Niobium-Centered C−C Coupling of Isonitriles

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*Summary: The complexes [NbI₂(CNtBu)₆]I (**1**), [NbI₂-(CNtBu)₄(tBuNHC≡CNHtBu)]I (**2**), and cis-[NbI(CO)₂-(CNR)₂dppe] (R = tBu (**3a**), Cy (**3b**)), have been prepared by oxidation of [Nb(CO)₆]⁻ with iodine in the presence of isonitrile either in a direct reaction (**1** and **2**) or, in the case of **3**, by substitution in the intermediate [NbI-(CO)₄dppe]. While **1** and **3** are generated in absolute THF, **2** forms in moist THF. The X-ray structure analysis of **1**·THF, **2**, and **3b**·toluene reveals trigonal-prismatic basic structures with the iodines capping tetragonal faces. **1** and **3b** exhibit interatomic C⋯C distances sufficiently close to enable C−C coupling. The relevance of the coupling product **2** for reductive C−C coupling mediated by low-valent niobium is discussed.*

Introduction

Reductive coupling of two CO or CNR groups in group 5 carbonyl and isonitrile complexes to form η^2-alkyne complexes has been documented: in the systems [MCl-(CO/CNR)₂(dmpe)₂] (M = V, Nb, Ta; dmpe = Me₂PCH₂-CH₂PMe₂), coupling is initiated by sodium amalgam or magnesium in the presence of Me₃SiY (Y is usually Cl or triflate). In most cases, formation of Me₃SiO-C≡COSiMe₃ has been achieved by coupling of two carbonyls,[1] but a cross-coupling between CO and CNR has also been observed.[2] The coupling of two CNR groups is a common feature in the reductive treatment (with Zn in wet THF) of [(Mo/W)Cl(CNR)₆]⁺, yielding [(Mo/W)Cl(CNR)₄(RHNC≡CNHR)]⁺.[3] To our knowledge, there is only one reported example in group 5 chemistry where two isonitriles are linked together to an acetylenic ligand, which then becomes coordinated to two niobium centers via the triple bond and the two nitrogens.[4] On a broader basis, vanadium-, niobium-, and tantalum-based catalysts have been employed in various reductive C−C coupling reactions.[5] An example involving isonitrile is the regioselective coupling of alkynes to nitriles.[6] The catalyst is either a low-valent group 5 metal halide such as "VCl₂" or an M^{IV/V} halide or alkoxide together with a reducing agent such as Zn

or AlEt₃, suggesting that the active species again is a low-valent metal center capable of coordinating and thus activating the substrate(s). Reactions supporting this view are the stoichiometric coupling of substrates to organic groups directly coordinated to the metal, such as the insertion of isonitrile into the Ta−Me bond to provide acetamidoyl[7] and the insertion of CO into the Ta−C_σ bond of a Ta(alkyl/aryl)(alkyne) fragment with concomitant coupling of the acyl/benzoyl group to the alkyne.[8]

Results and Discussion

Syntheses and Spectroscopic Characteristics. While the reaction between the hexacarbonyl*vanadate* [Et₄N][V(CO)₆], halogen, and isonitrile in absolute THF yields the hexacoordinated V^{II} complexes [VX₂(CNR)₄] (R = *cyclo*-C₆H₁₁ (Cy), *t*Bu; X = Br, I) and [VI-(CN*t*Bu)₅]I,[9] the corresponding reaction between CN*t*Bu, iodine, and hexacarbonyl*niobate*(−I) leads to the octa-coordinated Nb^{III} complex [NbI₂(CN*t*Bu)₆]I (**1**) in absolute THF. In wet THF (containing up to 0.03% water), the coupling product [NbI₂(CN*t*Bu)₄(*t*BuHN-C≡CNH*t*Bu)]I (**2**) is obtained. The source for the hydrogen in the coupling product **2** apparently is water. The complexes are obtained in good to medium yields (**1**, 87%; **2**, 45%). A direct conversion of **1** to **2**, using zinc as the reducing agent in analogy to the generation of Mo^{II}−alkyne from Mo^{II}−isonitrile complexes,[3] could not be achieved. The heptacoordinated Nb^{I} complexes cis-[NbI(CO)₂(CNR)₂dppe] (dppe = Ph₂PCH₂CH₂PPh₂; R = *t*Bu, **3a**; R = Cy, **3b**), which are isoelectronic with similar Mo^{II} complexes,[3] have been prepared in 83% yields by low-temperature CO substitution of THF solutions of [NbI(CO)₄dppe] in the presence of the isonitrile.[10] **3a** and **3b** exhibit strong similarities to the alkyne complexes [NbX(CO)₂(η^2-alkyne)(PR₃)₂], in which the alkyne acts as a four-electron donor. These alkyne complexes have been obtained either by direct interaction between [Nb(CO)₆]⁻, alkyne, phosphine, and halogen[10,11] or—starting from [NbCl(CO/CNR)₂(dmpe)₂]—by reductive coupling between CO and CO or between CO and CNR.[1,2]

1 and **2**, with Nb^{III} centers, show typical strong, broad, and asymmetric ν(C≡N) signals at 2153 and 2192 cm⁻¹, respectively, for the coordinated isonitriles. In addition, **2** exhibits ν(NH) at 3196 cm⁻¹ and ν(C=N) at 1557 cm⁻¹.

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Table 1. Crystal Data and Details of the Solution and Refinement of the Structures

	1·THF	**2**	**3b·toluene**
	$C_{34}H_{62}I_3N_6NbO$	$C_{30}H_{56}I_3N_6Nb$	$C_{49}H_{54}IN_2NbO_2P_2$
fw	1044.51	974.42	984.69
cryst syst	orthorhombic	orthorhombic	triclinic
space group	*Cmcm*	$P2_12_12_1$	$P\bar{1}$
a (Å)	11.473(2)	13.834(2)	10.258(2)
b (Å)	22.831(5)	14.811(3)	13.226(2)
c (Å)	23.187(5)	22.795(7)	17.727(2)
α (deg)			103.43(2)
β (deg)			94.99(2)
γ (deg)			104.55(2)
V (Å³)	6074(2)	4571(2)	2237.1(6)
Z	4	4	2
D_{calcd} (g/cm³)	1.142	1.386	1.462
λ (Å)	0.710 73	1.541 78	1.541 78
μ (mm⁻¹)	1.75	17.83	8.60
F(000)	2064	1912	1004
cryst size (mm)	0.5 × 0.5 × 0.4	0.2 × 0.1 × 0.1	0.3 × 0.2 × 0.1
temp (K)	153(2)	173(2)	173(2)
θ range (deg)	2.50−25.06	3.56−69.98	3.58−49.97
index range	−2 < h < 13, −2 < k < 27,	−17 < h < 0, −18 < k < 0,	−10 < h < 0, −12 < k < 13,
	−2 < l < 27	−28 < l < 0	−17 < l < 17
no. of reflns collected	4402	4975	4939
no. of indep rflns	2917	4919	4597
R_{int}	0.0280	0.0518	0.0346
no. of rflns with $I > 2\sigma I_0$		4175	
no. of params	136	376	504
R1 ($I > 2\sigma I_0$)	0.0585	0.0779	0.0485
wR2 ($I > 2\sigma I_0$)	0.1473	0.2115	0.0949
GOF	1.068	1.113	1.097
max/min diff peak (e/Å³)	+1.66/−1.20	+1.69/−1.71	+0.61/−0.45

Comparable IR characteristics have been reported for [(Mo/W)X(*t*BuNC)₄(*t*BuNHC≡CNH*t*Bu)]⁺.[3a] For the Nb[I] complexes [NbI(CO)₂(CNR)₂dppe], two almost equally intense ν(C≡N) signals (**3a**, 2131 and 2113 cm⁻¹; **3b**, 2135 and 2121 cm⁻¹; compare free *t*BuNC at 2134 cm⁻¹ and free CNCy at 2139 cm⁻¹) are observed. The greater electron density on the Nb[I] center weakens the C≡NR bond with respect to the free isonitrile by π back-donation. Comparison of the ν(CN) value for **3b** with that for [NbCl(CO)CNCy(dmpe)₂] (ν(CN) 1783 cm⁻¹)[12] shows that, in the latter complex with just one carbonyl, the isonitrile participates heavily in π back-donation. These differences in IR features are also reflected in the solid-state bonding parameters for the {Nb(CNCy)} moieties (*vide infra*). A further point of interest in this context of similar ligand properties of CO and CNR in **3** is the ⁹³Nb NMR signal at −1440 ppm. This is the same region where ⁹³Nb resonances for phosphine-stabilized carbonylniobium(I) halides are found,[10,13] indicative of comparable σ-donor/π-acceptor properties of carbonyl and isonitrile ligands in this complex. Two equally intense ν(CO) bands in **3b** (1799 and 1861 cm⁻¹) support the *all-cis* arrangement of the ligands. Since there is only a single ³¹P resonance (at 54.0 ppm), the two P atoms of the dppe ligand have to be equivalent. The only reasonable structure where this can be achieved is a capped trigonal prism with the pairs of carbonyls, isonitriles, and phosphorus functions each occupying one of the three edges formed at the junctions of the three rectangles. This structure is in fact also realized for **3b** in the solid state.

Structure Descriptions. Crystal data and further details from the X-ray diffraction analysis of **1**, **2**, and

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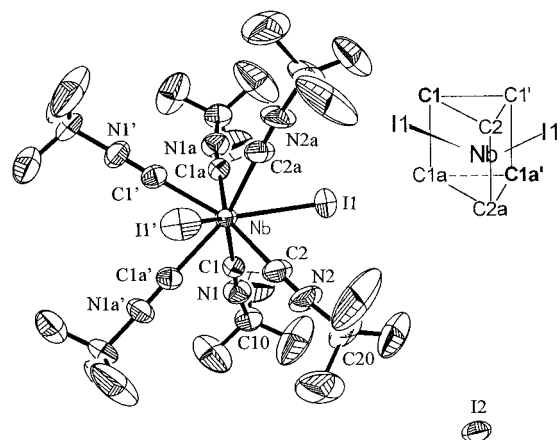
Figure 1. Molecular structure of the cation [NbI₂(CN*t*Bu)₆]⁺ of **1**, showing 50% probability thermal ellipsoids. The inset illustrates the basic geometry. Selected bond distances (Å) and angles (deg): Nb−I1 = 2.995(1), Nb−C1 = 2.210(6), Nb−C2 = 2.219(9), C1−N1 = 1.159(8), C2−N2 = 1.148(12), N1−C10 = 1.464(8), N2−C20 = 1.474-(12); I−Nb−C1 = 72.6(2), I−Nb−C2 = 73.99(7), C1−Nb−C1′ = 112.7(3), C1−Nb−C1a = 76.4(3), C1−Nb−C1a′ = 67.7(3), C1−Nb−C2 = 87.7(3), C2−Nb−C2a = 89.2(5), C2−Nb−C1a = 146.0(2), Nb−C1−N1 = 178.7(6), Nb−C2−N2 = 178.8(8), C1−N1−C10 = 171.4(7), C2−N2−C20 = 174.3-(11).

3b are provided in Table 1; plots of the molecules including the labeling schemes are given in Figures 1−3. Selected bonding parameters are given in the figure captions.

1 crystallizes with one molecule of THF in the orthorhombic space group *Cmcm*. The geometry of the cation [NbI₂(CN*t*Bu)₆]⁺ (Figure 1) is best described by a bicapped trigonal prism of C_{2v} symmetry, with the two iodo ligands capping two of the tetragonal planes. One of the mirror planes (containing Nb, C2, and C2a) bisects the tetragonal plane spanned by the C1 carbon atoms and creates the primed atoms; the other mirror

Figure 2. Molecular structure of the cation $[NbI_2(CNtBu)_4$-$(tBuNHC\equiv CNHtBu)I_2]^+$ of **2**. The inset illustrates how this structure relates to (or develops from) **1**. The bold line in inset **A** connects the two acetylenic carbons. Selected bond distances (Å) and angles (deg): Nb−I1 = 2.935(2), Nb−I2 = 2.908(2), Nb−C1 to Nb−C4 = 2.21−2.27(2), Nb−C5 and Nb−C6 = 2.07(2), C5−C6 = 1.38(2), C1−N1 to C4−N4 = 1.12−1.17(2), C5−N5 and C6−N6 = 1.34(3); I1−Nb−I2 = 89.51(6), C5−Nb−C6 = 38.8(7), I1−Nb−C1 = 75.1(5), I1−Nb−C2 = 75.4(5), I1−Nb−C3 = 88.3(5), I1−Nb−C4 = 77.7-(5), I1−Nb−C5 = 154.2(5), I1−Nb−C6 = 157.0(5), I2−Nb−C1 = 72.8(5), I2−Nb−C2 = 72.6(5), I2−Nb−C3 = 142.6(5), I2−Nb−C4 = 146.2(5), I2−Nb−C5 = 87.3(5), I2−Nb−C6 = 96.1(5), Nb−(C1−4)−(N1−4) = 172−174(2), (C1−4)−(N1−4)−(C10−40) = 69−178(2), Nb−C5−N5 = 160.9(14), Nb−C6−N6 = 160.6(14), C5−N5−C50 = 128(2), C6−N6−C60 = 130(2).
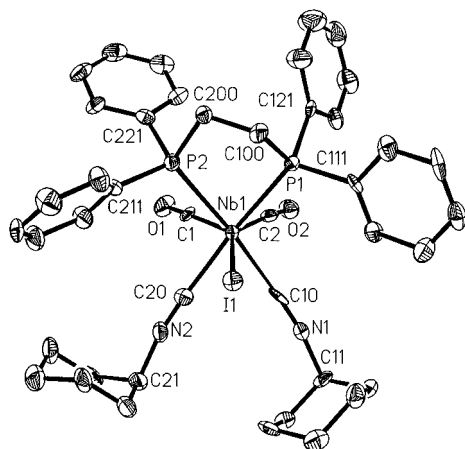

Figure 3. Molecular structure (50% probability thermal ellipsoids) of $[NbI(CO)_2(CNCy)_2dppe]$ (**3b**). Selected bond lengths (Å) and bond angles (deg): Nb−I = 2.9596(12), Nb−P1 = 2.653(2), Nb−P2 = 2.624(2), Nb−C1 = 2.040(10), Nb−C2 = 2.019(11), Nb−C10 = 2.177(11), Nb−C20 = 2.177(10), C1−O1 = 1.158(10), C2−O2 = 1.171(10), C10−N1 = 1.172-(11), C20−N2 = 1.160(10), N1−C11 = 1.456(11), N2−C21 = 1.467(12); I−Nb−C1 = 142.7(2), I−Nb−C2 = 147.4(2), P1−Nb−P2 = 72.78(7), C1−Nb−C2 = 68.7(3), C10−Nb−C20 = 72.4(3), C1−Nb−C20 = 74.8, C2−Nb−C10 = 73.6, Nb−C1−O1 = 177.6(7), Nb−C2−O2 = 176.2(7), Nb−C10−N1 = 176.7(7), Nb−C20−N2 = 177.0(8), C10−N1−C11 = 170.2(8), C20−N2−C21 = 169.9(9).

plane (containing Nb, I1, and I1′) creates the a-labeled atoms. The C_2 axis passes through the edge spanned by C2 and C2a and the center of the opposing plane. Among the C−Nb−C angles, ∠C1−Nb−C1a′ (67.7(3)°) is particularly narrow. This is also reflected in a rather close intramolecular nonbonding distance C1⋯C1a′ of 2.5 Å, and this edge might be considered to be the

coupling site for the generation of the acetylenic bond present in **2**. The angles at the carbons C1 and C2 are almost 180°, while those at N1 and N2 are slightly distorted from linearity. There are no significant interatomic contacts between the cation and its iodide counterion I2.

2 (see Figure 2 for the molecular structure) may be derived from **1** by bringing C1 and C1a′ in **1** together to the extent where formation of an acetylenic bond (C5 and C6 in **2**) occurs. If we take the alkyne as a unidentate ligand which coordinates through the center of the triple bond, the polyhedron spanned by the seven ligands may be viewed (*cf.* inset **B** in Figure 2) in terms of two trigonal pyramids with iodine (I1 and I2 in **2**, I1 and I1′ in **1**) in the apices that are corner-linked through the center of the alkyne and twisted so as to give rise to the angle I1−Nb−I2 of ca. 90°. If we view the alkyne as a bidentate ligand, the actual structure is that of a strongly distorted, bicapped trigonal prism (inset **A** in Figure 2), with ∠I1−Nb−I2 = 89.51(6)° and I1 moved away from and I2 bent toward the alkyne. The angles at the acetylenic carbons C5 and C6 (160°) deviate but slightly from linearity (the corresponding angles amount to *ca.* 150°[10,11] in alkyne−Nb[I] and to ca. 160° in alkyne−Mo[II] complexes[3b]), while the angles at the secondary nitrogens approach 130°. The four isonitriles remain essentially linear. The counterion I3 may be considered to be in weak hydrogen-bonding contact with the hydrogens on the amine nitrogens N5 and N6: the distances d(I3−H5) = 2.87 and d(I3−H6) = 2.94 Å are slightly below the lower limit of van der Waals contacts (3.15 Å).

3b (Figure 3) crystallizes with one molecule of toluene of solvation in the triclinic space group $P\bar{1}$. Nb is in the center of a capped trigonal prism. This structure type is quite typical for heptacoordinated complexes $[MXL_6]$ (M = V, Nb, Ta)[1b,12,14] although it is not the only type, as shown by the structures for X = H and M = V, Nb, Ta, which attain the geometry of a pentagonal bipyramid.[11c,15] As in structurally characterized complexes of the type $[MX(CO)_{6-n}p_n]$ (p_n = a *n*-dentate phosphine ligand; M = V, Nb, Ta),[1b,14a,d,e] the iodo ligand caps the rectangular face opposite the edge occupied by the two carbonyls. This is in accord with MO theoretical considerations and reflects the somewhat better π-acceptor capability of CO as compared to CNR and PR_3.[16] The angle C10−Nb−C20 formed between the two isonitriles and Nb amounts to 72.4(3)°, giving rise to a C10⋯C20 nonbonding contact of 2.6 Å, *i.e.* again on the order of magnitude where the C atoms come sufficiently close to each other to allow for coupling. While in the complexes $[(Nb/Ta)X(CO)CNR(dmpe)_2]$ and $[TaCl(CN$-$Me)_2(dmpe)_2]$[12] the isonitrile is strongly bent at the nitrogen (∠C−N−C(R) = 122−139°), implying significant contributions of a heteroallene structure for the M(CNR) moieties, the isonitrile in **3b** is only slightly bent (∠C−N−C(Cy) = *ca.* 170°). Correspondingly, the

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bond distances Nb−CNR are longer in **3b** (2.177(10) Å) than in [NbCl(CO)(CNCy)(dmpe)$_2$] (2.030(6) Å), and the distance NbC−NR is shorter in **3b** (1.160(10) and 1.172-(11) Å) than in [NbCl(CO)CNCy(dmpe)$_2$] (1.213(7) Å). These structural features are paralleled by the IR spectroscopic characteristics (*vide supra*), indicating structure agreement in the solid state and in solution. Quite unexpectedly, the cyclohexyls (in the chair conformation) occupy *axial* positions which, considering an undisturbed molecule, are the sterically less preferred positions. The axial attachments lead to a more spherical overall arrangement in the molecule, improving packing in the crystal. The expected *equatorial* position for Cy is realized in [NbCl(CO)CNCy(dmpe)$_2$].[12]

Conclusion

Isonitrile complexes are potential precursors in C−C coupling reactions. Starting from [Nb(CO)$_6$]$^-$, we have prepared three of these complexes with niobium in the oxidation states +I and +III in a hepta- or octacoordinated environment based on a trigonal prism as the basic structure. The ligand arrangements in **1** ([NbI$_2$-(CN*t*Bu)$_6$]I) and **3b** ([NbI(CO)$_2$(CNCy)$_2$dppe]) provide sufficiently close C···C nonbonding contacts for reductive coupling. One such coupling product, [NbI$_2$(CN*t*Bu)$_4$-(*t*BuNHC≡CNH*t*Bu)]I (**2**), containing a four-electron-donating diaminoacetylene coordinated to Nb^{III}, has been characterized. Despite the close structural relation between **1** and **2**, **1** should not be considered the precursor complex of **2**, since direct conversion of **1** to **2** with zinc/H$_2$O as an external reductant did not succeed. It is more likely that coupling takes place at an earlier stage, *i.e.* in an intermediate Nb^I complex such as **3a**, where the interatomic C···C distance of 2.6 Å and the availability of Nb^I as a two-electron reductant may enable reductive coupling. Hence, a low-valent metal center by itself acts as the electron source, contrasting with many other comparable C−C couplings, where an external source has been employed to provide the reduction equivalents.

Experimental Section

General Considerations. All manipulations were conducted under nitrogen and, if not noted otherwise, in strictly dried solvents, using common Schlenk techniques. ^{1}H, ^{13}C, and ^{31}P NMR (all in CD$_2$Cl$_2$) were scanned on a Bruker AM 360 spectrometer with the usual parameter settings. The ^{93}Nb NMR spectrum was obtained on a Varian Gemini 200 spectrometer as a *ca.* 0.02 M CD$_2$Cl$_2$ solution in a 5 mm diameter vial with the following measuring parameters: frequency 48.92 MHz, time domain 8K, pulse width 8°, no relaxation delay, line broadening factor 13 Hz. The δ(^{93}Nb) value is referenced against saturated [Et$_4$N][NbCl$_6$] in MeCN. IR spectra were measured as KBr pellets or Nujol mulls on a Perkin-Elmer 1720 FT spectrometer.

X-ray Analyses. For details of the crystal structure results, the structure determination, and the refinement, see Table 1. Data were collected on a Hilger & Watts (**1**·THF) or CAD 4 diffractometer (**2**, **3b**·toluene) equipped with a graphite monochromator in the $\theta/2\theta$ scan mode. All calculations were carried out with the SHELXL program package. Hydrogen atoms were calculated into fixed positions and refined isotropically. Non-hydrogen atoms were commonly refined anisotropically. The following special treatments were applied. **1**·THF: The carbon atoms C21, C22, and C23 of the methyl groups attached to C20 of CN*t*Bu were placed into fixed positions at 1.540-(1) Å with 50% population each. All distances in the THF of solvation were fixed to cope with disorder problems. **2**: Disorder problems were tackled by standardizing bond dis-

tances. The bond distances between the methyl carbons and the quaternary carbons of the *t*Bu groups were fixed at 1.54 Å and the through-space distances between the methyl carbons at 2.51 Å. Some of the U_{ij} values of the methyl carbons (U_{33} of C23, U_{22} of C42, and U_{33} of C43) were fixed at 0.5. Absorption corrections were applied for **2** and **3b**.

Preparation of Complexes. 1. A 394 mg (1.01 mmol) amount of [Et$_4$N][Nb(CO)$_6$]^{11a,17} was dissolved in 20 mL of dried (over LiAlH$_4$ and distilled under N$_2$) THF and this solution treated with 683 μL (6.04 mmol) of CN*t*Bu. After the reaction mixture was cooled to −40 °C by placing the Schlenk tube in an ethanol/liquid N$_2$ cold bath, 510 mg (2.01 mmol) of iodine was added to the stirred solution. Immediate development of CO was observed, and the solution turned from yellow to brown and finally to brown-black. The solution was stirred for 24 h, during which time it slowly regained room temperature. Stirring was continued for an additional 4 h. [Et$_4$N]I was filtered off; the filtrate was treated with 5 mL of pentane and cooled to −20 °C. Red crystals of **1**·THF separated within 2 days. Yield: 87%. IR (KBr): 2978 s, 2933 m, 2871 w, 2153 vs (broad and asymmetric). For the elemental analysis, the crystals were dried under high vacuum. Anal. Calcd (found) for **1**, C$_{30}$H$_{54}$I$_3$N$_6$Nb (M_r = 972.41): C, 37.06 (36.57); H, 5.60 (5.55); N, 8.64 (8.43). Efforts to convert **1** to **2** by a treatment with zinc and addition of some water to the THF solution were not successful.

2. The same procedure as described for the preparation of **1** was carried out with 426 mg (1.09 mmol) of the carbonylniobate, 491 μL (4.4 mmol) of CN*t*Bu, and 369 mg (1.45 mmol) of iodine in commercially available THF (Merck) of *pro analysi* quality, containing up to 0.03% of water (75 mg or 0.42 mmol of H$_2$O in 25 mL of THF). After 28 h of reaction time and removal of [Et$_4$N]I, 5 mL of pentane was added; the reaction mixture was placed into a warm bath (50 °C) equipped with a reflux condenser and refluxed for 30 min. The solution was then slowly cooled to room temperature. Orange-red crystals of **2** separated after 3 days. IR (KBr): 3196, 2978 s, 2933 m, 2871 w, 2192 vs (broad and asymmetric), 1557 cm^{-1}. Anal. Calcd (found) for C$_{30}$H$_{56}$I$_3$N$_6$Nb (M_r = 974.42): C, 36.98 (36.27); H, 5.79 (5.81); N, 8.62 (8.61).

3a,b. The preparation of these bis(isonitrile)niobium(I) complexes from [NbI(CO)$_4$dppe] and CNR (R = *t*Bu, **3a**; R = Cy, **3b**) has been described earlier.[10] Crystals of **3b**·toluene, suitable for an X-ray structure analysis, were obtained by allowing a solution of **3b** in hexane/toluene (1/3) to stand at −15 °C for 2 days. IR (Nujol): 2121 s, 2135 s (ν(CN)); 1861 vs, 1799 vs (ν(CO)) cm^{-1}. ^{1}H NMR (360 MHz): δ 1.29−1.77 (m, 24H, C*H*$_2$ of Cy and dppe), 3.87 (m, 2H, CNC*H*), 7.15−7.51 (m, 20H, Ph) ppm. ^{13}C NMR (90.52 MHz): δ 23.05 (incompletely resolved dd, PC*H*$_2$C*H*$_2$P), 25.11 (s, CNCH-C*H*$_2$C*H*$_2$), 25.47 (s, CNCHCH$_2$CH$_2$*C*H$_2$), 32.59 (s, CNCH*C*H$_2$), 32.97 (s, CN*C*H), 128.13−133.53 (m, Ph) ppm; the resonances for CO and C*N*Cy have not been observed. ^{31}P NMR (145.7 MHz, 210 K): δ 54.0 (s) ppm. ^{93}Nb NMR (48.9 MHz): δ −1440 ppm ($w_{1/2}$ = 7.3 kHz). Anal. Calcd (found) for **3b**·toluene, C$_{49}$H$_{54}$IN$_2$NbO$_2$P$_2$ (M_r = 984.69): C, 59.77 (59.26); H, 5.53 (5.56); N, 2.85 (3.34). Anal. Calcd (found) for **3a**·toluene, C$_{45}$H$_{50}$IN$_2$NbO$_2$P$_2$ (M_r = 932.66): C, 57.95 (56.30); H, 5.40 (5.37); N, 3.00 (3.70); I, 13.61 (14.3); P, 6.64 (6.70); Nb, 9.96 (10.0).

Supporting Information Available: Tables of bond lengths and angles, positional parameters, and anisotropic thermal parameters for the non-hydrogen atoms and figures giving unit cell views for **1**−**3** (16 pages). Ordering information is given on any current masthead page.

(17) Calderazzo, F.; Englert, U.; Pampaloni, G.; Pelizzi, G.; Zamboni, R. *Inorg. Chem.* **1983**, *22*, 1865.