that unwanted redox pathways are less likely for nucleophilic additions to **3**. Unlike **8**, the complexes **3** offer a pathway for functionalization of the coordinated cyclic π-hydrocarbon. Thus, there is precedent[21] for thermal migration of the σ-hydrocarbon in **5** to the arene to yield endo functionalized cyclohexadienyl complexes (redox-promoted migration probably will prove to be more convenient[22-24]). Through the intermediacy of **3**, such cyclohexadienyl complexes may be available with a wide range of endo substituents, and these may be converted to trans difunctionalized cyclohexadienes by using published procedures.[5]

Finally, we note that the chemistry described above can lead to C-H activation, at least with reactive C-H bonds. Thus, treatment of **1** with Me_3NO in furan was found to effect electrophilic substitution on the furan to give **5** as a σ-vinyl complex (ν_{CO} = 1950, 1897 cm^{-1} in CH_2Cl_2). Similarly, IR evidence strongly suggests C-H bond cleavage to give neutral σ-bonded complexes when oxiranes are added to a CH_2Cl_2 solution containing a mixture of **1** and Me_3NO.

Acknowledgment. We are grateful to Professor G. B. Carpenter for very useful discussions. This work was supported by a grant from the National Science Foundation (No. CHE-8521189).

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths, and bond angles for **7** (7 pages); tables of observed and calculated structure factors for **7** (22 pages). Ordering information is given on any current masthead page.

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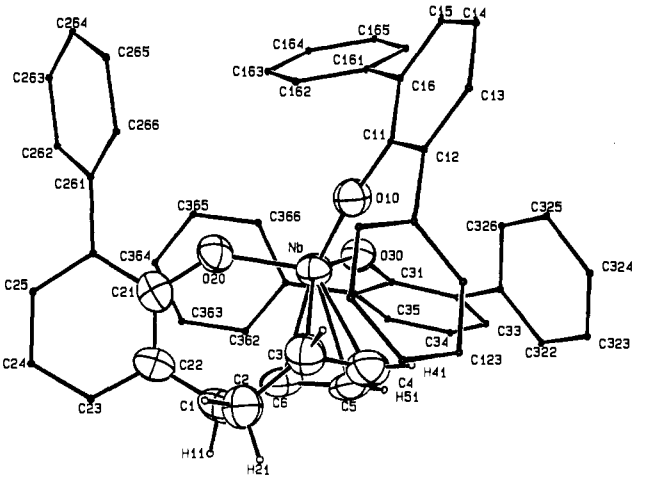
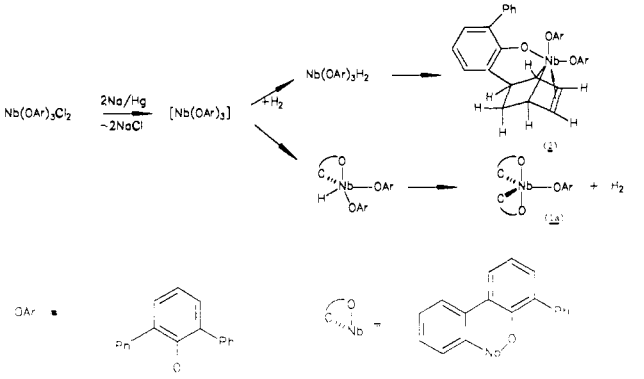


Figure 1. ORTEP view of $Nb(OC_6H_3Ph\text{-}\eta^4\text{-}C_6H_7)(OAr\text{-}2,6Ph_2)_2$ (**2**) emphasizing the central coordination sphere. Selected bond distances (Å) and angles (deg): Nb-O(10) = 1.928 (9); -O(20) = 1.923 (9); -O(30) = 1.932 (9); -C(3) = 2.27 (1); -C(4) = 2.27 (2); -C(5) = 2.37 (1); -C(6) = 2.40 (1); C(1)-C(2) = 1.52 (2); C(2)-C(3) = 1.51 (2); C(3)-C(4) = 1.41 (2); C(4)-C(5) = 1.40 (2); C(5)-C(6) = 1.38 (2); C(6)-C(1) = 1.52 (2); O(10)-Nb-O(20) = 107.8 (4); -O(30) = 107.3 (4); O(20)-Nb-O(30) = 108.9 (4); Nb-O(10)-C(11) = 165.8 (9); Nb-O(20)-C(21) = 138.8 (9); Nb-O(30)-C(31) = 147.8 (8).

Scheme I



Intramolecular Arene Hydrogenation by Niobium Aryloxide Compounds: Stereochemistry of Cyclohexadiene Formation

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The high-valent early d-block, lanthanide and actinide metal-hydride bond has been shown over the last few years to be an extremely important functional group, implicated in a wide range of stoichiometric and catalytic reactivity.[2-9] In this communication we wish to report on the observation of a very facile hydrogenation of an arene ring by a high-valent niobium aryloxy, hydride intermediate.[10-13]

The reduction of toluene solutions of the mixed chloro, aryloxide compounds $M(OAr\text{-}2,6Ph_2)_3Cl_2$ (M = Nb, Ta; OAr-2,6Ph_2 = 2,6-diphenylphenoxide)[14] with sodium amalgam (2 Na per M) takes place over a period of hours to produce yellow-brown suspensions. Workup allows the isolation of the bright yellow, biscyclometalated compounds $M(OC_6H_3Ph\text{-}C_6H_4)_2(OAr\text{-}2,6Ph_2)$ (M = Nb, **1a**; Ta, **1b**) in high yields (Scheme I). A previous single-crystal X-ray diffraction analysis of **1b** has been reported.[15] In the case of M = Nb, the reduction solution was found to also contain a second, deep-red minor component (**2**). The ^1H NMR

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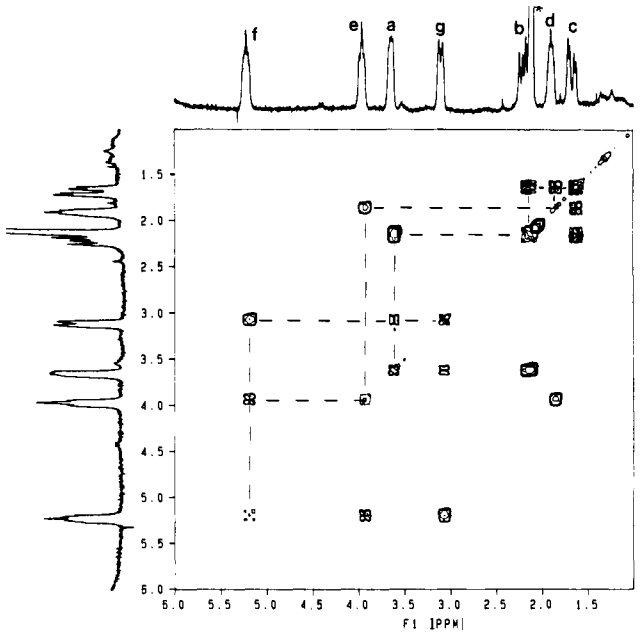
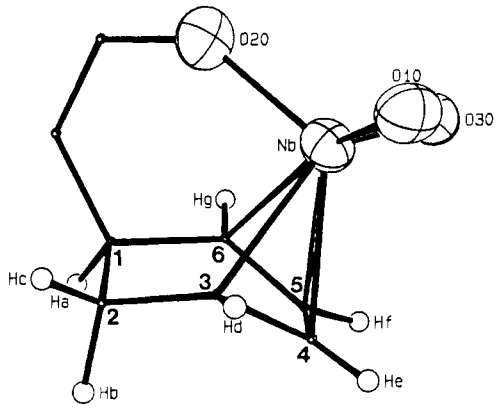


Figure 2. COSY 2D ^{1}H NMR spectrum of $Nb(OC_6H_3Ph\text{-}\eta^4\text{-}C_6H_7)(OAr\text{-}2,6Ph_2)_2$ (**2**) with proton assignments (see Table I).

spectrum of **2** showed it to contain seven separate resonances in the δ 1–6 ppm region of the spectrum. This combined with mass spectrometric data led us to formulate **2** as $Nb(OC_6H_3Ph\text{-}C_6H_7)(OAr\text{-}2,6Ph_2)_2$ containing a hydrogenated phenyl substituent.[16] Carrying out the reduction of $Nb(OAr\text{-}2,6Ph_2)_3Cl_2$ under 1 atm of H_2 was found to lead to deep-red solutions containing almost quantitative amounts of **2**. A single-crystal X-ray diffraction analysis of **2** confirmed that arene hydrogenation had taken place (Figure 1).[17] The niobium metal atom in **2** can be seen to be bound to three oxygen atoms arranged in a mutually pyramidal arrangement. The metal is also bound to four of the carbon atoms of the hydrogenated phenyl ring. The arene ring has undergone 1,2-hydrogenation leading to the ipso- and one ortho-carbon becoming hydrogenated. These two carbon atoms are not bound to the metal. The structure of the metal and central carbon framework in **2** can best be described as a 7-niobanorbornene in which the niobium is also strongly interacting with the olefinic bond. In this respect the d^2-metal has reduced the cyclohexadiene fragment in a fashion similar to that seen for early metal butadiene derivatives (Scheme I).[18]

The ^{1}H NMR spectrum of **2** in either C_6D_6 or $CDCl_3$ shows the presence of seven well-resolved, nonequivalent, equal intensity proton signals in the δ 1–6 ppm range (Figure 2). All other resonances are confined to the aromatic region. The reduction of $Nb(OAr\text{-}2,6Ph_2)_3Cl_2$ under 1 atm of D_2 causes two of these signals to diminish as well as the parent molecular ion in the mass spectrum of **2** to increase by two mass units.[16] A combination of 1D and 2D ^{1}H NMR experiments on **2** and the deuteriated compound allows the unequivocal assignment of the seven signals as well as all of the major (>1 Hz) coupling constants (Figure 2) (Table I). The ^{13}C NMR spectrum of **2** shows five carbon resonances upfield of the aromatic region. The sixth carbon resonance at $\sim\delta$ 120 ppm can be readily identified by obtaining

Table I. NMR Data (C_6D_6, 30 °C) for **2**

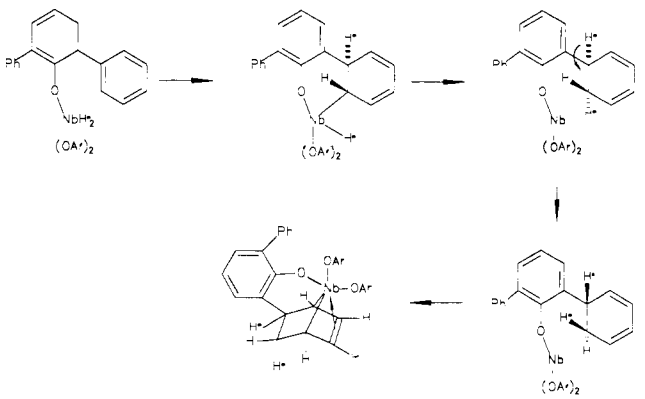


	δ (ppm)							
Ha[a]	3.61	He	3.94	C1	45.8	C4	103.7
Hb[a]	2.10	Hf	5.19	C2	33.2	C5	120.1
Hc	1.62	Hg	3.07	C3	82.5	C6	104.5
Hd	1.86						

	^{1}H coupling constants (Hz)				
Ha–Hg	2.9	Hc–Hd	4.1	He–Hf	5.0
Ha–Hb	7.0	Hd–He	4.5	He–Hg	1.0
Hb–Hc	12.9	Hd–Hf	2.5	Hf–Hg	7.7

[a] Ha, Hb disappear on deuteriation.

Scheme II



a 2D ^{13}C/^{1}H correlation spectrum. Combining the ^{1}H assignments with these results allows the chemical shifts of the six different ring carbon atoms in **2** to also be assigned (Table I). An important conclusion from the NMR experiments is that the two hydrogen atoms introduced are mutually cis to one another (Table I). However, their final position is opposite the side to which the metal atom is actually bound (Figure 2). We believe these observations can be explained as follows (Scheme II). Initial reduction produces an Nb(III) intermediate "$Nb(OAr\text{-}2,6Ph_2)_3$". This compound has the potential to undergo intramolecular CH bond activation to produce **1a**. However, in the presence of H_2, either added or generated in the production of **1a**, competing formation of a dihydride takes place.[19] Stepwise hydrogen transfer to a substituent phenyl group can then occur to produce a cyclohexadiene ring. However, due to the geometry of the aryloxide backbone it is difficult for the niobium atom to bind to the same face of the cyclohexadiene ring to which the hydrogen atoms were transferred. Rotation of the ring to present the opposite face to the metal overcomes this problem and allows chelation to take place with no strain being evident. The thermal stability of **2** (no decomposition at 80 °C) may also be attributable to this proposed hydrogenation/flip mechanism as the final geometry of **2** poses serious problems for a facile dehydrogenation of the ring by the niobium metal.[20] Further mechanistic studies are in progress.

(16) Anal. Calcd for $NbC_{54}H_{41}O_3$: C, 78.07; H, 4.97. Found: C, 78.38; H, 5.02. The mass spectrum of **2** showed a strong parent molecular ion at m/e = 830, while that of **2** obtained using D_2 was at m/e = 832.

(17) X-ray crystallographic data for $Nb(OC_6H_3Ph\text{-}\eta^4\text{-}C_6H_7)(OAr\text{-}2,6Ph_2)_2$ (**2**) at 21 °C: a = 9.339 (1) Å, b = 13.107 (1) Å, c = 20.681 (2) Å, α = 93.807 (8)°, β = 94.109 (9)°, γ = 105.992 (9)°, Z = 2, d_{calcd} = 1.302 g cm^{-3} in space group $P\bar{1}$. Of the 6274 unique data collected with Mo Kα radiation, 4° ≤ 2θ ≤ 45°, the 3612 with $I > 3\sigma(I)$ were used in the least-squares refinement to yield R = 0.055, R_w = 0.065. The seven hydrogen atoms on the unique ring were located and refined.

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Supplementary Material Available: A listing of fractional coordinates, anisotropic thermal parameters, and complete bond distances and angles for **2** (18 pages); listing of observed and calculated structure factors for **2** (31 pages). Ordering information is given on any current masthead page.

(20) Chelation of 2,6-diphenylphenoxide via an η^6-aryl interaction as well as η^2- and η^6-binding of aromatic rings to Ta(III) metal centers has been documented, see: (a) Kerschner, J. L.; Fanwick, P. E.; Rothwell, I, P. *J. Am. Chem. Soc.* **1987**, *109*, 5840. (b) Neithamer, D. R.; Parkanyi, L.; Mitchell, J. F.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 4421. (c) Brock, M. A.; Copenhaver, A. S.; Wigley, D. E. *J. Am. Chem. Soc.* **1987**, *109*, 6525.

Helichrome: Synthesis and Enzymatic Activity of a Designed Hemeprotein†

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A number of model compounds have been synthesized[1] in an effort to mimic the active sites of enzymes by combining functional groups with appropriate host molecules such as cyclodextrins,[2a] crown ethers,[2b] and cyclophanes.[2c] This approach has been quite successful in elucidating general mechanisms[3] of enzyme catalysis and has provided useful information on the design of molecules which possess specified catalytic functions.

Synthetic polypeptides with defined tertiary structures are more attractive candidates for the assembly of model enzymes. Recent advances in recombinant DNA technology coupled with the rapid accumulation of X-ray structural data on native proteins have contributed to defining the anticipated folding in such polypeptides.[3] Moreover, several recent successful examples[4] of de novo designed small proteins also encourage the synthesis of polypeptide based model enzymes. Neither substrate binding nor catalytic activity have, however, been reported for such model proteins. We wish to report here the synthesis,[5] characterization, and catalytic activity of an artificial hemeprotein **1** (Figure 1).

The overall topology of the molecule **1** was carefully designed so that peptide **2** has a high potential to form amphiphilic α-helix[6] (Figure 2) and to create a hydrophobic pocket for substrate binding

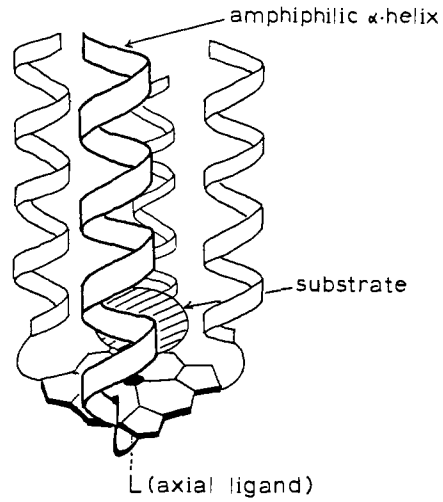

Figure 1. Proposed structure of helichrome **1** after folding of the peptide chains.

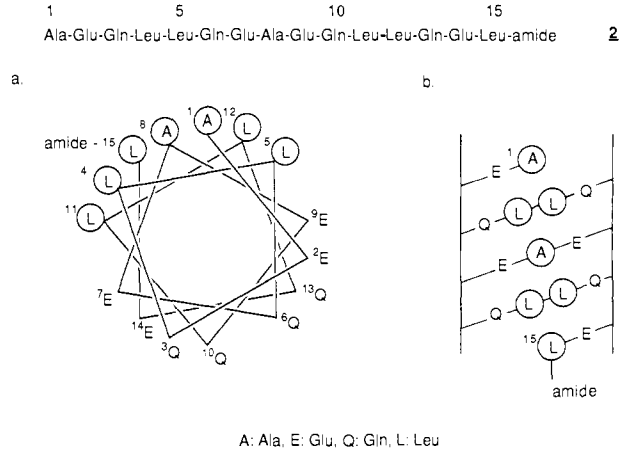

Figure 2. Amino acid sequence of peptide: (a) helix wheel and (b) helix diagram, in which the circle represents hydrophobic amino acids.

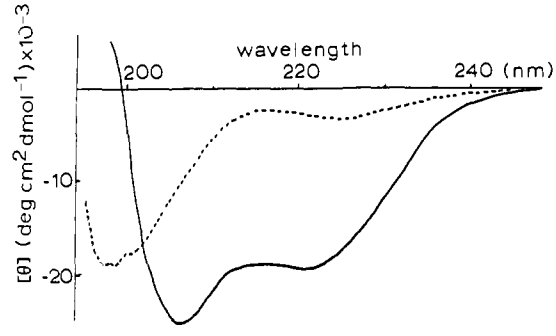

Figure 3. Circular dichroism spectra of helichrome (—, 7.95×10^{-5} M) and peptide alone (– –, 4.94×10^{-4} M) in 20 mM phosphate, 0.16 M KCl pH 7.5.

above the porphyrin ring after the expected folding of the peptide chains. The fully protected peptide segment **3** was synthesized[7a] via a fragment condensation of two small peptide segments (Boc-(1-7)-CO_2H and H_2N-(8-15)-$CONH_2$) which were prepared by utilizing oxime resin.[7b] After deprotection of the Boc group

† This paper is dedicated to the memory of Professor E. T. Kaiser.
‡ Deceased on July 18, 1988.

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