Pergamon

Polyhedron Vol. 14, No. 22, pp. 3293–3313, 1995

0277–5387/95 \$9.50+0.00

0277-5387(95)00063-1

INTRAMOLECULAR HYDROGENATION OF ARYLOXIDE LIGANDS AT NIOBIUM METAL CENTERS: STEREOCHEMICAL CONSEQUENCES OF REACTION REGIOCHEMISTRY

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Abstract—The sodium amalgam reduction (2Na per Nb) of hydrocarbon solutions of the niobium compounds [$Nb(OC_6H_3Ph_2\text{-}2,6)_3Cl_2$], **2a** ($OC_6H_3Ph_2$-2,6 = 2,6-diphenylphenoxide) and [$Nb(OC_6H_2Ph_3\text{-}2,4,6)_3Cl_2$], **2b** ($OC_6H_2Ph_3$-2,4,6 = 2,4,6-triphenylphenoxide) under 1 atm of H_2 leads to the deep-red, η^4-cyclohexadiene complexes [$Nb(OC_6H_3Ph\text{-}\eta^4\text{-}C_6H_7)(OC_6H_3Ph_2\text{-}2,6)_2$], **3a** and [$Nb(OC_6H_2Ph_2\text{-}\eta^4\text{-}C_6H_7)(OC_6H_2Ph_3\text{-}2,4,6)_2$], **3b**, respectively. The spectroscopic properties of **3a** and **3b** are consistent with one of the aryloxide ligands having undergone 1,2-hydrogenation of an *ortho*-phenyl substituent, leading to a cyclohexadiene group which is strongly coordinated to the metal center. This is confirmed by a single crystal X-ray diffraction analysis of **3a**, showing the coordination sphere about niobium to consist of two, normal 2,6-diphenylphenoxide ligands and one chelating, partially hydrogenated aryloxide group. The η^4-bonding of the chelated cyclohexadiene group is slightly distorted with Nb—C distances of 2.27(1), 2.27(2), 2.37(1) and 2.40(1) Å. Hydrocarbon solutions of **3a** and **3b** will react further with hydrogen (200–1200 psi) to produce upon hydrolysis 2-cyclohexyl-4-phenylphenol and 2,6-dicyclohexylphenol (for **3a**) and 2-cyclohexyl-4,6-diphenylphenol and 2,6-dicyclohexyl-4-phenylphenol (for **3b**). The intramolecular hydrogenation of aryl-phenoxide groups can also be achieved by treating mixtures of the chloride compounds [$Nb(OC_6H_3Ph_2\text{-}2,6)_nCl_{5-n}$] or [$Nb(OC_6HPh_4\text{-}2,3,5,6)_nCl_{5-n}$] ($n = 2,3$) with $(5-n)$ equivalents of Bu^nLi under hydrogen. Spectroscopic (^1H, ^{13}C NMR) analysis of the phenols obtained in all cases indicated that exclusive hydrogenation of *ortho*-phenyl groups occurs with no evidence of attack on either the *meta*- or *para*-phenyl substituents or upon the central phenoxy ring. The use of D_2 as reagent gas leads to dicyclohexylphenols containing up to 11 deuterium atoms per cyclohexyl ring due to the presence of H/D exchange processes. Analysis of the stereochemical positions of the remaining protons in the cyclohexyl rings indicates that the hydrogenation of the phenyl rings occurs via two regiochemically distinct reaction pathways. Crystal data at 183 K for $NbCl_3O_2C_{72}H_{54}$, **1c**: [$Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl_3$]$\cdot 2C_6H_6$, $a = 12.561(2)$, $b = 13.810(3)$, $c = 17.836(3)$ Å, $\alpha = 87.37(1)$, $\beta = 72.63(1)$, $\gamma = 76.85(1)^\circ$, $Z = 2$ in space group $P\bar{1}$; at 294 K for $NbO_3C_{36}H_{50}$, **3a**: [$Nb(OC_6H_3Ph\text{-}\eta^4\text{-}C_6H_7)(OC_6H_3Ph_2)_2$]$\cdot C_7H_7$, $a = 9.339(1)$, $b = 13.107(1)$, $c = 20.681(2)$ Å, $\alpha = 93.807(8)$, $\beta = 94.109(9)$, $\gamma = 105.992(9)^\circ$, $Z = 2$ in space group $P\bar{1}$. The trichloride compound **1c** adopts a square pyramidal geometry about the mononuclear niobium metal center with one axial and one basal aryloxide ligand.

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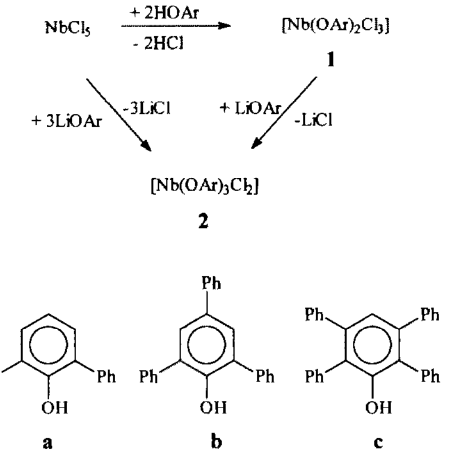


Scheme 1.

The ability to carry out the homogeneous hydrogenation of arene rings has been demonstrated for only a few transition metal systems.[1] Furthermore, the number of arene hydrogenation catalysts is dwarfed by the multitude of transition metal compounds able to carry out the corresponding homogeneous hydrogenation of olefins.[2] Despite the relative paucity of homogeneous arene hydrogenation catalysts some valuable mechanistic studies have been carried out.[3] During our studies of the organometallic chemistry of early transition metal aryloxide compounds we have discovered that mixed hydrido, aryloxide derivatives of tantalum and in particular niobium are able to carry out the hydrogenation of a variety of arene substrates.[4] Besides demonstrating both regioselectivity and stereoselectivity in the intermolecular hydrogenation of arene substrates, these systems will also intramolecularly saturate arene rings attached to ligands within the coordination sphere.[5] We report here on the stoichiometric hydrogenation of *o*-arylphenoxide ligands attached to niobium. The isolation and thorough characterization of cyclohexadiene intermediates as well as the stereochemistry of the reaction products produced by the use of deuterium reagents gives insight into the pathway of the intramolecular hydrogenation reactions.

RESULTS AND DISCUSSION

Synthesis and characterization of compounds

The ligand 2,6-diphenylphenol ($HOC_6H_3Ph_2$-2,6) is commercially available. Using slight adaptations of literature procedures we have been able to synthesize 2,4,6-triphenylphenol ($HOC_6H_2Ph_3$-2,4,6)[6] and 2,3,5,6-tetraphenylphenol (HOC_6HPh_4-2,3,5,6)[7] in reasonable quantities. These three phenols react with $NbCl_5$ in hydrocarbon solvents at room temperature to generate the trichloride compounds $[Nb(OC_6H_3Ph_2\text{-}2,6)_2Cl_3]$, **1a**, $[Nb(OC_6H_2Ph_3\text{-}2,4,6]_2Cl_3$, **1b**, and $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl_3]$, **1c**, respectively, along with liberated HCl (Scheme 1).[8] Further substitution by the parent phenol is slow. However, treatment of **1** with one equivalent of the corresponding lithium aryloxide (generated *in situ* from the phenol and one equivalent of Bu^nLi/hexane solution) or $NbCl_5$ with three equivalents of the lithium salt yields the niobium dichloride derivatives **2** (Scheme 1). The solid-state structure of **1c** (Fig. 1, Table 1) shows the presence of a mononuclear complex with no dimerization via either aryloxide or chloride bridges. The NbO_2Cl_3 core consists of a square pyramidal geometry with one axial and one equatorial aryloxide ligand. The geometry of **1c** is similar to that found in $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2Cl_3]$.[9] The ^1H and ^{13}C NMR spectra of **1** and **2** are uninformative due to the multitude of overlapping aromatic signals.

The sodium amalgam reduction of toluene solutions of the dichloride compounds **2a** and **2b** under an atmosphere of H_2 gas leads to dark-brown solutions from which deep-red crystals of the η^4-cyclohexadiene complexes $[Nb(OC_6H_3Ph\text{-}\eta^4\text{-}C_6H_7)(OC_6H_3Ph_2\text{-}2,6)_2]$, **3a**, and $[Nb(OC_6H_2Ph_2\text{-}\eta^4\text{-}C_6H_7)(OC_6H_2Ph_3\text{-}2,4,6)_2]$, **3b**, can be obtained (Scheme 2). In the absence of an atmosphere of H_2 the reduction of **2a** produces the bis(cyclometallated) compound $[Nb(OC_6H_3Ph\text{-}C_6H_4)_2(OC_6H_3Ph_2\text{-}2,6)]$, **4** (Scheme 3), as the major product along with small amounts of **3a**. Related work has shown that reduction of solutions of the corresponding tan-

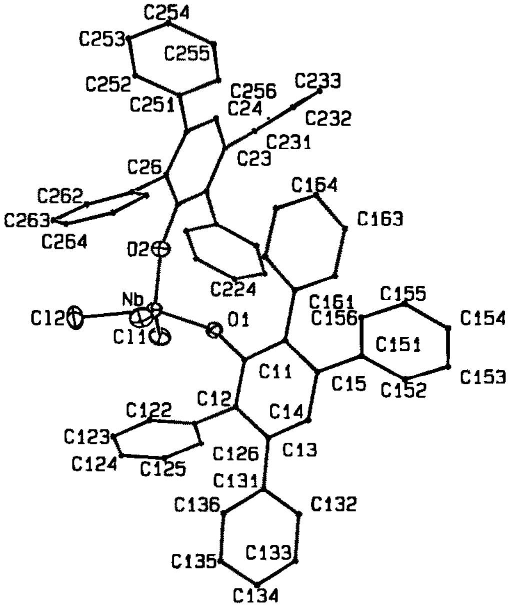
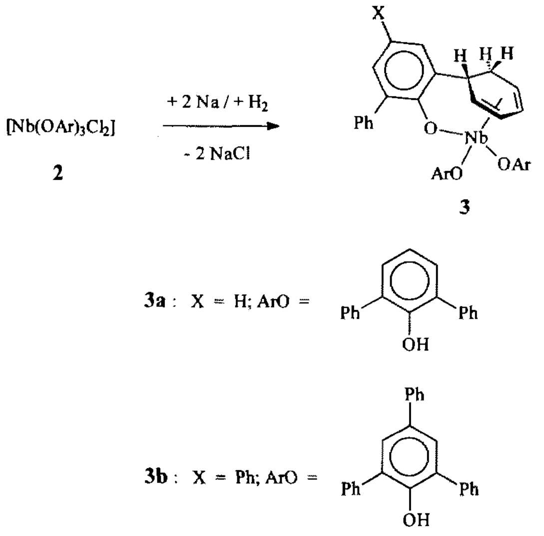


Fig. 1. Molecular structure of **1c**.

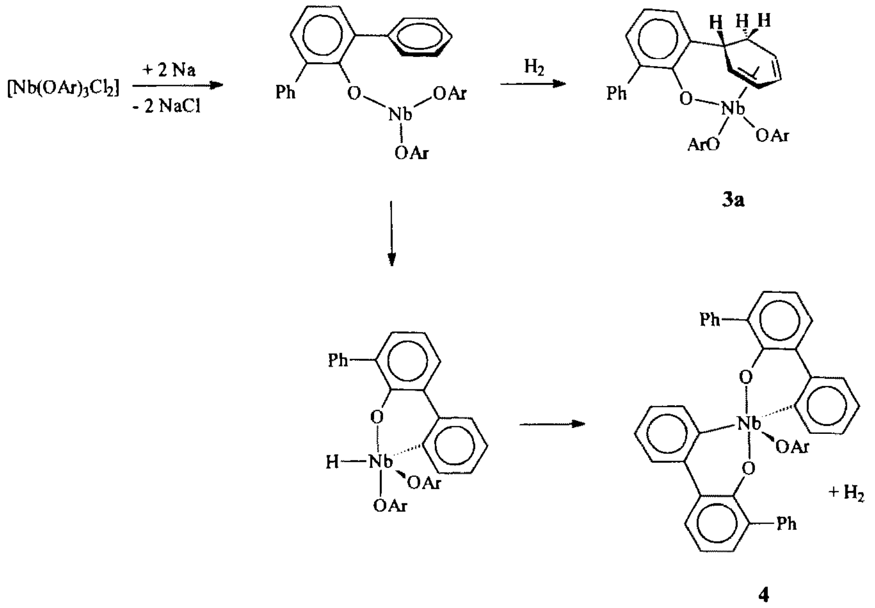
Table 1. Selected bond lengths (Å) and angles (°) for **1c**

Nb—Cl(1)	2.322(1)	Nb—Cl(2)	2.344(1)
Nb—Cl(3)	2.352(1)	Nb—O(1)	1.870(3)
Nb—O(2)	1.820(3)		
Cl(1)—Nb—Cl(2)	87.27(4)	Cl(1)—Nb—Cl(3)	153.94(4)
Cl(1)—Nb—O(1)	91.00(9)	Cl(1)—Nb—O(2)	104.05(9)
Cl(2)—Nb—Cl(3)	85.25(4)	Cl(2)—Nb—O(1)	154.68(9)
Cl(2)—Nb—O(2)	101.08(8)	Cl(3)—Nb—O(1)	85.31(9)
Cl(3)—Nb—O(2)	101.88(9)	O(1)—Nb—O(2)	103.8(1)
Nb—O(1)—C(11)	150.6(2)	Nb—O(2)—C(21)	162.5(2)



Scheme 2.

talum dichloride [$Ta(OC_6H_3Ph_2\text{-}2,6)_3Cl_2$] produces the bis(cyclometallated) compound [$Ta(OC_6H_3PhC_6H_4)_2(OC_6H_3Ph_2\text{-}2,6)$] (structurally characterized[10]) even under an atmosphere of hydrogen. We envisage the formation of both **3a** and **4** to occur via an intermediate [$Nb(OAr)_3$] (Scheme 3). In the absence of added hydrogen this complex can undergo intramolecular addition of an arene CH bond to generate an undetected monohydride which then forms **4** by a second cyclometallation and elimination of H_2. The presence of H_2 leads to **3a**, presumably via a dihydride intermediate (see mechanistic discussion). The small amount of **3a** formed in the absence of added H_2 presumably is a result of the tris(aryloxide) reacting with the hydrogen generated in the formation of **4** (Scheme 3). The formation of a highly reactive tris(siloxide) of tantalum by reduction of the corresponding dichloride has been demonstrated by Wolczanski *et al.*[11] Furthermore, these species react with hydrogen



Scheme 3.

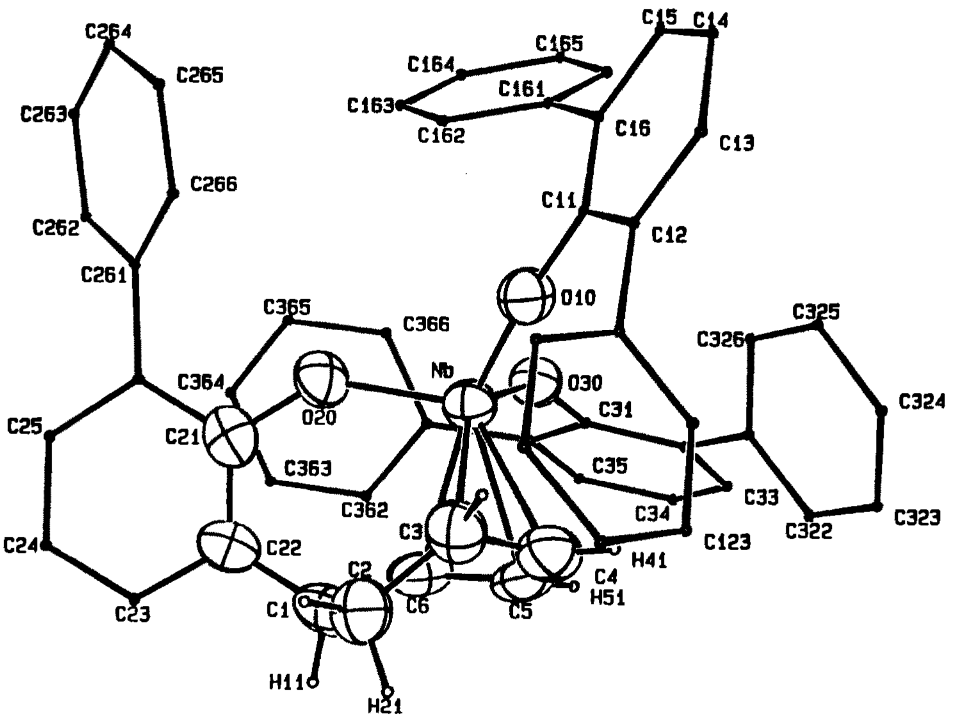


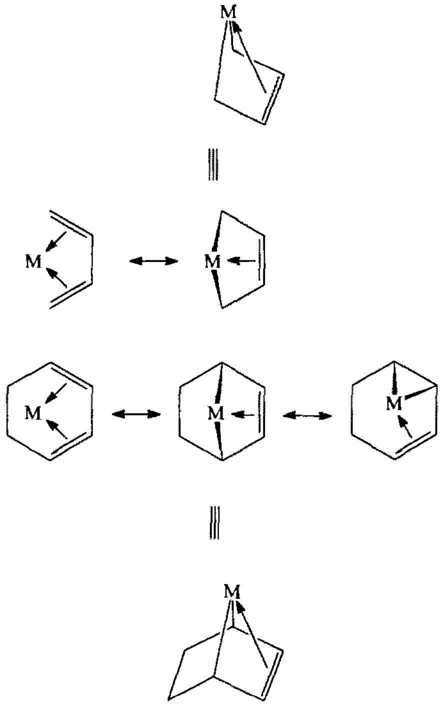
Fig. 2. Molecular structure of **3a**.

to form dihydrides and undergo ligand CH bond activation to form monohydrido, monometallated complexes.[11]

A single-crystal X-ray diffraction analysis of **3a** (Fig. 2, Table 2) shows a quasi-tetrahedral central coordination sphere made up of three oxygen donor atoms and an η^4-cyclohexadiene group which has been formed by the 1,2-hydrogenation of an *ortho*-phenyl group of one of the aryloxide ligands. The structural parameters for the coordination of this cyclohexadiene fragment are worthy of some discussion. There are now many examples in the literature of early *d*-block organometallic compounds which consist of d^2-metal fragments bound to 1,3-diene substrates. By far the largest examples involve cyclopentadienyl ancillary ligands such as the compounds [Cp_2M(diene)] (M = Ti, Zr, Hf)[12] and [$CpMCl_2$(diene)] (M = Nb, Ta).[13] In these compounds both s-*cis* and *trans*-η^4-diene complexes have been observed. In the case of the s-*cis* complexes the structural parameters indicate the importance of a metallacyclopent-3-ene resonance picture in describing these molecules (Scheme 4). An analogous analysis of the bonding of 1,3-cyclohexadiene to such metal fragments can lead to a "metallanorbornene" resonance picture to describe the resulting molecular structure (Scheme 4). The strong binding of arene rings to d^2-[$Ta(OAr)_3$] fragments has been described in terms of a "metallanorbornadiene" resonance structure.[14]

Table 2. Selected bond distances (Å) and angles (°) for [$Nb(OC_6H_3Ph$-η^4-$C_6H_7)(OC_6H_3Ph_2$-2,6$)_2$] (**3a**)

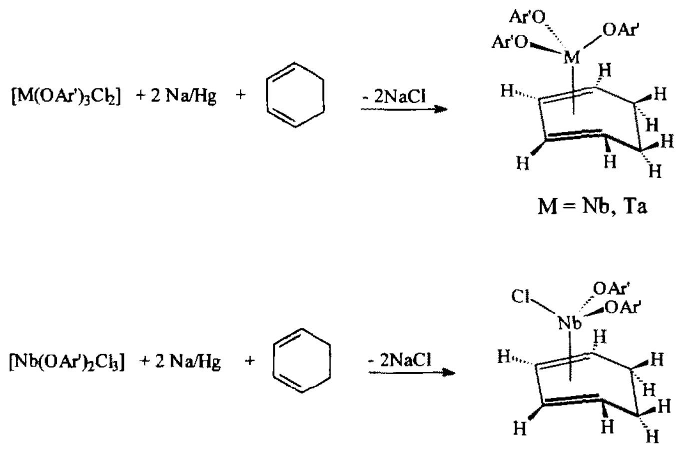
Nb—O(10)	1.928(9)	Nb—O(20)	1.923(9)
Nb—O(30)	1.932(9)	Nb—C(3)	2.27(1)
Nb—C(4)	2.27(2)	Nb—C(5)	2.37(1)
Nb—C(6)	2.40(1)	C(1)—C(2)	1.52(2)
C(1)—C(6)	1.52(2)	C(2)—C(3)	1.51(2)
C(3)—C(4)	1.41(2)	C(4)—C(5)	1.40(2)
C(5)—C(6)	1.38(2)		
O(10)—Nb—O(2)	107.8(4)	O(10)—Nb—O(30)	107.3(4)
O(20)—Nb—O(30)	108.9(4)	Nb—O(10)—C(11)	165.8(9)
Nb—O(20)—C(21)	138.8(9)	Nb—O(30)—O(31)	147.8(8)



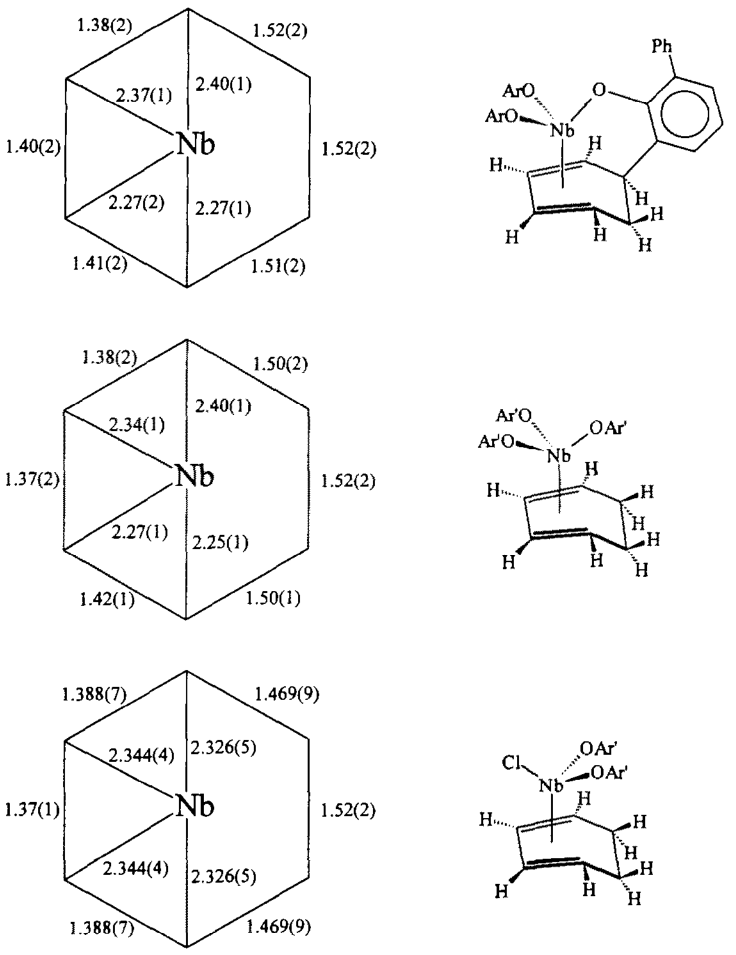
Scheme 4.

The structural parameters for **3a** show that there is a pronounced asymmetry in the interaction of the *ortho*-C_6H_7 fragment with the metal. Specifically, it can be seen (Table 2) that carbon atoms C(3) and C(4) are ~0.1 Å closer to the metal than C(5) and C(6). A corresponding slight increase in the C(3)—C(4) distance of 1.41(2) vs 1.38(2) Å for C(5)—C(6) is also observed. These structural parameters can be used to support a bonding picture involving the metal interacting more strongly with one of the diene olefin bonds to form a metallacyclopropane ring, while a weaker interaction occurs with the remaining olefin (Scheme 4). The Nb—C(3) and Nb—C(4) distances of 2.27(1) and 2.27(2) Å are not as short as the distances of 2.167(3) and 2.208(2) Å found for the complex $[Nb(OC_6H_3Pr^i_2)_2(OC_6H_3Pr^i\text{-}\eta^2\text{-}CMeCH_2)(thf)]$ which also has a much larger carbon–carbon distance of 1.453(4) Å.[15] We have recently isolated a series of 1,3-cyclohexadiene complexes of niobium and tantalum containing 2,6-diisopropylphenoxide (OAr′) ancillary ligation by reduction of the corresponding chlorides (Scheme 5).[16] All three complexes have been structurally characterized and the parameters for the metal–diene interaction for **3a** and the two niobium complexes are highlighted in Scheme 6. The tris(aryloxide) complex $[Nb(OAr')_3(\eta^4\text{-}C_6H_8)]$ has an asymmetric structure very similar to that in **3a**, while the monochloride $[Nb(OAr')_2(Cl)(\eta^4\text{-}C_6H_8]$ has a crystallographic mirror plane. It is interesting to note that the orientation of the three oxygen atoms bound to niobium in **3a** and $[Nb(OAr')_3(\eta^4\text{-}C_6H_8)]$ are identical to each other but are different from the orientation of the $NbClO_2$ unit on the face of the cyclohexadiene group in $[Nb(OAr')_2(Cl)(\eta^4\text{-}C_6H_8)]$ (Scheme 6). This implies that the slight asymmetry found in **3a** is not due to the presence of the chelate backbone but may have an electronic origin.

The spectroscopic properties of **3a** are consistent with it maintaining an identical molecular structure in solution. In the ^1H NMR spectrum, seven distinct resonances for the non-equivalent protons in the η^4-C_6H_7 ring are observed in the δ 1.5–6.0 ppm region of the ^1H NMR spectrum, while the six non-equivalent carbon atoms can be assigned in the ^{13}C NMR spectrum. A combination of 1D and 2D ^1H NMR experiments as well as $^1H/^{13}C$ HETCOR spectra allow unequivocal assignments of the proton and carbon resonances in the ring as well as the most significant proton–proton coupling constants



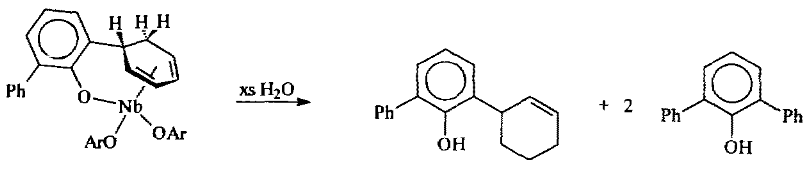
Scheme 5.



Scheme 6.

(Fig. 3, Table 3). The measured $^3J(^1H–^1H)$ coupling constants are consistent with the torsion angles observed in the solid-state structure of **3a**, e.g. the negligible coupling between H_a and H_c (H_aCCH_c torsion angle close to 90°). The non-symmetric bonding of the cyclohexadiene fragment is also evident from the fact that protons H_e and H_d and carbons C(3) and C(4) resonate to higher field than the corresponding resonances for H_g, H_f, C(5) and C(6) (Table 3).

The strong interaction of the chelated —C_6H_7 fragment with the metal center in **3a** is confirmed by analysis of the hydrolysis products. Addition of water to a benzene solution of **3a** was shown (^1H NMR) to generate two equivalents of 2,6-diphenylphenol and one equivalent of 2-(cyclohex-2-enyl)-6-phenylphenol (Scheme 7). The regiochemistry of the cyclohexene ring was determined by purification of the phenol and analysis of the ^1H NMR spectrum, specifically the downfield position of the proton H(1) and its coupling (lost upon selective decoupling) to both olefin protons. This result is consistent with the niobium metal center in **3a** having carried out the two-electron reduction of the cyclohexadiene ring, i.e. generating a chelated —$C_6H_7^{2-}$ group bound to a formally d^0-Nb^V metal center.



3a

Scheme 7.

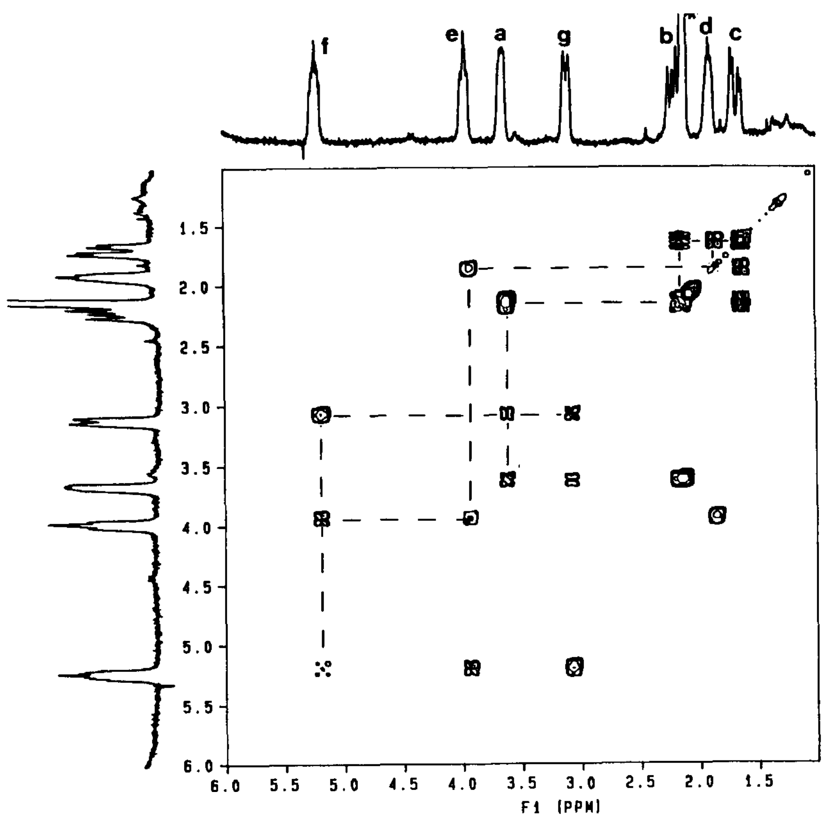


Fig. 3. ^{1}H COSY 200 MHz NMR spectrum of the aliphatic region of compound **3a**; for proton assignments see Table 3.

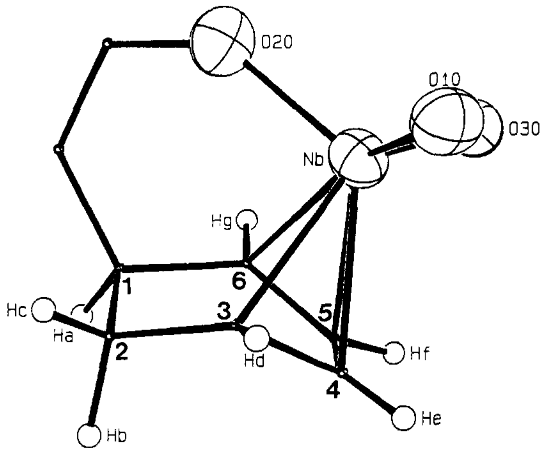
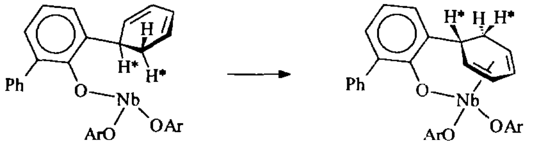


Table 3. NMR data for **3a**

δ (ppm)				Coupling constants (Hz)	
H_a	3.61	C_1	45.8	H_a—H_g	2.9
H_b	2.10	C_2	33.2	H_a—H_b	7.0
H_c	1.62	C_3	82.5	H_b—H_c	12.9
H_d	1.86	C_4	103.7	H_c—H_d	4.1
H_e	3.94	C_5	120.1	H_d—H_e	4.5
H_f	5.19	C_6	104.5	H_d—H_f	2.5
H_g	3.07			H_e—H_f	5.0
				H_e—H_g	1.0
				H_f—H_g	7.7

The use of D_2 as reagent gas leads to the formation of **3a**-d_2, which shows the loss of two resonances in the ^{1}H NMR spectrum compared to the protio complex. These protons are mutually *cis*, but located *exo* to the metallanorbornene framework, i.e. *trans* to the metal center (Table 3). We envisage this final stereochemical positioning of the added hydrogen atoms to be a consequence of the regiochemistry of the stoichiometric, intramolecular hydrogenation reaction. The addition of two hydrogen atoms to the 1,2-position of the *ortho*-phenyl ring produces a 1,3-cyclohexadiene which cannot chelate to the metal center without first rotating about the phenoxide–cyclohexadiene bond (Scheme 8). Hence, the resulting complex contains the added hydrogen atoms mutually *cis*, but on the opposite face to the metal center. This and the proposed reaction pathway are discussed in more detail in the mechanistic section (*vide infra*).



Scheme 8.

Hydrogenation studies

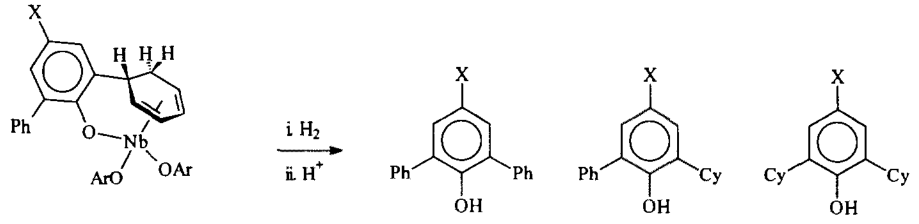
Exposure of hydrocarbon solutions **3a** to hydrogen (pressures >200 psi were typically used) resulted in the intramolecular hydrogenation of the *ortho*-phenyl groups of the aryloxide ligands. The direct analysis of the organometallic products of this reaction proved difficult. A deep-red solution of **3a** in C_6D_6 solvent was found to generate a dark brown solution on exposure to H_2. Analysis by ^1H NMR showed a mixture of products. The hydrolysis of these reaction mixtures, however, was informative in that it allowed the identification and quantitation of the aryloxide ligands present in solution by integration of the well resolved OH peaks of the resulting phenols in the ^1H NMR spectrum. The results of this study showed that after 6 days at 25°C under 1000 psi of hydrogen, essentially complete conversion of the original aryloxide ligands in **3a** into 2,6-dicyclohexylphenoxide groups had occurred (Scheme 9). At intermediate times hydrolysis yielded a mixture of 2,6-diphenylphenol, 2-phenyl-6-cyclohexylphenol and 2,6-dicyclohexylphenol. At higher temperatures, the hydrogenation of the *ortho*-phenyl groups of the aryloxide ligands occurs at a faster rate. When the cyclohexadiene complex $[Nb(OC_6H_2Ph_2\text{-}\eta^4\text{-}C_6H_7)(OC_6H_2Ph_3\text{-}2,4,6)_2]$, **3b**, was used as the substrate, hydrogenation was found to yield only 2-cyclohexyl-4,6-diphenylphenol and 2,6-dicyclohexyl-4-phenylphenol as products. No evidence for hydrogenation of the 4-phenyl ring was obtained (Scheme 9).

Other studies by our group have shown that reaction of the tantalum alkyls $[Ta(OC_6H_3Ph_2\text{-}2,6)_2(R)_3]$ (R = $CH_2C_6H_4$-4Me, CH_2SiMe_3) and $[Ta(OC_6HPh_4\text{-}2,3,5,6)_2(CH_2SiMe_3)_3]$ with H_2 (1200 psi, 80°C) in the presence of excess PMe_2Ph leads to the colorless seven-coordinate trihydride compounds $[Ta(OC_6H_3Cy_2\text{-}2,6)_2(H)_3(PMe_2Ph)_2]$ and $[Ta(OC_6HCy_2\text{-}2,6\text{-}Ph_2\text{-}3,5)_2(H)_3(PMe_2Ph)_2]$ containing 2,6-dicyclohexylphenoxide and 2,6-dicyclohexyl-3,5-diphenylphenoxide ligands respectively (Scheme 10).[4,17] The hydrogenolysis of the bis(alkyl) $[Ta(OC_6H_3Ph_2\text{-}2,6)_2(Cl)(CH_2SiMe_3)_2]$, however, generated the dihydride $[Ta(OC_6H_3Ph_2\text{-}2,6)_2(Cl)(H)_2(PMe_3)_2]$ (Scheme 10) in which intramolecular hydrogenation of the aryloxide ligands does not occur.[17]

An analogous reaction employing the niobium alkyl $[Nb(OC_6H_3Ph_2\text{-}2,6)_2(CH_2C_6H_4\text{-}4Me)_3]$ and PMe_2Ph was found to produce a reaction mixture from which a deep-green crystalline material could be obtained (Scheme 11). Hydrolysis of this product was found to generate 2,6-dicyclohexylphenol (^1H NMR) and PMe_2Cy (^1H and ^{31}P NMR). The ^1H NMR spectrum of the green niobium compound shows a very broad resonance at δ 9.8 ppm consistent with its formulation as a hydride species. A number of single-crystal X-ray diffraction analyses of the compound confirmed the presence of two 2,6-dicyclohexylphenoxide and two dimethylcyclohexylphosphine ligands bound to niobium. However, satisfactory refinement of the structure has not been possible due to disorder and other problems.[18] The niobium alkyls $[Nb(OC_6H_3Ph_2\text{-}2,6)_2(CH_2C_6H_4\text{-}4Me)_3]$ and $[Nb(OC_6H_3Ph_2\text{-}2,6)_3Me_2]$ prove to be useful precursors for the catalytic hydrogenation of arylphosphines,[4b] a reaction that occurs only very slowly for the corresponding tantalum systems. In the absence of added phosphine, both of these alkyls produce 2,6-dicyclohexylphenol upon hydrogenation followed by hydrolysis.

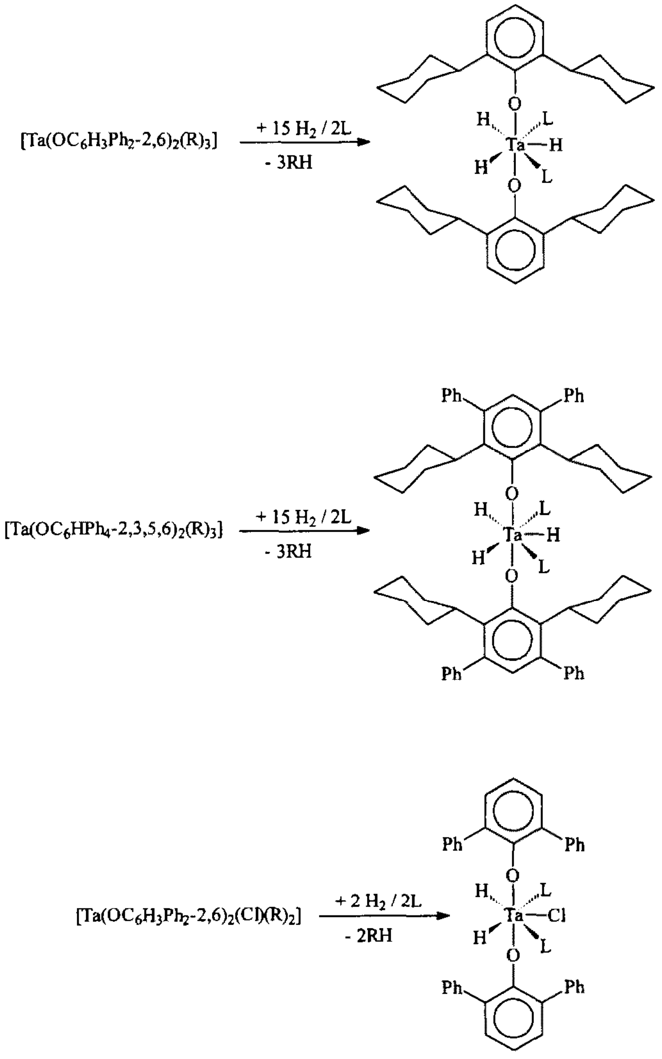
The reagents formed by mixing the dichlorides **1** or trichlorides **2** with either two or three equivalents of Bu^nLi in hydrocarbon solvents will also act as catalysts for the hydrogenation of arenes and arylphosphines.[19] The hydrolysis of the reaction mixtures formed by hydrogenation of either **1a** or **1c** plus $2Bu^nLi$ or either **2a** or **2c** plus $3Bu^nLi$ in benzene solvent is found to contain 2,6-dicyclohexyl- or 2,6-dicyclohexyl-3,5-diphenylphenol (Scheme 12). In no case was evidence obtained for hydrogenation of phenyl groups in the 3- or 5-positions or the central phenoxy ring.

Separation and purification of the cyclohexylphenols was readily achieved by preparative scale thin-layer chromatography. The aliphatic regions of the ^1H NMR spectra of the three 2,6-dicyclohexylphenols obtained in this study are shown in Fig. 4. The assignment of the seven non-equivalent protons (Table 4), which becomes important in the mechanistic studies, is based upon an analysis of the ^3J proton coupling constants (Table 4) as well as a combination of 1D–^1H, ^1H COSY and $^{13}C/^1H$ HETCOR NMR experiments. In all three compounds the methylene proton attached to C(1) appears as a well resolved triplet of triplets. The two $^3J(^1H\text{–}^1H)$ coupling constants that give rise to this pattern (Table 4) are typical of axial–axial and axial–equatorial coupling constants in cyclohexane rings,[20] i.e. this proton occupies an axial position in all three compounds. The *ortho*-cyclohexyl rings in all three phenols can hence be assigned a ground-state structure in which the central phenoxy ring occupies an equatorial site, as typically found for simple substituted cyclohexanes. In the case of 2,6-dicyclohexyl- and 2,6-dicyclohexyl-4-phenylphenol the positions of the remaining six proton resonances are very similar, with the three axial protons resonating to a higher field than the equatorial protons (Fig. 4). The chemical shifts of the cyclohexyl pro-

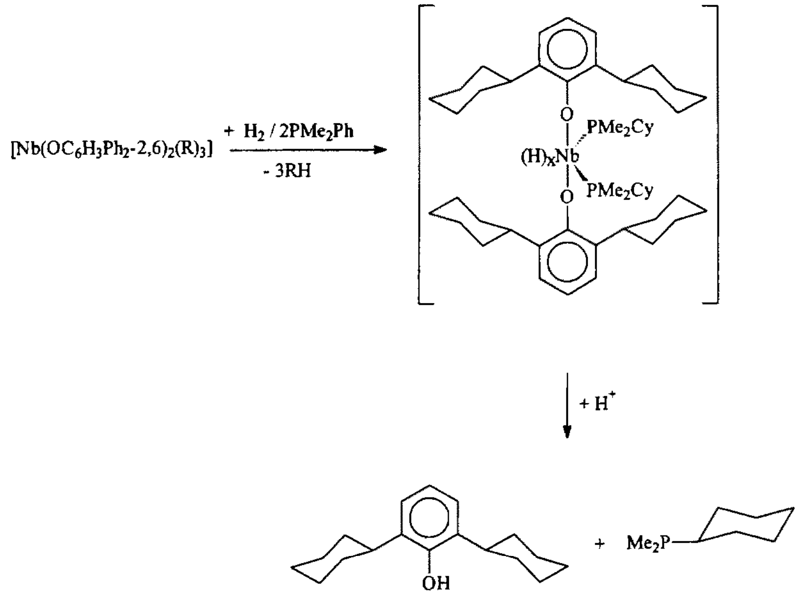


X	T/°C–	H_2 / psi	TIME	%	%	%
H	25	800	3 d	55	31	13
H	25	1000	6 d	2	2	96
H	80	500	18 h	4	6	90
Ph	25	800	3 d	30	45	25
Ph	80	500	18 h	2	3	95

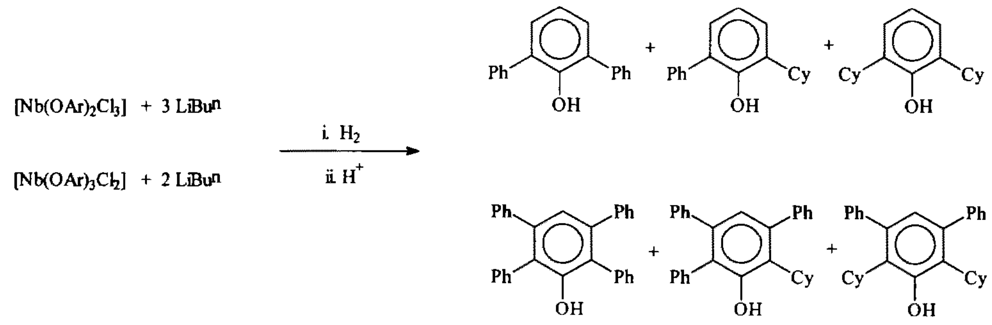
Scheme 9.



Scheme 10.



Scheme 11.



Scheme 12.

tons in 2,6-dicyclohexyl-3,5-diphenylphenol are, however, significantly different (Fig. 4). An obvious reason for a change in these proton chemical shifts is the presence of the phenyl substituents in the 3,5-positions. The proximity of these phenyl groups would be expected to lead to anisotropic shielding/deshielding of the protons on the adjacent cyclohexyl ring. The most important impact of the presence of these phenyl rings is, however, to change the preferred conformational structure of the phenol. This is shown by NOE experiments which indicate that in 2,6-dicyclohexyl- and 2,6-dicyclohexyl-4-phenylphenol, the proton H(1a) is in close proximity to the phenolic proton. In contrast, irradiation of the phenolic proton in 2,6-dicyclohexyl-3,5-diphenylphenol leads to an enhancement of the H(2a) signal. These results are consistent with the two preferred conformations for these molecules as shown in Scheme 13. The proximity to the phenolic group of H(2a) in the 3,5-diphenyl derivative also presumably accounts for its downfield chemical shift. The fact that H(1a) also resonates to lower field in this molecule may be a consequence of the diamagnetic anisotropy of the adjacent phenol rings, which in order to cause a downward shift would have to be approximately coplanar with the central phenoxy ring.

Mechanistic considerations

It is possible to envisage two pathways leading to the η^4-cyclohexadiene complex **3a**. The first involves a niobium dihydride intermediate which attacks one of the *ortho*-phenyl rings to generate either of two intermediate cyclohexadienyl, hydride complexes. The second pathway entails the formation of a niobium arene complex which then reacts with H_2 to form identical cyclohexadienyl, hydride intermediates (Scheme 14). The work of Wigley *et al.* shows that d^2-metal fragments such as $[Ta(OAr)_3]$ and $[Ta(OAr)_2Cl]$ can strongly bind arene rings (formed by cyclotrimerization of alky-

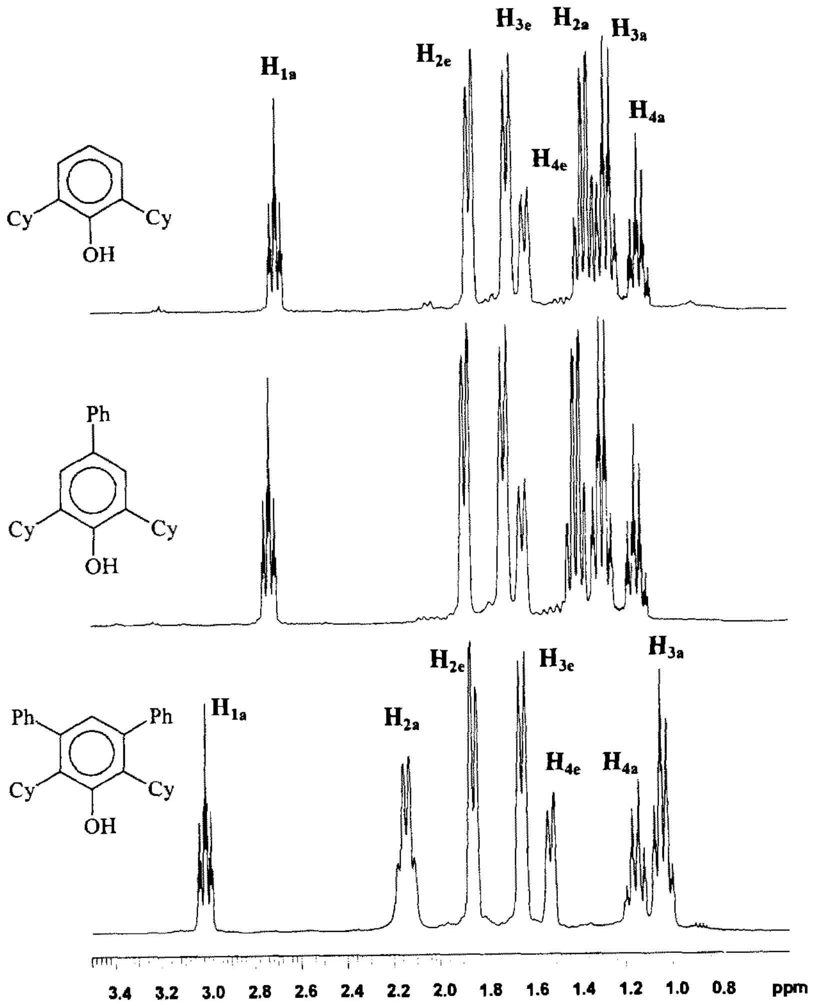


Fig. 4. The 500 MHz ^1H NMR spectra of the aliphatic protons of 2,6-dicyclohexyl-, 2,6-dicyclohexyl-4-phenylphenol- and 2,6-dicyclohexyl-3,5-diphenylphenol.

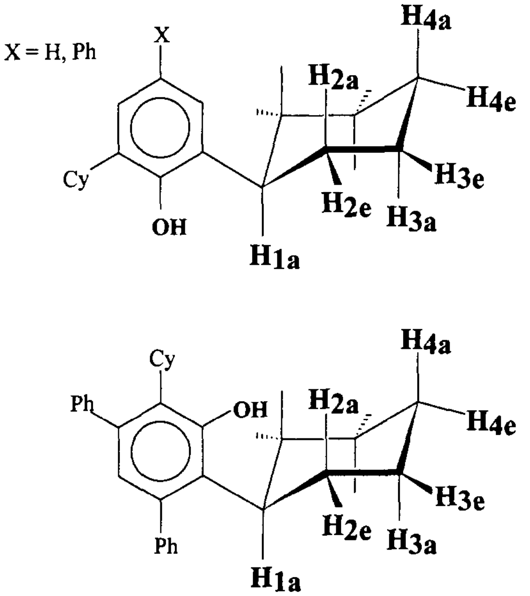
nes),[13] while Wolczanski and co-workers have shown the formation of benzene complexes from $[Ta(silox)_3]$.[21] The reduction of the arene nucleus by the metal center may lead to metallananorbornadiene species which undergo hydrogenolysis with H_2. This mechanistic uncertainty is highlighted by recent results obtained in the reactivity of a tungsten derivative of 2,3,5,6-tetraphenylphenoxide (Scheme 15).[22] The deep-green complex $[W(OC_6HPh_4\text{-}2,3,5,6)(OC_6HPh_3\text{-}\eta^6\text{-}C_6H_5)(PMe_2Ph)]$ reacts slowly with H_2 (1 atm) to produce a new organometallic derivative in which one of the *ortho*-phenyl rings has been converted to a cyclohex-1-enyl ring which is η^2-bound to tungsten. It is not known whether the reaction proceeds by direct hydrogenolysis of the tungsten-arene group or via initial formation of undetected tungsten hydride intermediates. In the case of the niobium systems it is known that in the absence of H_2 facile cyclometallation of the aryloxide ligands occurs with no detectable arene intermediates (Scheme 3). It therefore appears probable that complexes such as **3a** arise via a dihydride intermediate, although conclusive proof is presently absent. The ensuing reaction of **3a** with H_2 can be envisaged as involving hydrogenolysis of the incipient niobium–carbon bonds in the "niobanorbornene" or "niobacyclopropane" group.

The intramolecular hydrogenation of a pendant arene ring by a transition metal center can be envisaged to occur via a multitude of reaction pathways. It is possible to differentiate these pathways by analyzing the regiochemistry and stereochemistry of key intermediates, as well as the stereochemistry of the added hydrogen (deuterium) in the final cyclohexane ring. If one restricts the pathways to be considered to ones involving sequential, *cis* additions of two hydrogen atoms on adjacent carbon centers, then the hydrogenation of benzene with D_2 can produce only two distinguishable forms of cyclohexane, as shown (Scheme 16). A reagent which releases both intermediate 1,3-cyclohex-

Table 4. Chemical shifts and resolved coupling constants for the cyclohexyl ring protons in 2,6-dicyclohexyl-, 2,6-dicyclohexyl-4-phenyl- and 2,6-dicyclohexyl-3,5-diphenylphenol[a]

δ (ppm)							
OH	H_{1a}	H_{2a}	H_{2e}	H_{3a}	H_{3e}	H_{4a}	H_{4e}
4.45	2.71	1.37	1.87	1.28	1.71	1.13	1.63
4.50	2.74	1.41	1.89	1.30	1.73	1.15	1.64
5.10	3.01	2.15	1.86	1.04	1.65	1.16	1.52
Coupling constants/Hz							
		$^3J_{(H_{1a}-H_{2a})}$	$^3J_{(H_{1a}-H_{2e})}$	$^3J_{(H_{2a}-H_{3a})}$	$^3J_{(H_{2a}-H_{3e})}$	$^3J_{(H_{3a}-H_{4a})}$	$^3J_{H_{3a}-H_{4e}}$
		11.7	2.9	12.1	2.9	12.8	2.9
		11.7	3.1	12.5	2.8	12.8	3.1
		12.6	3.5	11.8	2.8	12.9	3.2
			$^2J_{(H_{2a}-H_{3a})}$	$^3J_{(H_{2e}-H_{3a})}$	$^2J_{(H_{3a}-H_{3e})}$	$^3J_{(H_{3e}-H_{4a})}$	$^3J_{(H_{4a}-H_{4e})}$
			11.7	2.9	12.8	3.7	12.5
			11.7	3.1	13.0	3.7	12.6
			12.6	3.2	13.0	3.3	12.7

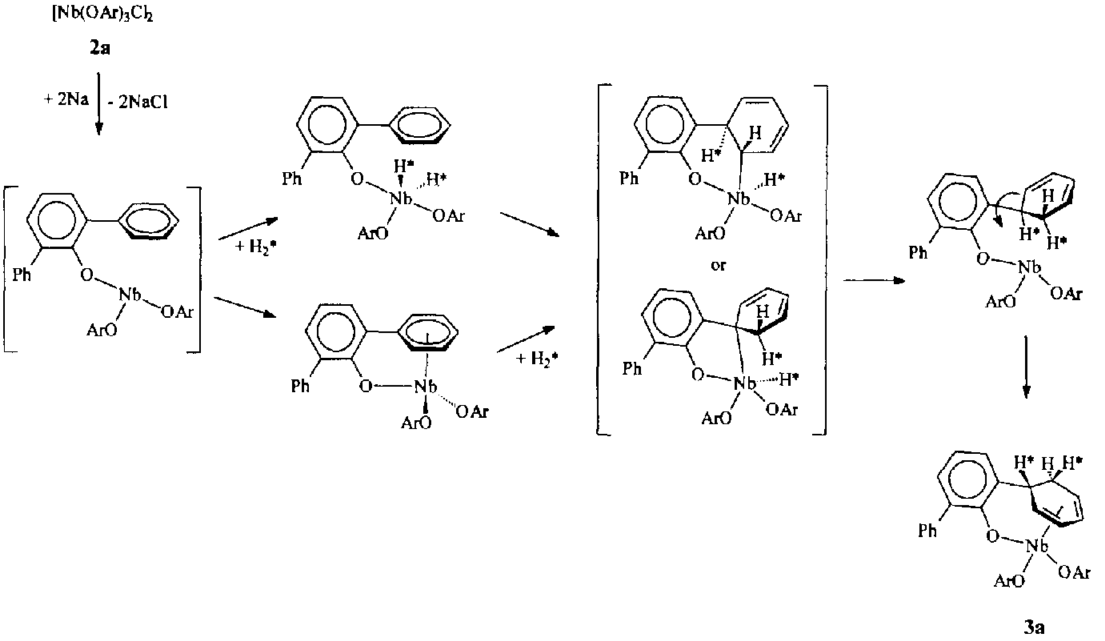
[a] The equatorial–equatorial couplings were not resolved.



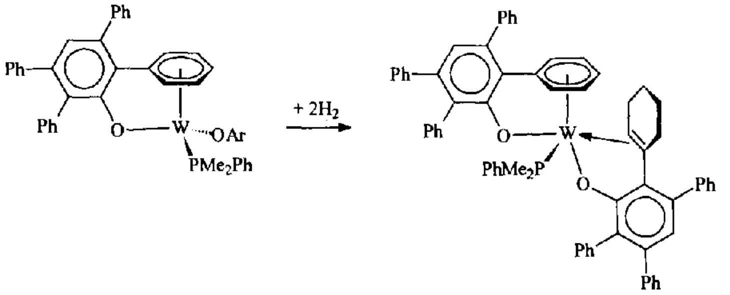
Scheme 13.

adiene or cyclohexene will produce a mixture containing one third of the all-*cis* isotopomer. The amount of the all-*cis* isotopomer will increase to 50% in a reaction in which either one of the intermediates remains bound to the metal center and a pure all-*cis* product will be generated exclusively only when the reagent/catalyst does not release any intermediates during the reaction.

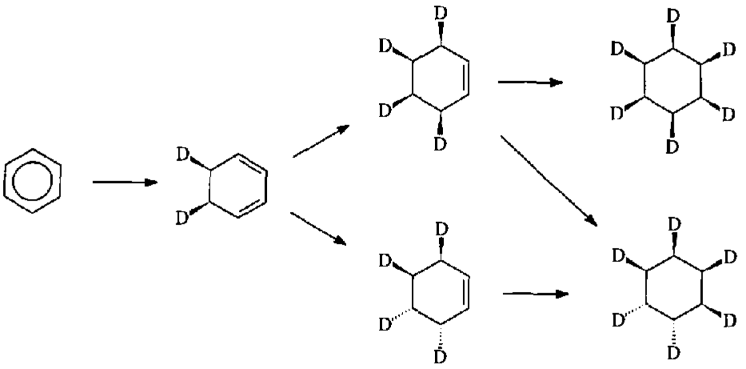
The presence of a single substituent on the arene ring will generate three regioisomers for the intermediate 1,3-cyclohexadiene and cyclohexene. Each of the three cyclohexene intermediates has two possible isotopomers involving the stereochemical arrangement of hydrogen and deuterium atoms (Scheme 17). A reagent or catalyst which demonstrates no electronic affinity for, or steric aversion to, the substituent and releases the intermediates will lead to a product containing equal amounts of four isotopomeric substituted cyclohexenes, as shown (Scheme 17). This even distribution will shift depending upon a combination of complex factors such as the reaction regiochemistry and how the reagent/catalyst interacts with the intermediates and the ring substituent. As with simple benzene, the all-*cis* isotopomer will form exclusively with a system that does not release any intermediates. A preference for the all-*cis* isotopomer will also be observed in a system which carries out an initial 1,2-hydrogenation and is sterically repelled by the arene substituent, i.e. the metal will preferentially interact with and hydrogenate the face of intermediates opposite to the ring substituent. A substituent which forms a strong, positive interaction with the metal center will, following an initial 1,2-hydrogenation, preferentially form isotopomer **D** (Scheme 17), with the last four deuterium atoms being added on the opposite face to the initial two. A similar stereochemical analysis can be applied to the other possible regiochemical pathways.



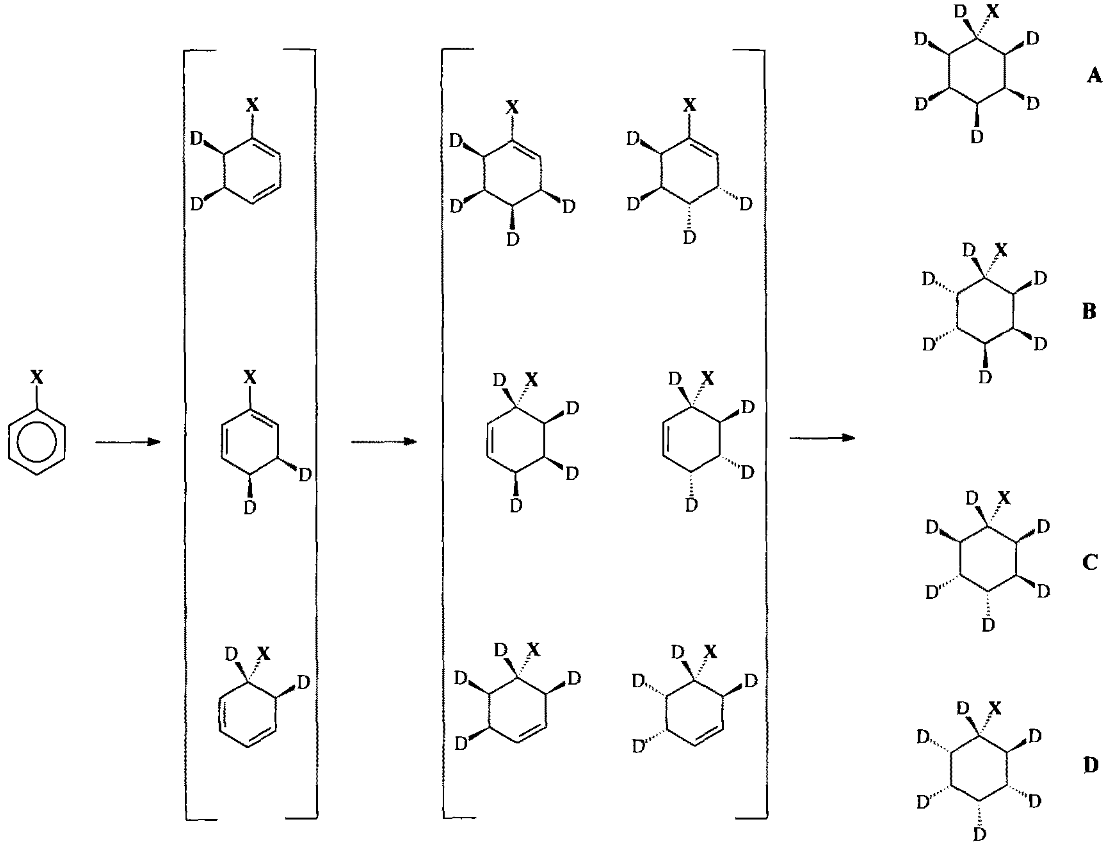
Scheme 14.



Scheme 15.



Scheme 16.

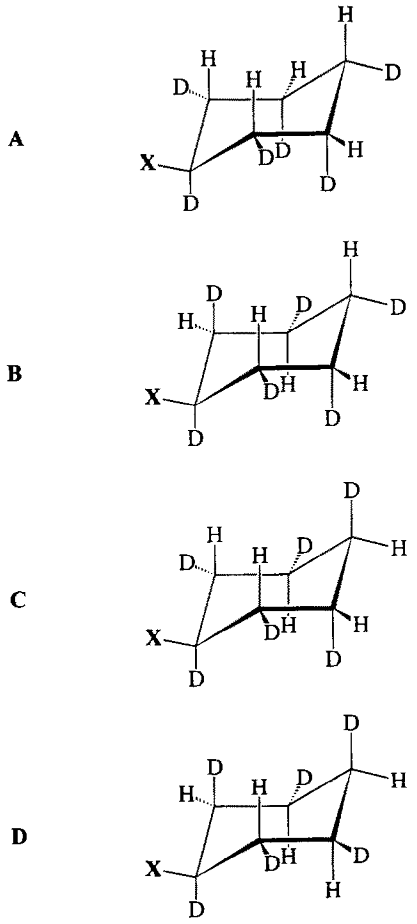


Scheme 17.

Reactions in which the initial hydrogenation does not occur at the 1,2-position will, assuming release of intermediates, invariably lead to a mixture of products.

The situation involving the intramolecular hydrogenation of *ortho*-phenyl rings entails a ring substituent (phenoxy group) which will remain strongly bound to the metal center throughout the course of the reaction. Hence, a reaction pathway involving initial 1,2-hydrogenation (as observed for compound **3a**) will lead to the formation of a single stereoisomer (**D**; Scheme 18) in which the last four deuterium atoms are introduced on the opposite face to the initial two. The constraints of the phenoxide chelate backbone preclude further hydrogenation on the same face once a hydrogen (deuterium) atom has been added to the ipso (1-position) carbon atom of the ring. A reaction pathway in which the 1,2-position is saturated last has the potential, assuming that the metal interacts strongly with the two intermediates, to produce an all-*cis* isotopomer (**A**; Scheme 18).

We have purified and analyzed the 2,6-dicyclohexylphenol produced by hydrogenation (using D_2 reagent gas) of a number of niobium 2,6-diphenylphenoxide substrates. In all cases it was found by mass spectrometric analysis that the products contained more than six deuterium atoms per cyclohexyl ring due to H/D scrambling processes. We are not able to say, based upon our experiments, whether H/D scrambling occurs during the hydrogenation sequence. However, we can say that H/D scrambling occurs both in the substrate 2,6-diphenylphenoxide ligand and in the product 2,6-dicyclohexylphenoxide group. Analysis of the 2,6-diphenylphenol obtained from partial hydrogenation of **3a** showed the presence of up to four deuterium atoms. This mass spectrometric result, coupled with integration of the aromatic region of the ^{1}H NMR spectrum, showed that H/D scrambling occurs exclusively into the *ortho*-positions of the 2,6-diphenyl rings. The origin of this deuterium incorporation is almost certainly due to reversible cyclometallation of the arene ring (Scheme 19), a process that is well documented. Facile H/D scrambling into saturated *ortho*-alkyl groups can also be demonstrated. Hence, exposure of a mixture of $[Nb(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_3]$ and 3 equiv. of Bu^nLi to D_2 gas was found to lead upon hydrolysis to 2,6-diisopropylphenol containing up to 14 deuterium atoms. The ^{2}H NMR of this sample showed incorporation exclusively into both the methyl and methyne pos-

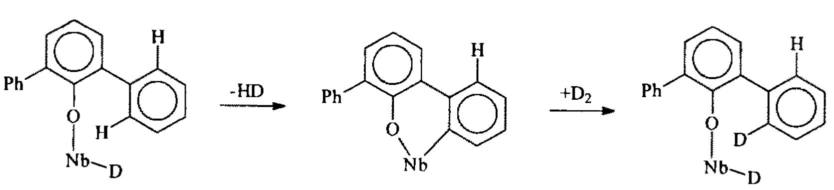


Scheme 18.

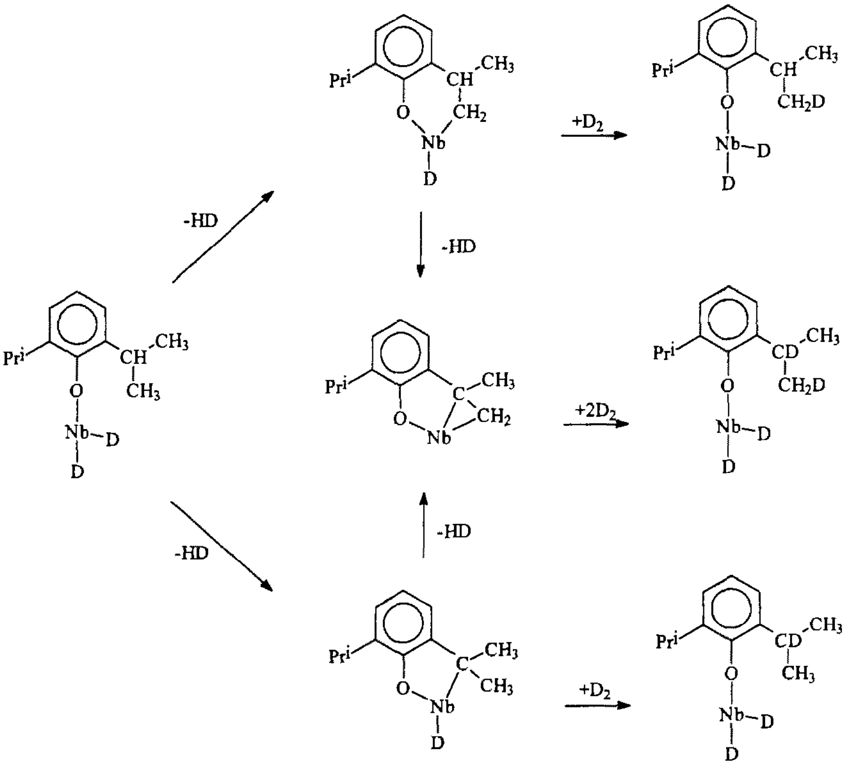
itions of the isopropyl groups. Reversible cyclometallation to form both five- and six-membered metallacycle rings can account for H/D scrambling, although it has also been shown that formation of chelated alpha-methylvinyl groups is feasible in that H/D scrambling may occur via reversible dehydrogenation/hydrogenation of *ortho*-alkyl groups that contain β-hydrogen atoms (Scheme 20). In the case of 2,6-dicyclohexylphenoxide these pathways are the reverse of the final stages of the hydrogenation reaction and complicate mechanistic analysis of the stereochemistry of the residual protons following reaction of 2,6-diphenylphenoxide with D_2 reagent gas.

The 2,6-dicyclohexylphenol obtained by reacting the η^4-cyclohexadiene complex **3a** with D_2 contains the majority of its proton intensity in the 4-equatorial and 3-axial positions. A similar pattern is observed for the 2,6-dicyclohexylphenol produced by reacting a mixture of $[Nb(OC_6H_3Ph_2\text{-}2,6)_3Cl_2]$ and 2Bu^{n}Li with D_2 gas in benzene (Fig. 5). The residual proton intensity in the ^{1}H NMR spectrum of these samples is consistent with the initial predominance of isotopomer **D** (Scheme 18) for the cyclohexyl rings followed by extensive H/D scrambling. This stereochemical arrangement of protons is exactly that predicted for a pathway which proceeds via initial 1,2-deuteration of the *ortho*-phenyl ring to form an intermediate such as **3a**, followed by addition of the remaining four deuterium atoms on the opposite face. The sample of 2,6-dicyclohexylphenol produced from the trichloride $[Nb(OC_6H_3Ph_2\text{-}2,6)_2Cl_3]$ and 3Bu^{n}Li under D_2 contains residual protons in the 2-axial, 3-equatorial and 4-axial positions as well as some intensity in the 3-axial and 4-axial sites (Fig. 5). The spectrum can be accounted for as resulting from a mixture of the two isotopomers **A** and **D** (Scheme 18), with the all-*cis* isotopomer (**A**) predominating. These results indicate that the intramolecular hydrogenation of the *ortho*-phenyl rings of 2,6-diphenylphenoxide can proceed via different regiochemical pathways, depending upon the metal substrate to which it is bound. This is confirmed by the tungsten chemistry shown in Scheme 15, where the remaining double bond occupies the 1,2-position,[22] the position hydrogenated first in **3a**. In the case of the niobium tris(aryloxides) there is clearly a strong preference for reactions proceeding via initial 1,2-hydrogenation. It should be borne in mind that this reaction is stoichiometric, with many possible intermediate niobium complexes containing ligands at various stages of hydrogenation. However, the fact that hydrolysis at intermediate times yielded only 2,6-dicyclohexyl- and 2-cyclohexyl-6-phenylphenol indicates, under the reaction conditions, that, once attacked, rings are saturated before other phenyl rings are hydrogenated.

In the case of the 2,3,5,6-tetraphenylphenoxide precursors $[Nb(OC_6HPh_4\text{-}2,3,5,6)_3Cl_2]$, **1c**, and $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl_3]$, **2c**, reaction with Bu^{n}Li under D_2 followed by hydrolysis yields the corresponding 2,6-dicyclohexylphenol which, based



Scheme 19.



Scheme 20.

upon mass spectrometric data, have undergone less extensive H/D scrambling. The ^1H NMR of both of these phenolic samples are very similar and show that the majority of the proton intensity lies at the 2-axial, 3-equatorial and 4-axial positions (Fig. 6). Furthermore, integration of the peaks against the phenolic OH peak allows a quantitative measure of the amount of H/D scrambling that has taken place at each position. It can be concluded that the 2,6-dicyclohexyl-3,5-diphenylphenol that is produced by both substrates contains predominantly (~ 70%) cyclohexyl rings with an all-*cis* stereochemical arrangement of protons (and hence deuterium atoms).

EXPERIMENTAL SECTION

All operations were carried out under a dry nitrogen atmosphere either in a Vacuum Atmospheres Dri-Lab or by standard Schlenck techniques. Hydrocarbon solvents were dried by distillation from sodium benzophenone and stored under a nitrogen atmosphere. 2,6-Diphenylphenol was purchased from Aldrich Chemical Co. (Milwaukee, Wisconsin) and used as is; 2,4,6-triphenylphenol and 2,3,5,6-tetraphenylphenol were synthesized by previously published procedures.[6,7] The compounds $[Nb(OC_6H_3Ph_2\text{-}2,6)_2Cl_3]$ (**1a**), $[Nb(OC_6H_2Ph_3\text{-}2,4,6)_2Cl_3]$ (**1b**), $[Nb(OC_6H_3Ph_2\text{-}2,6)_3Cl_2]$ (**2a**) and $[Nb(OC_6H_2Ph_3\text{-}2,4,6)_3Cl_2]$ (**2b**) were obtained by previously published procedures. The ^1H NMR spectra were recorded on either a Varian Associates Gemini 200 or 500 instrument; ^{13}C NMR spectra were recorded on a Varian Associates Gemini 200; HETCOR, COSY and NOEDIF spectra were recorded on a General Electric QE-300 instrument. Mass spectra and elemental analyses were recorded in-house at Purdue University.

Preparation of $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl_3]$ (**1c**)

To a stirred solution of $NbCl_5$ (6.3 g, 23.0 mmol) in 150 cm^3 of toluene was added 2,3,5,6-tetraphenylphenol (18.5 g, 47.0 mmol) portionwise. After the final addition, the solution was heated to reflux for 2 h and slowly cooled to room temperature. The solvent was removed *in vacuo* and the resulting red–orange solid was washed with hexane and dried. Yield = 20.5 g (21.0 mmol, 90%) of **1c**. Crystals suitable for an X-ray diffraction study were grown by the slow evaporation of a saturated benzene solution. ^1H NMR (C_6D_6, 30°C): δ 6.6–7.6 (m, aromatics).

Preparation of $[Nb(OC_6HPh_4\text{-}2,3,5,6)_3Cl_2]$ (**2c**)

To a stirred solution of $NbCl_5$ (5.0 g, 19.0 mmol) in 100 cm^3 of benzene was added a benzene/hexane

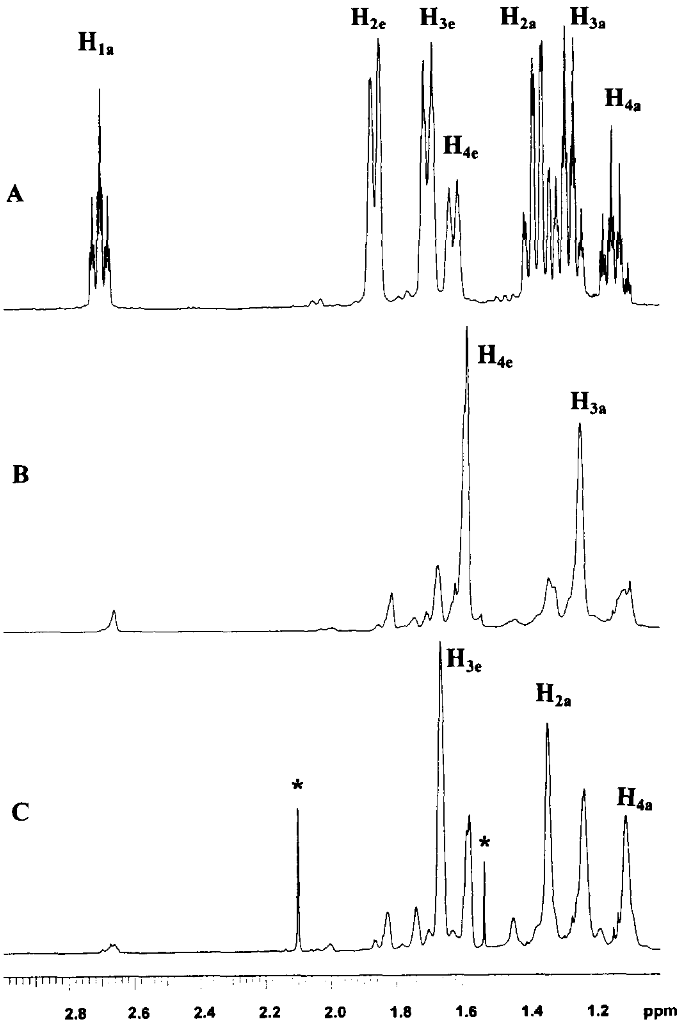


Fig. 5. The 500 MHz ^1H NMR spectra of the aliphatic protons of 2,6-dicyclohexylphenol (A) and the deuterated 2,6-dicyclohexylphenol formed from the reaction of (**2a**+2Bu^{n}Li) with D_2 (B) and (**1a**+3Bu^{n}Li) with D_2 (C).

solution of $LiOC_6HPh_4$-2,3,5,6 (generated by addition of one equivalent of Bu^{n}Li in hexane to a benzene solution of 2,3,5,6-tetraphenylphenol, 23.4 g, 58.0 mmol). The mixture lightened from dark red to orange. Stirring was continued overnight. The reaction mixture was filtered to remove the lithium salts and the solvent removed *in vacuo* from the filtrate to yield **2c** as an orange solid which was washed with hexane. Yield = 15.4 g (11.0 mmol, 60%). ^1H NMR (C_6D_6, 30°C): δ 6.6–7.6 (m, aromatics).

Preparation of $[Nb(OC_6H_3Ph\text{-}\eta^4\text{-}C_6H_7)(OC_6H_3Ph_2\text{-}2,6)_2]$ (**3a**)

A solution of **2a** (2.00 g, 2.22 mmol) in toluene (25 cm^3) was stirred over a sodium amalgam (0.11 g of Na, 4.89 mmol) under 1 atmosphere of hydrogen for 24 h. The solution was decanted off the mercury pool, filtered and evaporated *in vacuo* to yield a red solid. The crude solid was dissolved in a minimum amount of toluene and layered with hexane to yield 1.68 g (2.02 mmol, 91%) of **3a** as red crystals of the toluene solvate suitable for X-ray diffraction. The crystals were found to become opaque in the absence of an atmosphere of toluene. Calc. for $NbC_{54}H_{43}O_3$ (no toluene solvate): C, 77.78; H, 5.32. Found: C, 78.38; H, 5.02%. ^1H and ^{13}C NMR data are contained in Table 3.

Preparation of $[Nb(OC_6H_2Ph_2\text{-}\eta^4\text{-}C_6H_7)(OC_6H_2Ph_3\text{-}2,4,6)_2]$ (**3b**)

An essentially identical procedure to that used for the preparation of **3a** was followed except using **2b** (2.00 g, 1.77 mmol) stirred over a sodium amalgam (0.089 g, 3.55 mmol) under 1 atmosphere of hydrogen. Yield = 1.50 g (1.42 mmol, 80%). Calc.

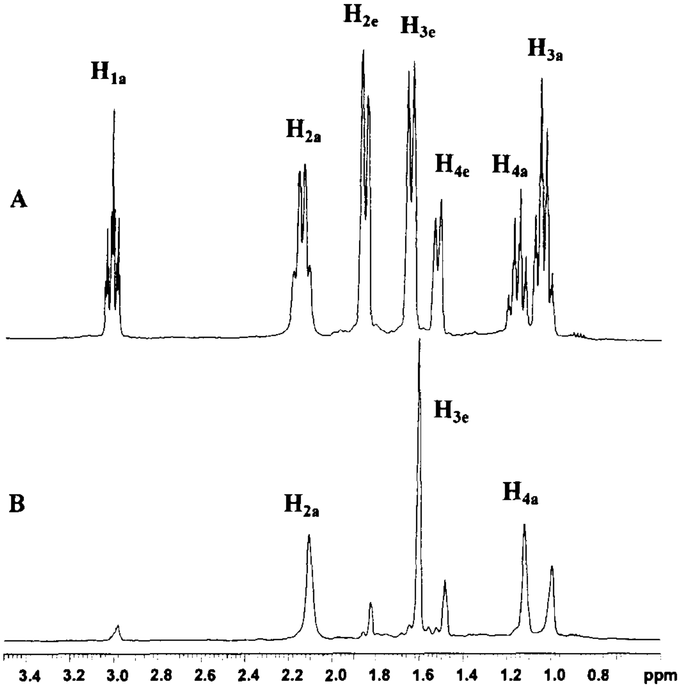


Fig. 6. The 500 MHz ^1H NMR spectra of the aliphatic protons of 2,6-dicyclohexyl-3,5-diphenylphenol (A) and the deuterated 2,6-dicyclohexyl-3,5-diphenylphenol phenol formed from the reaction of (**2c**+2Bu^{n}Li) with D_2 (B).

for $NbC_{72}H_{53}O_3$: C, 81.65; H, 5.04. Found: C, 81.52; H, 5.00%. ^1H NMR (C_6D_6, 30°C): δ 5.23(m), 3.96(m), 3.60(m), 3.15(m), 2.17(m), 1.93(m), 1.64(m).

Preparation of $[Nb(OC_6H_3Ph\text{-}C_6H_4)_2(OC_6H_3Ph_2\text{-}2,6)]$ (**4**)

A solution of **2a** (3.00 g, 3.3 mmol) in toluene (25 cm^3) was stirred over a sodium amalgam (0.18 g of Na, 7.67 mmol) for 24 h. The solution was decanted off the mercury pool, filtered and evaporated *in vacuo* to yield a brown solid. Washing with hexane gave the product as a yellow powder. Calc. for $NbC_{54}H_{39}O_3$: C, 78.26; H, 4.74. Found: C, 78.32; H, 4.98%. ^1H NMR (C_6D_6, 30°C): δ 6.5–7.7 (m, aromatic protons). ^{13}C NMR (C_6D_6, 30°C): δ 199.1 (Nb—C).

Preparation of 2-(cyclohex-2-enyl)-6-phenylphenol

A solution of **3a** (0.10 g, 0.12 mmol in 0.5 cm^3 of C_6D_6) was treated with a small drop of water and shaken. The resulting suspension was centrifuged and the phenolic products were quantified by integration of the OH protons in the supernatant solution. The 2-(cyclohex-2-enyl)-6-phenylphenol was separated by preparative thin layer chromatography on silica gel with hexane as the eluent. HRMS calc. for $C_{18}H_{18}O$: 250.1357; found: 250.1354. ^1H NMR ($CDCl_3$, 30°C): δ 5.39(s, O*H*), 3.72(br, H_1), 5.67(dd, H_2, $^3J_{H_2-H_3}$ = 10.1 Hz; $^3J_{H_2-H_1}$ = 2.6 Hz), 5.88(dq, H_3, $^3J_{H_3-H_{4,4'}}$ = 1.8 Hz; $^4J_{H_3-H_1}$ = 1.8 Hz), 1.3–2.0 (m, other aliphatics). ^{13}C NMR ($CDCl_3$, 30°C): δ 159.9, 130.2, 129.3, 129.2, 129.1, 128.6, 128.3, 127.6, 127.5, 127.3, 120.5, 35.7, 29.9, 24.9, 20.8.

Preparation of 2,6-dicyclohexylphenol

A solution of **3a** (0.20 g, 0.24 mmol in 3 cm^3 of benzene) was pressurized with 500 psi of hydrogen, heated at 80°C for 18 h and hydrolyzed to yield a mixture of phenols and insoluble niobium compounds. 2,6-Dicyclohexylphenol was purified using preparative thin layer chromatography on silica gel with hexane as the eluent. HRMS calc. for $C_{18}H_{26}O$: 258.1983; found: 258.1983. ^{13}C NMR (C_6D_6, 30°C): δ 151.1, 133.5, 125.0, 121.5 (aromatics), 38.1(C_1), 33.8(C_2), 27.5(C_3), 26.4(C_4). Deuterated 2,6-dicyclohexylphenol was prepared by pressurizing a benzene solution of **2a** (0.41 g, 0.46 mmol in 17 cm^3 of benzene) and Bu^{n}Li (0.064 g, 1.00 mmol) with 1150 psi of deuterium gas and heating at 60°C for 71 h. The reaction mixture was hydrolyzed and purified in a similar manner as for the protio compound. The hydrogenation of **3a** for shorter reaction times was found to produce significant quantities of 2-cyclohexyl-6-phenylphenol identified by NMR. ^1H NMR (C_6D_6, 30°C):

Table 5. Crystal data and data collection parameters

Formula	$NbCl_3O_2C_{72}H_{54}$	$NbO_3C_{63}H_{50}$
Formula weight	1150.50	948.01
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	12.561(2)	9.339(1)
b (Å)	13.810(3)	13.107(1)
c (Å)	17.836(3)	20.681(2)
α (°)	87.37(1)	93.807(8)
β (°)	72.63(1)	94.109(9)
γ (°)	76.85(1)	105.992(9)
V (Å^3)	2874(1)	2417.4(9)
Z	2	2
d_{calc} (g cm^{-3})	1.329	1.302
Crystal dimensions (mm)	0.63 × 0.31 × 0.30	0.25 × 0.25 × 0.22
Temperature (K)	183.	294.
Radiation (wavelength)	Mo-K_α (0.71073 Å)	Mo-K_α (0.70930 Å)
Monochromator	graphite	graphite
Linear abs. coef. (cm^{-1})	3.85	2.82
Absorption correction applied	empirical^a	none
Diffractometer	Enraf–Nonius CAD4	Enraf–Nonius CAD4
Scan method	ω–2θ	ω–2θ
h, k, l range	−13 to 13, −15 to 15, 0 to 19	−10 to 9, −14 to 14, 0 to 22
2θ range (°)	5.10–46.42	4.00–45.00
Scan width (°)	$0.51+0.92 \tan(\theta)$	$0.36+0.35 \tan(\theta)$
Take-off angle (°)	3.00	1.90
Programs used	Enraf–Nonius MolEN	Enraf–Nonius SDP
F(000)	1188.0	986.0
p-factor used in weighting	0.040	0.040
Data collected	8494	6274
Unique data	7928	6274
Data with $I > 3.0\sigma(I)$	6636	3612
Number of variables	703	585
Largest shift/e.s.d. in final cycle	0.15	0.24
R	0.046	0.055
R_W	0.060	0.065
Goodness of fit	1.804	0.987

δ 5.16(s, OH), 3.20(t,t; H_{1a}, $^3J_{H_{1a}-H_{2a}} = 8.8$ Hz, $^3J_{H_{1a}-H_{2e}} = 3.3$ Hz), 2.05(br d; H_{2e}, $^3J_{H_{2e}-H} = 12.5$ Hz), 1.78(br d, H_{4e}, $^3J_{H_{4e}-H} = 12.8$ Hz), 1.10–1.55(m, other aliphatic protons). ^{13}C NMR (C_6D_6, 30°C): δ 37.4(C_1), 32.9(C_2), 26.8(C_3), 26.1(C_4).

Preparation of 2,6-*dicyclohexyl*-4-*phenylphenol*

A benzene solution of **3b** (0.20 g, 0.19 mmol in 3 cm^3 of benzene) was pressurized with 500 psi of hydrogen and heated at 80°C for 18 h. Hydrolysis of the reaction products resulted in a mixture of phenols and insoluble niobium compounds. The 2,6-dicyclohexyl-4-phenylphenol was separated by preparative thin layer chromatography using hexane as the eluent. HRMS calc. for $C_{24}H_{30}O$: 334.2296; found: 334.2290. ^{13}C NMR (C_6D_6, 30°C): δ 149.7, 142.3, 134.1, 133.2, 128.5, 127.0, 126.3, 123.1 (aromatics), 37.7(C_1), 33.1(C_2), 26.9(C_3), 26.1(C_4).

Preparation of 2,6-*dicyclohexyl*-3,5-*diphenylphenol*

A benzene solution of **2c** (0.63 g, 0.46 mmol in 17 cm^3 of benzene) and Bu^{n}Li (0.064 g, 1.00 mmol) was pressurized with 1200 psi of hydrogen, heated at 60°C for 24 h and then hydrolyzed to yield a mixture of phenols and insoluble niobium compounds. 2,6-Dicyclohexyl-3,5-diphenylphenol was separated using preparative thin layer chromatography with a mixture of hexane/dichloromethane (95% : 5% v/v) as the eluent. HRMS calc. for $C_{30}H_{34}O$: 410.2610; found: 410.2597. ^{13}C NMR (C_6D_6, 30°C): δ 155.2, 143.3, 141.3, 130.3, 129.4, 128.2, 126.9, 125.4 (aromatics), 40.9(C_1), 31.2(C_2), 27.3(C_3), 26.5(C_4). Deuterated

2,6-dicyclohexyl-3,5-diphenylphenol was prepared by pressurizing a benzene solution of **1c** (0.46 g, 0.46 mol in 17 cm^3 of benzene) and Bu^{n}Li (0.096 g, 1.50 mmol) with 935 psi of deuterium gas and heating at 60°C for 48 h. The reaction mixture was hydrolyzed and purified in a similar manner as for the protio compound. 2-Cyclohexyl-3,5,6-triphenylphenol was identified in the reaction mixture by NMR. ^{1}H NMR (C_6D_6, 30°C): δ 5.20(s, O*H*), 3.10(t,t; H_{1a}), 2.60(br q; H_{2a}). ^{13}C NMR (C_6D_6, 30°C): δ 41.4(C_1), 30.4(C_2), 27.5(C_3), 26.6(C_4).

Crystallographic studies

The X-ray diffraction analyses of **1c** and **3a** were carried out in-house at the Purdue Chemistry Department Crystallographic Center. Crystal data and data collection parameters are collected in Table 5.

Acknowledgement—We thank the Department of Energy for financial support of this research.

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