3 and 5 are far more soluble than the ionic complexes, as exemplified by their solubilities of 0.060 and >0.25 M in cyclohexane and 0.0085 and 0.017 M in perfluoromethylcyclohexane, respectively. For 5, this indicates solubilities of >22 g/100 mL in cyclohexane and 1.5 g/100 mL in perfluoromethylcyclohexane. Addition of a third trimethylsilyl group leads to a significant increase in solubility, although the diketonate substituents also clearly play a role in solubility enhancement.

To the best of our knowledge, 1, 2, and 4 represent the first examples of cationic transition-metal complexes bearing an open coordination site that possess substantial solubilities in alkane and perfluoroalkane solvents. These species are probably tightly ion-paired in these media but still appear to be ionic, since the molecular complexes 3 and 5 exhibit considerably higher solubilities. The results of this study provide a rational basis for increasing the solubility of transition-metal complexes in nonpolar media through the use of polysilylated cyclopentadienes and substituted acetylacetonates. The fact that the worst case scenario (i.e., cationic complex solubility in cyclohexane and perfluoromethylcyclohexane) is easily achieved implies that simple ligand modification should allow the use of less reactive nonpolar solvents in cases where solvent coordination or reactivity is a problem. The extensive reaction chemistry of 1–5 will be reported in due course.

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Supplementary Material Available: Tables listing positional parameters, thermal parameters, complete bond lengths and angles, and full experimental details for data collection and refinement for 1 and 3, text giving experimental details for the preparation of 1–5, and tables of spectroscopic and analytical data for 1–5 (25 pages); tables of observed and calculated structure factors for 1 and 3 (48 pages). Ordering information is given on any current masthead page.

Vertical Four-Electron-Donor Alkyne Ligands in (Tris(3,5-dimethylpyrazolyl)borato)niobium Complexes

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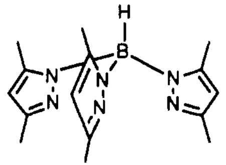
Summary: Reaction of $\mathrm{NbCl_3(DME)(PhC{\equiv}CMe)}$ with KTp′ in THF produces a high yield of $\mathrm{Tp'NbCl_2(PhC{\equiv}CMe)}$. The solid-state structure of $\mathrm{Tp'NbCl_2(PhC{\equiv}CMe)}$ has the alkyne ligand in the molecular mirror plane, and NMR data are compatible with retention of this alkyne orientation in solution.

Alkyne orientation is an important parameter in alkyne coordination chemistry. This informative probe, which has been particularly well studied in the field of four-electron alkyne ligands,[1] reflects the influence of both electronic and steric interactions.

Consider the geometries found for the extensive family of $\mathrm{Cp'MX_2(RC{\equiv}CR')}$ complexes ($\mathrm{Cp'} = \eta^5\text{-}\mathrm{C_5H_{5-x}Me_x}$; M = Nb, Ta; X = halide, alkyl, alkoxy; R or R′ = alkyl, aryl). For all but one category of alkyne, namely benzyne ligands, the alkyne has been shown to lie parallel to the cyclopentadienyl ring and perpendicular to the molecular mirror plane in the solid state; spectral data are compatible with retention of this alkyne orientation in solution.[2,3] An exception was revealed by the X-ray structure of $(\eta^5\text{-}\mathrm{C_5Me_5)TaMe_2(C_6H_4)}$,[4] where benzyne lies in the molecular mirror plane ("vertical"), and the low barrier to rotation, less than 9 kcal mol^{-1}, yields an average NMR signal for the ends of the alkyne even at −80 °C. For the whole series, the barrier to alkyne rotation about the metal–alkyne bond is low (ca. ≤11 kcal mol^{-1}).[2a] We report here the synthesis and structure of tris(3,5-dimethylpyrazolyl)borate (Tp′) derivatives of niobium of the type $\mathrm{Tb'NbX_2(PhC{\equiv}CMe)}$ that exhibit the vertical alkyne orientation as their ground-state geometry.

Reaction of $\mathrm{NbCl_3(DME)(PhC{\equiv}CMe)}$ (synthesized according to the method of Hartung and Pedersen[5]) with 1 equiv of KTp′ in THF overnight proceeds smoothly to give a red solution from which red crystals of $\mathrm{Tp'NbCl_2(PhC{\equiv}CMe)}$ (1) are isolated in 80% yield after workup (eq 1).[6]

$$\mathrm{NbCl_3(DMe)(PhC{\equiv}CMe)} + \mathrm{KTp'} \longrightarrow \underset{\mathbf{1}}{\mathrm{Tp'NbCl_2(PhC{\equiv}CMe)}} + \mathrm{KCl} \qquad (1)$$



Tp′

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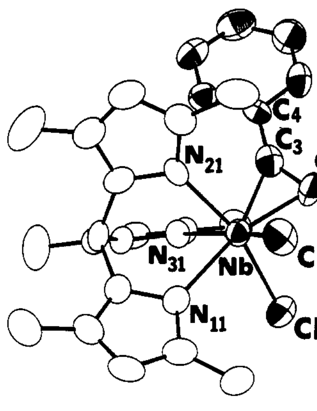

Figure 1. ORTEP drawing of $\mathrm{Tp'NbCl_2(PhC{\equiv}CMe)}$. Important bond distances (Å): Nb-Cl(1), 2.399 (3); Nb-Cl(2), 2.408 (3); Nb-C(2), 2.050 (9); Nb-C(3), 2.093 (9); Nb-N(11), 2.312 (7); Nb-N(21), 2.216 (6); Nb-N(31), 2.227 (6).

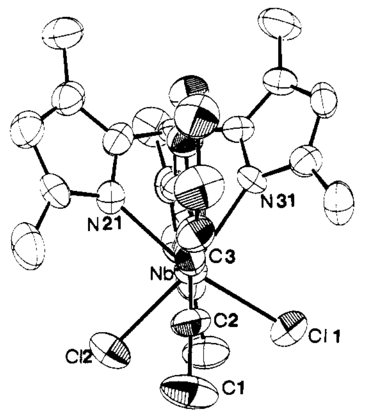

Figure 2. ORTEP drawing of $\mathrm{Tp'NbCl_2(PhC{\equiv}CMe)}$ emphasizing the vertical alkyne orientation in the effective mirror plane of the molecule.

Spectroscopic evidence for four-electron-donor behavior of the phenylpropyne ligand is found in the ^{13}C NMR spectrum of 1, where the coordinated carbons of the alkyne are found at low field (δ 265 and 219 ppm for the major isomer; δ 248 and 233 ppm for the minor isomer), typical of the range of such complexes.[1a] An important feature of both the ^{1}H and ^{13}C NMR room-temperature spectra of 1 is the observation of two sets of signals in a 6:1 ratio, which we attribute to two isomers. Furthermore, for each isomer, all of the sets of the Tp′ pyrazole ring signals appear in a 2:1 intensity pattern, indicating that a plane of symmetry exists for each isomer on the NMR time scale. The only way to fit these data is to orient the alkyne so that it lies in the molecular mirror plane. Two isomers will be observed depending on the alkyne substituent that points toward the Tp′ ligand (assuming the barrier to alkyne rotation about the Nb–alkyne axis is sufficiently high).

This geometrical hypothesis has been confirmed in the solid state by an X-ray diffraction analysis on a single crystal of 1.[7] An ORTEP drawing of the molecule is shown in Figure 1 with relevant metric parameters in the caption. If the alkyne is considered to occupy one coordination site, the niobium coordination geometry is roughly octahedral. The alkyne, including the phenyl ring, and the niobium are in the plane that bisects the Cl–Nb–Cl angle between two pyrazole rings. The phenyl group lies toward these cis-pyrazole rings, whereas the methyl group of the phenylpropyne points toward the chlorine atoms. The Nb–C(2) (2.050 (9) Å) and Nb–C(3) (2.093 (9) Å) bonds are short and approach the range expected for niobium–carbon double bonds. The C(2)–C(3) bond distance of 1.31 (1) Å for the former alkyne triple bond is appropriate for a short carbon–carbon double bond. The bend-back angles of the coordinated C–C bond of the alkyne and its substituents of 143° show a characteristic bending away from the metal.[2,3] These data show that, despite the vertical geometry of the alkyne, the bonding between the alkyne and the niobium can be described as containing a substantial amount of a metallacyclopropene resonance form with the metal in the 5+ oxidation state, in addition to the simple alkyne resonance structure with the metal in the 3+ oxidation state.[2-4]

We have been able to prepare the yellow dimethyl derivative of 1, $\mathrm{Tp'NbMe_2(PhC{\equiv}CMe)}$ (**2**), from the reaction of 1 with 2 equiv of methyllithium (eq 2).[8]

$$\mathrm{Tp'NbCl_2(PhC{\equiv}CMe)} + 2\mathrm{LiMe} \rightarrow \underset{\mathbf{2}}{\mathrm{Tp'NbMe_2(PhC{\equiv}CMe)}} + 2\mathrm{LiCl} \qquad (2)$$

As observed for the dichloro complex 1, two discrete isomers are evident at room temperature by ^{1}H and ^{13}C NMR spectroscopies. When the ca. 5:1 mixture of the two $\mathrm{Tp'NbMe_2(PhC{\equiv}CMe)}$ isomers was dissolved in toluene-d_8 and progressively heated to 100 °C in an NMR probe (no decomposition occurs even after prolonged heating), the only observed change in the ^{1}H NMR spec-

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(6) $\mathrm{NbCl_3(DME)(PhC{\equiv}CCH_3)}$ (2.00 g, 4.8 mmol) and KTp′ (1.61 g, 4.8 mmol) were stirred in THF (50 mL) overnight (room temperature, dinitrogen atmosphere). The THF was then stripped off, and toluene (75 mL) was added. The red solution was filtered through a pad of Celite that was then repeatedly washed with toluene. The solution was concentrated under vacuum, and hexane was added to induce crystallization. After 24 h, red crystals of $\mathrm{Tp'NbCl_2(PhC{\equiv}CMe)}$ (1) were collected by filtration, washed with hexane, and dried under vacuum (2.23 g, 3.8 mmol, 80%). Anal. Calcd for $\mathrm{C_{24}H_{30}BCl_2N_6Nb}$: C, 50.0; H, 5.2; N, 14.6. Found: C, 50.0; H, 5.3; N, 14.3. ^{1}H NMR ($\mathrm{C_6D_6}$): major isomers δ 6.94–6.82 (m, 3 H, *m*- and *p*-$\mathrm{C_6}H_5$), 6.76 (d, J_{HH} = 7.7 Hz, 2 H, *o*-$\mathrm{C_6}H_5$), 5.63 (s, 1 H, Tp′ C*H*), 5.37 (s, 2 H, Tp′ C*H*), 3.93 (s, 3 H, $\equiv$C—CH_3), 2.95, 2.13 (both s, 3 H, Tp′ CH_3), 2.00, 1.76 (both s, 6 H, Tp′ CH_3); minor isomer (some resonances obscured) δ 8.3 (d, J_{HH} = 8.0 Hz, 2 H, *o*-$\mathrm{C_6}H_5$), 7.37 (t, J_{HH} = 8.0 Hz, 2 H, *m*- or *p*-$\mathrm{C_6}H_5$), 5.62 (s, 1 H, Tp′ C*H*), 5.47 (s, 2 H, Tp′ C*H*), 2.95, 2.40 (both s, 3 H, Tp′ CH_3), 1.99, 1.91 (both s, 6 H, Tp′ CH_3). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): major isomer δ 264.5 ($\equiv$*C*—Ph), 218.7 ($\equiv$*C*—$\mathrm{CH_3}$), 153.9, 153.1, 144.2, 143.8 (Tp′ *C*—$\mathrm{CH_3}$), 138.2, 130.3, 129.8, 128.9 ($C_6\mathrm{H_5}$), 108.3, 108.1 (Tp′ *C*—H), 24.9 ($\equiv$C—$C\mathrm{H_3}$), 16.1, 15.3, 12.7, 12.4 (Tp′ $C\mathrm{H_3}$); minor isomer δ 247.6 and 232.6 ($\equiv$*C*–).

(7) $\mathrm{Tp'NbCl_2(PhC{\equiv}CMe)}$ crystallizes in the monoclinic $I2/a$ space group, with a = 17.546 (4) Å, b = 18.378 (4) Å, c = 19.090 (6) Å, β = 116.66 (2)°, V = 5501 (2) Å^3, and Z = 8. Use of Mo Kα radiation with λ = 0.709 30 Å, μ_{calcd} = 6.4 cm^{-1}, and ρ_{calcd} = 1.39 g cm^{-3} produced final residuals of R = 5.3% and R_{w} = 6.9% for 308 variables refined against 2483 data with $I > 2.5\sigma(I)$. Analysis of spectroscopic data leads us to believe that the crystal chosen corresponds to the major isomer.

(8) To a vigorously stirred toluene solution (20 mL) of 1 (0.500 g, 0.85 mmol) was added dropwise (0 °C, dinitrogen atmosphere) a solution of methyllithium (1.1 mL of a 1.6 M solution in diethyl ether, 1.70 mmol). Instantaneously, the solution turned from red to light yellow and a precipitate formed. The solution was stirred 30 min at room temperature. It was then filtered through a pad of Celite that was washed repeatedly with toluene. The solution was concentrated to ca. 2–3 mL; then hexane (15 mL) was added and the solution cooled to −78 °C for 24 h. The yellow crystals of $\mathrm{Tp'Nb(CH_3)_2(PhC{\equiv}CMe)}$ (**2**) that deposited were collected by filtration at low temperature and briefly dried under vacuum. They were found to contain a half-molecule of toluene (0.400 g, 0.69 mmol, 80%). Anal. Calcd for $\mathrm{C_{26}H_{36}BN_6Nb\cdot{}^1/_2C_7H_8}$: C, 60.9; H, 6.9; N, 14.4. Found: C, 60.5; H, 6.6; N, 14.0. ^{1}H NMR ($\mathrm{C_6D_6}$): major isomer δ 7.20–6.85 (m, 5 H, $\mathrm{C_6}H_5$), 5.83 (s, 1 H, Tp′ C*H*), 5.50 (s, 2 H, Tp′ C*H*), 3.62 (s, 3 H, $\equiv$C—CH_3), 2.50, 2.27 (both s, 3 H, Tp′ CH_3), 2.11, 1.67 (both s, 6 H, Tp′ CH_3), 1.14 (s, 6 H, Nb—CH_3); minor isomers δ 8.02 (d, J_{HH} = 8 Hz, *o*-$\mathrm{C_6}H_5$), 7.42 (t, J = 8 Hz, *m*- or *p*$\mathrm{C_6}H_5$) (other phenyl resonances obscured), 5.80 (s, 1 H, Tp′ C*H*), 5.56 (s, 2 H, Tp′ C*H*), 2.65 (s, 3 H, $\equiv$C—CH_3), 2.53, 2.25 (both s, 3 H, Tp′ CH_3), 2.09, 1.88 (both s, 6 H, Tp′ CH_3), 1.25 (s, 6 H, Nb—CH_3). ^{13}C{^{1}H} NMR (toluene-d_8, −60 °C): major isomer δ 249.2 ($\equiv$*C*—Ph), 222.5 ($\equiv$*C*—$\mathrm{CH_3}$), 151.0, 150.7, 143.6, 143.5 (Tp′ *C*—$\mathrm{CH_3}$), 108.0, 106.9 (Tp′ *C*—H), 53.6 (Nb—$C\mathrm{H_3}$), 22.8 ($\equiv$C—$C\mathrm{H_3}$), 15.1, 14.6, 12.9, 12.8 (Tp′ $C\mathrm{H_3}$); minor isomer δ 236.9, 235.0 ($\equiv$*C*–), 54.6 (Nb—$C\mathrm{H_3}$).

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trum was a slight broadening of the signals, so there is no evidence of interconversion of the two isomers at this temperature; this suggests a *lower* limit to the alkyne rotation barrier of ca. 20 kcal mol^{-1}. This is in sharp contrast with observations on related vertical (C_5Me_5) benzyne derivatives of Nb and Ta, where an *upper* limit to benzyne rotation was estimated around 9 kcal mol^{-1} ($(C_5Me_5)TaMe_2(C_6H_4)$).[4a] For the more general horizontal geometry (with the alkyne axis parallel to the C_5Me_5 plane) the barrier to alkyne rotation in one example, $(C_5Me_5)Ta(Cl)(OMe)(PhC{\equiv}CPh)$, is 11 kcal mol^{-1} (^{13}C NMR data).[2a] The computed barrier is around 6 kcal mol^{-1} in the symmetrical model complex $CpNbCl_2(HC{\equiv}CH)$(EHMO calculations).[3b]

Thus, these results suggest that when a Tp′ ligand replaces a cyclopentadienyl ligand in these group 5 four-electron-donor alkyne complexes, the ground-state structure, in both the solid state and in solution, adopts the vertical geometry. Furthermore, the energy difference between the two orthogonal alkyne orientations increases substantially. The physical basis for this behavior is probably both electronic and steric, but since the bonding parameters for coordinated alkynes in all of the known X-ray structures, regardless of whether the alkyne is perpendicular or parallel, are so similar, we believe that the main contribution is steric. The utilization of these properties in organic transformations of the coordinated alkyne ligands in these and related complexes is under active investigation.

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Supplementary Material Available: Tables of crystal data, positional and thermal parameters, bond lengths, bond angles, and torsion angles for 1 and additional drawings of 1 (12 pages); a listing of calculated and observed structure factors for 1 (14 pages). Ordering information is given on any current masthead page.

Characterization of Rhodium Olefin Complexes Chemisorbed onto γ-Alumina by Solid-State ^{13}C NMR and EXAFS Spectroscopies

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Summary: Rhodium olefin and carbonyl complexes $[RhClL]_2$ (L = 1,5-cyclooctadiene (cod), $(C_2H_4)_2$, $(CO)_2$), chemisorbed onto partially dehydroxylated γ-alumina, are characterized by solid-state NMR and extended X-ray absorption fine structure (EXAFS) spectroscopies. ^{13}C NMR data indicate that the olefin ligands observed in the immobilized species remain bound to the rhodium centers. EXAFS studies reveal a ligand-dependent, reversible disruption of the Rh–Cl bonds upon chemisorption.

The manner in which transition metal-based catalysts are bound to support materials is of fundamental interest in the field of heterogeneous catalysis.[1] For many systems metal-support interactions are known to play important roles in their overall reactivity.[2] Unfortunately, the interactions between functional groups on the surface of a support and single metal atoms or aggregate assemblies remain obscure.[3] In this regard solid-state NMR methods utilizing cross polarization and magic angle spinning (CPMAS)[4] and EXAFS[5] spectroscopy have emerged as two important techniques capable of providing new and detailed information about surface-bound species in amorphous materials.[6,7]

Supported rhodium catalysts have been studied extensively due to the number of economically important pro-

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