(Hydrotris(3,5-dimethylpyrazolyl)borato)niobium Alkyne Complexes: Dichloro and Dialkyl Derivatives and Formation of a Butadienyl Complex with an α-Agostic Interaction

Michel Etienne,*,† Fabienne Biasotto,† René Mathieu,† and Joseph L. Templeton‡

Laboratoire de Chimie de Coordination du CNRS, UPR 8241, 205 Route de Narbonne, 31077 Toulouse Cedex, France, and Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290

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A high-yield one-pot synthesis of Tp*$NbCl_2$(alkyne) is described [Tp* = hydrotris(3,5-dimethylpyrazolyl)borate; alkyne = PhC≡CCH_3 (**1a**), PhC≡CCH_2CH_3 (**1b**), PhC≡CCH_2CH_2-CH_3 (**1c**), CH_3C≡CCH_3 (**1d**), PhC≡CPh (**1e**)]. It involves treatment of $NbCl_3$(DME) (DME = 1,2-dimethoxyethane) with first an alkyne and then with KTp*. The dimethyl derivatives Tp*Nb$(CH_3)_2$(alkyne) (alkyne = PhC≡CCH_3 (**2a**), PhC≡CCH_2CH_3 (**2b**), PhC≡$CCH_2CH_2CH_3$ (**2c**)) and the dibenzyl complex Tp*Nb$(CH_2Ph)_2$(PhC≡CCH_3) (**3a**) have been obtained from the appropriate dichloro complex and 2 equiv of either methyllithium or benzylmagnesium chloride, respectively. These 16-electron niobium(III) d^2 complexes, **1a-e**, **2a-c**, and **3a**, have been characterized spectroscopically. In all cases the alkyne is shown to occupy the molecular mirror plane. The barrier to alkyne rotation is high and could be measured only in the case of **1d** (68 kJ mol^{-1} at 358 K). On the basis of qualitative arguments, the structure of these complexes is basically governed by steric interactions. A comparison with the isoelectronic cyclopentadienyl derivatives is provided. When **1a** is treated with 2 equiv of ethylmagnesium chloride, the formal dehydrogenation of an ethyl group results in the alkyne-coupled product Tp*Nb(CH_2CH_3)[C(Ph)C(CH_3)CHCH_2] (**4a**), which has been spectroscopically characterized. ^{1}H and ^{13}C NMR data suggest that an α-agostic interaction is present in the ethyl group in this complex.

Introduction

According to the more recent reviews,[1] the chemistry of the group 5 transition metals with hydrotris(pyrazolyl)borates is clearly underdeveloped. With vanadium, much effort has been devoted to model histidine (imidazole)−metal interactions thought to be present in the enzyme bromoperoxidase.[2] Only recently have such complexes been utilized as catalysts in Ziegler−Natta polymerization.[3] For the heavier niobium and tantalum, the organometallic chemistry has been renewed since we discovered an efficient route to niobium(III) complexes containing four-electron donor alkynes with hydrotris(3,5-dimethylpyrazolyl)borate (Tp*).[4] These complexes are useful starting materials for further chemistry. In many cases, unexpected structures and reactivity are observed,[5] particularly when comparison is made with related complexes containing a more or less substituted cyclopentadienyl (Cp′). In this article, we report full accounts of the syntheses and characterizations of dichloro and dialkyl derivatives[4] and a discussion of the stereoelectronic effects of Tp* bonding in these complexes. An unexpected dehydrogenation reaction of an ethyl group leading to an alkyne coupling product is also described.

Results

Dichloro Complexes. As earlier communicated,[4] the alkyne complexes $NbCl_3$(DME)(alkyne)[6] (DME = 1,2-dimethoxyethane) serve as useful starting materials. Reaction of these complexes with a stoichiometric amount of KTp* in THF leads cleanly to the corresponding Tp*$NbCl_2$(alkyne) complexes in *ca.* 80% yield (eq 1). However, isolation of pure $NbCl_3$(DME)(alkyne) is sometimes cumbersome. Thus we have now devised a one-pot synthesis which avoids this step. It takes advantage of the high stability of Tp*$NbCl_2$(alkyne) toward hydrolysis. A few hours after addition of KTp* to a crude solution of $NbCl_3$(DME)(alkyne) the reaction solution is extracted with toluene or dichloromethane, and then the remaining byproducts can be conveniently removed by washing the crude residue with ethanol. The Tp*$NbCl_2$(alkyne) products are obtained as red purple to dark orange solids in *ca.* 60−70% yields after recrystallization, with alkyne = PhC≡CCH_3 (**1a**), PhC≡CCH_2-

† Laboratoire de Chimie de Coordination. E-mail: "etienne@lcctoul.lcc-toulouse.fr".

‡ University of North Carolina.

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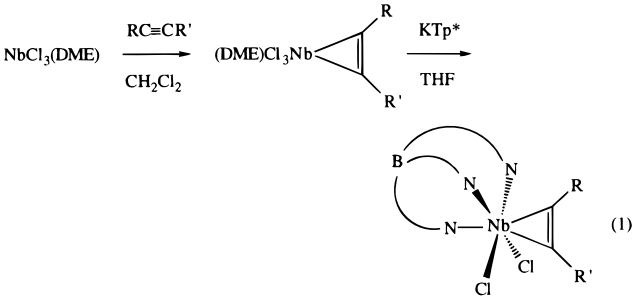


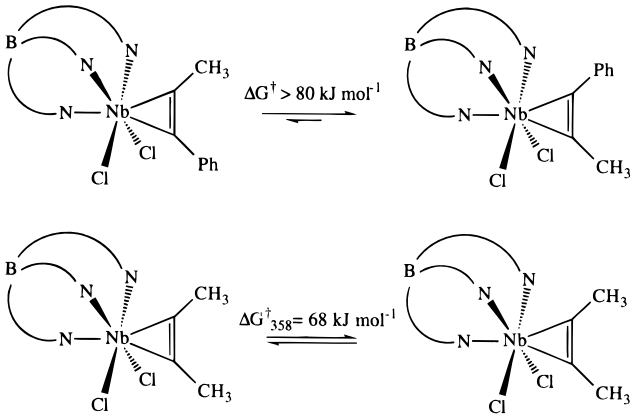
R = Ph, R' = CH_3 (**1a**), CH_2CH_3 (**1b**), $CH_2CH_2CH_3$ (**1c**); R = R' = CH_3 (**1d**); R = R' = Ph (**1e**)

CH_3 (**1b**), $PhC{\equiv}CCH_2CH_2CH_3$ (**1c**), $CH_3C{\equiv}CCH_3$ (**1d**), and PhC≡CPh (**1e**). The diphenylethyne complex is by far the least soluble and is best extracted in dichloromethane. These complexes are air stable in the solid state for weeks. Toluene solutions exposed to air show no sign of decomposition after 24 h.

These complexes have been characterized by elemental analysis and by ^1H and ^{13}C NMR spectroscopies. The ^1H NMR spectra indicate a plane of symmetry for these complexes, as judged from the 1:2 intensity pattern observed for the methine protons and the methyl groups of Tp*. For the symmetrical alkyne complexes **1d**,**e**, the alkyne substituents give separate signals at room temperature. For the 2-butyne complex **1d**, alkyne methyl protons are observed at δ 3.58 and 2.15 as slightly broad singlets. In the case of the diphenylethyne complex **1e**, two inequivalent phenyl groups are observed as well. Similarly, in the $^{13}C\{^1H\}$ NMR spectra of **1d**,**e** two deshielded resonances are observed for the coordinated alkyne carbons, and phenyl and methyl groups give two types of signals. These data clearly indicate that the alkyne lies in the molecular mirror plane which bisects the Cl−Nb−Cl angle and contains the pyrazole ring *trans* to alkyne as depicted geometrically in (1). In this geometry one of the alkyne substituents sits between two *cis* pyrazole rings, whereas the other one is directed toward the chlorides. In the former case, the ring currents exerted by the pyrazoles lead to a shielding of the protons. Thus for **1d**, we ascribe the shielded ^1H NMR signal at δ 2.15 to the protons of the alkyne methyl group proximal to the pyrazole rings. For **1e**, the signals of the phenyl group proximal to the pyrazole rings cluster around δ 6.90. The other phenyl group gives well-separated signals for ortho-, meta-, and para-protons which appear at lower field (*ca.* δ 8.5, 7.4 and 7.2, respectively). Thus these signals allow an unequivocal distinction of the two types of alkyne substituents. The observation of two distinct signals for the symmetrical alkynes means that there is a high barrier to alkyne rotation about the niobium−alkyne bond (see below).

For complexes **1a-d** which contain unsymmetrical alkynes, two sets of NMR signals are observed at room temperature in accord with the presence of two isomers. In the ^1H NMR spectra, each set shows a 1:2 intensity pattern for the Tp* signals and we conclude that the alkyne sits in the molecular mirror plane. The barrier to alkyne rotation is high enough for two sets of resonances to be observed. The ratio of the two isomers depends on the alkyne substituent. Following the analysis made for the chemical shifts of the phenyl and methyl groups in the case of symmetrical alkynes, it can be inferred that the major isomer in every case is the one with the phenyl group lying between the two proximal *cis*-pyrazole rings. Interactions between pyrazoles and phenyl π-systems could account for this preference, as suggested elsewhere.[7] However the isomer ratio clearly increases with increasing steric demand of the alkyne alkyl group. In benzene-d_6, the ratios are *ca.* 1:6, 1:9, and 1:15 for the phenylpropyne, phenylbutyne, and phenylpentyne complexes **1a**−**c**, respectively. For $Tp^*NbCl_2(PhC{\equiv}CCH_2CH_2Ph)$, which we have synthesized by deprotonation of **1a** followed by alkylation with benzyl bromide,[8] this ratio is *ca.* 1:18. For **1a**, variable-temperature ^1H NMR experiments in toluene-d_8 show no broadening of the signals up to 373 K, indicating that the barrier to alkyne rotation is at least 80−85 kJ mol^{-1}. In the case of the 2-butyne complex **1d**, the alkyne methyls signals, which are slightly broad at room temperature, coalesce at 358 K. The slow-exchange regime is reached below 253 K, and the frequency difference between the two alkyne methyls signals leads to a barrier to 2-butyne rotation of 68 kJ mol^{-1} (250 MHz spectrometer). These events are depicted and summarized in Chart 1. This is the only barrier, hence the lowest one, we have been able to measure by coalescence techniques. Most of the less sterically congested terminal alkynes are cyclotrimerized by $NbCl_3(DME)$[6] so that no terminal alkyne is available from our synthetic route. The last spectroscopic data we would like to emphasize is the ^{13}C NMR chemical shifts of the coordinated alkyne carbons. These resonances appear at low field, in the region δ 220−270. Such chemical shifts are characteristic of four-electron donor alkynes,[9] where both π-systems are involved in bonding to the transition metal. This behavior has been reviewed for the group 6 metals,[10] and several group 5 metal complexes have also been described.[11] Thus complexes **1a-e** are formally 16-electron species with a niobium(III), d^2 center. However, the four-electron donor alkynes partially oxidize the metal and resonance forms with a niobium(V), d^0 center must be considered. To make it clear that the alkyne is not a conventional two-electron ligand we have adopted the latter resonance form in the drawings.

Chart 1



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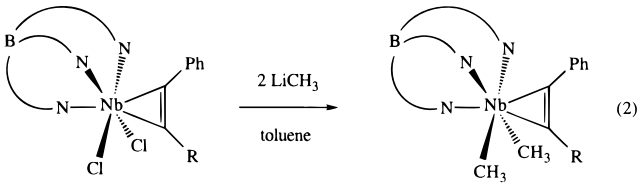
The crystal structure of **1a** has been described previously.[4] We simply summarize here the main data and conclusions. The geometry found in the solid state around the niobium is that of a distorted octahedron if the alkyne is considered to occupy one coordination site. It is the same as that adopted in solution; *i.e.* the phenylpropyne bisects the Cl−Nb−Cl angle. The phenyl group points toward the two *cis*-pyrazole rings, the orientation found for the major isomer in solution. According to the four-electron donor description,[10] the niobium-coordinated alkyne carbons bond lengths are short (Nb−C = 2.050(9) and 2.093(9) Å) and approach the range expected for niobium−carbon double bonds. The coordinated carbon−carbon bond length of the alkyne is 1.31(1) Å, appropriate for a short carbon−carbon double bond. The alkyne exerts a strong *trans*-influence. The niobium−*trans*-nitrogen bond length is 2.312(7) Å, *ca.* 0.1 Å longer than the other two. Finally, the Cl−Nb−Cl angle is obtuse (102.0(1)°). Similar bonding parameters for the alkyne linkage have been observed for the isoelectronic $Cp^*TaCl_2(PhC{\equiv}CPh)$ and $(C_5H_4CH_3)NbCl_2(ArC{\equiv}CAr)$.[11b,c]

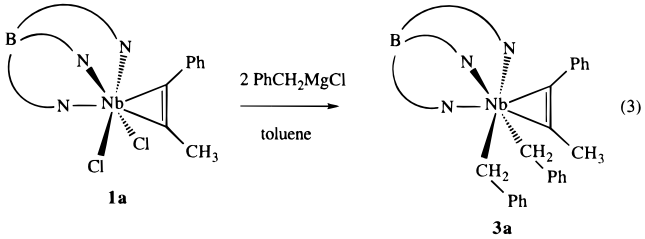
Dialkyl Complexes. Yellow crystalline dimethyl complexes $Tp^*Nb(CH_3)_2$(alkyne) (**2a-c**) are straightforwardly synthesized in virtually quantitative yields from the dichloro complexes **1a-c** and 2 equiv of methyllithium in toluene (eq 2).



1a-c R = CH_3 (**2a**), CH_2CH_3 (**2b**), $CH_2CH_2CH_3$ (**2c**)

The 1:2 intensity patterns for the Tp* hydrogens and carbons in the ^1H and ^{13}C NMR spectra testify of the presence of a symmetry plane in **2a-c**. The equivalent niobium-bound methyl groups give a single ^1H NMR signal in the range δ 1.1−1.3. At room temperature, these methyl groups give a niobium-broadened ^{13}C NMR signal around δ 54. For **2a**, the signal sharpens at 213 K. For **2c**, the gated-decoupled spectrum reveals a quartet with a normal $^1J_{CH}$ of 119 Hz. Similar chemical shifts and coupling constants are recorded in the Cp′ series.[12] The coordinated alkyne carbons appear at low field in the range δ 220−250. Two discrete isomers are observed at room temperature. For the phenylpropyne complex **2a**, no coalescence is observed up to 373 K in toluene-d_8, so that the barrier to alkyne rotation is at least *ca.* 80−85 kJ mol^{-1}. For **2a-c**, we find isomer ratios of 1:5, 1:6, and 1:8, respectively. Although the isomer ratio for **2a-c** follow the same trend as that for **1a-c**, it is systematically lower in the case of the dimethyl complexes. Slightly increased steric congestion on going from chloro to methyl ligands might decrease the preference for the alkyne alkyl group orientation toward these ligands.

Important steric effects are also observed in the case of the dibenzyl phenylpropyne complex $Tp^*Nb(CH_2Ph)_2(PhC{\equiv}CCH_3)$ (**3a**). In **3a**, we estimate the isomer ratio to be on the order of 1:100. Steric effects are also important in the synthesis of this dibenzyl complex and in the attempts we have made to synthesized other dialkyl complexes. The reaction between the dichloro phenylpropyne complex **1a** and 2 equiv of benzylmagnesium chloride proceeds very slowly to give **3a**. In a toluene:diethyl ether mixture (1:1 by volume), at least 18 h at room temperature are needed for the completion of the reaction (eq 3).



1a **3a**

In fact the first 1 equiv reacts within 1 h but the second substitution is much slower. Attempts to make a bis((trimethylsilyl)methyl) complex starting from **1a** have failed, even in the more polar solvent THF. The reaction stops at the monosubstitution stage, as $Tp^*Nb(Cl)[CH_2Si(CH_3)_3](PhC{\equiv}CCH_3)$ forms slowly.[13] It is not possible to heat this reaction mixture since, as reported for other chloro alkyl complexes, thermally induced internal alkyl exchange between the niobium and the alkyne occurs.[5b] The dibenzyl complex **3a** is isolated as blood-red crystals and is characterized spectroscopically. The methylene protons of each benzyl group are diastereotopic, but because of the plane of symmetry, they are also pairwise equivalent. Thus one AB pattern is observed in the ^1H NMR of **3a**, each doublet (δ 3.23 and 2.82, $^2J_{HH}$ = 11.2 Hz) integrating for two protons. In the ^{13}C NMR spectrum, the niobium-bound carbon resonates at δ 88.6 as a triplet with $^1J_{CH}$ = 119 Hz. Similar data have been obtained for a related dibenzyl(imido)niobium(V) complex.[14] When this dibenzyl imido complex is heated in the presence of PMe_3, the X-ray characterized benzylidene complex is formed.[14] Under similar reaction conditions (excess PMe_3, toluene 353 K), **3a** leads only to decomposition.

We have also attempted to synthesize dialkyl complexes in which the alkyl groups bear β-hydrogens. We have shown previously that the chloro ethyl complex $Tp^*Nb(Cl)(\mu\text{-H-}CHCH_3)(PhC{\equiv}CCH_3)$ exhibited ^1H and ^{13}C NMR data consistent with the presence of an α-agostic interaction.[5a] A thermally induced intramolecular exchange of alkyl groups was observed, leading to the methyl phenylbutyne complex $Tp^*Nb(Cl)(CH_3)(PhC{\equiv}CCH_2CH_3)$.[5b] Upon addition of 2 equiv of ethylmagnesium chloride to a toluene:diethyl ether

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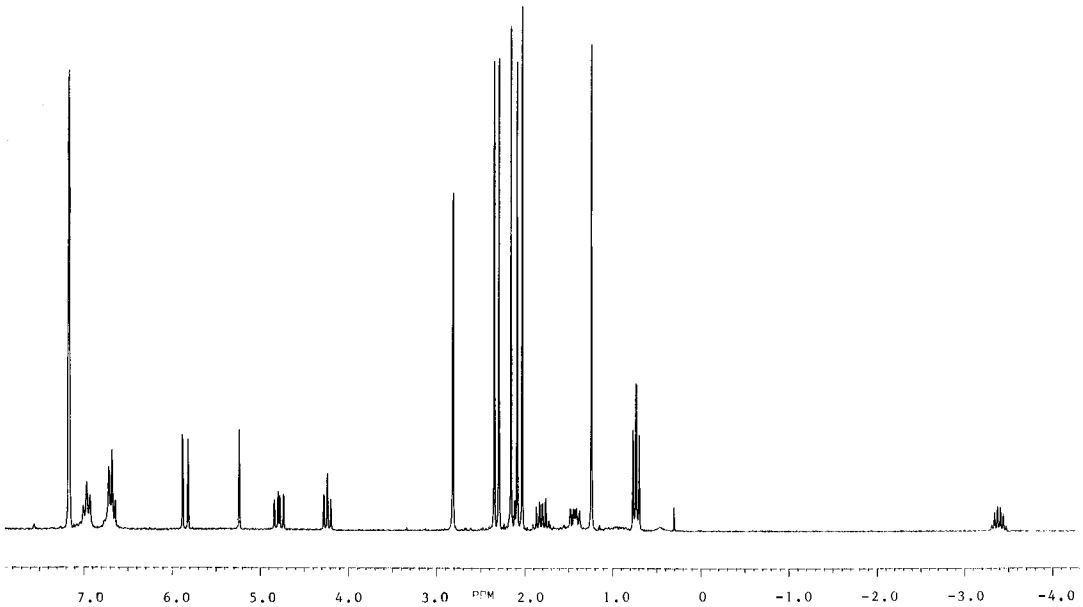
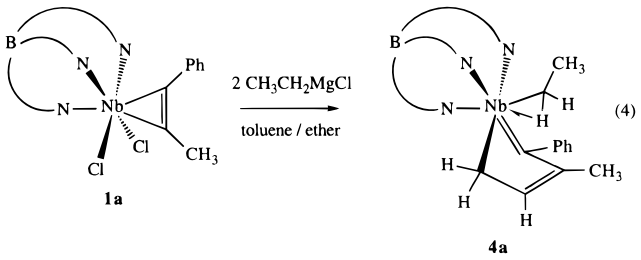


Figure 1. 200 MHz ^{1}H NMR spectrum of Tp*Nb(CH_2CH_3)[C(Ph)C(CH_3)$CHCH_2$] (**4a**) in benzene-d_6.

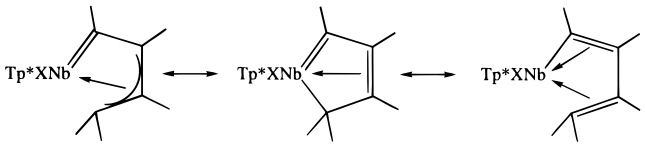
mixture (1:1 by volume) solution of **1a**, the color changes rapidly to orange, the characteristic color of Tp*Nb(Cl)-(μ-H-$CHCH_3$)(PhC≡CCH_3).[5a] An extremely sluggish reaction then takes place, although no intermediate is observed. After several days, the green five-membered niobacycle Tp*Nb(CH_2CH_3)[C(Ph)C(CH_3)$CHCH_2$] (**4a**) is isolated in 64% yield (eq 4).



We have no mechanistic information, but the net result of this reaction is the formal dehydrogenation of one ethyl group which has been coupled to the coordinated phenylpropyne. Similar five-membered nioba- and tantalacycles resulting from acyl−alkyne,[12,15] iminoacyl−alkyne,[12] and allyl−alkyne[5c] coupling reactions are documented. The η^1-vinyl complex Tp*Nb(Cl)-[CPh=$C(CH_2CH_3)_2$](PhC≡CCH_3) is thermally stable[16] so that, whatever its mechanism, the dehydrogenation of one ethyl group to a vinyl group is unlikely to occur prior to alkyne coupling.

Complex **4a** has been characterized by elemental analysis and by ^{1}H and ^{13}C NMR spectroscopies. The ^{1}H NMR spectrum of **4a** is shown in Figure 1. All assignments are supported by homodecoupling experiments and a full analysis including COSY ^{1}H, ^{1}H and HMQC ^{1}H, ^{13}C on a 400 MHz machine (see the Supporting Information). As opposed to the other compounds in this study, **4a** is chiral and, as such, three methine and six methyl resonances are observed for Tp* in the ^{1}H and ^{13}C NMR spectra. Let us first consider the five-membered niobacycle itself. As previously,[5c] we assign the α-position to the phenyl attached carbon. The Nb−CH_2−CH− fragment is characterized as follows. Hγ resonates as a doublet of doublets ($^3J_{HH}$ = 8.5, 12.5 Hz) centered at δ 4.78. It is coupled to the two protons of the methylene group in the δ-position at δ 4.23 (t, $^3J_{HH}$ = 8.0 Hz, $^2J_{HH}$ = 8.0 Hz) and δ 1.42 (dd, $^3J_{HH}$ = 12.5 Hz, $^2J_{HH}$ = 8.0 Hz). These chemical shifts are characteristic of *syn* and *anti* positions, respectively. In the related complex Tp*Nb(Cl)[C(Ph)C(CH_3)$CHCHCH_3$],[5c] the *anti* H$_\delta$ resonates as a doublet of quartets at δ 1.62 (dq, $^3J_{HH}$ = 12.4 Hz, $^3J_{HH}$ = 5.2 Hz) and H$_\gamma$ is observed at δ 5.49 (d, $^3J_{HH}$ = 12.4 Hz). In the ^{13}C NMR spectrum of **4a**, the corresponding carbon C$_\delta$ is observed at δ 73.0 as a slightly niobium-broadened doublet of doublets with $^1J_{CH}$ of 158 and 140 Hz. C$_\gamma$ is isochronous with one of the Tp*CH carbon in benzene-d_6. It has been unequivocally observed during the full analysis conducted on a 400 MHz machine at δ 105.1 in dichloromethane-d_2. In the related niobacycles Tp*Nb(Cl)[C(Ph)C(CH_3)CHCH-CH_3] and Tp*Nb(OCH_3)[C(Ph)C(CH_3)C(CH_3)O],[5c,15] it is observed at δ 112 and 136, respectively. Quaternary C$_\beta$, bearing the methyl group of the formerly phenylpropyne, resonates at δ 115 whereas C$_\alpha$, bound to niobium, gives a broad carbene-like resonance at δ 233.5. Some resonances structures in agreement with these data are depicted in Chart 2. As described elsewhere, they are characteristic of η^n-C$_n$R$_{n+1}$ metallacycles.[5c]

Chart 2



The niobium-bound ethyl group of **4a** exhibits peculiar ^{1}H and ^{13}C NMR features. In the ^{1}H NMR spectrum (Figure 1), the inequivalent diastereotopic methylene protons appear as pseudosextets (doublets of quartets) with $^2J_{HH}$ = 13.4 Hz. However, while one of these protons has a "normal" chemical shift of δ 1.80, the other one is highly shielded and resonates at δ −3.40. The methyl group gives a doublet of doublets ($^3J_{HH}$ = 6.6,

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(16) Etienne, M. Unpublished data.

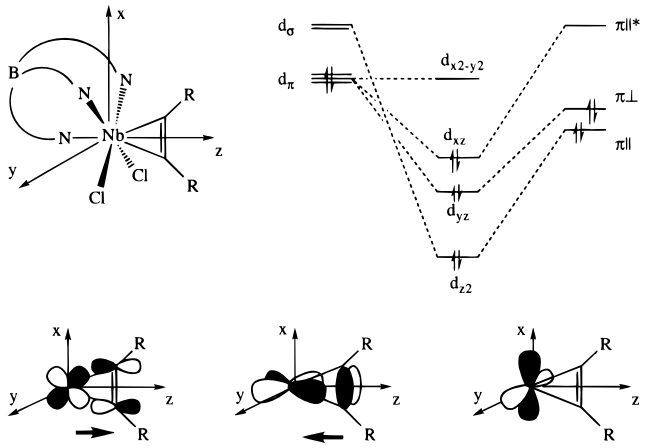
7.6 Hz) at δ 0.73. The large chemical shift difference of 5.20 ppm for the two methylene protons, coupled to the notably high-field resonance of one of these protons, would suggest an α-agostic interaction, although these criteria are not conclusive by themselves.[17] Such misleading examples in tantalum chemistry have appeared recently.[18] In the ^{13}C NMR spectrum, this niobium-bound carbon gives a very broad doublet of doublets at δ 78.2. This broadening causes large errors on the measured coupling constants ($^1J_{CH} \approx 120$, 107 Hz). However, we have been able to measure these $^1J_{CH}$ from the ^{13}C satellites of the main proton resonances in the 400 MHz ^1H NMR spectrum of **4a**. For the isolated shielded proton at δ −3.40, an accurate value of 104 Hz is obtained. The fact that the highly shielded proton is associated with the reduced $^1J_{CH}$ allows us to infer the presence of an α-agostic bond in this niobium−ethyl complex.[17] This is another rare example where an α-agostic interaction is preferred to β-agostic bonding when β-hydrogens are available. As suggested previously for Tp*Nb(Cl)(μ-H-CHCH$_3$)(PhC≡CCH$_3$)[5a] and for [Cp*$_2$Hf(μ-H-CHCH(CH$_3$)$_2$)(PMe$_3$)]$^+$,[19] steric congestion around the metal prevents the sterically demanding bending of the alkyl group necessary for the β-agostic interaction to occur.

Discussion

In this discussion, we focus on some comparisons between the Tp* complexes reported herein and related isoelectronic Cp′ complexes. Cp′MX$_2$(RC≡CR′) have been described in several instances (M = Nb, Ta; X = halogen, alkyl, methoxide, amide; R = R′ = hydrogen, aryl, alkyl).[11b,c,12,20] In all cases but one, the alkyne lies in a plane parallel to that of the Cp′. Furthermore the highest barrier to alkyne rotation (46 kJ mol^{-1} at 218 K) has been reported for the relatively crowded Cp*Ta(Cl)(OCH$_3$)(PhC≡CPh).[11b] EHMO calculations for the model compound CpNbCl$_2$(HC≡CH) indicate a barrier of *ca.* 25 kJ mol^{-1}.[11c] The only known exception in that of Cp*Ta(CH$_3$)$_2$(C$_6$H$_4$), where benzyne lies in the molecular mirror plane perpendicular to Cp* plane.[21] Here again the barrier to alkyne rotation is low and an upper limit was estimated around 37 kJ mol^{-1}.

The question is raised as to the origin of the orthogonal geometry in the Tp* alkyne complexes. Simple qualitative considerations using the axis framework in Chart 3 indicate that the observed bisecting geometry is not the result of orbital interactions. In a first approximation, Tp*NbCl$_2$ is an ML$_5$ fragment devoid of π-acceptor ligand so that it is virtually of cylindrical symmetry. Subsequent breaking of the symmetry only leads to small perturbations. This cannot induce large splittings in the d_π set, and consequently, no clear preference for π-bonding in one plane or the other will occur. From Chart 3 (only the interactions of the d_π set are drawn), the d_{xy} and d_{z^2} orbitals (d_σ set) are stabilized

Chart 3



by σ-bonding. In particular, the empty d_{z^2} strongly interacts with the filled $\pi_\|$ orbital of the alkyne. This interaction does not depend on the alkyne orientation. In the remaining d_π set, d_{xz} and d_{yz} point toward the alkyne. In the bisecting geometry, d_{xz} has the right symmetry to interact with the vacant $\pi_\|^*$ of the alkyne. In our d^2 system this molecular orbital is filled and constitutes the HOMO. The empty d_{yz} is then well suited to interact with the filled $\pi_\perp$. We verify here that the alkyne acts as both a π-acid and a π-base, as established for the four-electron donor description.[10] If the alkyne is now rotated by 90° around the *z* axis, d_{xz} and d_{yz} simply change their roles and similar orbital interactions lead to an equally viable geometry. Second-order splittings between d_{xz} and d_{yz} will not induce large energy differences in both geometries. In this scheme, $d_{x^2-y^2}$ remains in a nonbonding situation and represents the LUMO of the system. This is maybe the main difference if we compare our analysis to the EHMO calculations on CpNbCl$_2$(HC≡CH).[11c]

We would like also to briefly discuss the obtuse Cl−Nb−Cl angle (*ca.* 102°) observed in the X-ray crystal structure of **1a**. This may be ascribed to orbital interactions as follows. Consider the π-interactions of the p_{Cl} orbitals. There is one linear combination which has the correct symmetry to interact with d_{xz}. Since d_{xz} is occupied, this leads to a destabilizing overlap which is relieved when the Cl−Nb−Cl angle increases. At the same time, there is increased overlap with the orthogonal d_{yz}. Overall, increasing the Cl−Nb−Cl angle leads to a net energy gain. It should be noted here that similar π-interactions are present in the horizontal geometry since, in the crystal structure of (C$_5$H$_4$CH$_3$)NbCl$_2$(ArC≡CAr), the Cl−Nb−Cl angle is 99°.[11c] When π-acceptors like CO are considered, similar interactions lead to a decreased OC−Nb−CO angle in d^4 complexes.[22]

Whatever the discussion in the preceding paragraph, we conclude that the bisecting geometry in Tp*NbCl$_2$(alkyne) complexes is not the result of orbital interactions. When the alkyne rotates by 90°, there are obvious steric interactions between the pyrazole methyls and the alkyne which are avoided when the alkyne adopts the bisecting geometry. Furthermore, given the small

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d_π splitting, alkyne rotation barrier is also governed by the same steric interactions. Indeed we have been able to measure this barrier in the case of 2-butyne only. The observed barrier is *ca.* 68 kJ mol^{-1} at 358 K, much higher than 46 kJ mol^{-1} at 218 K observed for Cp*Ta(Cl)(OCH_3)(PhC≡CPh), the highest reported for a Cp′ system.[11b] Thus it can be proposed that, at least in the absence of strong π-acceptors as X ligands, the geometry and dynamic behavior of Tp*NbX_2(alkyne) will be governed largely by steric interactions. The α-agostic interactions in Tp*Nb(Cl)(μ-H-$CHCH_3$)(PhC≡CCH_3)[5a,b] and Tp*Nb(μ-H-$CHCH_3$)[C(Ph)C(CH_3)$CHCH_2$] (**4a**) are examples of such a behavior. We have recently synthesized the unsubstituted hydrotris(pyrazolyl)borato analog of **1a**: the same bisecting geometry is found in the crystal, but a low barrier to alkyne rotation is observed in solution.[23]

Experimental Section

All reactions and workup procedures were performed under an atmosphere of dried dinitrogen using conventional vacuum line and Schlenck tube techniques. THF and toluene were dried and distilled by refluxing over sodium−benzophenone under argon. *n*-Hexane and dichloromethane were dried and distilled over CaH_2 under argon. Methyllithium (1.6 M in diethyl ether), benzylmagnesium chloride (1.0 M in diethyl ether), and ethylmagnesium chloride (2.0 M in diethyl ether) were purchased. Benzene-d_6, toluene-d_8, and chloroform-d_1 were stored over molecular sieves under dinitrogen. ^{1}H NMR data were acquired at 200 or 250 MHz, and ^{13}C NMR data at 50.3 or 62.9 MHz. Some NMR spectra were obtained at 400 MHz when specified (see main text). Elemental analyses were performed in the Analytical Service of our laboratory. Solvents quoted in the elemental analyses were observed and integrated in the ^{1}H NMR of the complexes. $NbCl_3$(DME),[24] $NbCl_3$(DME)(alkyne),[6] and KTp*[25] were synthesized according to published procedures.

Syntheses of Tp*$NbCl_2$(alkyne) (1a-e). All compounds were prepared according to the same general procedure described here in detail for **1a**. According to the reported procedure,[6] $NbCl_3$(DME) (3.98 g, 13.74 mmol) and PhC≡CCH_3 (1.73 mL, 1.38 mmol) were stirred in dichloromethane (50 mL) for 16 h yielding a red-brown solution of $NbCl_3$(DME)(PhC≡CCH_3). This solution was filtered through a Celite pad, which was subsequently rinsed with dichloromethane. The volatiles were removed under vacuum to leave a dark oily residue. The dynamic vacuum was applied for *ca.* 1 h. Degassed solid KTp* (4.64 g, 13.8 mmol) was added to this residue, followed by THF (50 mL). This slurry was stirred for 16 h. After addition of toluene (50 mL), the volatiles were removed and the residue was extracted several times with toluene. The extracts were filtered through Celite, and the toluene was stripped off. This process induced the precipitation of dark red microcrystals, which were washed with hexanes and dried under vacuum. This material was then washed several times with absolute ethanol (*ca.* 3 × 30 mL) to remove brownish byproducts and dried under vacuum. In most cases, it was found pure by ^{1}H NMR and used as such for subsequent syntheses (5.80 g, 3.35 mmol, 73% yield). Alternatively, the compounds can be recrystallized from either toluene/hexanes or dichloromethane/hexanes mixtures without significant losses to give analytical samples. In the synthesis of the least soluble diphenylethyne complex **1e**, the extraction step is best carried out with dichloromethane instead of toluene. **1a-d** are red purple whereas **1e** is dark orange.

Tp*$NbCl_2$(PhC≡CCH_3) (1a). Anal. Calcd for $C_{24}H_{30}BCl_2N_6Nb$: C, 50.0; H, 5.2; N, 14.6. Found: C, 50.0; H, 5.3; N, 14.3. ^{1}H NMR (benzene-d_6): major isomer δ 6.94−6.76 (m, 5H, C_6H_5), 5.63 (1H, Tp*C*H*), 5.37 (2 H, Tp*C*H*), 3.93 (3 H, ≡CCH_3), 2.95, 2.13 (3H each, Tp*CH_3), 2.00, 1.76 (6H each, Tp*CH_3); minor isomer (some resonances obscured) δ 8.3 (d, J = 8, 2H, *o*-C_6H_5), 7.37 (t, J = 8, 2H, *m*-C_6H_5), 7.17 (t, J = 8, 1H, *p*-C_6H_5), 5.62 (1H, Tp*C*H*), 5.47 (2 H, Tp*C*H*), 2.98, 2.40 (3H each, Tp*CH_3), 1.99, 1.91 (6H each, Tp*CH_3); isomer ratio 6:1. ^{13}C{^{1}H} NMR (benzene-d_6): major isomer δ 264.5 (≡*C*Ph), 218.7 (≡*C*CH_3), 153.9, 153.1, 144.2, 143.8 (Tp**C*CH_3), 138.2, 130.3, 129.8, 128.9 (C_6H_5), 108.3, 108.1 (Tp**C*H), 24.9 (≡*C*CH_3), 16.1, 15.3, 12.7, 12.4 (Tp**C*H_3); minor isomer δ 247.6, 232.6 (≡*C*).

Tp*$NbCl_2$(PhC≡CCH_2CH_3) (1b). Anal. Calcd for $C_{25}H_{32}BCl_2N_6Nb$: C, 50.8; H, 5.5; N, 14.2. Found: C, 51.1; H, 5.5; N, 14.4. ^{1}H NMR (benzene-d_6): major isomer δ 7.00−6.75 (m, 5H, C_6H_5), 5.63 (1H, Tp*C*H*), 5.35 (2 H, Tp*C*H*), 3.99 (q, J = 7.6, 2H, ≡CCH_2CH_3), 2.97, 2.12 (3H each, Tp*CH_3), 1.99, 1.81 (6H each, Tp*CH_3), 1.80 (t, J = 7.6, 3H, ≡CCH_2CH_3); minor isomer (some resonances obscured) δ 8.39 (d, J = 8, 2H, *o*-C_6H_5), 7.40 (t, J = 8, 2H, *m*-C_6H_5), 5.60 (1H, Tp*C*H*), 5.53 (2 H, Tp*C*H*), 2.82 (q, J = 7.4, 2H, ≡CCH_2CH_3), 2.98, 2.40 (3H each, Tp*CH_3), 1.98, 1.97 (6H each, Tp*CH_3), 0.64 (t, J = 7.4, 3H, ≡CCH_2CH_3); isomer ratio 9:1. ^{13}C{^{1}H} NMR (benzene-d_6): major isomer δ 267.0 (≡*C*Ph), 219.7 (≡*C*CH_2), 154.2, 153.5, 144.5, 144.1 (Tp**C*CH_3), 138.5, 131.1, 130.0, 129.2 (C_6H_5), 108.7, 108.5 (Tp**C*H), 33.7 (≡*C*CH_2CH_3), 16.5, 15.8, 13.1, 12.9, 12.8 (Tp**C*H_3 and ≡CCH_2CH_3); minor isomer δ 247.6, 232.6 (≡*C*−).

Tp*$NbCl_2$(PhC≡$CCH_2CH_2CH_3$) (1c). Anal. Calcd for $C_{26}H_{34}BCl_2N_6Nb$: C, 51.6; H, 5.7; N, 13.9. Found: C, 51.1; H, 5.5; N, 13.6. ^{1}H NMR (benzene-d_6): major isomer δ 7.00−6.75 (m, 5H, C_6H_5), 5.63 (1H, Tp*C*H*), 5.36 (2 H, Tp*C*H*), 4.42 (pseudo t, J = 7.5, 2H, ≡CCH_2CH_2), 2.38 (sextet, J = 7.5, 2H, ≡$CCH_2CH_2CH_3$), 2.96, 2.12 (3H each, Tp*CH_3), 2.00, 1.83 (6H each, Tp*CH_3), 1.19 (t, J = 7.5, 3H, ≡$CCH_2CH_2CH_3$); minor isomer not reported; isomer ratio 15:1. ^{13}C{^{1}H} NMR (chloroform-d_1): major isomer δ 266.5 (≡*C*Ph), 221.0 (≡*C*CH_2), 153.3, 152.9, 144.2 (Tp**C*CH_3), 137.1, 130.3, 129.5, 128.4 (C_6H_5), 108.1, 108.0 (Tp**C*H), 41.8 (≡*C*CH_2CH_2), 21.3 (≡$CCH_2CH_2CH_3$), 15.6, 15.0, 13.1, 12.9, 12.6 (Tp**C*H_3 and ≡$CCH_2CH_2CH_3$).

Tp*$NbCl_2$(CH_3C≡CCH_3) (1d). Anal. Calcd for $C_{19}H_{28}BCl_2N_6Nb\cdot{}^1/_2CH_2Cl_2$: C, 42.0; H, 5.2; N, 15.1. Found: C, 42.3; H, 5.4; N, 15.1. ^{1}H NMR (benzene-d_6): δ 5.57 (1H, Tp*C*H*), 5.46 (2 H, Tp*C*H*), 3.58, 2.15 (3H each, ≡CCH_3), 2.90, 2.08 (3H each, Tp*CH_3), 1.96, 1.95 (6H each, Tp*CH_3). ^{13}C{^{1}H} NMR (chloroform-d_1): δ 262.2, 230.2 (≡*C*CH_3), 153.3, 151.7, 144.4, 144.2 (Tp**C*CH_3), 108.1, 107.9 (Tp**C*H), 23.1, 22.5 (≡CCH_3), 15.5, 15.1, 12.9, 12.6 (Tp**C*H_3).

Tp*$NbCl_2$(PhC≡CPh) (1e). Anal. Calcd for $C_{29}H_{32}BCl_2N_6Nb$: C, 54.5; H, 5.0; N, 13.1. Found: C, 54.2; H, 5.6; N, 12.9. ^{1}H NMR (benzene-d_6): δ 8.54 (d, J = 8, 2H, *o*-C_6H_5), 7.42 (t, J = 8, 2H, *m*-C_6H_5), 7.21 (t, J = 8, 1H, *p*-C_6H_5), 7.00−6.75 (m, 5H, C_6H_5), 5.62 (1H, Tp*C*H*), 5.36 (2 H, Tp*C*H*), 2.98, 2.14 (3H each, Tp*CH_3), 2.01, 1.87 (6H each, Tp*CH_3). ^{13}C{^{1}H} NMR (chloroform-d_1): δ 251.3, 222.8 (≡*C*Ph), 153.4, 153.0, 144.4, 144.3 (Tp**C*CH_3), 139.5, 137.3, 130.0, 129.9, 129.8, 128.6, 128.5 (C_6H_5), 108.2, 108.1 (Tp**C*H), 15.9, 15.2, 13.0, 12.7 (Tp**C*H_3).

Synthesis of Tp*$Nb(CH_3)_2$(alkyne) (2a-c). To a vigorously stirred toluene solution (20 mL) of **1a** (0.500 g, 0.85 mmol) maintained at 0 °C with an ice-water bath was added dropwise *via* syringe an ethereal solution of methyllithium (1.7 mmol, 1.1 mL of a 1.6 M solution). The solution turned immediately from red purple to yellow. The solution was then stirred at room temperature for 1 h, during which time a light precipitate formed. The solution was filtered through Celite and concentrated to an oil (*ca.* 1 mL). Hexanes (10 mL) were added and crystallization started almost immediately. After the mixture was standing for several hours at −30 °C, yellow microcrystals of **2a** were collected, washed rapidly with cold

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hexanes, and dried under vacuum (0.400 g, 0.69 mmol, 80%). **2b**,**c** were prepared similarly.

Tp*Nb(CH$_3$)$_2$(PhC≡CCH$_3$) (2a). Anal. Calcd for $C_{26}H_{36}BN_6Nb\cdot{}^1/_2C_7H_8$: C, 60.9; H, 6.9; N, 14.4. Found: C, 60.5; H, 6.6; N, 14.0. ^{1}H NMR (benzene-d_6): major isomer δ 7.20−6.85 (m, 5H, C_6H_5), 5.83 (1H, Tp*C*H*), 5.50 (2 H, Tp*C*H*), 3.62 (3 H, ≡CC*H*$_3$), 2.50, 2.27 (3H each, Tp*C*H*$_3$), 2.11, 1.67 (6H each, Tp*C*H*$_3$), 1.14 (6H, NbC*H*$_3$); minor isomer (some resonances obscured) δ 8.02 (d, J = 8, 2H, *o*-C_6H_5), 7.42 (t, J = 8, 2H, *m*-C_6H_5), 5.80 (1H, Tp*C*H*), 5.56 (2 H, Tp*C*H*), 2.65 (3 H, ≡CC*H*$_3$), 2.53, 2.25 (3H each, Tp*C*H*$_3$), 2.09, 1.88 (6H each, Tp*C*H*$_3$), 1.25 (6H, NbC*H*$_3$); isomer ratio 5:1. ^{13}C{^{1}H} NMR (toluene-d_8, 213 K): major isomer δ 249.2 (≡*C*Ph), 222.5 (≡*C*CH$_3$), 151.0, 150.7, 143.6, 143.5 (Tp**C*CH$_3$), 108.0, 106.9 (Tp**C*H), 53.6 (Nb*C*H$_3$), 22.8 (≡C*C*H$_3$), 15.1, 14.6, 12.9, 12.7 (Tp**C*H$_3$); minor isomer δ 236.9, 235.0 (≡*C*−), 54.6 (Nb*C*H$_3$).

Tp*Nb(CH$_3$)$_2$(PhC≡CCH$_2$CH$_3$) (2b). Anal. Calcd for $C_{27}H_{39}BN_6Nb$: C, 59.5; H, 6.1; N, 15.4. Found: C, 59.8; H, 6.3; N, 15.2. ^{1}H NMR (benzene-d_6): major isomer δ 7.20−6.88 (m, 5H, C_6H_5), 5.84 (1H, Tp*C*H*), 5.51 (2 H, Tp*C*H*), 4.08 (q, J = 7.5, 2 H, ≡CC*H*$_2$CH$_3$), 2.53, 2.28 (3H each, Tp*C*H*$_3$), 2.12, 1.71 (6H each, Tp*C*H*$_3$), 1.79 (t, J = 7.5, 3 H, ≡CCH$_2$C*H*$_3$), 1.24 (6H, NbC*H*$_3$); minor isomer (some resonances obscured) δ 8.02 (d, J = 8, 2H, *o*-C_6H_5), 7.46 (t, J = 8, 2H, *m*-C_6H_5), 5.79 (1H, Tp*C*H*), 5.56 (2 H, Tp*C*H*), 3.10 (q, J = 7.4, 2H, ≡CC*H*$_2$-CH$_3$), 2.50, 2.25 (3H each, Tp*C*H*), 2.11, 1.92 (6H each, Tp*C*H*$_3$), 1.28 (6H, NbC*H*$_3$), 0.81 (t, J = 7.4, 3H, ≡CCH$_2$C*H*$_3$); isomer ratio 6:1.

Tp*Nb(CH$_3$)$_2$(PhC≡CCH$_2$CH$_2$CH$_3$) (2c). Anal. Calcd for $C_{28}H_{40}BN_6Nb$: C, 59.6; H, 7.1; N, 14.9. Found: C, 59.4; H, 7.1; N, 14.7. ^{1}H NMR (benzene-d_6): major isomer δ 7.20−6.90 (m, 5H, C_6H_5), 5.85 (1H, Tp*C*H*), 5.53 (2 H, Tp*C*H*), 4.08 (pseudo t, J = 7.5, 2 H, ≡CC*H*$_2$CH$_2$CH$_3$), 2.53, 2.30 (3H each, Tp*C*H*$_3$), 2.36 (sextet, J = 7.5, 2 H, ≡CCH$_2$C*H*$_2$CH$_3$), 2.15, 1.72 (6H each, Tp*C*H*$_3$), 1.25 (t, J = 7.5, 3 H, ≡CCH$_2$CH$_2$C*H*$_3$), 1.21 (6H, NbC*H*$_3$); minor isomer (some resonances obscured) δ 8.00 (d, J = 8, 2H, *o*-C_6H_5), 7.46 (t, J = 8, 2H, *m*-C_6H_5), 5.82 (1H, Tp*C*H*), 5.60 (2 H, Tp*C*H*), 3.05 (pseudo t, J = 7.5, 2 H, ≡CC*H*$_2$CH$_2$CH$_3$), 2.48, 2.26 (3H each, Tp*C*H*$_3$), 2.13, 1.96 (6H each, Tp*C*H*$_3$), 1.26 (6H, NbC*H*$_3$), 0.71 (t, J = 7.5, 3 H, ≡CCH$_2$-CH$_2$C*H*$_3$); isomer ratio 8:1. ^{13}C NMR (benzene-d_6): major isomer δ 250.5 (≡*C*Ph), 224.6 (≡*C*CH$_3$), 151.3, 151.1, 143.8, 143.7 (Tp**C*CH$_3$), 139.6, 130.4, 128.8, 127.5 (C_6H_5), 108.2, 107.2 (Tp**C*H), 54.3 (q, $^1J_{CH}$ = 119, Nb*C*H$_3$), 40.4 (≡C*C*H$_2$), 22.1 (≡CCH$_2$*C*H$_2$CH$_3$), 15.4, 15.3, 14.7, 12.9, 12.8 (Tp**C*H$_3$ and ≡CCH$_2$CH$_2$*C*H$_3$).

Synthesis of Tp*Nb(CH$_2$Ph)$_2$(PhC≡CCH$_3$) (3a). To a vigorously stirred toluene/ether (1/1 by volume) solution (40 mL) of **1a** (0.430 g, 0.745 mmol) maintained at 0 °C with an ice-water bath was added dropwise *via* syringe an ethereal solution of benzylmagnesium chloride (1.6 mmol, 1.6 mL of a 1.0 M solution). The solution turned immediately from red purple to bright orange-red. The solution was then stirred at room temperature for 16 h, during which time it darkened. It was concentrated to *ca*. 15 mL, and an equal volume of hexanes was added. The resulting slurry was filtered through Celite and concentrated to an oil (*ca*. 1 mL). Hexanes (10 mL) were added and crystallization occurred after standing several hours at −30 °C. Dark orange-red crystals were then collected, washed with cold hexanes, and dried under vacuum (0.370 g, 0.54 mmol, 72%). Anal. Calcd for $C_{38}H_{44}BN_6Nb$: C, 66.3; H, 6.4; N, 12.2. Found: C, 65.8; H, 6.7; N, 12.3. ^{1}H NMR (benzene-d_6): δ 7.20−6.80 (m, *ca*. 10 HH, C_6H_5), 5.74 (1H, Tp*C*H*), 5.52 (2H, Tp*C*H*), 3.23 (d, J = 11.2, 2H, NbC*H*$_2$Ph), 2.99 (3 H, ≡CC*H*$_3$), 2.82 (d, J = 11.2, 2H, NbC*H*$_2$Ph), 2.68, 2.28 (3H each, Tp*C*H*$_3$), 2.16, 1.43 (6H each, Tp*C*H*$_3$). ^{13}C NMR (benzene-d_6): δ 249.6 (≡*C*Ph), 233.6 (≡*C*CH$_3$), 153.5, 152.5, 151.8 (Tp**C*CH$_3$ and *ipso*-$C_6H_5CH_2$), 144.8, 144.6 (Tp**C*CH$_3$), 139.8, 129.4, 128.3, 127.5, 122.8 (other C_6H_5), 109.5, 108.1 (Tp**C*H), 88.6 (br-t, J_{CH} = 120, Nb*C*H$_2$Ph), 24.5 (≡C*C*H$_3$), 17.2, 15.9, 13.5 (Tp**C*H$_3$).

Synthesis of Tp*Nb(CH$_2$CH$_3$)[C(Ph)C(CH$_3$)CHCH$_2$] (4a). Following the procedure used for **3a**, **1a** (0.580 g, 1.0 mmol) and ethylmagnesium chloride (1.25 mL, 2.50 mmol) were stirred in the dark at room temperature for 7 days to give a deep red solution. This solution was concentrated to *ca*. 15 mL, and an equal volume of hexanes was added. The resulting slurry was filtered through Celite and concentrated to an oil (*ca*. <1 mL). Hexanes (10 mL) were added, and crystallization occurred after standing several hours at −30 °C. Green microcrystals of **4a** (0.230 g, 0.64 mmol, 64%) were then collected, washed with cold hexanes, and dried under vacuum. Anal. Calcd for $C_{28}H_{38}BN_6Nb$: C, 59.8; H, 6.8; N, 14.9. Found: C, 60.1; H, 7.0; N, 14.7. ^{1}H NMR (benzene-d_6): δ 7.03−6.63 (m, 5H, C_6H_5), 5.87, 5.81, 5.23 (1H each, Tp*C*H*), 4.78 (dd, J = 12.5, 8.5, 1H, C*H*CH$_2$), 4.23 (t, J = 8.0, 1H, CHC*H*$_2$), 2.81, 2.34, 2.29, 2.15, 2.08, 2.03, 1.24 (3H each, CC*H*$_3$ and Tp*C*H*$_3$), 1.80 (m, J = 13.5, 7.6, 1H, NbHC*H*CH$_3$), 1.42 (m, J = 12.5, 8.0, 1H, CHC*H*$_2$), 0.73 (dd, J = 7.4, 6.7, 3H, NbHCHC*H*$_3$), −3.40 (m, J = 13.3, 6.6, 1H, Nb*H*CHCH$_3$). ^{13}C NMR (benzene-d_6) (one *C*H resonance obscured): δ = 233.5 (Nb*C*Ph), 152.4, 152.4, 150.7, 145.0, 144.7, 144.5 (Tp**C*CH$_3$), 142.0 (*ipso*-C_6H_5), 128.8, 128.5, 125.1 (other C_6H_5), 115.0 (*C*CH$_3$), 107.9, 106.7 (Tp**C*H*), 78.2 (dd, J_{CH} = 120, 107, NbH*C*HCH$_3$), 73.0 (dd, J_{CH} = 158, 140, CH*C*H$_2$), 18.3, 17.2, 16.8, 15.8, 15.7, 13.5, 13.5, 13.2 (NbHCH*C*H$_3$, C*C*H$_3$ and Tp**C*C*H$_3$). ^{13}C NMR (dichloromethane-d_2): δ 106.46, 106.22, 106.21 (Tp**C*H*), 105.11 (NbCPhCCH$_3$*C*H).

Supporting Information Available: Full NMR analysis for complex **4a** including ^{1}H (with an expansion showing the ^{13}C satellites for the shielded proton), ^{13}C{^{1}H}, GE-COSY ^{1}H, ^{1}H and GE-HMQC ^{1}H, ^{13}C spectra (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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