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Probing the Niobium Metallaaziridine Functionality

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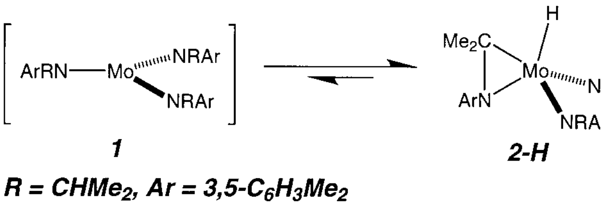
*Summary: Borane abstraction from **4-BH$_4$** was used to access the metallaaziridine-hydride functionality in a niobium system. Unlike its known molybdenum analog, proposed intermediate **4-H** displays reactivity characteristic of electrophilic early transition-metal hydride complexes.*

Reactive metal fragments stabilized by β-hydrogen-containing amide ligands have been shown recently to activate small-molecule substrates, e.g. dinitrogen, in addition to organic compounds incorporating nitriles, ketones, and alkynes.[1−4] Interestingly, although the reactive molybdenum(III) amide Mo(N[^{i}Pr]Ar)$_3$ (**1**) was found to exist as its metallaaziridine−hydride tautomer HMo(η^2-Me$_2$C=NAr)(N[^{i}Pr]Ar)$_2$ (**2-H**),[2] all of the compound's reactions studied thus far are explicable in terms of reaction out of three-coordinate **1**, in accord with the equilibrium of eq 1.



(1)

Insertions into the hydride functionality of **2-H** have not been observed, a circumstance leading to the description of **2-H** as a masked or latent form of three-coordinate molybdenum(III).[2−4] Intrigued by the possibility that the metallaaziridine−hydride ligand combination could be extended to other systems to provide the functional equivalent of a low-coordinate metal fragment, we undertook the synthesis of the niobium analogue of **2-H** as detailed herein.

Reported previously in the context of heterodinuclear dinitrogen cleavage,[5] dichloride **3-Cl$_2$** (Scheme 1) served as a precursor to metallaaziridine borohydride **4-BH$_4$** via treatment first with silver triflate to generate **3-Cl(OTf)**[6] and subsequently with an excess of lithium borohydride. The silver triflate step was necessitated by an observed lack of reaction of **3-Cl$_2$** with lithium borohydride directly. Formation of **4-BH$_4$** likely proceeds via the intermediate **3-Cl(BH$_4$)** (not observed), which is susceptible under the reaction conditions to borane loss and dihydrogen ejection, the latter process furnishing a means for closure of the metallaaziridine ring.[7] Further substitution of chloride then provides **4-BH$_4$**, which was isolated in 70% yield based on the **3-Cl$_2$** employed. X-ray crystallography showed **4-BH$_4$** to feature an η^3-borohydride ligand located cis to the niobium−carbon bond (Figure 1). The structure of **4-BH$_4$** features a pseudo mirror plane passing through the metallaaziridine ring and the boron atom while relating the two *N*-isopropylanilide NC$_2$ planes. Further characterization data for **4-BH$_4$** include a well-resolved ^{11}B NMR quintet (δ −2.24 ppm, $^1J_{BH}$ = 53 Hz, 100 °C), indicative of fluxional behavior for the BH$_4$ ligand.

The complex **4-BH$_4$** is formally an adduct between borane and the target molecule **4-H**, and it is synthetically signficant in view of its ready preparation from dichloride **3-Cl$_2$**. Borane abstraction from **4-BH$_4$** in the presence of a substrate was expected to provide the product of substrate addition to either **4-H** or its tautomer Nb(N[^{i}Pr]Ar)$_3$ (**3**). Quinuclidine was used for borane abstraction on the basis of literature precedent.[8−10] Recognizing that the reaction of known[5] **3-Cl** with sodium benzophenone ketyl (Scheme 1) provides the crystallographically characterized η^2-benzophenone complex **3-OCPh$_2$** (Figure 2), we elected to effect borane abstraction in the presence of benzophenone. Germane to this choice also is the observation that the molybdenum metallaaziridine hydride **2-H** reacts with benzophenone to provide the adduct Mo(η^2-OCPh$_2$)(N[^{i}Pr]-Ar)$_3$ (**1-OCPh$_2$**).[2] It is interesting to note that the O−C bond distance of 1.413(3) Å observed for the niobium benzophenone adduct **3-OCPh$_2$** is elongated slightly relative to that (1.377(6) Å) for its molybdenum counterpart, suggestive of a greater degree of carbonyl activation in the former.

Contrasting behavior is observed for niobium, inasmuch as the adduct **3-OCPh$_2$** is not produced upon treatment of **4-BH$_4$** with quinuclidine in the presence of benzophenone. Instead, the mode of substrate addition ostensibly entailed carbonyl insertion into the niobium−hydrogen bond of putative transient **4-H**, as depicted in Scheme 1.[11] Thus, we obtained diphenylmethoxide **4-OC(H)Ph$_2$** in 47% yield, its metallaaziri-

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[1] Berno, P.; Gambarotta, S. *Organometallics* **1995**, *14*, 2159.

[2] Tsai, Y.-C.; Johnson, M. J. A.; Mindiola, D. J.; Cummins, C. C.; Klooster, W. T.; Koetzle, T. F. *J. Am. Chem. Soc.* **1999**, *121*, 10426.

[3] Mindiola, D. J.; Tsai, Y.-C.; Hara, R.; Chen, Q.; Meyer, K.; Cummins, C. C. *Chem. Commun.* **2001**, 125.

[4] Tsai, Y.-C.; Diaconescu, P. L.; Cummins, C. C. *Organometallics* **2000**, *19*, 5260.

[5] Mindiola, D. J.; Meyer, K.; Cherry, J.-P. F.; Baker, T.; Cummins, C. C. *Organometallics* **2000**, *19*, 1622.

[6] The complex **3-Cl(OTf)** was isolated and characterized fully; see the Supporting Information for more details.

[7] Closure of the metallaaziridine ring is postulated initially to lead to **4-Cl**, a compound similar in composition to that reported by Berno and Gambarotta as being derived from dicyclohexylamide niobium chemistry.[1]

[8] Bannwart, E.; Jacobsen, H.; Furno, F.; Berke, H. *Organometallics* **2000**, *19*, 3605.

[9] Furno, F.; Fox, T.; Schmalle, H. W.; Berke, H. *Organometallics* **2000**, *19*, 3620.

[10] Liang, F. P.; Jacobsen, H.; Schmalle, H. W.; Fox, T.; Berke, H. *Organometallics* **2000**, *19*, 1950.

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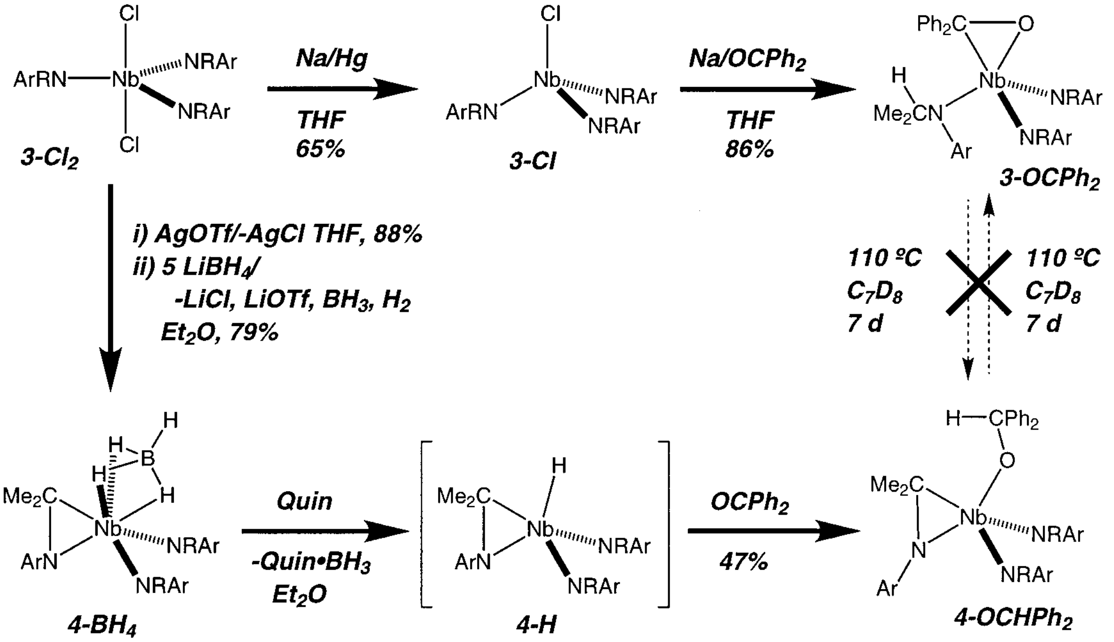
Scheme 1



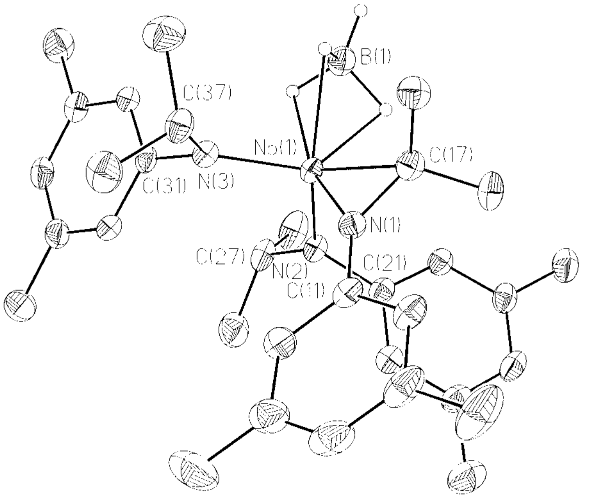


Figure 1. Structural drawing of **4-BH$_4$** with thermal ellipsoids at the 35% probability level. Selected distances (Å) from both of the independent molecules in the asymmetric unit: Nb(1)−N(1), 1.967(3); Nb(1)−N(2), 1.966(3); Nb(1)−N(3), 1.968(3); Nb(1)−H(6), 2.048(33); Nb(1)−H(7), 2.134(29); Nb(1)−H(8), 2.209(30); Nb(1)−C(17), 2.184(3); Nb(2)−N(4), 1.971(3); Nb(2)−N(5), 1.980(3); Nb(2)−N(6), 1.953(3); Nb(2)−H(2), 2.101(30); Nb(2)−H(3), 2.126(31); Nb(2)−H(4), 2.093(29); Nb(2)−C(67), 2.179(3).

dine ring still intact, as verified by X-ray crystallography (Figure 3). The relatively low isolated yield of the substance is attributable to its high lipophilicity; spectroscopic analysis of the crude product mixture indicated that **4-OC(H)Ph$_2$** forms in greater than 95% yield via the indicated regimen. Exhibited by the diphenylmethoxide ligand is a ^{1}H NMR signal at 6.61 ppm assigned to the O−C*H* proton, a downfield shift similar to that seen recently for the product of benzophenone insertion into a Mo−H bond.[10]

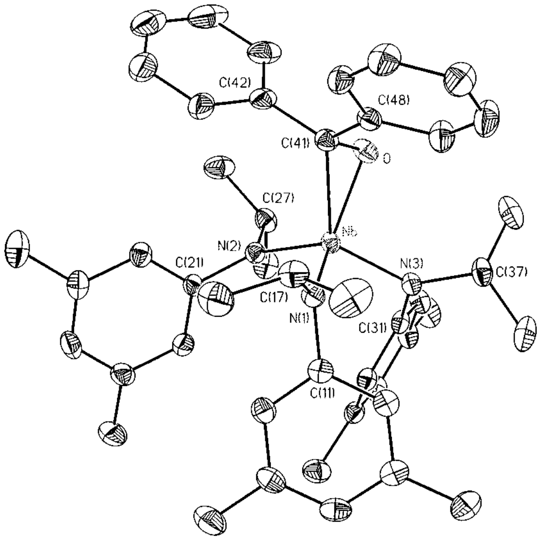


Figure 2. Structural drawing of **3-OCPh$_2$** with thermal ellipsoids at the 35% probability level. Selected distances (Å) and angles (deg): Nb−O, 1.955(2); Nb−N(1), 1.996(2); Nb−N(2), 1.965(2); Nb−N(3), 2.017(2); Nb−C(41), 2.218(3); O−C(41), 1.413(3); Nb−O−C(41), 38.95(9); Nb−O−C(41), 80.62(14); O−C(41)−Nb, 60.43(12).

Unlike its molybdenum analogue **2-H**, the putative metallaaziridine hydride **4-H** would be formally d^0 and would be expected to display reactivity characteristic of a Lewis acid. Perhaps this explains the contrasting modes of benzophenone addition for the two complexes, but it should be noted that borane abstraction from **4-BH$_4$** in the *absence* of benzophenone did *not* lead cleanly to **4-H** or to dinitrogen chemistry thereof (1 atm of N$_2$) but rather to a mixture of products.[12] Stored under similar conditions, the molybdenum analogue **2-H** has been shown to bind dinitrogen and to effect its six-electron reductive cleavage.[2] And indeed, the chemistry leading to **4-BH$_4$** recalls the method of Berno and Gambarotta for isolation of a dinitrogen-bridged dinio-

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(11) The data do not rule out a less plausible alternative scenario whereby quinuclidine (Quin) abstracts BH$_3$ from **4-BH$_4$**, Quin·BH$_3$ reduces benzophenone, and hydride for alkoxide exchange provides **4-OC(H)Ph$_2$**.

(12) Details to be provided in an upcoming paper.

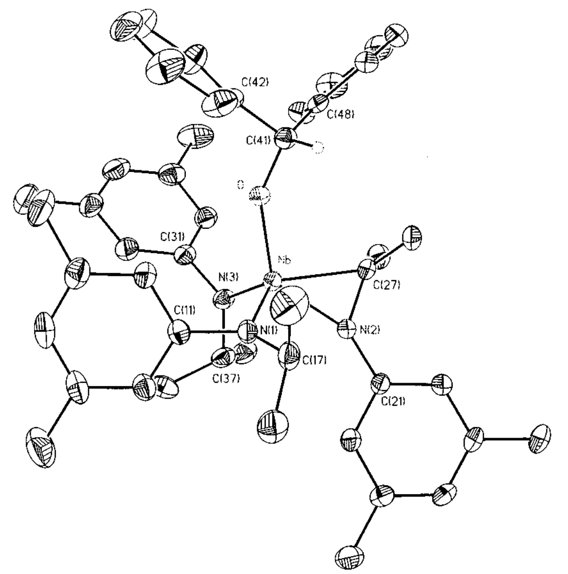

Figure 3. Structural drawing of **4-OC(H)Ph$_2$** with thermal ellipsoids at the 35% probability level. Selected distances (Å) and angles (deg): Nb−O, 1.914(2); Nb−N(2), 1.943(3); Nb−N(3), 1.976(3); Nb−N(1), 1.979(3); Nb−C(27), 2.166(4); O−C(41), 1.417(4); N(2)−C(27), 1.414(4); O−Nb−N(2), 131.77(11); O−Nb−N(3), 109.88(11); N(2)−Nb−N(3), 104.00(12); O−Nb−N(1), 104.11(12); N(2)−Nb−N(1), 92.45(13); N(3)−Nb−N(1), 113.29(12); O−Nb−C(27), 95.49(12); N(2)−Nb−C(27), 39.81(12); N(3)−Nb−C(27), 109.94(14); N(1)−Nb−C(27), 121.90(13); C(41)−O−Nb, 147.8(2).

bium complex supported by a complement of six dicyclohexylamide ligands: addition of NaHBEt$_3$ to a metallaaziridine chloride precursor.[1] Kinetically facile modes of decomposition evidently are available to transient **4-H** in the absence of the aggressive trap benzophenone.

The isomers **4-OC(H)Ph$_2$** and **3-OCPh$_2$** differ merely by the transposition of a β-hydrogen, making it of interest to determine whether they could be interconverted thermally. The complex **4-OC(H)Ph$_2$** was heated in toluene solution at 110 °C for ca. 1 week, conditions that left the sample pure and unchanged. The tautomer **3-OCPh$_2$** likewise was found to be immune to transformation when treated similarly (Scheme 1), leaving unresolved the issue of thermodynamic preference while highlighting the system's robust nature.

An emerging theme for dicyclohexylamide and *N*-isopropylanilide complexes of niobium and molybdenum is the metallaaziridine functionality,[1−4] shown herein to be compatible with halide, borohydride, and alkoxide coligands. When the metallaaziridine is present together with hydride ligation, the situation is particularly intriguing, the present work giving an indication of traditional hydride insertion chemistry. Evidence from the literature suggests tantalizingly that the metallaaziridine−hydride combination *on niobium* is capable of tautomerization and ensuing small-molecule-activation reaction manifolds,[1] as has been demonstrated conclusively for molybdenum.[2−4] Niobium systems tuned properly for a clear illustration of this dichotomy remain attractive as synthetic targets.

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Supporting Information Available: Text and tables giving experimental details and data for the X-ray crystallographic studies, synthetic procedures, and spectroscopic and analytical data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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