmed that they are key intermediates in the polymerization of olefins, a reaction that these complexes catalyze efficiently.[1] Detailed thermodynamic and kinetic studies of alkene binding, ion pairing, migratory insertion (i.e. chain growth), and β-H and β-alkyl eliminations (i.e. chain transfer and chain termination) have been carried out on discrete, highly reactive cationic alkyl complexes of these and related metals.[2] A combination of these efforts at the molecular level has resulted in considerable improvements in catalyst design and ultimately to process development. One of the seminal advances in this field was the discovery that alkyl cations of the group 4 metallocene complexes could indeed be generated and stabilized.

Although simple vanadium compounds are used industrially for ethylene/propylene copolymerization and related reactions,[3] polymerization of olefins with complexes of the heavier group 5 metals (Nb, Ta) has received considerably less attention.[4] With a range of stable oxidation states, these metals offer an opportunity to study in more depth the influence of charge, electron count, and other variables on the various steps of the polymerization process. These complexes may also be more tolerant to functional groups than the oxophilic species derived from group 4 metals: their use as selective catalysts may then parallel mechanistic insights. In some instances, group 5 catalysts have been shown to have reactivity comparable to that of group 4 systems, such as in the recently described trimerization of ethylene to 1-hexene catalyzed by $TaMe_2Cl_3$.[5] In addition, group 5 systems have produced creditable performances in terms of product polydispersity, if not in terms of catalyst activity. Most attempts to develop active group 5 catalysts have been inspired by isoelectronic, isolobal, or isostructural relationships with known group 4 metal complexes. Thus, complexes based on cyclopentadienyl (sandwich and half-sandwich complexes),[6] amidinate,[7] imido,[7,8] diamido,[7] borollide,[9] tribenzylidenemethane,[10] diene,[11] amidopyridine,[12] and tris(pyrazolyl)borate[13] ligands—or combinations thereof—have all been explored. However, simple alkyl cations (or related ion pairs or base adducts) that *also* polymerize ethylene or higher olefins have rarely been characterized for the heavier group 5 metals.[12b,14] Consequently, associated mechanistic studies are extremely rare, and no information is available concerning the details of the polymerization process. We report herein that the use of the Tp^{Me2} (Tp^{Me2} = hydrotris(3,5-dimethyl)pyrazolylborate) ligand and the nature of the counterion are critical for the full characterization (including an X-ray crystal structure) of a rare ether adduct of a niobium alkyl cation, [$Tp^{Me2}NbMe(OEt_2)$-

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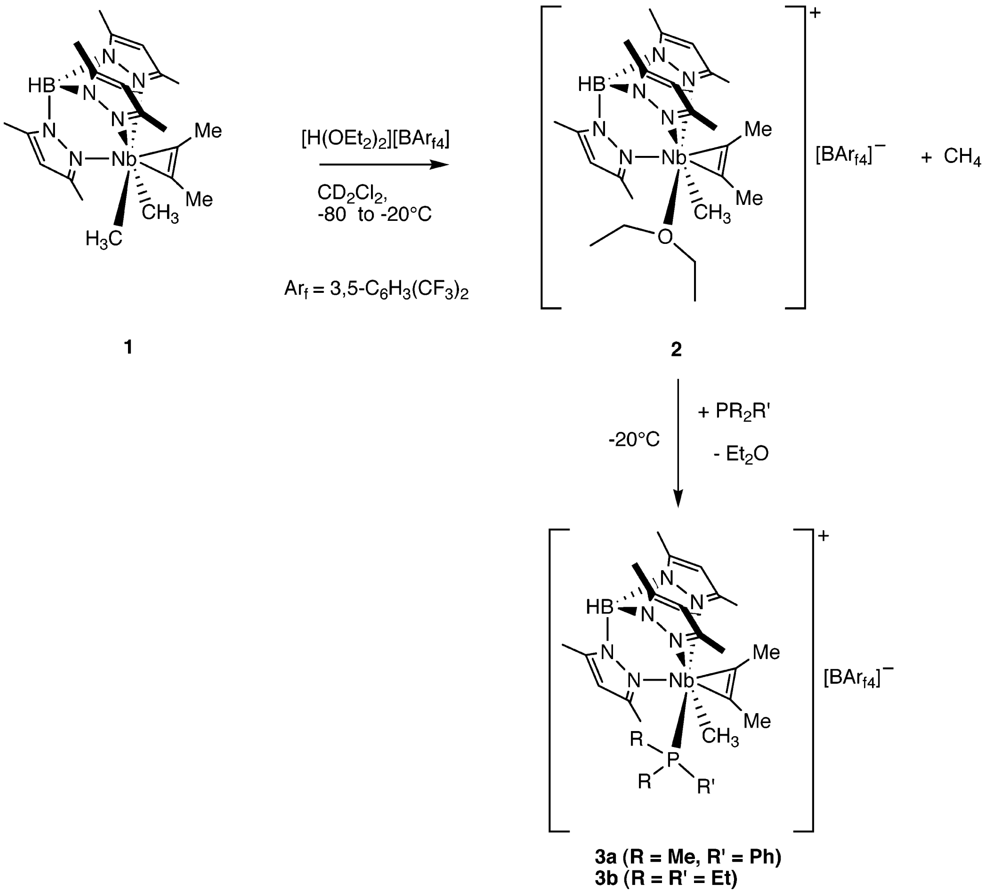
Scheme 1



$(MeC{\equiv}CMe)]^+$.[15] Preliminary substitution reactions indicate that the chemistry of this complex can be developed further.

The system $[Tp'NbMe_2(PhC{\equiv}CMe)]/B(C_6F_5)_3$ (Tp′ = Tp, Tp^{Me2}, $Tp^{Me2,4-Cl}$) polymerizes ethylene, as described earlier.[13] Attempts to observe the putative intermediate ion pair $[Tp^{Me2}Nb^+Me(PhC{\equiv}CMe)(\mu\text{-}Me)B^-(C_6F_6)_3]$ by in situ NMR tube reactions at low temperatures in various solvents (toluene-d_8, dichloromethane-d_2) were frustrated by extensive decomposition, possibly through electrophilic cleavage of the B−N bond of Tp^{Me2}, a known phenomenon in Tp′-based chemistry. A route to $[Tp^{Me2}NbMe(L)(alkyne)]^+$ was thus sought through the dimethyl complex. Pioneering work on the group 4 systems employed $[HNMe_2Ph][BPh_4]$ as the combined proton donor, Lewis base, and nonnucleophilic, noncoordinating anion source.[1a,b] In our hands, $[HNMe_2Ph][BPh_4]$ did not protonate $[Tp^{Me2}NbMe_2(PhC{\equiv}CMe)]$. The stronger acid $[H(OEt_2)_2][BAr_{f4}]$ (Ar_f = 3,5-C_6H_3-$(CF_3)_2$)[16] has been used extensively to generate labile ether adducts of late-transition-metal alkyl complexes,[17] including Tp′-containing complexes.[18] Reactions of this acid with early-transition-metal alkyl complexes have not often been reported,[19] although half-sandwich cationic chromium alkyls which polymerize olefins have been generated via this route.[20]

Protonation of the yellow dimethyl complex[21] $[Tp^{Me2}NbMe_2(MeC{\equiv}CMe)]$ (**1**) with 1 equiv of $[H(OEt_2)_2][BAr_{f4}]$ in dichloromethane-d_2 at −80 °C quantitatively generates methane (δ 0.17) and bright orange $[Tp^{Me2}NbMe(OEt_2)(MeC{\equiv}CMe)][BAr_{f4}]$ (**2**), as indicated by ^1H and ^{13}C NMR spectroscopy (Scheme 1). Note that triflic acid, HOTf, protonates the dimethyl complex $[Cp^*TaMe_2(\eta^4\text{-isoprene})]$ to yield the structurally characterized $[Cp^*TaMe(OTf)(\eta^4\text{-isoprene})]$ with a covalent Ta−OTf bond, a complex that only serves as a very crude model for a base-stabilized cation.[11a] $[Tp^{Me2}NbMe(Cl)(MeC{\equiv}CMe)]$ can be obtained by treatment of **1** with HCl in diethyl ether.[19]

Prominent features in the NMR spectra of **2** are (i) the appearance of a 3 × 1H and a 6 × 3H pattern for the Tp^{Me2} protons, indicating the absence of a symmetry plane, (ii) Nb−Me signals at δ 1.77 and 75.0 (q, $^1J_{CH}$ = 122 Hz) in the ^1H and ^{13}C NMR spectra, respectively, and (iii) diastereotopic OEt_2 methylene protons at δ 4.24, 4.11, 3.55, and 3.30 (all m), with their associated ^{13}C resonances at δ 75.2 and 74.5. These assignments

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(15) A few base-stabilized niobium alkyl cations exist, but they only bear a distant resemblance to olefin polymerization catalysts; see for example, the following. (a) Antinolo, A.; Otero, A.; Fajardo, M.; Gil-Sanz, R.; Herranz, M. J.; Lopez-Mardomingo, C.; Martin, A.; Gomez-Sal, P. *J. Organomet. Chem.* **1997**, *533*, 87−96. (b) $[Cp_2Nb(N^tBu)]$-$[MeB(C_6F_5)_3]$ is a separated ion pair, see: Humphries, M. J.; Douthwaite, R. E.; Green, M. L. H. *Dalton* **2000**, 2952−2959.

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(21) Unpublished data. For similar dimethyl complexes, see: Etienne, M.; Biasotto, F.; Mathieu, R.; Templeton, J. L. *Organometallics* **1996**, *15*, 1106−1112.

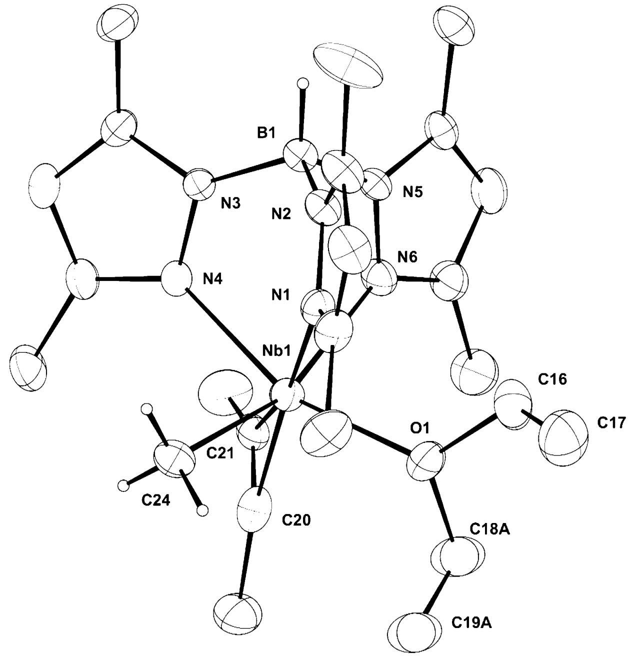

Figure 1. Structure of the cation of [Tp^{Me2}NbMe(OEt$_2$)(MeC≡CMe)][BAr$_{f4}$] (**2**), as determined by X-ray diffraction at 180 K. Ellipsoids are drawn at the 30% probability level. Salient distances (Å) and angles (deg): Nb(1)−C(24), 2.182(7); Nb(1)−O(1), 2.186(5), Nb(1)−C(20) = 2.104(8), Nb(1)−C(21) = 2.047(7), C(20)−C(21) = 1.234(10); O(1)−Nb(1)−C(24), 108.9(2).

have all been confirmed by ^{1}H/^{13}C correlation experiments. Complex **2** is stable in solution up to −20 °C for ca. 12 h. At this temperature, migratory insertion of the 4e alkyne[22] (^{13}C NMR δ 254.7, 245.4 (C≡C); at lower field than those in *neutral* [Tp^{Me2}NbRCl(MeC≡CMe)])[23] into the Nb−Me bond is not observed. Although quite reactive toward air and moisture, complex **2** has produced X-ray-quality crystals from a concentrated dichloromethane-d_2 solution. The X-ray diffraction experiment,[24] carried out at 180 K, confirmed the formulation (Figure 1). However, one ethyl group of the Et$_2$O ligand was disordered. Data collection at 120 K on crystals selected from an independent batch did not solve this disorder problem. Salient bond lengths and angles are included in the caption of Figure 1. The Nb−C bond (2.182(7) Å) lies at the shorter end of the range of Nb−C bond lengths we have observed in our series of *neutral* [Tp^{Me2}NbCl(alkyl)(RC≡CMe)] complexes[22] and is slightly shorter than that in [Tp^{Me2}NbMe$_2$(MeC≡CMe)] (Nb−C = 2.210(4), 2.213(4) Å),[19] in accord with the higher electrophilicity of the metal center in the cation.[25] The Tp^{Me2} ligand plays its characteristic directing role in **2**: one ethyl group of the OEt$_2$ ligand occupies the wedge between two of the three pyrazole rings, with the other (disordered) one pointing away from the pendant Me groups of Tp^{Me2}. The Nb−OEt$_2$ and Nb−C bond lengths are almost identical, with no Nb−O (2.186(5) Å) shortening apparent from the possible involvement of Nb−O π-bonding,[26] a conclusion supported by the normal Nb−(4e alkyne) distances (Figure 1).[27] Although the esd is somewhat large, the coordinated C−C bond of the alkyne is slightly shorter than in the related neutral species [Tp^{Me2}NbRCl(MeC≡CMe)].[22] Clearly, [H(OEt$_2$)$_2$][BAr$_{f4}$] provides the necessary ingredients to generate and stabilize 16e alkyl cations of niobium (either d^2 or d^0 depending on how the 4e alkyne is described)[21] also involved in ethylene polymerization. Under kinetically controlled conditions, there is no evidence of Tp^{Me2} decomposition or κ^2-Tp^{Me2} formation via protonation of a pyrazolyl ring.

Excess PMe$_2$Ph quantitatively replaces the Et$_2$O ligand in **2** between −60 and −20 °C to give [Tp^{Me2}NbMe(PMe$_2$Ph)(MeC≡CMe)][BAr$_{f4}$] (**3a**), which has been spectroscopically characterized at −60 °C (Scheme 1). In the ^{1}H and ^{13}C NMR spectra of **3a**, prominent resonances at δ 1.68 and 95.1 (q, $^1J_{CH}$ = 122 Hz), respectively, correspond to the Nb−Me moiety; this shows no coupling with the phosphine ligand (^{31}P NMR δ −1.75). The diastereotopic methyl groups of the phosphine resonate at δ 1.93 and 1.25 in the ^{1}H NMR spectrum. Free ether and phosphine signals were narrow enough to confirm that no exchange occurs between the coordinated phosphine and other potential ligands. Solutions of **3a** are stable for 24 h below −20 °C. In a similar vein, PEt$_3$ produces [Tp^{Me2}NbMe(PEt$_3$)(MeC≡CMe)][BAr$_{f4}$] (**3b**: ^{1}H NMR δ 1.70; ^{13}C NMR δ 94.7; ^{31}P NMR δ 15.3), indicating that the cone angle and basicity of the phosphine can be varied.

Although **2** has limited thermal stability, its ability to catalyze the polymerization of ethylene was tested. In contrast to the system [Tp′NbMe$_2$(PhC≡CMe)]/B(C$_6$F$_5$)$_3$, which polymerizes ethylene (q.v.),[13] only a few milligrams of polyethylene precipitated when a dichloromethane solution of **2** was exposed to 1 bar of ethylene. In view of the behavior of similar group 4 complexes,[1a] this is not surprising, since a vacant coordination site is required for ethylene coordination prior to migratory insertion and chain growth. In our search for bulkier ligands that dissociate more readily than diethyl ether, we have preliminary evidence that the diisopropyl ether complex [Tp^{Me2}NbMe(O*i*Pr$_2$)(MeC≡CMe)]$^+$[BAr$_{f4}$] can be made.

In summary, we have prepared rare examples of alkyl cations of niobium directly related to the active species in ethylene polymerization. Stabilization is effected by the unique electronic and steric properties of Tp^{Me2} and the 4e alkyne ligands, in tandem with the noncoordinating properties of the BAr$_{f4}$$^-$ anion. Our next task will be the study of alkene and/or alkyne binding to the

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[24] X-ray data for **2**: C$_{56}$H$_{53}$B$_2$F$_{24}$N$_6$NbO, triclinic, $P\bar{1}$, T = 180 K, a = 12.7185(6) Å, b = 13.0870(7) Å, c = 18.5693(10) Å, α = 91.249(4)°, β = 94.824(4)°, γ = 99.599(9)°, V = 3034.7(3) Å^3, Z = 2, 17 779 reflections collected, 8700 unique reflections (R_{int} = 0.0437), 6918 reflections with $I > 2\sigma(I)$, 48 restraints, 820 parameters, R1 = 0.0793, wR2 = 0.2155 on F^2.

[25] In [Cp$_2$TaMe$_2$][(C$_6$F$_5$)$_3$Al(μ-Me)Al(C$_6$F$_5$)$_3$], the Ta−C bond lengths are 2.166(3) and 2.188(3) Å.[14] Neutral [L$_2$NbMe(PhC≡CSiMe$_3$)] (L = 6-methyl-2-((trimethylsilyl)amido)pyridine) has an Nb−C bond length of 2.195(13) Å, whereas in the ion pair [L$_2$Nb(PhC≡CSiMe$_3$)(μ-Me)B(C$_6$F$_5$)$_3$], it is significantly elongated to 2.611(5) Å.[12b]

[26] See, for example: Guo, G.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1994**, *13*, 1424−1432 and references therein.

[27] In 4e alkyne complexes in particular, definitive assignment of an oxidation state to the metal is a matter of debate. The bond distances in **2** indicate that the alkyne is partially oxidized, so that the niobium center is between the two extremes of Nb(III) (d^2)/Nb(V) (d^0).[22]

naked cation [Tp^{Me2}NbMe(MeC≡CMe)]$^{+}$, generated in situ by dissociation of the bulky ligand L from [Tp^{Me2}NbMe(L)(MeC≡CMe)]$^{+}$.

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Supporting Information Available: Crystallographic data for **2**, as a CIF file or in tabular format, and text giving experimental details and characterization data for **2** and **3a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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