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Carbon Monoxide Insertion and Coupling Reactions of Niobium Alkyne Complexes

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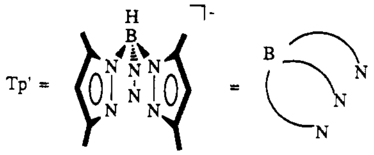
Treatment of the dichloroniobium alkyne complexes Tp′$NbCl_2(PhC{\equiv}CR')$ (R′ = CH_3 (**1**), CH_2CH_3 (**2**)) (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate) with sodium methoxide gives good yields of the corresponding chiral chloro methoxy derivatives Tp′$Nb(Cl)(OCH_3)(PhC{\equiv}CR')$ (R′ = CH_3 (**3**), CH_2CH_3 (**4**)). Methyl and phenyl methoxy complexes Tp′$Nb(CH_3)(OCH_3)(PhC{\equiv}CR')$ (R′ = CH_3 (**5**), CH_2CH_3 (**6**)) and Tp′$Nb(C_6H_5)(OCH_3)(PhC{\equiv}CH_2CH_3)$ (**8**) are obtained in high yields upon reaction of either **3** or **4** with methyllithium or phenyllithium. These complexes have been characterized spectroscopically. Due to chirality at niobium, the ethyl groups in **4** and **6** give AMX_3 type ^1H NMR spectra; in complex **8**, a deceptively simple A_2X_3 pattern is observed, regardless of the solvent or temperature, even though rotation about the niobium—phenyl bond can be frozen out. Complexes **5**, **6**, and **8** react with carbon monoxide to form five-membered oxaniobiacycles Tp′$(CH_3O)\overline{Nb[C(Ph)C(R)C(CH_3)O}]$ (R = CH_3 (**9**), CH_2CH_3 (**10**)) and Tp′$(CH_3O)\overline{Nb[C(Ph)C(CH_2CH_3)C(Ph)O}]$ (**12**), respectively, resulting from the regioselective coupling of the coordinated alkyne with an acetyl or benzoyl group. An X-ray structure has been obtained for **9** (monoclinic, $P2_1/n$, a = 12.804(3) Å, b = 16.822(4) Å, c = 13.496(3) Å, β = 110.92(2)°, Z = 4, refinement of 334 parameters over 2890 unique reflections with $I > 2.5\sigma(I)$ led to R = 0.043 and R_w = 0.057). The oxaniobiacycle is folded like an envelope about the C_α—O axis with the C_α—Nb—O triangle constituting the flap. Examination of metric parameters within the ring and comparison with related complexes indicate that an analogy between the oxaniobiacycle and the bonding description for a metallacyclopentatriene is appropriate.

Introduction

The hydridotris(3,5-dimethylpyrazolyl)borate (Tp′) ligand has been an important ancillary unit in pursuing reactions of other ligands in molybdenum and tungsten monomers. Diastereoselective η^2-acyl reactions[1] and four electron donor alkyne[2] elaborations have been performed. Importantly, optical resolution of some of these complexes has been described.[3,4] By way of contrast, the pyrazolylborate chemistry of the group 5 metals remains largely unexplored.[5] A straightforward synthesis of niobium alkyne complexes[6] Tp′$NbX_2(PhC{\equiv}CCH_3)$ (X = Cl, CH_3) has been achieved, and alkyne elaboration in these and related chiral-at-metal complexes has been demonstrated.[7] We report here syntheses of alkyl and aryl alkoxy complexes of the type Tp′$Nb(R)(OCH_3)(PhC{\equiv}CR')$ (R = CH_3, C_6H_5; R′ = CH_3, CH_2CH_3) that react with carbon monoxide. These reactions underline the subtle differences observed for the ligating properties of Tp′ when compared to those of the extensively studied cyclopentadienyl ligand.[6,8]



Results and Discussion

Syntheses of Methoxy Complexes. Orange crystalline methoxy complexes Tp′$Nb(Cl)(OCH_3)(PhC{\equiv}CR')$ (R′ = CH_3 (**3**), CH_2CH_3 (**4**)) can be conveniently synthesized in more than 80% yield via treatment of the dichloro complexes Tp′$NbCl_2(PhC{\equiv}CR')$ (R′ = CH_3 (**1**), CH_2CH_3 (**2**))[6,7] with sodium methoxide in THF followed by recrystallization from toluene/hexanes (eq 1). The new complexes **3** and **4** have been characterized by elemental analysis and ^1H and ^{13}C NMR spectroscopies (see Experimental Section). The observation of six methyl and three methine resonances for the Tp′ signals in the ^1H and ^{13}C NMR spectra reflects the absence of a symmetry plane in these chiral-at-niobium complexes. In addition, com-

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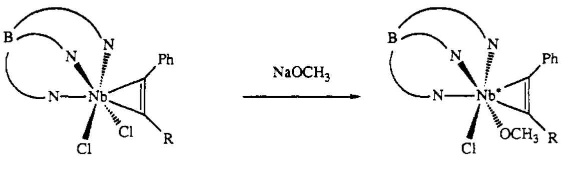


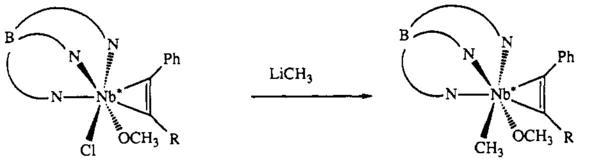
(1)

(1), R= CH$_3$ (3), R= CH$_3$

(2), R= CH$_2$CH$_3$ (4), R= CH$_2$CH$_3$

plex 4 exhibits a distinctive AMX$_3$ pattern in its ^{1}H NMR spectrum (δ_{HA} 4.32, δ_{HM} 3.97, δ_{HX} 1.71; J_{AM} = 15 Hz, J_{AX} = J_{MX} = 7.5 Hz), attributed to the alkyne bound ethyl group. ^{1}H and ^{13}C NMR signals for the methoxy ligand are also observed.

Derivative chiral complexes may be obtained via treatment of the chloro methoxy complexes 3 and 4 with 1 equiv methyllithium in toluene (eq 2). Good yields of the yellow crystalline methyl methoxy complexes Tp′Nb(CH$_3$)(OCH$_3$)(PhC≡CR′) (R′ = CH$_3$ (5), CH$_2$CH$_3$ (6)) are obtained.



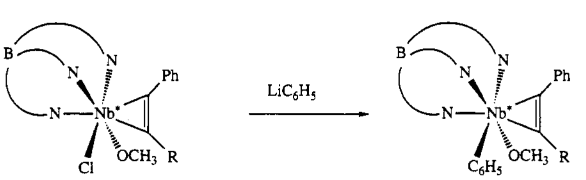
(2)

(3), R= CH$_3$ (5), R= CH$_3$

(4), R= CH$_2$CH$_3$ (6), R= CH$_2$CH$_3$

Chirality is evident for 5 and 6. The number of methyl and methine resonances of the Tp′ ligand is 6 and 3, respectively. In the ^{1}H NMR spectrum of 6, a characteristic AMX$_3$ pattern is observed for the alkyne ethyl group, the methylene protons being diastereotopic and inequivalent (δ_{HA} 4.06, δ_{HM} 3.72, δ_{HX} 1.68; J_{AM} = 15.0 Hz, J_{AX} = J_{MX} = 7.5 Hz). Signals integrating for three protons at δ 1.46 and 1.47 for 5 and 6, respectively, and in the ^{13}C NMR of 6, a broadened resonance at δ 38.2 ($\omega_{1/2} \sim 30$ Hz), appearing as a quartet in the ^{1}H gated spectrum with $^1J_{CH}$ = 120 Hz, are attributed to the niobium bound methyl group in 5 and 6.

Similar treatment of the chloro methoxy complex 4 with phenyllithium allows the orange phenyl methoxy derivative Tp′Nb(C$_6$H$_5$)(OCH$_3$)(PhC≡CH$_2$CH$_3$) (8) to be isolated in nearly quantitative yield (eq 3). In the room temperature ^{1}H NMR spectrum of 8 (benzene-d_6) two different groups of phenyl protons are observed. One well resolved group gives overlapping triplets and doublets between δ 7.10 and 6.80, and these signals are attributed to the alkyne phenyl group by comparison with other compounds in this study. The other aromatic signals, markedly broadened around δ 7.25 and severely broadened between δ 7.4 and 8.0, are ascribed to the niobium phenyl group (see below for a variable temperature ^{1}H NMR experiment). Evidence for a phenyl quaternary carbon bound to niobium is found in the ^{13}C NMR spectrum where a broad, deshielded signal is observed at δ 198.1. A similar chemical shift (δ 177.6, br) has been recently reported in a related diphenyl complex Cp*Nb(C$_6$H$_5$)$_2$(NR)(PMe$_3$).[9] A peculiar feature in the ^{1}H NMR spectrum of 8 is the appearance of a deceptively simple A$_2$X$_3$ pattern for the ethyl protons of the coordinated phenylbutyne [δ 3.79 (q, J = 7.6 Hz, 2H, CH_2CH$_3$); δ 1.51 (t, J = 7.6 Hz, 3H, CH$_2$CH_3)]. This is the only case in the Tp′Nb(X)(OCH$_3$)(PhC≡CCH$_2$CH$_3$) (X = Cl, CH$_3$, C$_6$H$_5$) series where the methylene protons, although diastereotopic by virtue of chirality at niobium, have been found equivalent. Moreover, changing the NMR solvent benzene-d_6 for chloroform-d_1, toluene-d_8, or acetone-d_6 does not modify the quartet–triplet feature at room temperature. A ^{1}H NMR variable temperature experiment has been carried out in toluene-d_8. Restricted rotation about the Nb—C$_6$H$_5$ bond is evidenced when the temperature is progressively lowered to 213 K: six signals, of which three are well resolved [δ 8.80 (d, J = 7.2 Hz), 7.66 (t, J = 7.1 Hz), and 6.70 (d, J = 7.2 Hz); the others are obscured by the alkyne phenyl resonances] are observed. Although the niobium bound phenyl group does not rotate rapidly at 213 K, the methylene protons still exhibit a simple quartet pattern, now partially overlapping the methoxy proton resonance. Above room temperature, and up to 373 K, when the barrier to rotation around the niobium—phenyl bond is overcome, the alkyne ethyl signals as well as the three more shielded Tp′ methyl signals become broad. At these temperatures kT is now approaching the energy barrier to alkyne rotation,[6] but in no case has a splitting of the methylene signal been observed, whatever the temperature or the solvent chosen for the experiment. Thus efforts aimed at understanding the possible reasons for the observation of a deceptively simple spectrum[10] for the diastereotopic methylene protons of Tp′Nb(C$_6$H$_5$)(OCH$_3$)(PhC≡CCH$_2$CH$_3$) (8) have been frustrated.



(3)

(4), R= CH$_2$CH$_3$ (8), R= CH$_2$CH$_3$

As shown previously for complex 1 and its dimethyl derivative,[6] these Tp′ complexes exist as equilibrating mixtures of isomers: the alkyne lies in the molecular mirror plane (or pseudomirror plane for the chiral complexes) that bisects two *cis*-pyrazole rings, and two isomers will be observed depending on which alkyne substituent points toward these *cis*-pyrazole rings. Thus, these isomers are rotamers, and in all cases so far they exhibit high energy barriers to alkyne rotation about the Nb—alkyne axis (see above; for Tp′Nb(CH$_3$)$_2$(PhC≡CH$_3$), $\Delta G > 20$ kcal mol^{-1}). Recall that in the related cyclopentadienyl–Nb and –Ta complexes,[11,12] the alkyne lies parallel to the cyclopentadienyl plane,[13] a geometry orthogonal to that of our Tp′ complexes, and that the barrier to alkyne rotation is below 11 kcal mol^{-1}.[12a] In the major isomer, the phenyl group of the alkyne points toward the *cis*-pyrazole rings, as shown. For the chloro methoxy complexes 3 and 4, the rotamer ratio is *ca.* 6:1 and 9:1, respectively, for the methyl methoxy derivatives 5 and 6 the ratio is *ca.* 4:1 and 5:1, respectively, and finally, for the phenyl methoxy complex the ratio is *ca.* 15:1.

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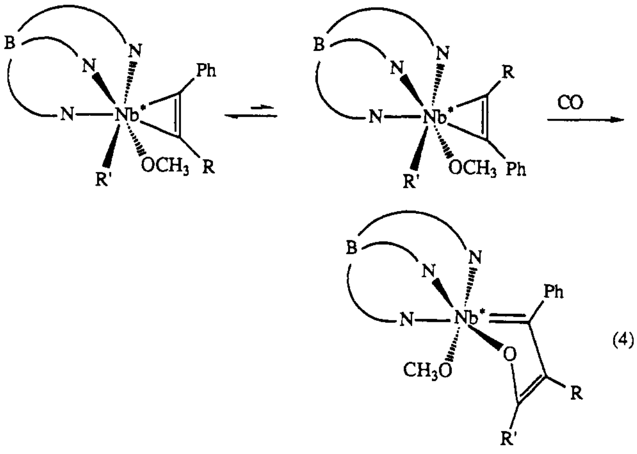
Carbonylation Reactions. Given the orthogonality of the alkyne in these complexes compared to their Cp′ congeners, is there any significant difference in chemical behavior? A simple way to address this question was to subject our complexes to a carbon monoxide atmosphere. Curtis and co-workers[14] have shown that the dialkyl complex $CpTa(CH_3)_2(PhC{\equiv}CPh)$ readily reacts with CO, but no product was isolated, and characterization was therefore limited to ^1H NMR spectroscopy. The oxatantalacyclopentatriene formulation $Cp(CH_3)Ta[C(Ph)C(Ph)C(CH_3)O]$ was astutely proposed for the carbon monoxide reaction product on the basis that a similar, structurally characterized, azatantalacycle $Cp(CH_3)Ta[C(Ar)C(Ar)C(CH_3)N(^tBu)]$, was formed by rearrangement of the η^2-iminoacyl complex $CpTa(CH_3)[\eta^2\text{-}CN(^tBu)CH_3](ArC{\equiv}CAr)$. No insertion reaction was described for the analogous niobium complexes.

When CO is bubbled through a toluene solution of alkoxy complex **5**, **6**, or **8**, the orange yellow color of the solution turns rapidly dark green. After *ca.* 24 h under carbon monoxide, dark green crystals can be isolated in yields exceeding 70%. In all three cases, the same ligand arrangement is deduced from analytical, spectroscopic, and in one case, X-ray diffraction data (see below). These complexes result from the coupling of CO with the niobium bound methyl (in **5** and **6**) or phenyl (in **8**) and the coordinated alkyne to give "oxaniobiacyclopentatriene"[14] complexes (eq 4). One striking feature of these coupling reactions is that they are regioselective. The alkyne carbon bearing the phenyl group remains attached to niobium, and the alkyne carbon bearing the alkyl (whether methyl or ethyl) is coupled to either an acetyl group in $Tp'(CH_3O)Nb[C(Ph)C(R)C(CH_3)O]$ ($R = CH_3$, (**9**), CH_2CH_3, (**10**)) or a benzoyl group in $Tp'(CH_3O)Nb[C(Ph)C(CH_2CH_3)C(Ph)O]$ (**12**). It is noteworthy that this does not depend on the rotamer ratio which differs in the three alkyne complexes **5**, **6**, and **8**. In **12**, the methylene protons are diastereotopic and accordingly appear as overlapping doublets of quartets in the ^1H NMR spectrum, just as for compound **10**. In the ^{13}C NMR spectrum of **10** and **12**, the C_α resonance is found around δ 208, a chemical shift indicative of alkylidene character.[9,14,15] The C_β carbons of the metallacycle are observed at δ 137 and 135 for the oxygen bound carbon of **10** and **12**, respectively, and at δ 110 and 112 for the ethyl bound carbon of **10** and **12**, respectively. In the closely related azatantalacycle[14] $Cp(CH_3)Ta[C(C_6H_4CH_3)C(C_6H_4CH_3)C(CH_3)N(^tBu)]$, C_α resonates at δ 228 and the C_β carbons give signals at δ 98 and 118. In an effort to trap or observe a postulated η^2-acyl intermediate[14] in our coupling reactions, the reactions were studied by ^1H NMR at ambient and low (0 and −20 °C) temperatures, but no signal attributable to an intermediate acyl complex was observed. At −20 °C, the reactions are extremely sluggish. Hence, although an acyl is a conceptually attractive intermediate, it appears to be too reactive with respect to the coupling reaction to be observed. Despite this fact, the coupling reaction is regioselective: the electron deficient acyl carbon couples to the more electron rich alkyl bound carbon of the alkyne, whatever the rotamer ratio in the starting complex. For the acyl to couple selectively to the alkyl bound carbon of the alkyne, it is necessary that the alkyne, in the minor rotamer, rotates by 180°. Since we have observed energy barriers to alkyne rotation of at least 20 kcal mol^{-1} (see ref 6 and above), the rate of exchange is about 10^{-2} s^{-1} at 298 K, which therefore gives a *rough* estimate of the lifetime of the putative acyl complex. Although we have no direct evidence of the relative orientation of the acyl and alkyne ligands in the intermediate, it seems likely that the alkyne remains in the pseudosymmetry plane of the molecule. Note that in the Cp case the alkyne and η^2-iminoacyl ligands are both in a plane parallel to that of the Cp ring, as observed for the alkyl precursor.[14]



(4)

X-ray Crystal Structure of $Tp'(CH_3O)Nb[C(Ph)C(CH_3)C(CH_3)O]$ (9).

An ORTEP plot of **9** is shown in Figure 1. Crystallographic data and atomic coordinates are gathered in Tables I and II, respectively. Table III provides relevant bond lengths and angles as well as torsional angles. The result of the X-ray diffraction analysis confirms the regioselective coupling reaction between phenylpropyne and acetyl ligands within the coordination sphere of niobium to give a five-membered oxaniobiacycle.

The Nb—C(1) distance (1.983(5) Å) is appropriate for a niobium—carbon double bond, in agreement with the ^{13}C NMR data. In a true alkylidene complex[9] $Cp^*Nb({=}CHPh)(NR)(PMe_3)$ the Nb=C bond length is 2.026(4) Å, and for a niobiacyclopentenylidene complex[16] $Cp_2Nb[{=}C(CH_2CH_3){-}C(CH_2CH_3){=}C(CO_2Me){-}CH(CO_2Me)]$, the Nb=C distance reaches 2.087(2) Å, close to that reported for a dithiolylidene complex $Cp_2Nb[C(CF_3){=}CH(CF_3)][{=}C{-}S{-}C(CF_3){=}C(CF_3){-}S]$ (2.06(4) Å).[17]

The Nb—O(4) distance (2.016(3) Å) indicates an alkoxy type of bonding, to be compared with the Nb—O(7) bond length of 1.942(3) Å as a reference for such an interaction. True Nb=O double bonds are substantially shorter [$(C_5H_4Me)_2Nb(O)(CH_2SiMe_3)$, 1.74(3) Å],[18] whereas dative bonding leads to longer Nb—O bonds (2.226(2) and 2.345(2) Å in $NbCl_3(THF)_2(PhC{\equiv}CSi(^tBu)Me_2)$).[19]

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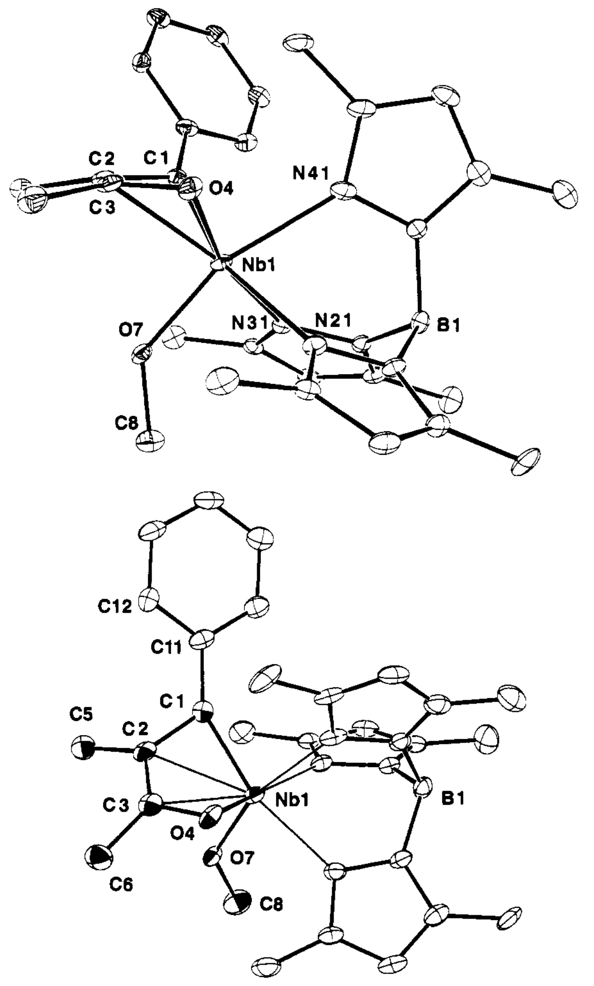

Figure 1. Two different views of the molecular structure of 9 (ORTEP plots).

The C(1)—C(2) (1.443(7) Å) and C(2)—C(3) (1.413(7) Å) bonds are marginally different. These distances lie between those of single and double carbon—carbon bonds. These atoms are sp^2 hydridized, the organic atoms of the niobiacycle being coplanar although conjugation is not fully operative (see torsional angles, Table II). The C(3)—O(4) bond length (1.351(6) Å) is consistent with this formulation, a C(8)—O(7) distance of 1.404(6) Å being observed within the methoxide ligand. Carbons C(2) and C(3) are within the bonding distance of Nb (Nb—C(2) = 2.378(5) Å; Nb—C(3) = 2.384(5) Å (see for example, Nb—C single bonds: 2.305(2) and 2.297(5) Å in, respectively, $Cp_2Nb[=C(CH_2CH_3)—C(CH_2CH_3)=C(CO_2Me)—CH(CO_2)Me]$ and $Cp_2Nb[C(CO_2Me)=CH(CO_2Me)](Me_3SiC\equiv CSiMe_3)$,[16] and for the $Nb—CH_2CH_3$ bond of $Cp_2Nb(C_2H_4)(CH_2CH_3)$, 2.316(8) Å.[20] These close contacts accompany the folding of the niobiacycle by 63° about the C(1)—O(4) axis.

Table I. Crystal Data and Experimental Details of the X-ray Diffraction Analysis of 9

formula	$NbO_2N_6C_{27}BH_{36}$
mol wt	580.33
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	12.804(3)
b, Å	16.822(4)
c, Å	13.496(3)
β, deg	110.92(2)
V, Å^3	2716(1)
Z	4
cryst dimens, mm	0.20 × 0.20 × 0.20
D(calcd), Mg m^{-3}	1.420
λ(Mo Kα), Å	0.709 30
μ, mm^{-1}	0.46
F(000)	1200
T, K	123
scan type	$\theta/2\theta$
$2\theta_{max}$, deg	44.9
h,k,l ranges	$-13 \leq h \leq 12, 0 \leq k \leq 18, 0 \leq l \leq 14$
no. of reflns	4592
no. of unique reflns	3537
no. of reflns with $I > 2.5\sigma(I)$	2890
no. of params	334
R	0.043
R_w	0.057
goodness of fit	1.85
max. shift/σ ratio	0.019

Table II. Atomic Parameters and B_{iso} Values (Å^2) with Esd's for 9

atom	x	y	z	B_{iso}
Nb(1)	0.31168(4)	0.621173(24)	0.13455(3)	1.27(3)
C(1)	0.2853(4)	0.6294(3)	0.2703(4)	1.29(22)
C(2)	0.1962(4)	0.5728(3)	0.2255(4)	1.63(24)
C(3)	0.2145(5)	0.5087(3)	0.1660(4)	1.88(25)
O(4)	0.3135(3)	0.50212(20)	0.15207(25)	1.76(16)
C(5)	0.0784(4)	0.5878(3)	0.2227(4)	1.92(24)
C(6)	0.1260(5)	0.4530(3)	0.1008(4)	2.5(3)
O(7)	0.1723(3)	0.64203(19)	0.01823(24)	1.53(15)
C(8)	0.1464(5)	0.6811(3)	−0.0796(4)	2.3(3)
C(11)	0.3154(4)	0.6635(3)	0.3768(4)	1.60(23)
C(12)	0.2827(4)	0.6291(3)	0.4564(4)	1.67(23)
C(13)	0.3214(4)	0.6588(3)	0.5590(4)	2.1(3)
C(14)	0.3946(4)	0.7227(3)	0.5856(4)	2.1(3)
C(15)	0.4271(4)	0.7583(3)	0.5085(4)	1.98(25)
C(16)	0.3876(4)	0.7285(3)	0.4056(4)	1.81(25)
B(1)	0.5413(5)	0.7149(3)	0.1121(5)	1.5(3)
N(21)	0.3983(3)	0.61289(22)	0.0135(3)	1.45(19)
N(22)	0.4859(3)	0.66107(23)	0.0146(3)	1.49(20)
C(23)	0.5143(4)	0.6454(3)	−0.0705(4)	1.77(23)
C(24)	0.4445(5)	0.5849(3)	−0.1269(4)	2.0(3)
C(25)	0.3751(4)	0.5663(3)	−0.0723(4)	1.49(22)
C(26)	0.6062(5)	0.6873(3)	−0.0920(4)	2.6(3)
C(27)	0.2852(5)	0.5044(3)	−0.0995(4)	2.3(3)
N(31)	0.3566(3)	0.75188(23)	0.1316(3)	1.32(18)
N(32)	0.4554(3)	0.77676(23)	0.1195(3)	1.37(19)
C(33)	0.4586(4)	0.8568(3)	0.1210(4)	1.55(24)
C(34)	0.3636(4)	0.8845(3)	0.1334(4)	1.66(24)
C(35)	0.3018(4)	0.8175(3)	0.1398(3)	1.43(23)
C(36)	0.5555(5)	0.9024(3)	0.1118(5)	2.5(3)
C(37)	0.1915(5)	0.8160(3)	0.1523(4)	2.03(25)
N(41)	0.4988(4)	0.61876(24)	0.2369(3)	1.75(20)
N(42)	0.5769(3)	0.66257(23)	0.2120(3)	1.44(19)
C(43)	0.6811(4)	0.6474(3)	0.2825(4)	1.94(25)
C(44)	0.6694(5)	0.5926(3)	0.3541(4)	2.2(3)
C(45)	0.5568(5)	0.5759(3)	0.3242(4)	1.9(3)
C(46)	0.7839(5)	0.6852(3)	0.2787(4)	2.7(3)
C(47)	0.5039(5)	0.5195(3)	0.3755(4)	2.7(3)

Hence, the situation here is that cleverly analyzed by Curtis and co-workers[14] for the azatantalacyclopentatriene complex discussed above and also for the related molybdacyclopentatriene $CpMo(Cl)[=C(Ph)—C(Ph)=C(Ph—C(Ph)]$. Recent work from the Rothwell laboratory[21] describes a new tungsten metallacyclopentatriene complex and provides a nice overview of work in this area. The geometric features in our Nb complex compare well with those in the Ta and Mo complexes. Curtis and co-workers concluded that the folding of the metallacycles is due to relief of antibonding interactions between the metal and the β carbons of the metallacycle and that a metallacyclopentatriene description (A) is more appropriate than

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(20) Guggenberger, L. J.; Meakin, P.; Tebbe, F. N. *J. Am. Chem. Soc.* **1974**, *96*, 5420.

(21) Kriley, C. E.; Kerschner, J. L.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1993**, *12*, 2051.

a metallacyclopentadiene formulation (B), an alternate resonance form.

A B

The niobium in **9**, **10**, and **12** has a d^0 configuration in the +5 oxidation state with 16 electrons according to resonance structure A. Note that five-membered oxamolybda- and oxatungstacycles with 18 electrons obtained from reactions of an alkyne with acyl ligands, Cp*(CO)$_2$W[C(R)=C(R)C(R)O] and Tp′(CO)$_2$Mo[C(CH$_2$CH$_3$)=C(CH$_2$CH$_3$)C(CH$_2$CH$_3$)O],[22] whatever the orientation of the metallacycle, are planar. In the 18-electron complex of niobiocene Cp$_2$Nb=C(CH$_2$CH$_3$)C(CH$_2$CH$_3$)=C(CO$_2$Me)—CH(CO$_2$Me)] discussed by Herberich and Mayer,[16] the folding about the α-carbons axis has been interpretated in terms of π-bonding and subsequent distortion at the alkylidene carbon. Finally, we note that the orientation of the oxaniobiacycle with respect to Tp′ is identical to that of the azatantalacycle and molybdacycle with respect to the Cp ligand,[14] the geometric features of more or less distorted octahedra being adopted.

Conclusion

We have synthesized methoxo complexes in the chloro and alkyl or aryl series Tp′Nb(X)(OCH$_3$)(PhC≡CR) (X = Cl, CH$_3$, C$_6$H$_5$). The methyl and phenyl complexes react readily with CO to give unusual alkyne coupled products. Although two rotamers are populated in the starting materials as a consequence of the vertical orientation of the alkyne, the coupling reactions are regioselective. Although related cyclopentadienyl tantalum complexes form according to the insightful report by Curtis and coworkers, it does not lead to isolable products. The niobium products here provide additional testimony to the stabilization effect imparted by Tp′ ligands. For kinetic reasons, it has not been possible to characterize a putative η^2-acyl intermediate akin to an η^2-iminoacyl tantalum complex which is an isolated intermediate in the formation of a related azatantalacycle. The rapidity of cyclization following acyl formation has been ascribed to the electrophilic reactivity of an η^2-acyl ligand.

Experimental Section

All reactions were performed under a dry dinitrogen atmosphere with use of standard Schlenk techniques. All solvents were dried and distilled under an argon atmosphere: THF from purple sodium–benzophenone just before use, toluene from purple sodium–benzophenone, hexane and pentane from calcium hydride. Solvents were stored over molecular sieves under a dinitrogen atmosphere. NMR spectra were recorded on Bruker AC 200 and WM 250 instruments [200.13 MHz (^{1}H), 50.32 and 62.90 MHz (^{13}C), respectively] with benzene-d_6 as solvent unless stated otherwise. Elemental analyses were performed at the Laboratoire de Chimie de Coordination in Toulouse. The synthesis of Tp′NbCl$_2$(PhC≡CCH$_3$) (**1**) was reported previously[6] and Tp′NbCl$_2$ (PhC≡CCH$_2$CH$_3$) (**2**) was prepared similarly.[7]

Table III. Selected Bond Lengths (Å) and Bond Angles and Torsional Angles (deg) for 9

Bond Lengths			
Nb(1)–C(1)	1.983(5)	Nb(1)–C(2)	2.378(5)
Nb(1)–C(3)	2.384(5)	Nb(1)–O(4)	2.016(3)
Nb(1)–O(7)	1.942(3)	C(1)–C(2)	1.443(7)
C(1)–C(11)	1.466(7)	C(2)–C(3)	1.413(7)
C(2)–C(5)	1.516(7)	C(3)–C(6)	1.492(7)
C(3)–O(4)	1.351(6)	C(8)–O(7)	1.404(6)
Bond Angles			
Nb(1)–C(1)–C(2)	86.4(3)	C(1)–C(2)–C(3)	118.3(5)
Nb(1)–C(1)–C(11)	149.5(4)	C(1)–C(2)–C(5)	122.1(4)
C(2)–C(1)–C(11)	124.1(4)	C(3)–C(2)–C(5)	118.6(4)
C(1)–Nb(1)–O(7)	108.9(2)	C(2)–C(3)–O(4)	119.8(4)
C(1)–Nb(1)–O(4)	87.7(2)	C(2)–C(3)–C(6)	124.7(5)
Nb(1)–O(4)–C(3)	87.9(3)	O(4)–C(3)–C(6)	114.7(4)
Nb(1)–O(7)–C(8)	133.3(3)		
Torsional Angles			
Nb(1)–C(1)–C(2)–C(3)	40.7(5)		
C(2)–C(3)–O(4)–Nb(1)	–39.4(5)		
O(4)–Nb(1)–C(1)–C(2)	–50.5(3)		
C(1)–C(2)–C(3)–O(4)	–0.3(7)		
C(3)–O(4)–Nb(1)–C(1)	52.1(3)		

Tp′Nb(Cl)(OCH$_3$)(PhC≡CCH$_3$) (3) and Tp′Nb(Cl)(OCH$_3$)(PhC≡CCH$_2$CH$_3$) (4). Both compounds are prepared by identical procedures from the corresponding dichloro complex **1** or **2**. A solution of Tp′NbCl$_2$(PhC≡CCH$_3$) (**1**) (0.800 g, 1.4 mmol) is stirred with a suspension of NaOCH$_3$ (0.120 g, 2.2 mmol) in THF (15 mL) for 36 h at room temperature. The red color of **1** is slowly replaced by an orange yellow color, typical of complex **3**. The THF is then removed under vacuum. Toluene (15 mL) is added and the slurry evaporated to dryness, in order to remove traces of THF that may solubilize some salts. Toluene (15 mL) and hexane (10 mL) are sequentially added, and the mixture is filtered through a Celite pad. The Celite is washed several times with hexane and the clear orange yellow solution evaporated to dryness. Crystallization is effected by dissolving the oily residue in toluene (*ca.* 3 mL) and adding hexane (*ca.* 10 mL). Complex Tp′Nb(Cl)(OCH$_3$)(PhC≡CCH$_3$) (**3**) is obtained as orange crystals in 82% yield (0.640 g, 1.1 mmol) that are washed with pentane and dried under vacuum.

For **3**: ^{1}H NMR (major isomer) δ 7.10–6.85 (m, 5H, C$_6$*H*$_5$), 5.68, 5.61, 5.28 (all s, 1H, Tp′C*H*), 3.71, 3.62 (s, 3H, ≡C—C*H*$_3$ and OC*H*$_3$), 2.78, 2.15, 1.99, 1.86, 1.76 (all s, 3,6,3,3,3H, Tp′C*H*$_3$); ^{1}H NMR (minor isomer) (some resonances obscured) δ 8.39 (dd, *J* 8, 1 Hz, *o*-C$_6$*H*$_5$), 7.44 (t, *J* 8 Hz, *m*-C$_6$*H*$_5$), 5.73, 5.67, 5.36 (all s, 1H, Tp′C*H*), 3.85 (s, 3H, OC*H*$_3$ or ≡C—C*H*$_3$), 2.80, 2.40, 2.11, 1.97, 1.95 (all s, 3H, Tp′C*H*$_3$); isomer ratio; *ca.* 6:1; ^{13}C{^{1}H} NMR (major isomer) δ 219.3 (≡*C*—Ph), 189.6 (≡*C*—CH$_3$), 152.2, 152.0, 151.9, 144.0, 143.6, 143.5 (Tp′*C*CH$_3$), 138.2, 129.9, 128.7 (*C*$_6$H$_5$), 107.6, 107.5 (Tp′*C*H), 63.9 (O*C*H$_3$), 20.1 (≡C—*C*H$_3$), 15.4, 14.6, 14.3, 13.0, 12.7, 12.5 (Tp′*C*H$_3$). Anal. Calcd for C$_{25}$H$_{33}$BClN$_6$NbO: C, 52.4; H, 5.8; N, 14.7. Found: C, 52.5; H, 5.6; N, 14.1.

For **4**: ^{1}H NMR (major isomer) δ 7.02–6.85 (m, 5H, C$_6$*H*$_5$), 5.68, 5.60, 5.30 (all s, 1H, Tp′C*H*), 4.32 (dq, *J* 15.0, 7.5 Hz, 1H, C*H*$_2$CH$_3$), 3.97 (dq, *J* 15.0, 7.5 Hz, 1H, C*H*$_2$CH$_3$), 3.71 (s, 3H, OC*H*$_3$), 2.77, 2.15, 2.14, 2.00, 1.94, 1.74 (all s, 3H, Tp′C*H*$_3$), 1.71 (t, *J* 7.5 Hz, 3H, CH$_2$C*H*$_3$); ^{1}H NMR (minor isomer) (some resonances obscured) δ 8.34 (dd, *J* 8, 1 Hz, *o*-C$_6$*H*$_5$), 7.44 (t, *J* 8 Hz, *m*-C$_6$*H*$_5$), 5.71, 5.65, 5.34 (all s, 1H, Tp′C*H*), 3.85 (s, 3H, OC*H*$_3$), 2.12, 2.09, 1.99 (all s, 3H, Tp′C*H*$_3$), 0.64 (t, *J* 7.4 Hz, 3H, CH$_2$C*H*$_3$); isomer ratio, *ca.* 9:1; ^{13}C{^{1}H} NMR (major isomer) δ 223.5 (≡*C*—Ph), 188.5 (≡*C*—CH$_2$), 152.7, 152.2, 144.3, 143.9, 143.8 (Tp′*C*CH$_3$), 139.4, 130.6, 128.7, 128.3 (*C*$_6$H$_5$), 107.9, 107.7, 107.5 (Tp′*C*H), 64.5 (O*C*H$_3$), 30.9 (≡C—*C*H$_2$), 15.7, 15.2, 14.6, 13.9, 13.3, 13.1, 12.9 (CH$_2$*C*H$_3$ and Tp′*C*H$_3$). Anal. Calcd for C$_{26}$H$_{35}$BClN$_6$NbO: C, 53.2; H, 6.0; N, 14.3. Found: C, 53.5; H, 6.2; N, 14.1.

Tp′Nb(CH$_3$)(OCH$_3$)(PhC≡CCH$_3$) (5) and Tp′Nb(CH$_3$)(OCH$_3$)(PhC≡CCH$_2$CH$_3$) (6). Both complexes are prepared according to identical procedures starting from **3** or **4**. A solution of Tp′Nb(Cl)(OCH$_3$)(PhC≡CCH$_3$) (**3**) (0.360 g, 0.63 mmol) in toluene (15 mL) is cooled to −20 °C and an ethereal solution of LiCH$_3$ (1.6 M, 0.4 mL, 0.64 mmol) is added with vigorous stirring. The cooling bath is kept at −20 °C for 15 min and then allowed to slowly reach room temperature. After 1 h,

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(22) (a) Alt, H. G.; Engelhardt, H. E.; Thewalt, U.; Riede, J. *J. Organomet. Chem.* **1985**, *288*, 165. (b) Rusik, C. A.; Collins, M. A.; Gamble, A. S.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 2550.

the brownish green mixture is concentrated to *ca.* 5 mL and hexane (10 mL) is added. The mixture is filtered through Celite, the Celite is washed with hexane, and the resulting clear yellow green solution is evaporated to an oily residue. Toluene (<1 mL) is added, followed by pentane (5 mL). If any cloudiness is evident, the solution is quickly filtered. Yellow crystals of $Tp'Nb(CH_3)(OCH_3)(PhC{\equiv}CCH_3)$ (**5**) deposit. Further crystallization is achieved by cooling to −20 °C. The product is isolated by filtration, washed with cold pentane, and dried under vacuum. Yield: 0.290 g, 0.52 mmol, 83%. Analytical samples are obtained after a second crystallization.

For **5**: ^1H NMR (major isomer) δ 7.13–6.92 (m, 5H, C_6H_5), 5.77, 5.63, 5.40 (all s, 1H, Tp′C*H*), 3.84 (s, 3H, OCH_3), 3.42 (s, 3H, $\equiv C{-}CH_3$), 2.60, 2.22, 2.18, 2.06, 1.85, 1.70 (all s, 3H, $Tp'CH_3$), 1.46 (s, 3 H, $Nb{-}CH_3$); ^1H NMR (minor isomer) (some resonances obscured) δ 8.07 (dd, *J* 1.3, 8.0 Hz, 2H, *o*-C_6H_5), 7.46 (t, *J* 7.3 Hz, 2H, *m*-C_6H_5), 7.26 (t, *J* 7.5 Hz, 1H, *p*-C_6H_5), 5.74, 5.71, 5.44 (all s, 1H, Tp′C*H*), 3.98 (s, 3H, OCH_3), 2.64 (s, 3H, $\equiv C{-}CH_3$), 2.61, 2.20, 2.16, 2.04, 1.87 (all s, 3H, $Tp'CH_3$), 1.43 (s, 3H, $Nb{-}CH_3$); isomer ratio, *ca.* 4:1. Anal. Calcd for $C_{26}H_{36}BN_6NbO$: C, 56.6; H, 6.5; N, 15.2. Found: C, 56.6; H, 6.9; N, 15.3.

For **6**: ^1H NMR (major isomer) δ 7.11–6.91 (m, 5H, C_6H_5), 5.77, 5.61, 5.43 (all s, 1H, Tp′C*H*), 4.06 (dq, *J* 15.0, 7.5 Hz, 1H, $\equiv CCH_2CH_3$), 3.86 (s, 3H, OCH_3), 3.72 (dq, *J* 15.0, 7.5 Hz, 1H, $\equiv C{-}CH_2CH_3$), 2.60, 2.22, 2.17, 2.07, 1.82, 1.78 (all s, 3H, $Tp'CH_3$), 1.68 (t, *J* 7.5 Hz, 3H, CH_2CH_3), 1.47 (s, 3H, $Nb{-}CH_3$); ^1H NMR (minor isomer) (some resonances obscured) δ 8.02 (dd, *J* 1.0, 8.0 Hz, 2H, *o*-C_6H_5), 7.46 (t, *J* 8.0 Hz, 2H, *m*-C_6H_5), 7.22 (t, *J* 7. Hz, 1H, *p*-C_6H_5), 5.73, 5.70, 5.44 (all s, 1H, Tp′C*H*), 3.97 (s, 3H, OCH_3), 3.24 (dq, *J* 15.0, 7.5 Hz, 1H, $\equiv CCH_2CH_3$), 2.83 (dq, *J* 15.0, 7.5 Hz, 1H, $\equiv CCH_2CH_3$), 2.61, 2.20, 2.06, 1.94 (all s, 3H, $Tp'CH_3$), 1.44 (s, 3H, $Nb{-}CH_3$), 0.89 (t, *J* 7.5 Hz, CH_2CH_3); isomer ratio, *ca.* 5:1; ^{13}C NMR (major isomer) δ 226.3 ($\equiv C{-}Ph$), 200.0 ($\equiv C{-}CH_2$), 152.5, 151.3, 150.8, 144.2, 143.6, 143.5 ($Tp'C{-}CH_3$), 140.8 (*ipso*-C_6H_5), 130.1, 128.9, 127.7 (*m,o,p*-C_6H_5), 107.7, 107.4, 107.3 (Tp′CH), 64.4 (q, J_{CH} 141 Hz, OCH_3), 38.2 (br-q, J_{CH} 120 Hz, $Nb{-}CH_3$), 28.4 (CH_2CH_3), 14.8, 14.7, 14.3, 13.4, 13.2, 13.0 (1:1:2:1:1:1, $Tp'CH_3$ and CH_2CH_3); ^{13}C NMR (minor isomer) δ 216.3, 216.0 ($\equiv C$), 39.3 ($Nb{-}CH_3$). Anal. Calcd for $C_{27}H_{38}BN_6NbO$: C, 57.3; H, 6.7; N, 14.8. Found: C, 57.7; H, 7.0; N, 14.7.

$Tp'Nb(C_6H_5)(OCH_3)(PhC{\equiv}CCH_2CH_3)$ (8). Complex **8** is prepared according to the procedure described previously for **5** and **6** except that a cyclohexane/ether solution of LiC_6H_5 is used instead of $LiCH_3$. The reaction mixture has an amber color. Starting from 0.510 g (0.87 mmol) of $Tp'Nb(Cl)(OCH_3)(PhC{\equiv}CCH_2CH_3)$ (**4**), orange crystals of $Tp'Nb(C_6H_5)(OCH_3)(PhC{\equiv}CCH_2CH_3)$ (**8**) are isolated in 90% yield (0.490 g, 0.78 mmol). ^1H NMR (room temperature): (major isomer) δ 8.0–7.4, 7.25 (v br, $Nb{-}C_6H_5$), 7.10–6.83 (m, 5H, $\equiv CC_6H_5$), 5.62, 5.56, 5.48 (all s, 1H, Tp′C*H*), 3.87 (s, 3H, OCH_3), 3.79 (q, *J* 7.6 Hz, 2H, $\equiv CCH_2CH_3$), 2.20, 2.14, 1.83, 1.76, 1.53 (all s, 3,6,3,3,3H, $Tp'CH_3$), 1.51 (t, *J* 7.6 Hz, 3H, CH_2CH_3); (minor isomer) (some resonances obscured) δ 5.76, 5.51 (all s, 1H, Tp′C*H*), 3.97 (s, 3H, OCH_3), 2.19, 2.17, 2.13, 1.89, 1.81, 1.61 (all s, 3H, $Tp'CH_3$), 0.86 (t, *J* 7.6 Hz, 3H, CH_2CH_3). Isomer ratio: *ca.* 15:1. ^{13}C NMR (room temperature): (major isomer) δ 218.4 ($\equiv CPh$), 200.5 ($\equiv CCH_2$), 193.1 (br, Nb-*ipso*-C_6H_5), 153.2, 152.8, 152.1, 144.3, 143.9, 143.8 ($Tp'CCH_3$), 141.4 ($\equiv C$-*ipso*-C_6H_5), 137.7 (br d, J_{CH} 155 Hz, Nb-*m*-C_6H_5), 129.4 (d, J_{CH} 159 Hz, $\equiv C$-*m*-C_6H_5), 128.7 (d, J_{CH} 159 Hz, $\equiv C$-*o*-C_6H_5), 127.6 (d, J_{CH} 138 Hz, $\equiv C$-*p*-C_6H_5), 127.0 (br d, J_{CH} 151 Hz, Nb-*o*-C_6H_5), 124.9 (d, J_{CH} 135 Hz, Nb-*p*-C_6H_5), 107.8, 107.6 (1:2, d, J_{CH} 175 Hz, Tp′CH), 64.5 (q, J_{CH} 142 Hz, OCH_3), 26.7 (t, J_{CH} 127 Hz, CH_2CH_3), 15.8, 14.6, 14.5, 14.1, 13.4, 13.2, 13.1 ($Tp'CH_3$ and CH_2CH_3). Anal. Calcd for $C_{32}H_{40}BN_6NbO$: C, 61.2; H, 6.4; N, 13.4. Found: C, 61.2; H, 6.7; N, 13.2.

$Tp'(CH_3O)\overline{Nb[C(Ph){-}C(R){-}C(R'){-}O}]$ ($R' = CH_3$, $R = CH_3$ (9), CH_2CH_3 (10); $R' = C_6H_5$, $R = CH_2CH_3$ (12)). The three compounds are synthesized following an identical procedure that follows. $Tp'Nb(CH_3)(OCH_3)(PhC{\equiv}CCH_2CH_3)$ (**6**) (0.190 g, 0.34 mmol) is dissolved in toluene (15 mL), and CO is gently bubbled through the solution for *ca.* 2 h. At that time the color of the solution has turned from yellow to dark green. The clear solution is then stirred for 24 h under a CO atmosphere. The resulting intense dark green solution is filtered and concentrated under vacuum to *ca.* 3 mL. Hexane (6 mL) is added and the solution filtered after a while (*ca.* 1 h) to remove a small amount of brownish powder. Slow cooling provides dark green crystals of complex **10** collected after 48 h, which are washed with pentane and dried under vacuum. Yield: 0.145 g, 0.24 mmol, 72%.

For **10**: ^1H NMR δ 7.02 (t, *J* 7.5 Hz, 2H, *m*-C_6H_5), 6.72 (d, *J* 8.4 Hz, 2H, *o*-C_6H_5), 6.63 (t, *J* 7.3 Hz, 1H, *p*-C_6H_5), 5.88, 5.60, 5.23 (all s, 1H, Tp′C*H*), 3.41 (s, 3H, OCH_3), 2.94 (dq, *J* 7.6, 15.2 Hz, 1H, CH_2CH_3), 2.68 (dq, *J* 7.6, 15.2 Hz, 1H, CH_2CH_3), 2.56, 2.42, 2.30, 2.28, 2.17, 2.05 (all s, 3H, $Tp'CH_3$ and $OC(CH_3)$), 1.56 (t, *J* 7.6 Hz, 3H, CH_2CH_3), 1.42 (s, 3H, $Tp'CH_3$); ^{13}C NMR δ 208.1 (br, $\omega_{1/2}$ = 20 Hz, NbC), 152.4, 151.8, 150.0, 145.3, 144.2, 143.8 ($Tp'CCH_3$), 141.6 (*ipso*-C_6H_5), 137.3 ($OCCH_3$), 129.0, 128.2 (*m*- and *o*-C_6H_5), 123.7 (*p*-C_6H_5), 110.3 [$NbC(Ph)C(CH_2CH_3)$], 107.5, 107.3, 106.9 (Tp′CH), 60.0 (OCH_3), 24.4 (CH_2CH_3), 18.2, 15.1, 14.9, 14.0, 13.3, 12.6 (1:1:2:1:2:1, $Tp'CH_3$ and CH_2CH_3 and $OCCH_3$). Anal. Calcd for $C_{28}H_{38}BN_6NbO_2$: C, 56.6; H, 6.4; N, 14.1. Found: C, 57.1; H, 6.6; N, 14.2.

For **9**: ^1H NMR δ 7.02 (t, *J* 7.8 Hz, 2H, *m*-C_6H_5), 6.69 (d, *J* 8.5 Hz, 2H, *o*-C_6H_5), 6.64 (t, *J* 7.3 Hz, 1H, *p*-C_6H_5), 5.86, 5.60, 5.25 (s, 1H, Tp′C*H*), 3.44 (s, 3H, OCH_3), 2.51, 2.42, 2.35, 2.27, 2.22, 2.17, 2.06 (all s, 3H, $Tp'CH_3$ and $OCCH_3$), 1.43 (s, 3H, $Tp'CH_3$). Anal. Calcd for $C_{27}H_{36}BN_6NbO_2$: C, 55.9; H, 6.2; N, 14.5. Found: C, 56.1; H, 6.4; N, 14.6.

For **12**: ^1H NMR δ 8.12 (d, *J* 7.5 Hz, 2H, *o*-OCC_6H_5), 7.34 (t, *J* 7.5 Hz, 2H, *m*-OCC_6H_5), 7.20 (t, *J* 7.5 Hz, 1H, *p*-OCC_6H_5), 7.02 (t, *J* 7.5 Hz, 2H, $\equiv C$-*m*-C_6H_5), 6.80 (d, *J* 7.5 Hz, 2H, *o*-C_6H_5), 6.65 (t, *J* 7.5 Hz, 1H, *p*-C_6H_5), 5.91, 5.43, 5.27 (all s, 1H, Tp′CH), 3.43 (s, 3H, OCH_3), 3.36 (dq, *J* 15.0, 7.5 Hz, 1H, CH_2CH_3), 2.96 (dq, *J* 15.0, 7.5 Hz, 1H, CH_2CH_3), 2.42, 2.28, 2.13, 2.11, 2.04, 1.55 (all s, 3H, $Tp'CH_3$), 1.35 (t, *J* 7.5 Hz, 3H, CH_2CH_3); $^{13}C\{^1H\}$ NMR δ 207.6 (NbC), 152.5, 151.9, 150.4, 145.3, 144.3, 143.9 ($Tp'CCH_3$), 141.6, 140.0 (both *ipso*-C_6H_5), 135.4 (OCC_6H_5), 131.1, 128.9, 128.5, 128.3, 123.9, (other C_6H_5), 112.3 [$NbC(Ph)C(CH_2CH_3)$], 107.6, 107.4, 107.0 (Tp′CH), 59.6 (OCH_3), 23.2 (CH_2CH_3), 15.2, 15.1, 14.5, 13.9, 13.3, 12.5 (1:1:1:1:2:1, $Tp'CH_3$ and CH_2CH_3). Anal. Calcd for $C_{33}H_{34}BN_6NbO_2$: C, 60.4; H, 6.1; N, 12.8. Found: C, 61.0; H, 6.5; N, 12.6.

X-ray Crystal Structure of $Tp'(CH_3O)\overline{Nb[C(Ph)C(CH_3)C(CH_3)O}]$ (9). Crystals of **9** were grown from a toluene solution. Diffraction data were collected on a Rigaku automated diffractometer at 123 K. Details are gathered in Table I. Cell parameters were obtained and refined from 44 reflections in the 2θ range 30.0–33.0°. 2890 reflections with $I > 2.5\sigma(I)$ were used in the structure solution and refinement.[23,24] The position of the niobium atom was deduced from a three-dimensional Patterson function. The positions of the remaining non-hydrogen atoms were determined through subsequent Fourier and Fourier difference calculations. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated and their isotropic thermal parameters were derived from the anisotropic values for the atoms to which they were connected. Final least-squares refinement resulted in the residuals $R = 0.043$ and $R_w = 0.057$ ($R = \sum(\|F_o| - |F_c\|)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$). The final difference Fourier map had no peak greater than 0.98 e/Å^3.

Supplementary Material Available: Full textual details of the X-ray structure analysis of **9**, along with a figure with full numbering scheme and tables of atomic parameters, anisotropic temperature factors, and complete bond lengths and angles (9 pages). Ordering information is given on any current masthead page.

OM9302599

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[23] Programs used during solution and refinement were from the NRCVAX structure determination package: Gabe, E. J.; Le Page, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

[24] Scattering factors were taken from: Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.