

Intramolecular Arene Hydrogenation at Niobium Metal Centres: Stereochemical Consequences

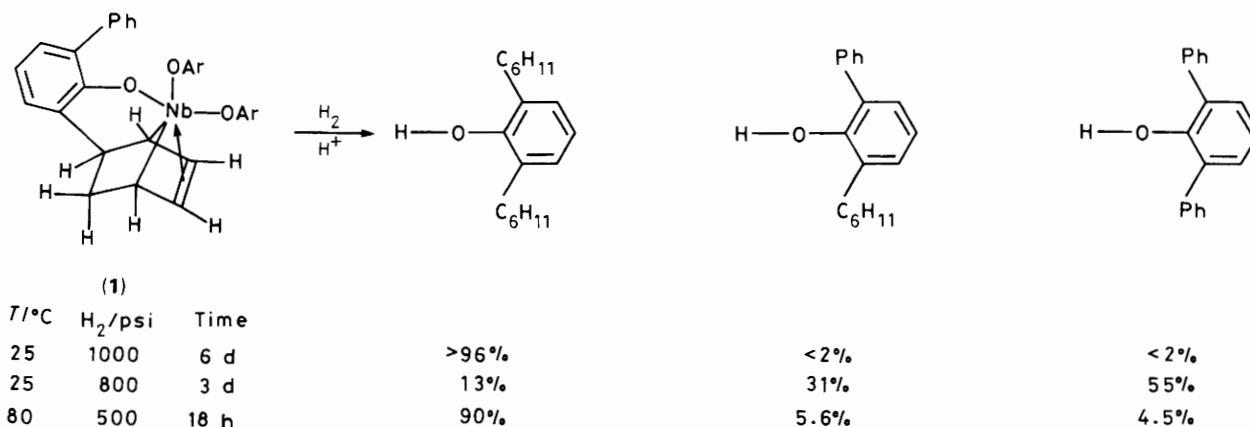
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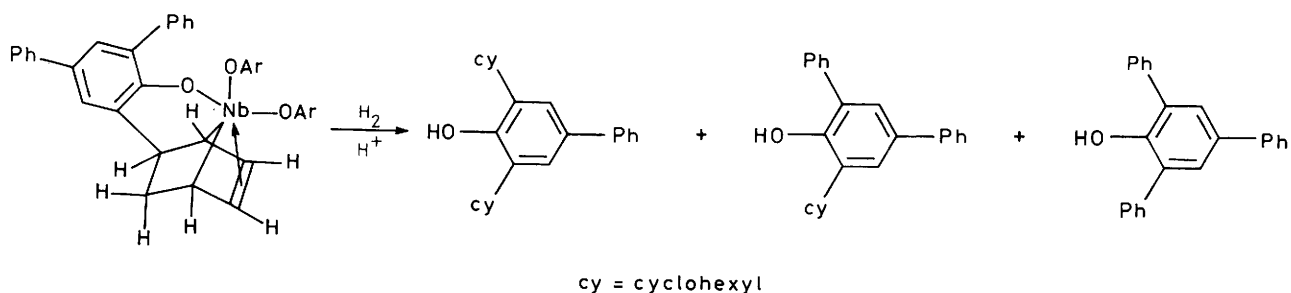
Selective hydrogenation of 2,6-diphenylphenoxide to 2,6-dicyclohexylphenoxide ligands takes place at niobium(v) metal centres.

During our studies of the chemistry of low valent early d-block metal compounds supported by aryloxy ancillary ligation¹ we have found that two-electron reduction of $\text{Nb}(\text{OC}_6\text{H}_3\text{Ph}_2-2,6)_3\text{Cl}_2$ ($\text{OC}_6\text{H}_3\text{Ph}_2-2,6 = 2,6$ -diphenylphenoxide) in the presence of H_2 leads to a cyclohexadiene compound $\text{Nb}(\text{OC}_6\text{H}_3\text{Ph}-\eta^4-\text{C}_6\text{H}_7)(\text{OC}_6\text{H}_3\text{Ph}_2-2,6)_2$ (**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 aryloxy ligands to 2,6-dicyclohexylphenol can be achieved after sufficient reaction times (Scheme



Scheme 1



Scheme 2

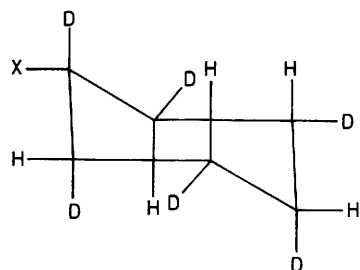
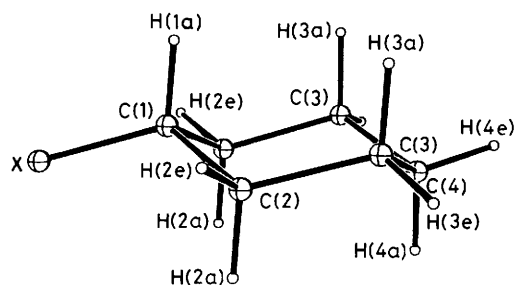


Figure 1



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 D₂ 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/¹³C HETCOR NMR spectroscopic experiments. The treatment of (1) with D₂ (900 psi, 80 °C, 24 h) in toluene solution followed by hydrolysis leads to the formation of cyclohexylphenols but in lower yields than when H₂ 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 OC₆H₃Ph₂-2,6 ligands occurs, presu-

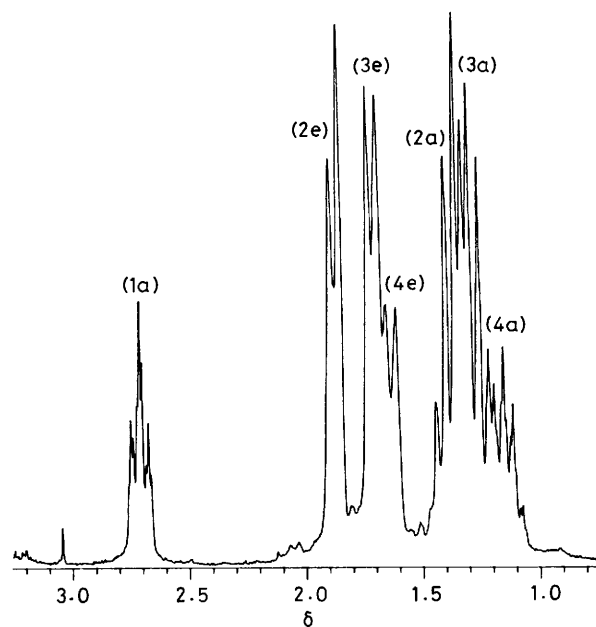


Figure 2. ¹H NMR spectrum (300 MHz, C₆D₆, 30 °C) of 2,6-dicyclohexylphenol obtained by hydrogenation/hydrolysis of (1). The aliphatic region of the spectrum is assigned.

mably being reversed by hydrogenolysis (by H₂ or D₂) of the resulting Nb-C(aryl) bond. The ¹H NMR spectrum of the 2,6-dicyclohexylphenol obtained by treatment of (1) with D₂ 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 OC₆H₃Ph₂-2,6 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

[†] 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.

