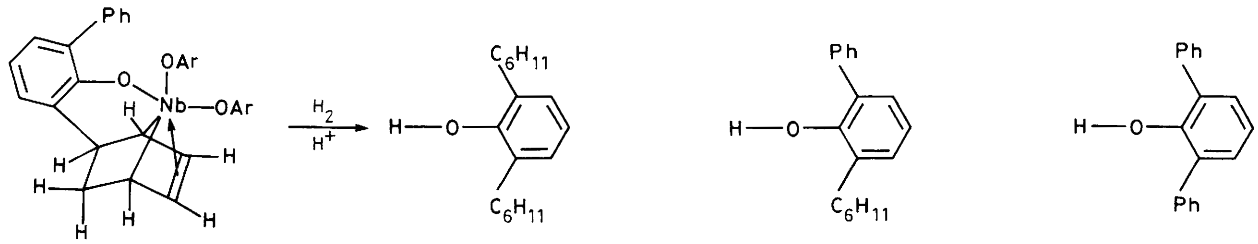
Intramolecular Arene Hydrogenation at Niobium Metal Centres: Stereochemical Consequences

Bryan D. Steffey and Ian P. Rothwell*

Department of Chemistry, Purdue University, West Lafayette, IN 47907, U.S.A.

Selective hydrogenation of 2,6-diphenylphenoxide to 2,6-dicyclohexylphenoxide ligands takes place at niobium(v) metal centres.

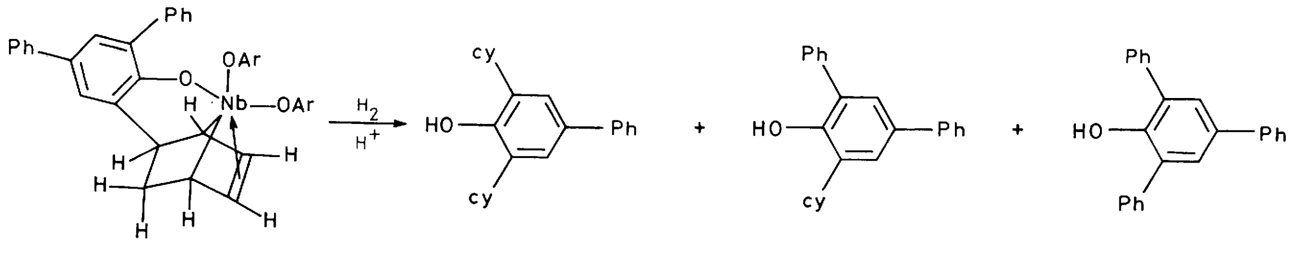
During our studies of the chemistry of low valent early d-block metal compounds supported by aryloxide ancillary ligation[1] we have found that two-electron reduction of $Nb(OC_6H_3Ph_2\text{-}2,6)_3Cl_2$ ($OC_6H_3Ph_2$-2,6 = 2,6-diphenylphenoxide) in the presence of H_2 leads to a cyclohexadiene compound $Nb(OC_6H_3Ph\text{-}\eta^4\text{-}C_6H_7)(OC_6H_3Ph_2\text{-}2,6)_2$ (**1**) (Scheme 1)[2] in high yield. The cyclohexadiene ring is generated by hydride reduction of an arene ring *via* a dihydride intermediate. An interesting feature of (**1**) concerns the fact that the two hydrogen atoms introduced at the 1,2-positions of the ring are mutually *cis*, but on the opposite side of the ring to the chelated niobium metal atom.[2] Further treatment of toluene solutions of (**1**) with H_2 at pressures of 200—1000 psi results in the further hydrogenation of substituent aryl rings.[3—5] Hydrolysis of the final mixtures after various reaction times leads to the isolation of cyclohexylphenols. Total hydrogenation of essentially all the aryloxide ligands to 2,6-dicyclohexylphenol can be achieved after sufficient reaction times (Scheme



(**1**)

T/°C	H_2/psi	Time			
25	1000	6 d	>96%	<2%	<2%
25	800	3 d	13%	31%	55%
80	500	18 h	90%	5.6%	4.5%

Scheme 1



cy = cyclohexyl

Scheme 2

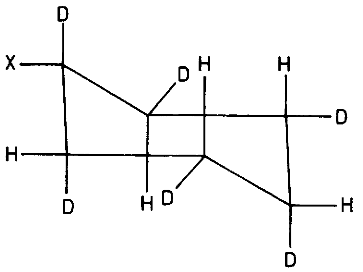


Figure 1

1).† The use of 2,4,6-triphenylphenoxide ligation in the synthesis of (**1**) followed by hydrogenation and hydrolysis leads only to 2,6-dicyclohexyl-4-phenylphenol as the final product (Scheme 2). No evidence for hydrogenation of either the 4-phenyl ring or the central phenoxy ring was obtained. Hence, it appears that hydrogenation is taking place *via* a series of niobium–hydrido intermediates which selectively attack only the phenyl rings *ortho* to the phenoxide oxygen atom.

The isolation and total characterization of (**1**)[2] has an important stereochemical consequence. If initial hydrogenation occurs to produce cyclohexadiene groups chelated to the metal as in (**1**), then the final cyclohexane ring formed by further hydrogenation should not contain all six new hydrogen atoms bound mutually *cis*. Instead the use of D_2 as reagent gas should lead to 2,6-dicyclohexylphenol in which the deuterium atoms are contained in the specific positions shown (Figure 1). The ^1H NMR spectrum of unlabelled 2,6-dicyclohexylphenol in the aliphatic region is consistent with the phenoxide ring (X, Figure 1) preferring an equatorial position, and the proton resonances can be readily assigned as shown on the basis of 1D and 2D ^1H-COSY and $^1H/^{13}C$ HETCOR NMR spectroscopic experiments. The treatment of (**1**) with D_2 (900 psi, 80 °C, 24 h) in toluene solution followed by hydrolysis leads to the formation of cyclohexylphenols but in lower yields than when H_2 was used as the reagent gas. The mass spectrum of the three phenolic products indicates that deuterium is incorporated into all three. In the case of recovered 2,6-diphenylphenol, a maximum of four deuterium atoms were found to be contained in the molecules. Furthermore, ^1H and ^2D NMR spectroscopy showed the label to be incorporated exclusively into the *ortho*-CH bonds of the substituent phenyl rings. This result indicates that during the thermal hydrogenation of (**1**) cyclometallation of the $OC_6H_3Ph_2$-2,6 ligands occurs, presumably being reversed by hydrogenolysis (by H_2 or D_2) of the resulting Nb–C(aryl) bond. The ^1H NMR spectrum of the 2,6-dicyclohexylphenol obtained by treatment of (**1**) with D_2 is shown in Figure 3. It can be seen that the majority of the proton intensity resides specifically in the axial site at the 4-position and the equatorial site at the 3-position. The lack of ^1H in either of the sites at the 2-position can be accounted for by H/D scrambling at these positions in the initial $OC_6H_3Ph_2$-2,6 ligation or after hydrogenation has occurred. The residual hydrogen atoms are located almost exclusively as shown (Figure 3) this provides strong evidence for the intramolecular

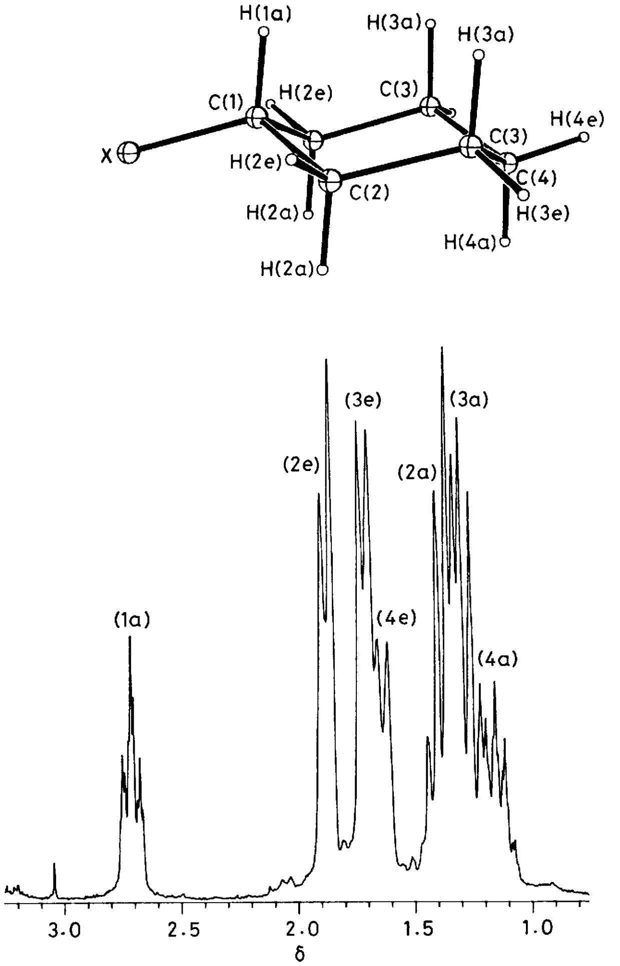


Figure 2. ^1H NMR spectrum (300 MHz, C_6D_6, 30 °C) of 2,6-dicyclohexylphenol obtained by hydrogenation/hydrolysis of (**1**). The aliphatic region of the spectrum is assigned.

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† Separation of the phenolic products was achieved using preparation scale thin layer chromatography with hexane as eluent. High resolution mass spectrum of isolated 2,6-dicyclohexylphenol, calc. 258.1983; found 258.1983.

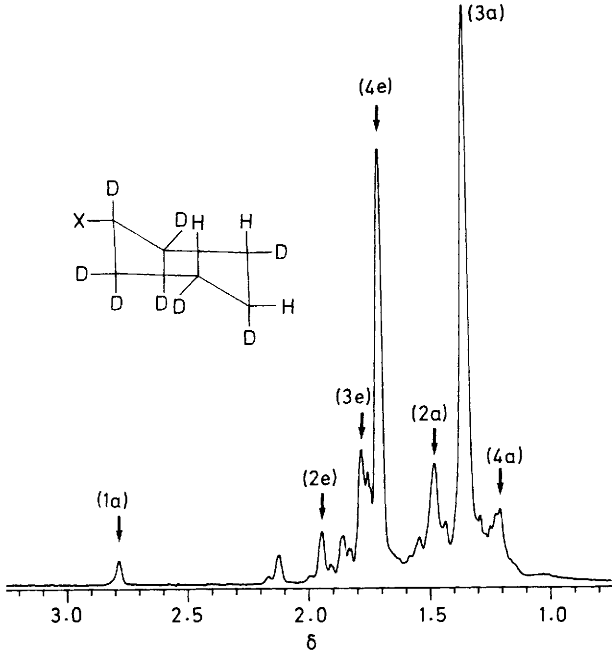

Figure 3. ^1H NMR spectrum (300 MHz, C_6D_6, 30 °C) of 2,6-dicyclohexylphenol obtained by treatment of (**1**) with D_2.

hydrogenation of these aryl rings occurring in a [2 + 4] sequence; *i.e.*, two hydrogen or deuterium atoms on one face, the subsequent other four on the opposite face. Hence, a hydrogenation sequence proceeding *via* chelated cyclohexadiene ligands as contained in (**1**) is strongly implicated. The generation of 2,6-dicyclohexylphenol has also been achieved by hydrogenation of the di-alkyl compound $Nb(OC_6H_3Ph_2\text{-}2,6)_3(Me)_2$,[6] the initial step presumably involving hydrogenolysis of the Nb–Me bonds. Furthermore, treatment of $Ti(OC_6H_3Ph_2\text{-}2,6)_2(Ph)_2$,[6] $Ta(OC_6H_3Ph_2\text{-}2,6)_2(Me)_3$,[6] and $W(OC_6H_3Ph\text{-}\eta^6\text{=}Ph)OC_6H_3Ph_2\text{-}2,6)(dppm)$ [dppm = bis(diphenylphosphino)methane][7] with H_2 (900 psi, 80 °C) leads to 2,6-dicyclohexylphenol after hydrolysis.[8]

We thank the National Science Foundation for support of this research.

Received, 1st September 1989; Com. 9/03732B

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