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Synthesis and Characterization of New Niobium Hydridotris(3,5-dimethylpyrazol-1-yl)borato Complexes

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Reaction of the binuclear alkoxide species $[Nb(Cl)_3(OR)_2]_2$ (R = Me, Et) with potassium hydridotris(3,5-dimethylpyrazol-1-yl)borate, KTp*, leads to Tp*Nb(O)(Cl)(OR) (R = Me (**1**), Et (**2**)). These complexes react with Me_3SiCl or PCl_3 to give $Tp^*Nb(O)(Cl)_2$ (**3**). The binuclear complex $[\{Tp^*Nb(O)(Cl)\}_2(\mu\text{-}O)]$ (**4**) was prepared by the controlled hydrolysis of **1** or **2**. Finally, complex **3** reacts with $(Me_3Si)_2NMe$ or $LiN(SiMe_3)_2\cdot Et_2O$ to give $Tp^*Nb(O)(HNSiMe_3)_2$ (**5**) as the only isolated niobium product. Compounds **4** and **5** were characterized by X-ray diffraction.

Introduction

Poly(pyrazol-1-yl)borato-containing complexes are well-documented, and in recent years, a significant number of complexes with most metals of the periodic table have been prepared.[1] Several classes of niobium poly(pyrazol-1-yl)borato complexes containing halide, alkoxide, alkyl, imido, oxo, or alkyne ancillary ligands have been prepared.[2] As a result of our investigation into niobium complexes with N-donor ligands, some of us reported[3] the preparation of several complexes of the type $TpNb(Cl)_2(RC{\equiv}CR')$ and the Tp- and Cp-containing complex $TpCpNb(Cl)(PhC{\equiv}CMe)$, where Tp = hydridotris(pyrazol-1-yl)borato and Cp = $\eta^5\text{-}C_5H_5$. We subsequently became interested in the study of new tris(pyrazol-1-yl)borato-containing niobium complexes, and this paper focuses on the preparation and structural details of some niobium hydridotris(3,5-dimethylpyrazol-1-yl)borato compounds.

Results and Discussion

We have found that $[Nb(Cl)_3(OR)_2]_2$ compounds react readily with KTp* (Tp* = hydridotris(3,5-dimethylpyrazol-1-yl)borato), giving rise to the complexes Tp*Nb(O)(Cl)(OR) (R = Me (**1**), Et (**2**)) (eq 1). The initial step of

$$^1/_2[NbCl_3(OR)_2]_2 + KTp^* \xrightarrow{-KCl} Tp^*Nb(Cl)_2(OR)_2 \xrightarrow{\text{hydrolysis}} Tp^*Nb(O)(Cl)(OR) + HCl + ROH \quad (1)$$

the reaction is presumably formation of $Tp^*Nb(Cl)_2(OR)_2$ with elimination of KCl, although an alternative elimination of KOR cannot be ruled out. This step is then followed by hydrolysis, in which a chloride−alkoxide substitution by an oxo group would take place, to give the final product **1** or **2**. The formation of ROH (R = Me, Et) was detected by gas chromatography. The process occurs even when the solvent (THF) was carefully dried. Similar behavior has been described[4] in the reaction of $[Nb(Cl)_2(OMe)_3]$ with KTp. The IR spectra of **1** and **2** show a characteristic band at 919 and 917 cm^{-1}, respectively, which corresponds to $\nu(Nb{=}O)$. The ^1H and $^{13}C\{^1H\}$ NMR spectra exhibit resonances for three distinct sets of pyrazol-1-yl units, indicating that the three pyrazolyl rings are not equivalent, and additional resonances corresponding to the alkoxide ligand are also present (see Experimental Section). It is noteworthy in the ^1H NMR spectrum of **2** that an ABX_3 system is observed for the ethoxy group, which appears as a pseudotriplet for the methyl group coupled to the methylene unit and two multiplets due to the methylene unit itself. A computer simulation of the ABX_3 system was also carried out, and the spectrum obtained agrees

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(1) Trofimenko, S. *Chem. Rev.* **1972**, *72*, 497. (b) Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 115. (c) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943.

(2) Hubert-Pfalzgraf, L. G.; Tsunoda, M. *Polyhedron* **1983**, *2*, 203. (b) Bradley, D. C.; Hursthouse, M. B.; Newton, J.; Walker, N. P. C. *J. Chem. Soc., Chem. Commun.* **1984**, 188. (c) Sundermeyer, J.; Putterlik, J.; Foth, M.; Field, J. S.; Ramesar, N. *Chem. Ber.* **1994**, *127*, 1201. (d) Etienne, M.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 3801. (e) Etienne, M.; White, P. S.; Templeton, J. L. *Organometallics* **1993**, *12*, 4010. (f) Etienne, M.; Zeline, P.; Templeton, J. L.; White, P. S. *New J. Chem.* **1993**, *17*, 515. (g) Etienne, M. *Organometallics* **1994**, *13*, 410. (h) Etienne, M.; Biasotto, F.; Mathieu, R. *J. Chem. Soc., Chem. Commun.* **1994**, 1661. (i) Biasotto, F.; Etienne, M.; Dahan, F. *Organometallics* **1995**, *14*, 1870. (j) Etienne, M., Biasotto, F.; Mathieu, R.; Templeton, J. L. *Organometallics* **1996**, *15*, 1106. (k) Lorente, P.; Carfagna, C.; Etienne, M.; Donnadieu, B. *Organometallics* **1996**, *15*, 1090. (l) Etienne, M.; Mathieu, R.; Donnadieu, B. *J. Am. Chem. Soc.* **1997**, *119*, 3218. (m) Mashima, K.; Oshiki, T.; Tani, K. *Organometallics* **1997**, *16*, 2760.

(3) Etienne, M.; Donnadieu, B.; Mathieu, R.; Fernández-Baeza, J.; Jalón, F. A.; Otero, A.; Rodrigo-Blanco, M. E. *Organometallics* **1996**, *15*, 4597.

(4) Hubert-Pfalzgraf, L. G.; Riess, J. G. *Inorg. Chim. Acta* **1980**, *47*, 7.

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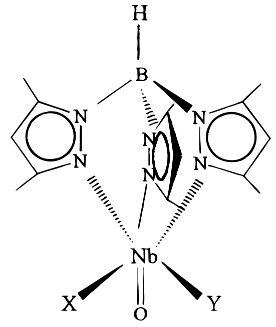

X = Cl, Y = OMe (1), OEt (2); X = Y = Cl (3); X = Y = HN(SiMe$_3$) (5)

Figure 1. Proposed structure of complexes **1**−**3** and **5**.

very well with the experimental spectrum. The two methylenic protons are diastereotopic because the niobium atom in this molecule is a chiral center. The spectroscopic results agree with an octahedral environment for **1** and **2** (Figure 1).

Moreover, **1** and **2** react with an excess of Me$_3$SiCl or PCl$_3$ to give the complex Tp*Nb(O)(Cl)$_2$ (**3**) (eqs 2 and 3). The process with Me$_3$SiCl has been found to be

$$\mathrm{Tp^*Nb(O)(Cl)(OR) + Me_3SiCl \rightleftharpoons Tp^*Nb(O)(Cl)_2 + Me_2SiOR} \quad (2)$$

$$\mathrm{R = Me, Et}$$

$$\mathrm{Tp^*Nb(O)(Cl)(OR) + PCl_3 \rightarrow Tp^*Nb(O)(Cl)_2 + PCl_2OR} \quad (3)$$

reversible; thus, complexes **1** and **2** can easily be obtained by reaction of **3** with an excess of the appropriate trimethylsilyl alkoxide, Me$_3$SiOR. Complex **3** was previously prepared by Sundermeyer et al.[2c] by reacting Nb(O)(Cl)$_3$ with KTp*.

The spectroscopic data (IR and ^{1}H and ^{13}C{^{1}H} NMR; see Experimental Section) for **3** agree with those previously described.[2c] An interesting hydrolytic process was found when **1** or **2** was treated with water. In fact, **1** or **2** reacts with H$_2$O, in a 1:1 molar ratio, to give the binuclear μ-oxo complex [{Tp*Nb(O)(Cl)}$_2$(μ-O)] (**4**; eq 4). Several polynuclear niobium complexes have been

$$\mathrm{Tp^*Nb(O)(Cl)(OR)} \xrightarrow[-\mathrm{ROH}]{+\mathrm{H_2O}} \mathrm{Tp^*Nb(O)(Cl)(OH)} \xrightarrow{-\mathrm{H_2O}} {}^{1}/_{2}[\{\mathrm{Tp^*Nb(O)(Cl)}\}_2(\mu\text{-O})] \quad (4)$$

described with oxygen bridging, and these are prepared in most cases by hydrolysis from niobium halide species. Several of these examples contain cyclopentadienyl as an ancillary ligand.[5] However, to the best of our knowledge, compound **4** is the first example of a niobium complex containing oxygen bridging with a tris(pyrazol-1-yl)borato ligand. The IR spectrum of **4** exhibits two characteristic bands at 926 and 804 cm^{-1}, which correspond to ν(Nb=O) and ν_{asym}(Nb−O−Nb), respectively. The high value for ν_{asym}(Nb−O−Nb) indicates an appreciable degree of π-bonding character in the Nb−O bond of the Nb−O−Nb unit[5d] with an Nb−O−Nb angle of 169.8° [5d] (see discussion below). The ^{1}H and ^{13}C{^{1}H} NMR spectra show resonances for six distinct sets of pyrazol-1-yl units, indicating the existence of two isomers, *meso* and *rac*, in a 1:1 ratio. When a displacement reagent ((*S*)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol) was added to the sample in the NMR tube, the ^{1}H NMR resonances of the *rac* isomer were doubled (see Experimental Section). A ^{1}H ^{13}C correlation experiment (HETCOR) carried out on these isomers has allowed us to assign the resonances corresponding to the different types of carbon atoms.

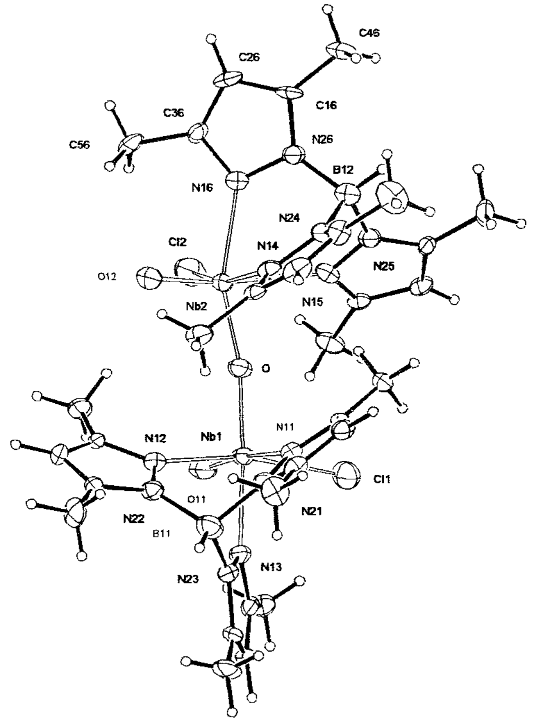

Figure 2. View of complex **4** with the atomic numbering scheme. Selected distances (Å): Nb1−Cl1, 2.360(3); Nb1−O, 1.920(5); Nb2−Cl2, 2.380(3); N2−O, 1.910(5); Nb1−O11, 1.783(5); Nb2−O12, 1.727. Selected angles (deg): Nb1−O−Nb2, 169.8(3); O−Nb1−O11, 100.1(2); O−Nb2−O12, 102.8(2); Cl1−Nb1−O11, 98.7(2); Cl2−Nb2−O12, 97.6(2).

An X-ray crystal structure determination was carried out for **4**. An ORTEP drawing is shown in Figure 2, and a summary of X-ray and refinement data can be found in Table 1. The structure consists of dimeric complexes [{Tp*Nb(O)(Cl)}$_2$(μ-O)] and benzene molecules of solvation. The coordination around the Nb atoms is distorted octahedral with the metal atoms surrounded by three N atoms from a Tp* ligand, a Cl atom, and a terminal O atom; the sixth position is occupied by a bridging O atom. As a result of the ligand distribution this complex is chiral, and in the dimeric units the configuration number is 44 and the chirality symbol **C** for Nb1 and **A** for Nb2 (*meso* form in reference to the complex shown in Figure 2). The Nb1−O11 and Nb2−O12 bond distances of 1.783(5) and 1.727(6) Å, respectively, are indicative of a high degree of π-bonding character. In addition, the Nb−O (bridging) bond distances of 1.920(5) and 1.910(5) Å together with the

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[5] Selected examples: (a) de la Mata, J.; Fandos, R.; Gómez, M.; Gómez-Sal, P.; Martínez-Carrera, S.; Royo, P. *Organometallics* **1990**, *9*, 2486. (b) Bottomley, F.; Boyle, P. D.; Karslioglu, S. *Organometallics* **1993**, *12*, 4090. (c) Gómez, M.; Martínez de Ilarduya, J. M.; Royo, P. *J. Organomet. Chem.* **1989**, *369*, 197. (d) Andreu, A. M.; Jalón, F. A.; Otero, A.; Royo, P.; Manotti Lanfredi, A. M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1987**, 953.

a bond angle value for Nb1−O−Nb2 of 169.8° are indicative of significant π bonding between the bridging oxygen and niobium atoms. These latter bond distances and angle are in accordance with those found in eight related parent structures[6] retrieved from the Cambridge Structural Database System files.[7] In these complexes the Nb−O bond distances ranges from 1.876 to 1.943 Å and the Nb−O−Nb bond angles from 169.3 to 180°. The deformation of the coordination polyhedron is due mainly to the double-bond character of the Nb−O bonds, and indeed, the greatest increases of the bond angle values (from 90°) involve the oxygen atoms. Moreover, the terminal oxygen atoms exert a strong trans influence, the trans Nb−N bonds being elongated *ca.* 0.2 Å (Nb1−N11 = 2.429(6) Å, Nb1−N12 = 2.245(6) Å, Nb1−N13 = 2.233(6) Å; Nb2−N15 = 2.401(6) Å, Nb2−N16 = 2.254(7) Å, Nb2−N14 = 2.223(6) Å).

Finally, we have explored the reactivity of **3** toward $(Me_3Si)_2NMe$ and $LiN(SiMe_3)_2{\cdot}Et_2O$ (1:2 molar ratio), which gives rise to the same complex as the final product $Tp^*Nb(O)(HN(SiMe_3))_2$ (**5**; eq 5). The bis(amide) derivative probably results from a hydrolytic process involving the proposed intermediate $Tp^*Nb(O)(N(SiMe_3)_2)_2$, and in this way the byproduct $(Me_3Si)_2O$, from a condensation process of Me_3SiOH, was detected. The reaction of **3** with $(Me_3Si)_2NMe$ implies, probably, the breaking of a N−C bond at room temperature, although we do not yet have conclusive proof to establish the nature of this unprecedented process. Attempts to avoid the breaking of the N−Si bonds in the proposed bis(amide) intermediate by hydrolysis were unsuccessful even when the solvents were carefully dried. The IR spectrum of **5** show characteristic bands at 3432 and 982 cm^{-1} for the ν(N−H) and ν(Nb=O) modes, respectively. The ^{1}H and ^{13}C{^{1}H} NMR spectra of **5** exhibited two distinct sets of pyrazol-1-yl resonances, indicating the existence of two types of pyrazol-1-yl rings in a 2:1 ratio (see Experimental Section). An octahedral environment for **5** (see Figure 1) can be proposed on the basis of the spectroscopic data.

$$\mathrm{Tp^*Nb(O)(Cl)_2} \xrightarrow[\mathrm{2LiN(SiMe_3)_2\cdot Et_2O}]{\mathrm{2(Me_3Si)_2NMe}} \mathrm{Tp^*Nb(O)(N(SiMe_3)_2)_2} \xrightarrow[\mathrm{-2Me_3SiOH}]{\mathrm{2H_2O}} \mathrm{Tp^*Nb(O)(HN(SiMe_3))_2} \quad (5)$$

Table 1. Crystal Data and Structure Refinement Details for Compounds 4 and 5

	4	5
empirical formula	$C_{30}H_{44}B_2Cl_2N_{12}Nb_2O_3{\cdot}1.5C_6H_6$	$C_{21}H_{42}BN_8NbOSi_2$
fw	1016.26	582.53
wavelength (Å)	0.710 70	0.710 70
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a (Å)	10.667(2)	11.342(2)
b (Å)	13.378(4)	14.1570(10)
c (Å)	17.466(5)	18.717(4)
α (deg)	102.75(2)	90.0
β (deg)	102.13(2)	95.64(2)
γ (deg)	95.22(2)	90.0
V (Å^3)	2352(1)	2990.8(9)
Z	2	4
density (calcd), (g/cm^3)	1.435	1.294
abs coeff (cm^{-1})	6.50	5.10
F(000)	1042	1224
cryst size (mm)	0.15 × 0.28 × 0.35	0.3 × 0.3 × 0.2
θ range for data collection (deg)	3−25	2.02−27.00
index ranges	$-12 \le h \le 12$, $-15 \le k \le 15$, $0 \le l \le 20$	$0 \le h \le 14$, $0 \le k \le 18$, $-23 \le l \le 23$
no. of indep rflns	8269	6525
no. of obsd rflns ($I > 2\sigma(I)$)	4077	1985
GOF	0.735	1.071
R	0.0488	0.1045
R_w	0.0668	0.2449
largest diff peak and hole (e/Å^3)	0.72 and −0.59	1.084 and −1.237

Suitable crystals for an X-ray molecular structure study of **5** were obtained. The molecular structure of **5** is shown in Figure 3, and a summary of X-ray and refinement data can be found in Table 1. The geometry around the niobium atom is approximately octahedral, with the metal atom surrounded by three N atoms from a Tp* ligand and by a terminal O atom; in addition, two positions are occupied by the amide ligands. The molecular structure is not of high quality because of the relatively poor quality of the crystals obtained. However, because of the highly unusual nature of the molecule, and since spectroscopic data and microanalytical results are in good agreement with the established structure, we feel that the overall features of the structure are worth describing, although caution must be taken in reading too much into actual bond lengths and angles obtained. The geometry around the Nb atom can be described as a distorted octahedron, due mainly to the double-bond character of the Nb−O bond (the Nb−O distance is 1.703(8) Å). As for complex **4**, the oxygen atom exerts a strong trans influence, the trans Nb−N bonds being elongated *ca.* 0.2 Å (Nb1−N12 = 2.28(1) Å, Nb−N22 = 2.411(9) Å, Nb1−N32 = 2.264(9) Å). The Si−N−Nb angles are larger than those of the theoretical value for a sp^3 hybridization (155.7(5) and 166.3(5)°) but there are nearly the same as those found for NHR ligands in V and Zr complexes.[8]

In conclusion, we have explored new methods for the synthesis of Tp*-containing niobium complexes. A series of oxo-containing Tp* niobium species have been prepared, and in particular, the X-ray molecular structures of both an oxo-bridging binuclear niobium compound with appreciable π-bonding character in the Nb−

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[6] Skripkin, Yu. V.; Eremenko, I. L.; Pasynskii, A.V.; Volkov, O. G.; Bakum, S. I.; Porai-Koshits, M. A.; Antsyshkina, A. S.; Dikareva, L. M.; Ostrikova, V. N.; Sakharov, S. G.; Struchkov, Yu, T. *Koord. Khim.* **1985**, *11*, 995. (b) Roesky, H. W.; Liebermann, J.; Noltemeyer, M.; Schmidt, H. G. *Chem. Ber.* **1989**, *122*, 1641. (c) Bottomley, F.; Keizer, P. N.; White, P. S.; Preston, K. F. *Organometallics* **1990**, *9*, 1916. (d) Green, M. L. H.; Hughes, A. K.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **1991**, 1407. (e) Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Rees, G. V. *Acta Crystallogr., Sect. B* **1974**, *30*, 2290. (f) Kirillova, N. I.; Lemenovskii, D. A.; Baukova, T. V.; Struchkov, Yu. T. *Koord. Khim.* **1977**, *3*, 1600. (g) Prout, K.; Daran, J. C. *Acta Crystallogr., Sect. B* **1979**, *35*, 2882. (h) Mandimutsira, B. S.; Chen. S. J.; Demadis, K. D.; Coucouvanis, D. *Inorg. Chem.* **1995**, *34*, 2267.

[7] Allen, F. H.; Bellard, S.; Brice, M. D.; Cartwright, B. A.; Doubleday, A.; Higgs, H.; Hummelink, T.; Hummelink-Peters, B. G.; Kennard, O.; Motherwell, W. D. S.; Rodgers, J. R.; Watson, D. E. *Acta Crystallogr., Sect. B* **1979**, *35*, 2331.

[8] de With, J.; Horton, A. D. *Organometallics* **1993**, *12*, 1493. (b) Schaller, C. P.; Cummins, C. C.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1996**, *118*, 591.

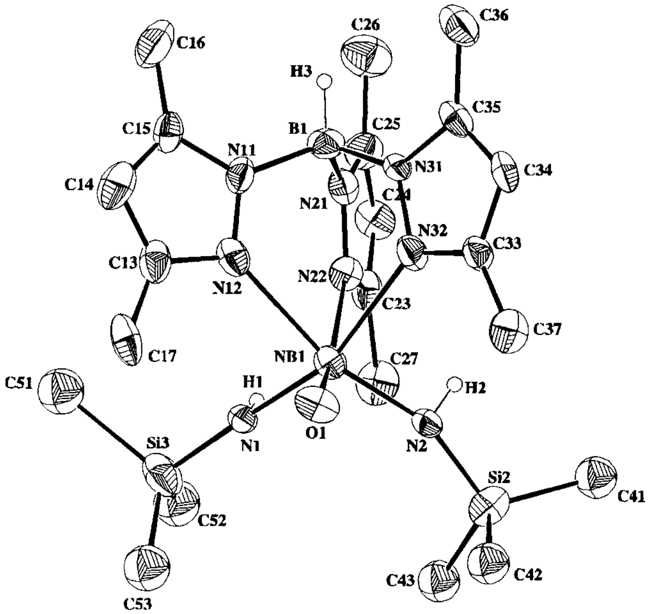

Figure 3. View of complex **5** with the atomic numbering scheme. Selected distances (Å): Nb1−O1, 1.703(8); Nb1−N1, 1.890(8); Nb1−N2, 1.883(8); N2−Si2, 1.632(9); N1−Si3, 1.593(8). Selected angles (deg): Si3−N1−Nb1, 166.3(5); Si2−N2−Nb1, 155.7(5); O1−Nb1−N2, 100.9(4); O1−Nb1−N1, 101.2(4).

O−Nb unit and an unusual bis(amide) complex resulting from the hydrolysis of N−Si bonds has been described.

Experimental Section

All operations were performed under an inert atmosphere using standard vacuum line (Schlenk) techniques. Solvents were purified by distillation from appropriate drying agents before use. NMR spectra were recorded on a Varian Unity FT-300 instrument. IR spectra were recorded as Nujol mulls between CsI plates (in the region between 4000 and 200 cm^{-1}) on a Perkin-Elmer PE 883 IR spectrophotometer. Elemental analyses were performed on a Perkin-Elmer 2400 microanalyzer. Potassium hydridotris(3,5-dimethylpyrazol-1-yl)borate[9] and $[Nb(Cl)_3(OR)_2]_2$[10] were prepared as previously reported.

Synthesis of Tp*Nb(O)(Cl)(OMe) (1). A solution of $[Nb(Cl)_3(OMe)_2]_2$ (0.381 g, 1.46 mmol) in THF (50 mL) was cooled to −40 °C, and potassium hydridotris(3,5-dimethylpyrazol-1-yl)borate (0.491 g, 1.46 mmol) was added with vigorous stirring. The solution turned from colorless to light yellow, and a white precipitate was formed. After 1 h at −40 °C, the mixture was concentrated under vacuum. Extraction with dicholoromethane (10 mL), addition of hexane (30 mL), and filtration through a Celite pad gave a yellow solution. Precipitation occurred upon slow concentration followed by addition of hexane. The resulting white solid **1** (0.414 g, 0.88 mmol, 60%) was isolated by filtration and then dried under vacuum. Anal. Calcd for $C_{16}H_{25}BClN_6NbO_2$: C, 40.7; H, 5.3; N, 17.8. Found: C, 41.0; H, 4.9; N, 17.7. IR (Nujol mull): 2550 (m, ν(B−H)), 1536 (s, ν(C=N$_{pz}$)), 919 (s, ν(Nb=O)), 529 (m, ν(Nb−OR)), 339 (m, ν(Nb−Cl)) cm^{-1}. ^{1}H NMR (300 MHz, benzene-d_6): δ 5.55, 5.38, 5.34 (all s, 1H, Tp*CH), 4.26 (s, 3H, OCH_3), 3.01, 2.60, 2.52, 2.09, 1.96, 1.94 (all s, 3H, Tp*CH_3). ^{13}C{^{1}H} NMR: δ 154.3, 152.5, 152.4, 145.4, 144.9, 143.5 (Tp**C*CH_3), 107.2, 106.9, 106.8 (Tp*CH), 66.1 (OCH_3), 15.5, 14.3, 14.2, 12.4, 12.2 (1:1:1:1:2:1, Tp*CH_3).

Tp*Nb(O)(Cl)(OEt) (2). The synthetic procedure was the same as for complex **1**, using $[Nb(Cl)_3(OEt)_2]_2$ (0.276 g, 0.95 mmol) and potassium hydridotris(3,5-dimethylpyrazol-1-yl)borate (0.319 g, 0.95 mmol); it gave complex **2** (0.379 g, 0.78 mmol, 82%) as a white solid. Anal. Calcd for $C_{17}H_{27}BClN_6NbO_2$: C, 41.9; H, 5.6; N, 17.3. Found: C, 41.5; H, 5.6; N, 17.3. IR (Nujol mull): 2543 (m, ν(B−H)), 1538 (s, ν(C=N$_{pz}$)), 917 (s, ν(Nb=O)), 584 (m, ν(Nb−OR)), 337 (m, ν(Nb−Cl)) cm^{-1}. ^{1}H NMR (300 MHz, benzene-d_6): δ 5.56, 5.41, 5.34 (all s, 1H, Tp*CH), 4.88, 4.60, 1.35 (m, 1H$_A$; m, 1H$_B$; t, 3H$_X$; J_{AB} = 12 Hz, J_{AX} = J_{BX} = 7 Hz, ABX$_3$ system of OCH_2CH_3), 3.00, 2.65, 2.52, 2.10, 1.98, 1.95 (all s, 3H, Tp*CH_3). ^{13}C{^{1}H} NMR: δ 154.2, 152.5, 152.4, 145.6, 144.7, 143.5 (Tp**C*CH_3), 107.2, 106.8 (1:2 Tp*CH), 75.5 (O*C*H_2CH_3), 17.8, 15.5, 14.5, 14.3, 12.5, 12.4 (Tp*CH_3), 12.2 (OCH_2*C*H_3).

Tp*Nb(O)(Cl)$_2$ (3). To a solution of Tp*Nb(O)(Cl)(OMe) (**1**; 0.899 g, 1.90 mmol) or Tp*Nb(O)(Cl)(OEt) (**2**; 0.925 g, 1.90 mmol) in toluene (50 mL) was added Me_3SiCl (0.206 g, 1.90 mmol) or PCl_3 (0.261 g, 1.90 mmol). The solution turned from colorless to light yellow, and a white precipitate was formed. After 4 days, the mixture was filtered through a Celite pad to give a yellow solution. Precipitation occurred upon slow concentration followed by addition of hexane. The resulting light yellow solid of **3** (0.895 g, 1.88 mmol, 99%) was isolated by filtration and then dried under vacuum. Anal. Calcd for $C_{15}H_{22}BCl_2N_6NbO$: C, 37.7; H, 4.6; N, 17.6. Found: C, 37.8; H, 4.8; N, 17.3. IR (Nujol mull): 2553 (m, ν(B−H)), 1538 (s, ν(C=N$_{pz}$)), 933 (s, ν(Nb=O)), 337 (m, ν(Nb−Cl)) cm^{-1}. ^{1}H NMR (300 MHz, benzene-d_6): δ 5.50, 5.20 (both s, 1H, 2H, Tp*CH), 2.82, 2.72, 2.06, 1.83 (all s, 3H, 6H, 3H, 6H Tp*CH_3). ^{13}C{^{1}H} NMR: δ 154.5, 154.2, 146.1, 143.7 (1:2:1:2, Tp**C*CH_3), 107.7, 107.4 (1:2, Tp*CH), 15.7, 15.2, 12.3, 12.1 (1:2:1:2, Tp*CH_3).

[{Tp*Nb(O)(Cl)}$_2$(μ-O)] (4). To a solution of Tp*Nb(O)(Cl)(OMe) (**1**; 0.300 g, 0.63 mmol) or Tp*Nb(O)(Cl)(OEt) (**2**; 0.307 g, 0.63 mmol) in toluene (50 mL) was added H_2O (11 μL). The solution turned from colorless to light yellow, and a white precipitate was formed. After 2 days, the white solid **4** (0.228 g, 0.25 mmol, 82%) was isolated by filtration and then dried under vacuum. Anal. Calcd for $C_{30}H_{44}B_2Cl_2N_{12}Nb_2O_3$: C, 40.1; H, 4.9; N, 18.7. Found: C, 39.7; H, 5.0; N, 18.5. IR (Nujol mull): 2540 (m, ν(B−H)), 1538 (s, ν(C=N$_{pz}$)), 926 (s, ν(Nb=O)), 804 (s, ν_{asym}(O−Nb−O), 336 (m, ν(Nb−Cl)) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *meso* isomer, δ 5.97, 5.77, 5.47 (all s, 1H, Tp*CH), 2.98, 2.76, 2.37, 1.02 (all s, 3H, 3H, 9H, 3H, Tp*CH_3); *rac* isomer, δ 5.83, 5.81, 5.39 (all s, 1H, Tp*CH), 3.27, 2.71, 2.39, 2.33, 2.31, 1.06 (all s, 3H, Tp*CH_3). ^{13}C{^{1}H} NMR: δ 153.8, 153.7, 153.5, 153.4, 153.0, 145.9, 145.3, 145.2, 145.1, 144.6, 143.6, 143.4 (Tp**C*CH_3); *meso* isomer, δ 108.0, 107.3, 107.1 (Tp*CH), 16.9, 16.2, 16.1, 13.3, 12.8, 11.4 (Tp*CH_3); *rac* isomer, δ 107.6, 107.4, 106.6 (Tp*CH), 17.0, 16.0, 13.1, 12.9, 11.5, 11.3 (Tp*CH_3).

Tp*Nb(O)(HNSiMe$_3$)$_2$ (5). This complex was prepared by two different methods.

Method A. To a solution of Tp*Nb(O)(Cl)$_2$ (**3**; 0.350 g, 0.73 mmol) in toluene (50 mL) was added $(Me_3Si)_2NMe$ (0.256 g, 1.46 mmol). After 2 days, the yellow solution was concentrated under vacuum and hexane (20 mL) was added. The mixture was filtered through a Celite pad to give a colorless solution. This solution was cooled to −4 °C to give white microcrystals of **5** (0.106 g, 0.18 mmol, 25%). $(Me_3Si)_2O$ was isolated from the mother liquor and was characterized by comparison with the spectroscopic data of an authentic sample (^{1}H NMR ($CDCl_3$) δ 0.07 ppm; ^{13}C NMR ($CDCl_3$) δ 2.0 ppm).

Method B. To a solution of Tp*Nb(O)(Cl)$_2$ (**3**; 0.231 g, 0.48 mmol) in THF (50 mL) was added $LiN(SiMe_3)_2 \cdot Et_2O$ (0.232 g, 0.96 mmol). After 3 days, the solution turned from colorless to light yellow and a white precipitate formed. The mixture was filtered through a Celite pad to give a yellow solution. Precipitation occurred upon slow concentration followed by addition of hexane. The resulting white solid **5** (0.168 g, 0.29 mmol, 60%) was isolated by filtration and then dried under

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[9] Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170.

[10] Antiñolo, A.; Otero, A.; Urbanos, F.; Garcia-Blanco, S.; Martinez-Carrera, S.; Sanz-Aparicio, J. *J. Organomet. Chem.* **1988**, *350*, 25.

vacuum. Anal. Calcd for $C_{21}H_{42}BN_8NbOSi_2$: C, 43.3; H, 7.3; N, 19.2. Found: C, 43.1; H, 7.2; N, 19.0. IR (Nujol mull): 3432 (s, ν(N−H)), 2543 (m, ν(B−H)), 1543 (s, ν(C=N_{pz})), 982 (s, ν(Nb=O)) cm^{-1}. ^1H NMR (300 MHz, benzene-d_6): δ 5.62, 5.47 (both s, 1H, 2H, Tp*CH), 2.83, 2.55, 2.11, 2.01 (all s, 6H, 3H, 3H, 6H, Tp*CH_3), 0.34 (s, 18H, $SiMe_3$). $^{13}C\{^1H\}$ NMR: δ 152.4, 150.7, 144.6, 143.1 (2:1:1:2 Tp*CCH_3), 106.5, 106.1 (1:2 Tp*CH), 15.5, 15.2, 12.5, 12.1 (2:1:1:2 Tp*CH_3), 2.2 ($SiMe_3$). Mass spectrum (*m*/*z*, assignment, percent intensity): 585D [M + 3], 45; 489D [M − $C_4H_6N_2$ - $2CH_3$ + O]$^+$, 100.

X-ray Data Collection, Structure Determination, and Refinement of Complexes 4 and 5. Crystals of **4** and **5** were grown from a solution of benzene by slow evaporation of solvent and from a solution of hexane cooled to −4 °C, respectively. Suitable crystals of these complexes were sealed in Lindeman capillaries under dry nitrogen and used for data collection. Accurate unit-cell parameters were determined for **4** by least-squares refinement of the setting angles of 26 randomly distributed and carefully centered reflections with θ in the range 11−18°. The data collection was performed on a Philips PW 1100 diffractometer using the $\theta/2\theta$ scan mode, at 293 K, with a variable scan speed of 3−9.6° min^{-1} and a scan width of $1.20 + 0.34 \tan \theta$. One standard reflection was monitored every 100 measurements; no significant decay was noticed over the time of data collection. The individual profiles have been analyzed following the method of Lehmann and Larsen.[11] Intensities were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SIR 92[12]) and refined first isotropically by full-matrix least-squares using the SHELX-76 program[13] and then anisotropically by blocked full-matrix least-squares for all the non-hydrogen atoms. All the hydrogen atoms were placed at their geometrically calculated positions (d(C−H) = 0.96 Å) and refined "riding" on their parent carbon atoms, except for those of the solvent molecules. All calculations were carried out on the ENCORE 91 computer of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma, Italy.

The crystals of **5** were of poor quality and diffracted rather weakly; unfortunately, no other crystals could be obtained. Whereas the X-ray structural determination of **5** was not accurate enough for an in-depth investigation of the structural parameters for this compound, it does show the overall structural features and hence has been included for this reason. The structure was solved by a combination of direct methods (SIR92)[14] and Fourier techniques with refinement being performed using the least-squares methods on F^2 (SHELXL93).[14] For the final cycles of refinement all non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included in calculated positions but not refined. The programs Parst[15] and ORTEP[16] were also used. The final atomic coordinates for **4** and **5** are provided in the Supporting Information.

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Supporting Information Available: For **4** and **5**, final atomic coordinates for the non-hydrogen and hydrogen atoms (Tables SI, SI′, SII, and SII′), anisotropic thermal parameters (Tables SIII and SIII′), all bond distances and angles (Tables SIV and SIV′), and all crystallographic data (Tables SV and SV′) (14 pages). Ordering information is given on any current masthead page.

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[11] Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A* **1974**, *30*, 580.

[12] Attomare, A.; Cascarano, G.; Giacovazzo, C.; Gualiardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. J. *Appl. Crystallogr.* **1994**, *27*, 435.

[13] Sheldrick, G. M. SHELX-76: Program for the Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1976.

[14] Sheldrick, G. M. SHELXL93: Program for the Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1993.

[15] Nardelli, M. *Comput. Chem.* **1983**, SHELXL93, 95.

[16] Johnson, C. K. ORTEP; Report ORNL-3794, revised; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.