Alkyne and Nitrile as η^2(3e) Ligands in [Tris(pyrazolyl)borato]niobium(I) Complexes. Synthesis, Structure, and Coupling Reaction

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Received November 17, 1995⊗

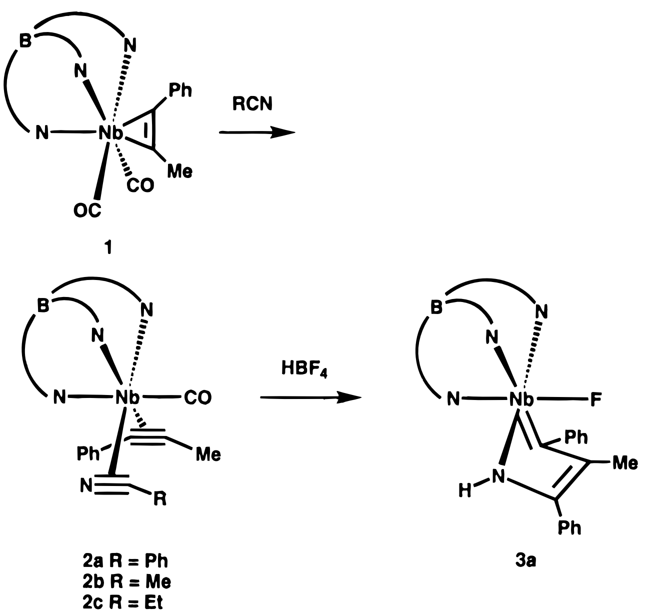
*Summary: Treatment of the 4e-alkyne complex [Tp*Nb(CO)$_2$(PhCCMe)] with the nitrile RCN (R = Ph, Me, Et) yields the first mixed 3e-alkyne−η^2(3e)-nitrile complexes, [Tp*Nb(CO)(PhCCMe)(RCN)], which have been spectroscopically and structurally characterized. Upon addition of HBF$_4$, the protonated coupling product [Tp*Nb(F)(CPhCMeCPhNH)] (R = Ph) is formed.*

Although nitriles act as either η^1 or η^2 two-electron (2e) donor ligands,[1] their behavior as η^2(4e) donors has been recognized only recently.[2] The involvement of both π-systems of the CN triple bond parallels that now well-established for alkynes.[3] We report here the first examples of mixed alkyne−nitrile complexes [Tp*Nb(CO)(PhCCMe)(RCN)] (Tp* = hydridotris(3,5-dimethylpyrazolyl)borate, R = Me, Et, Ph), where these η^2-bound ligands formally contribute three electrons each to the total electron count at niobium(I). Protonation with HBF$_4$ induces intramolecular ligand coupling in the benzonitrile complex, giving the niobacycle [Tp*Nb(F)(CPhCMeCPhNH)].

For some years, we have been developing the chemistry of niobium(III) Tp* alkyne complexes and we have shown that the stereoelectronic properties of Tp* have important structural and reactivity consequences.[4] The present study represents an unprecedented entry into niobium(I) Tp* chemistry.

Treatment of the yellow-green symmetrical (4e-phenylpropyne)dicarbonylniobium(I) complex [Tp*Nb(CO)$_2$(PhCCMe)] (**1**; ν(CO) 1960, 1855 cm^{-1}; ^{13}C NMR δ 259.4, 212.2 (Ph*CC*Me))[5] with the nitrile RCN in refluxing tetrahydrofuran proceeds smoothly to give, after CO evolution, the unsymmetrical complexes [Tp*Nb(CO)(PhCCMe)(RCN)] (R = Ph, **2a**, 67%; R = Me, **2b**, 30%; Et, **2c**, 30%) (see Scheme 1). They are isolated as orange crystals after washing the crude reaction residue with diethyl ether. Chirality in **2a**−**c** is evident by the observation of three methine and six methyl resonances in the ^{1}H and ^{13}C NMR spectra.[6] Diastereotopic propionitrile methylene hydrogens are inequivalent in **2b**.

Scheme 1



Spectroscopic[6] and crystallographic[7] data are consistent with an η^2(3e)-nitrile description. In the three cases, *three* quaternary carbon resonances (^{13}C NMR) are observed in the region δ 174−187. We ascribe two of these signals to the contact carbons of a 3e-alkyne[3] and one to the nitrile carbon bound to niobium. ^{13}C NMR data have been reported for η^1(2e)- or η^2(4e)-nitriles[2a,b] but, unfortunately, have not been detailed in the few

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⊗ Abstract published in *Advance ACS Abstracts,* February 1, 1996.

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(6) Data for **2a** are as follows. Anal. Calcd for $C_{32}H_{35}BN_7NbO$: C, 60.3; H, 5.5; N, 15.4. Found: C, 60.3; H, 5.6; N, 15.0. Infrared (KBr): ν(CO) 1947, ν(C≡C, C≡N) 1737, 1725 cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.66, 1.99, 2.06, 2.14, 2.31, 2.40 (all s, 3 H each, Tp**Me*), 3.12 (s, 3 H, PhCC*Me*), 5.19, 5.39, 5.90 (all s, 1 H each, Tp*C*H*), 6.70−7.03 (m, 5 H, *Ph*CCMe), 7.29 (t, *J* 7 Hz, 2 H, *m-Ph*CN), 8.53 (d, *J* 7 Hz, 2 H, *o-Ph*CN), *p-Ph*CN obscured by solvent. ^{13}C{^{1}H} NMR ($CDCl_3$, 243 K): δ 13.0, 13.3, 14.7, 15.0, 15.5 (Tp**Me*), 18.8 (PhC≡C*Me*), 106.3, 106.5, 107.5 (Tp**C*H), 125.9, 127.0, 127.7, 129.0, 130.8, 132.3, 138.5 (*Ph*C≡CMe and *Ph*C≡N), 143.2, 143.4, 144.4, 149.8, 150.7, 153.4 (Tp**C*Me), 176.5, 176.8, 186.7 (Ph*CC*Me and Ph*C*N), 230.1 (*C*O). Data for **2b** are as follows. Anal. Calcd for $C_{27}H_{33}BN_7NbO$: C, 56.4; H, 5.8; N, 17.0. Found: C, 56.2; H, 5.6; N, 16.6. Infrared (KBr): ν(CO) 1920, ν(C≡C, C≡N) 1785, 1728 cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.62, 1.98, 2.08, 2.15, 2.19, 2.38 (all s, 3 H, Tp**Me*), 2.87 (s, 3 H, *Me*CN), 2.95 (s, 3 H, PhCC*Me*), 5.28, 5.37, 5.82 (all s, 1 H, Tp*C*H*), 6.72−7.02 (m, 5 H, *Ph*CCMe). ^{13}C{^{1}H} NMR ($CDCl_3$, 233 K): δ 17.5, 17.8 (*Me*CN and PhCC*Me*), 174.6, 177.3, 180.9 (Ph*CC*Me and Me*C*N), 230.3 (*C*O). Data for **2c** are as follows. Infrared (KBr): ν(CO) 1894, ν(C≡C, C≡N) 1789, 1729 cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.38 (t, *J* 7 Hz, 3 H, *Me*CH$_2$CN), 3.21, 3.31 (both dq, *J* 14, 7 Hz, 1 H each, MeC*H*$_2$CN), 2.98 (s, 3H, PhCC*Me*). ^{13}C{^{1}H} NMR ($CDCl_3$, 233 K): δ 14.1 (*Me*CH$_2$CN), 17.4 (PhCC*Me*), 26.6 (Me*C*H$_2$CN), 174.6, 177.0, 183.8 (Ph*CC*Me and Et*C*N), 230.4 (*C*O).

(7) Crystal data for **2a**: $C_{32}H_{35}BN_7NbO$, monoclinic, space group $P2_1/c$, $a = 12.647(2)$ Å, $b = 16.468(3)$ Å, $c = 15.190(3)$ Å, $\beta = 96.28(1)°$, $V = 3144.6(8)$ Å^3, $Z = 4$, $F(000) = 1320$, λ(Mo Kα) = 0.710 73 Å, $\rho_{calcd} = 1.346$ Mg m^{-3}, $\mu = 40.01$ mm^{-1}. The final residuals for 207 parameters refined against 1546 unique data with $I > 3\sigma(I)$ were $R = 0.0373$ and $R_w = 0.0414$.

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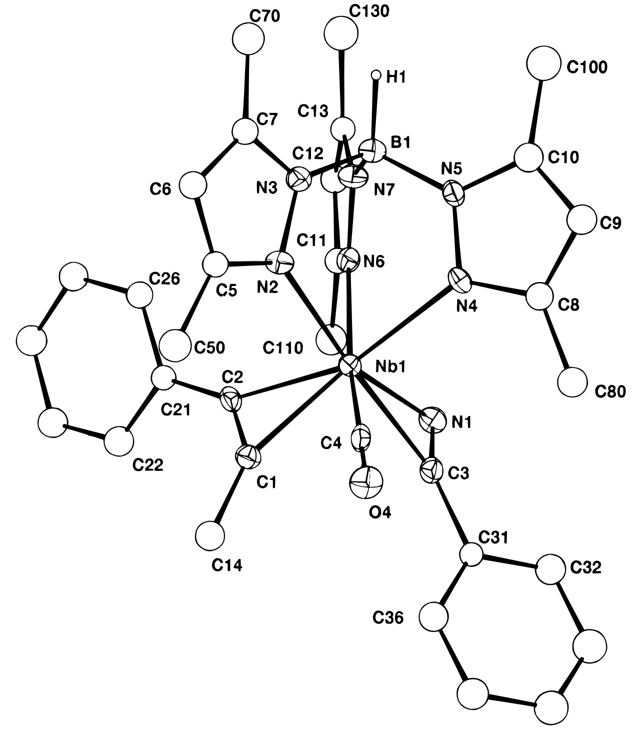

Figure 1. Plot of the molecular structure of [Tp*Nb(CO)(PhCCMe)(PhCN)] (**2a**). Selected bond lengths (Å) and angles (deg): Nb(1)−N(1), 2.139(8); Nb(1)−N(2), 2.339(6); Nb(1)−N(4), 2.312(7); Nb(1)−N(6), 2.335(7); Nb(1)−C(1), 2.166(9); Nb(1)−C(2), 2.118(8); Nb(1)−C(3), 2.17(1); Nb(1)−C(4), 2.06(1); C(1)−C(2), 1.21(1); N(1)−C(3), 1.21(1); C(2)−C(1)−C(14), 138.4(9); C(1)−C(2)−C(21), 139.1(9), N(1)−C(3)−C(31), 135.2(10).

cases of X-ray-characterized η^2(2e) coordination.[8,16] η^2-(4e)-Nitriles have low-field resonances comparable to those of η^2(4e)-alkynes.[2a,b] η^1(2e)-Nitriles usually give resonances at higher field, more comparable to those of free nitriles. Except for a slight broadening, the ^{1}H NMR of **2b** is temperature-independent (183−333 K, C_7D_8). The solid-state infrared spectra reveal two medium-intensity absorptions in the region 1725−1790 cm^{-1}, which are readily ascribed to coordinated C≡C and C≡N stretches. The X-ray crystal structure[7] of **2a** confirms the η^2-coordination mode for the nitrile (see Figure 1). Both the coordinated CC and CN bonds are parallel to the Nb−CO axis, leading to optimized orbital interactions (see below).[3] The alkyne methyl group and the nitrile phenyl group are directed toward the CO. The lengths of the Nb(1)−N(1) and Nb(1)−C(3) bonds indicate multiple-bonding character (2.139(8) and 2.17(1) Å, respectively). The Nb−phenylpropyne bonding exhibits similar parameters, which are longer than those for the 4e-phenylpropyne complex [Tp*NbCl$_2$(PhCCMe)] (Nb−C = 2.050(9) and 2.093(9) Å).[4] Recently described η^2(4e)-nitrile tungsten complexes have virtually equal metal−nitrogen and metal−carbon bonds around 2.00 Å.[2b] The η^2(2e)-nitrile complex[8a] $(C_5H_5)_2$Mo(MeCN) displays metal−nitrogen and metal−carbon bond lengths of 2.22 and 2.11 Å, respectively. The C−N bond length in **2a** is 1.21(1) Å. For the η^2(4e)-nitrile complexes, it is in the range 1.27−1.22 Å,[2b] whereas in the η^2(2e) case, it is slightly shortened to 1.20 Å.[8a] To our knowledge, complexes **2a**−**c** are the first η^2-nitrile complexes of the group 5 transition metals.[16] It is also the first time that a nitrile behaves formally as a 3e donor.

As analyzed previously for bis(alkyne) group 6 metal complexes,[3] the 3e-donor formulation is a formal one and does not involve any odd-electron chemistry. It is the involvement of *two* 3e-donor ligands, one alkyne and one nitrile, for a total of six electrons donated to the metal which leads to such a description. From a molecular orbital standpoint, it is the absence of a suitable metal orbital for interaction with the out-of-phase combination of $\pi_\perp$ ligand orbitals that rationalizes the bonding situation. We note here that the isoelectronic cationic mixed alkyne−nitrile group 6 carbonyl complex [Tp*W(CO)(PhCCMe)(MeCN)][BF$_4$] contains 4e-alkyne and η^1(2e)-nitrile ligands.[9] Undoubtedly, this reflects the fact that the tungsten(II) center in the cationic complex is harder than the niobium(I) center in neutral **2a**−**c** or, alternatively,[2b] that nitriles having low-energy π^*(CN) orbitals stabilize more efficiently the relatively electron-rich niobium(I) in **2a**−**c**.

Although stereoselective stepwise reduction of acetonitrile has been realized in [Tp*W(CO)(PhCCMe)(η^1-MeCN)][BF$_4$],[10] η^2-coordination has been suggested to activate the nitrile toward methanol attack in [MCl(MeCN)(dmpe)][BPh$_4$] (M = Cr, Mo).[2c,11] Protonation of [Cp$_2$Mo(η^2-MeCN)] in MeCN yields [Cp$_2$Mo(η^1-MeCN)(η^1-NH=CHMe)][BF$_4$]$_2$.[12] Addition of HBF$_4$ to [Tp*Nb(CO)(PhCCMe)(PhCN)] (**2a**) in dichloromethane at −20 °C gives a red-brown solution in which no CO stretch may be observed by infrared spectroscopy. Extraction with toluene and precipitation from hexane give the neutral complex [Tp*Nb(F)(CPhCMeCPhNH)] (**3a**) in 65% yield (see Scheme 1).[13] Evidence for the NH group comes from (i) the ^{1}H NMR spectrum, where a broad singlet is observed at δ 8.31 which slowly disappears upon addition of D_2O, and (ii) the solid-state infrared spectrum, which displays an NH stretch at 3382 cm^{-1}. The fluoride bound to niobium gives a ^{19}F NMR signal at δ 117.1 ($w_{1/2}$ = 30 Hz, external CF_3CO_2D) and a strong Nb−F stretch at 554 cm^{-1}. The five-membered niobacycle is well-defined from the ^{13}C NMR spectrum of **3a**. Quaternary signals are observed at δ 219.4 as a niobium-broadened alkylidene-like signal, assigned to the α-carbon, and at δ 93.6 and δ 121.8, ascribed to β- and γ-carbons. Similar ^{13}C NMR data have been obtained for related oxa- or azametallacycles resulting from either acyl−alkyne or iminoacyl−alkyne coupling reactions in the coordination sphere of niobium or

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tantalum.[14] These species are heteroatom analogs of η^4-C_4R_4H butadienyl complexes formed *via* allyl−alkyne coupling in Tp* niobium chemistry.[15] As observed in the X-ray structure of **2a**, the alkyne and the nitrile are well set up for this regioselective coupling. The first step of a mechanism leading to **3a** is presumably protonation of the η^2(3e)-nitrile lone pair, which is not involved in the bonding. This gives a cationic iminoacyl complex which would readily lose CO and undergo iminoacyl−alkyne coupling *via* carbon−carbon bond formation. Tetrafluoroborate is nucleophilic enough to transfer a fluoride to this highly electrophilic unsaturated niobium cation, leading to **3a**. We are actively attempting to trap one of these putative intermediates.

In conclusion, we have described the first examples of formally η^2(3e)-nitrile complexes. The second 3e ligand in the metal coordination sphere, namely an alkyne, readily couples to the nitrile upon protonation.

Acknowledgment. C.C. and M.E. thank the LCC and the European Union for a grant to C.C. under the Human Capital and Mobility Program (Contract No. ERBCHBGCT 930417).

Supporting Information Available: Text and tables giving full details of the X-ray structure determination for **2a** (10 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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(16) During the time this paper was being printed, we became aware of a study reporting ^{13}C NMR data for some η^2(2e)-MeCN complexes. The molybdenum-bound carbon of MeCN in $(C_5H_5)_2Mo(\eta^2\text{-MeCN})$ is found at δ 170.8. The niobium-bound carbon of MeCN in $(C_5H_5)_2Nb(SnMe_3)(\eta^2\text{-MeCN})$ is found at δ 179.8 and 165.1 (*exo* and *endo* isomers). See: Green, M. L. H.; Hughes, A. K.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **1991**, 1407.