structure and function of the enzymic Ni–Fe center.

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Supplementary Material Available: Tables of positional parameters for the five compounds in footnote 10 (8 pages). Ordering information is given on any current masthead page.

Intramolecular Alkane Dehydrogenation and Functionalization at Niobium Metal Centers

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The last 10 years have seen an explosion of interest in the transition-metal chemistry associated with ancillary aryl oxide ligation.[1–3] A particularly popular ligand is the 2,6-diisopropylphenoxide group due to its steric size as well as its apparent reluctance to undergo cyclometalation chemistry.[4,5] We report here on the facile dehydrogenation[6,7] of the substituent alkyl groups of this ligand at niobium metal centers as well as upon the ensuing reactivity of the resulting metallacyclopropane.

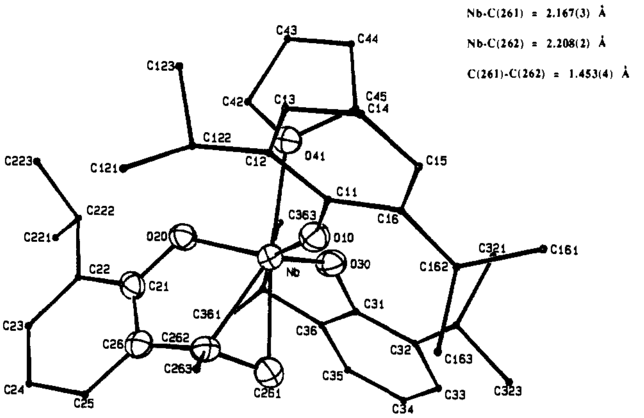

Figure 1. ORTEP view of **2** emphasizing the central coordination sphere. Selected bond distances (Å) and angles (deg): Nb–O(10), 1.875 (2); Nb–O(20), 1.949 (2); Nb–O(30), 1.967 (2); Nb–O(41), 2.293 (2); Nb–C(261), 2.167 (3); Nb–C(262), 2.208 (2); C(261)–C(262), 1.453 (4); Nb–O(10)–C(11), 157.6 (2); Nb–O(10)–C(21), 120.0 (1); Nb–O(30)–C(31), 137.7 (2).

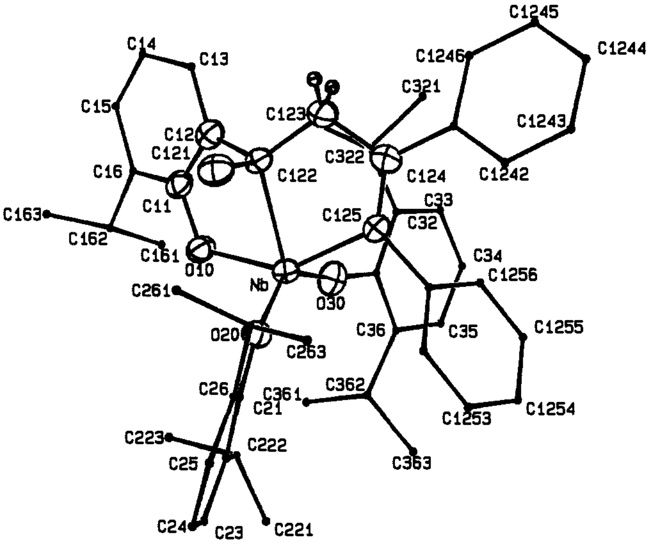

Figure 2. ORTEP view of **3**. Selected bond distances (Å) and angles (deg): Nb–O(10), 1.943 (4); Nb–O(20), 1.873 (4); Nb–O(30), 1.882 (4); Nb–C(122), 2.261 (6); Nb–C(125), 2.125 (6); C(122)–C(123), 1.532 (8); C(123)–C(124), 1.501 (9); C(124)–C(125), 1.349 (8); Nb–O(10)–C(11), 123.0 (4); Nb–C(122)–C(123), 114.0 (4); Nb–C(125)–C(124), 125.1 (5).

The room temperature reduction of thf solutions of the dichloride $Nb(OC_6H_3Pr^i_2\text{-}2,6)_3Cl_2$ (**1**)[8] with sodium amalgam (2 Na/Nb) results in the formation of dark solutions from which the deep-green crystalline complex $Nb(OC_6H_3Pr^i_2\text{-}2,6)_2(OC_6H_3Pr^i\text{-}\eta^2\text{-}CMe{=}CH_2)(thf)$ (**2**) can be obtained in high yield (Scheme I). A reasonable pathway for the formation of **2** from **1** involves intramolecular oxidative addition of an isopropyl CH bond (either primary or tertiary) in an intermediate Nb(III) compound $[Nb(OC_6H_3Pr^i_2\text{-}2,6)_3]$ followed by elimination of H_2.[9] The new vinyl phenoxide group in **2** is clearly indicated in solution spectra. The $CMeCH_2$ protons appear as a singlet and AB pattern in the ratio of 3:1:1 in the ^1H NMR spectrum. In the ^{13}C NMR spectrum the two carbon atoms coordinated to the metal center resonate at δ 95.9 and 90.1 ppm, the latter appearing as a triplet with $^1J(^{13}C\text{–}^1H) = 140.8$ Hz. A single-crystal X-ray diffraction analysis of **2**[8] clearly shows the new ligand strongly chelated to the metal center (Figure 1). In particular the short Nb–C distances of 2.167 (3) and 2.208 (2) Å and C–C distance of 1.453 (4) Å coupled with the significant bending back of the methylene group protons are more consistent with a metallacyclopropane

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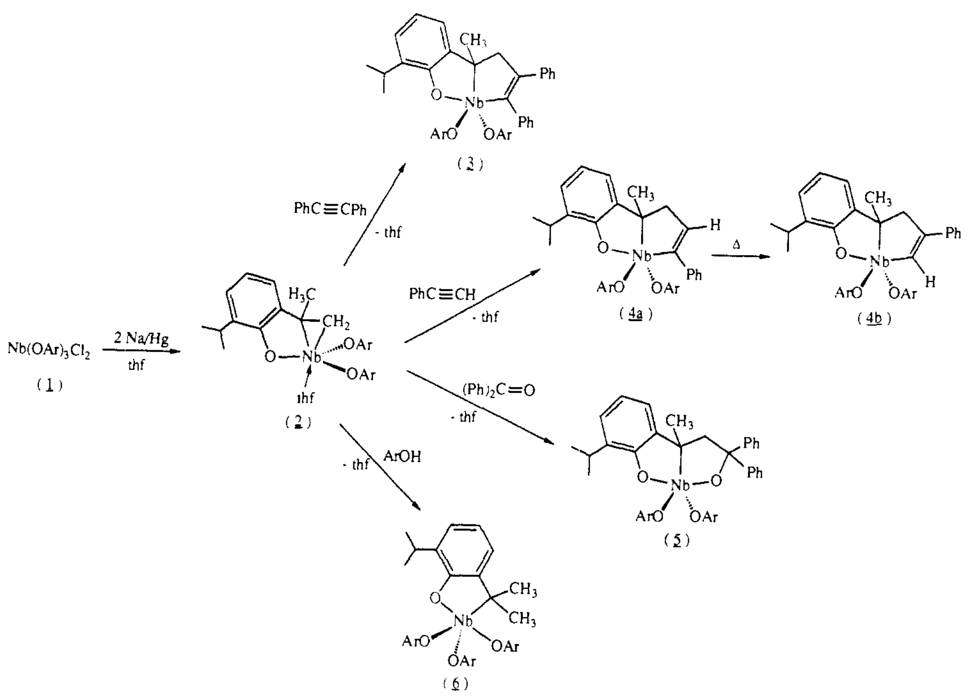
Scheme I[a]



[a] OAr = 2,6-diisopropylphenoxide; thf = tetrahydrofuran.

description of the bonding rather than as a niobium(III) olefin complex.[10]

The metallacyclopropane ring in **2** will undergo coupling (ring expansion) with a number of unsaturated molecules with displacement of the coordinated thf (Scheme I). Reaction with $PhC\equiv CPh$ takes place to yield the metallacyclopentene complex $[Nb(OC_6H_3Pr^i_2\text{-}2,6)_2(OC_6H_3Pr^iCMeCH_2CPh{=}CPh)]$ (**3**) in almost quantitative yields.[8] In **3** the $OC_6H_3Pr^iCMeCH_2C(Ph){=}C(Ph)$ methylene protons appear as a well-resolved AB pattern in the ^1H NMR spectrum. A single-crystal X-ray diffraction analysis of **3** (Figure 2) shows the metallacyclopentene ring to be essentially planar. The coordination to the metal via the aryl oxide oxygen atom results in the formation of two five-membered metallacycle rings which appear to be readily accommodated with little strain being evident (Figure 2). The reaction of **2** with the nonsymmetric alkyne $PhC\equiv CH$ initially leads to the formation of a metallacyclopentene (**4a**) in which the phenyl substituent is adjacent to the metal center. This kinetic product slowly isomerizes at room temperature in solution to the thermodynamically more stable isomer (**4b**) in which the phenyl substituent is present at the 3-position of the ring (Scheme I). Thermolysis of solutions of **4a** at 100 °C for minutes yields **4b** with no evidence in the ^1H NMR spectra for any residual **4a**. Reaction of the metallacyclopropane compound **2** with $Ph_2C{=}O$ leads to the oxametallacyclopentane compound $[Nb(OC_6H_3Pr^i_2\text{-}2,6)_2(OC_6H_3Pr^iCMeCH_2CPh_2O)]$ (**5**) (Scheme I).

Compound **2** will also undergo reactions with protic reagents. Treatment of green **2** with 1 equiv of $HOC_6H_3Pr^i_2\text{-}2,6$ results in the formation over minutes of the new metallacycle compound $[Nb(OC_6H_3Pr^i_2\text{-}2,6)_4(OC_6H_3Pr^iCMe_2)]$ (**6**) along with 1 equiv of thf (Scheme I). The formulation of **6** as containing a five-membered metallacycle ring is based upon NMR spectroscopic data as well as preliminary X-ray data.[12] Further studies into the mechanism and possible generality of the dehydrogenation reaction are currently underway.

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Supplementary Material Available: Details of the analytical and spectroscopic data as well as of the crystallographic studies, tables of positional parameters, general temperature factors, and bond distances and angles for **2** and **3** (34 pages); tables of observed and calculated structure factors for **2** and **3** (33 pages). Ordering information is given on any current masthead page.

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Preparation and Structure of $[(W(CO)_3)_6(Te_2)_4]^{2-}$: A 14-Membered Cluster with a Novel Shape

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Historically, the chemistry of transition-metal selenides and tellurides has not been well developed, but recently it has come under increased investigation. This is because their chemistry is substantially different from that of the sulfides,[1] and also because they are finding use as convenient precursors to solid materials.[1b,2] We have been investigating the reactions of soluble polyselenide and polytelluride anions with various classes of metal complexes.[3] One class of compounds that has an exceptionally rich chemistry

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