A nucleophilic niobium(v) nitride prepared by isocyanate decarbonylation

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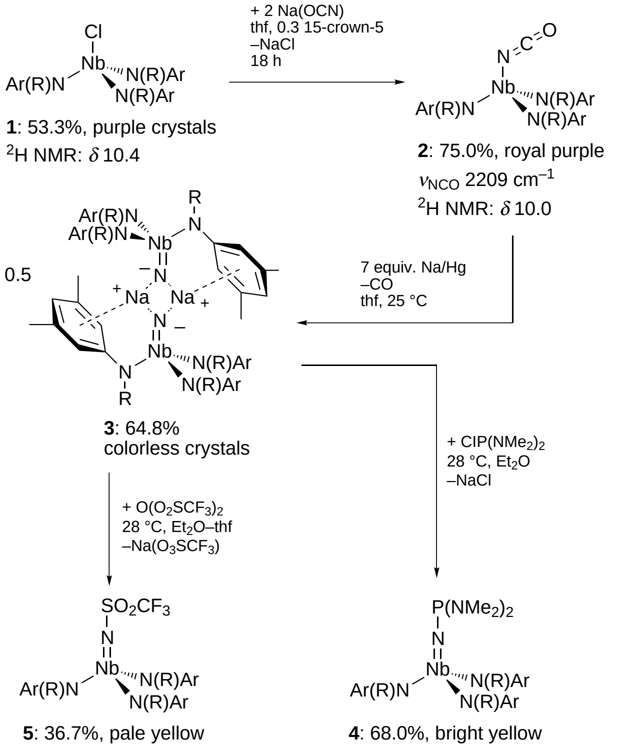
Carbon monoxide is lost upon sodium amalgam reduction of [(OCN)Nb{N(R)Ar}$_3$] [R = C(CD$_3$)$_2$CH$_3$, Ar = C$_6$H$_3$Me$_2$-3,5] to give crystallographically characterized [Na{NNb-[N(R)Ar]$_3$}]$_2$, a nucleophilic niobium(v) nitride which reacts with ClP(NMe$_2$)$_2$ and O(SO$_2$CF$_3$)$_2$ to give P- and S-substituted imido complexes, respectively.

New synthetic routes to d^0 transition-metal complexes containing the terminal nitride functionality have emerged in recent years.[1] Various small molecules or ions, including N$_2$,[2,3] N$_2$O,[4] NO,[5] N$_3^-$,[6] and organic nitriles,[7] have been identified as N-atom sources for metal–nitrogen triple bond formation. This work describes the finding that cyanate ion NCO$^-$ can be added to the foregoing list in the context of niobium chemistry.

A handful of niobium complexes bearing sterically demanding amido ligands such as NPh$_2$,[8,9] N(SiMe$_3$)$_2$,[8,10] and N(c-C$_6$H$_{11}$)$_2$,[11] have been described in recent years. Given the demonstrated effectiveness of the N(R)Ar [R = C(CD$_3$)$_2$CH$_3$, Ar = C$_6$H$_3$Me$_2$-3,5) ligand in molybdenum chemistry,[2,4,12] and the convenience of the ^{2}H NMR spectroscopic handle afforded by it,[13] this ligand was selected for our investigation of niobium isocyanate chemistry.‡ Accordingly, treatment of [NbCl$_4$(thf)$_2$] with 3 equiv. of Li[N(R)Ar](OEt$_2$) in hexane led to formation of purple [ClNb{N(R)Ar}$_3$] **1**, which was obtained in 53% yield as a hydrocarbon- and diethyl ether-soluble crystalline solid (Scheme 1). Toluene solutions of compound **1** exhibit an EPR signal (g_{iso} = 1.966, a_{iso} = 105.1 G) characteristic of a d^1 niobium (^{93}Nb, I = 9/2) center, along with a single ^{2}H NMR signal (δ 10.4, $\Delta\nu_{1/2}$ 116 Hz); the compound exhibits a μ_{eff} of 2.1 μ_{B} ([^{2}H$_6$]benzene).[14] The pseudotetrahedral monomeric nature of **1** has been confirmed in preliminary fashion by an X-ray diffraction study showing that **1** is isostructural with the related compound [SMo{N(R)Ar}$_3$],[15] with which **1** is isoelectronic.



Scheme 1

Displacement of chloride by isocyanate was effected by treating, for 18 h, a 28 °C thf solution of **1** with an excess of sodium cyanate (2 equiv.) in the presence of 15-crown-5 (0.30 equiv). Compound **2** [(OCN)Nb{N(R)Ar}$_3$], was obtained subsequently as dark purple needles in 75% yield by recrystallization from pentane; the compound exhibits a μ_{eff} of 2.2 μ_{B} ([^{2}H$_6$]benzene). A strong band at 2209 cm^{-1} in the IR spectrum of **2** is attributable to ν_{NCO},[16] consistent with the proposal of an N-bound, η^1 mode of ligation for the NCO$^-$ ion. The decarbonylation chemistry of **2** (see below) likewise is suggestive of its isocyanate character.

Decarbonylation occurred upon treatment of **2** with an excess of 0.5% sodium amalgam (7 equiv. Na, unoptimized) in thf for 18 h at 28 °C. Trapping experiments to be described in detail elsewhere confirmed that a substantial fraction of the carbon monoxide lost is evolved as free CO. The anionic niobium(v) nitride [Na{NNb[N(R)Ar]$_3$}]$_2$, **3**, was obtained as a thf-free, benzene-soluble, colorless solid in 65% yield subsequent to trituration with hexane and recrystallization from ether. Compound **3** was found by X-ray crystallography to adopt a dimeric structure in the solid state (Fig. 1),§ the dimer possessing a center of inversion about a central Na$_2$N$_2$ square core. The environment about sodium involves two nitrido nitrogens and η^6-aryl complexation, with Na–C$_{\mathrm{aryl}}$ distances averaging 2.94 Å. Interaction of alkali-metal cations with benzene-like organic π systems is a well documented phenomenon,[17] and in the present case this interaction serves to explain the ready isolation of **3** in thf-free form. NMR spectra of diamagnetic **3** are

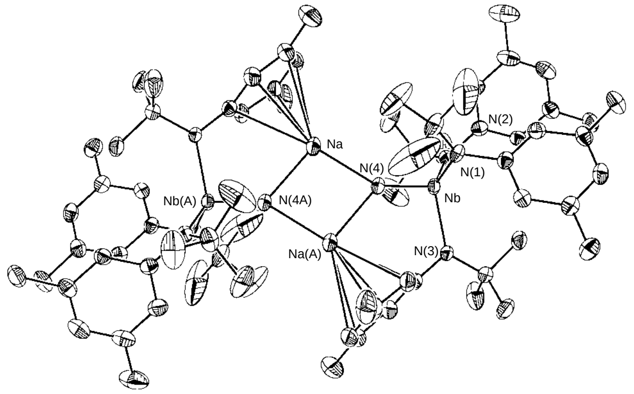


Fig. 1 Structural drawing of **3** with thermal ellipsoids at the 35% probability level. Selected bond lengths (Å) and angles (°): Nb–N(4) 1.718(3), Nb–N(1) 2.041(3), Nb–N(2) 2.074(3), Nb–N(3) 2.089(3), N(4)–Na 2.351(4), N(4)–Na(A) 2.336(4); Nb–N(4)–Na 129.0(2), Nb–N(4)–Na(A) 148.5(2), N(4)–Na–N(4A) 96.62(12), N(4)–Nb–N(1) 104.3(2), N(4)–Nb–N(2) 105.7(2), N(4)–Nb–N(3) 101.3(2), N(1)–Nb–N(2) 115.61(14), N(1)–Nb–N(3) 113.40(13), N(2)–Nb–N(3) 114.42(13).

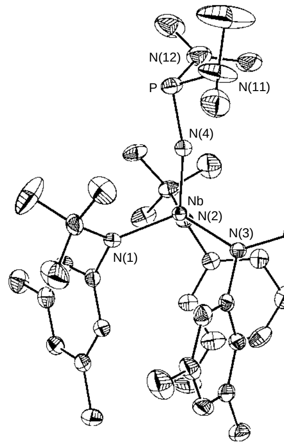


Fig. 2 Structural drawing of **4** with thermal ellipsoids at the 35% probability level. Selected bond lengths (Å) and angles (°): Nb–N(4) 1.796(3), Nb–N(1) 2.010(3), Nb–N(2) 2.018(4), Nb–N(3) 2.021(3), N(4)–P 1.687(4), P–N(11) 1.744(5), P–N(12) 1.658(4); Nb–N(4)–P 166.5(2), N(4)–Nb–N(1) 108.0(2), N(4)–Nb–N(2) 109.5(2), N(4)–Nb–N(3) 108.0(2), N(4)–P–N(11) 99.4(2), N(4)–P–N(12) 106.5(2), N(11)–P–N(12) 99.0(3).

consistent with its solid-state structure if a fluxional process is invoked to explain the observed equivalence of the N(R)Ar ligands on the NMR timescale at 25 °C. The enthalpic driving force for the decarbonylation producing **3** is understandable in terms of formation of a very strong Nb–N multiple bond, free carbon monoxide, and solvated sodium ion. Despite its evident favorability the latter transformation appears to be unique in isocyanate coordination chemistry. The reverse reaction, isocyanate formation by intramolecular coupling of N and CO ligands, has been described in at least one report.[18]

The utility of **3** stems from its nucleophilic character as evinced by its reactions with chlorobis(dimethylamino)phosphine and triflic anhydride, producing the unusual imido derivatives **4** and **5**, respectively. (A related nucleophilic vanadium nitride anion, $[NV(NPh_2)_3]^-$, was reported recently.[9]) Compound **4**, $[(Me_2N)_2PNNb\{N(R)Ar\}_3]$, was obtained in 68% yield as a bright yellow lipophilic crystalline solid. Diamagnetic **4** exhibits a single broad ^{31}P NMR signal at δ 135.0 ($\Delta\nu$ 101 Hz), the breadth of which is attributable to ^{93}Nb coupling. X-Ray crystallography confirmed that **4** is a pseudotetrahedral monomer (Fig. 2) with a relatively linear Nb–N–P linkage (166.5°) and a $Nb–N_{imido}$ distance [1.796(3) Å] that is short by comparison with the $Nb–N_{amido}$ distances [av. 2.016(3) Å].§

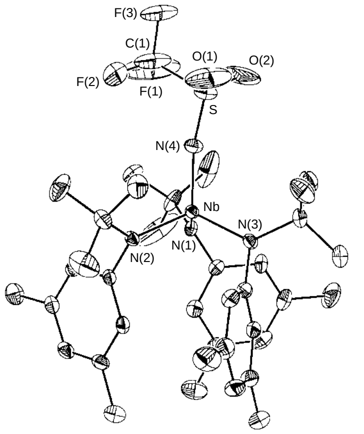


Fig. 3 Structural drawing of **5** with thermal ellipsoids at the 35% probability level. Selected bond lengths (Å) and angles (°): Nb–N(4) 1.853(5), Nb–N(1) 1.978(5), Nb–N(2) 1.988(5), Nb–N(3) 1.983(5), N(4)–S 1.550(5), S–O(1) 1.415(7), S–O(2) 1.398(7), S–C(1) 1.807(12); Nb–N(4)–S 167.0(4), N(4)–Nb–N(1) 109.8(2), N(4)–Nb–N(2) 110.5(2), N(4)–Nb–N(3) 110.2(2), N(4)–S–O(1) 113.5(4), N(4)–S–O(2) 113.2(4), N(4)–S–C(1) 104.2(4), O(1)–S–O(2) 117.7(7), O(1)–S–C(1) 102.3(5), O(2)–S–C(1) 103.7(7).

'Triflimide' **5**, $[(CF_3SO_2)NNb\{N(R)Ar\}_3]$, was also characterized by X-ray diffraction (Fig. 3).§ The compound exhibits a relatively long $Nb–N_{imido}$ distance [1.853(5) Å] reflective of the highly electron-withdrawing nature of the trifluoromethanesulfonyl substituent. Interestingly, compound **5** appears to be the first example of a triflimide transition-metal complex. Although the formation of **5** appears to proceed smoothly according to the ^1H NMR spectrum of the crude reaction mixture, the compound, a pale yellow solid, was obtained in moderate (37%) yield after a diethyl ether wash.

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Footnotes and References

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‡ All manipulations were carried out under an atmosphere of dry nitrogen using solvents purified by standard methods. The new compounds **1**–**5** gave satisfactory elemental analyses (C, H, and N).

§ *Crystallographic data*: **3**: monoclinic, space group $P2_1/c$, a = 18.149(4), b = 13.682(2), c = 16.306(2) Å, β = 113.009(8)°, U = 3727.0(11) Å^3, Z = 4, T = 183 K, μ(Mo-Kα) = 0.362 mm^{-1}, no. of unique reflections = 5146, data/parameter ratio = 14, R_1 = 0.0432, wR_2 = 0.1288, GOF = 1.111, residuals based on $I > 2\sigma(I)$.

4: orthorhombic, space group $P2_12_12_1$, a = 12.336(2), b = 13.182(2), c = 25.894(3) Å, U = 4210.9(10) Å^3, Z = 4, T = 183 K, μ(Mo-Kα) = 0.357 mm^{-1}, no. of unique reflections = 6042, data/parameter ratio = 14, R_1 = 0.0372, wR_2 = 0.0800, GOF = 0.913, residuals based on $I > 2\sigma(I)$.

5: monoclinic, space group $C2/c$, a = 30.0096(7), b = 10.6464(3), c = 24.3461(7) Å, β = 93.8780(10)°, U = 7760.6(4) Å^3, Z = 8, T = 183 K, μ(Mo-Kα) = 0.414 mm^{-1}, no. of unique reflections = 5562, data/parameter ratio = 13, R_1 = 0.0714, wR_2 = 0.1372, GOF = 1.277, residuals based on $I > 2\sigma(I)$. CCDC 182/595.

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