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COMMUNICATION

FORMATION AND REACTIVITY OF 1,3-CYCLOHEXADIENE COMPLEXES OF NIOBIUM AND TANTALUM CONTAINING ARYLOXIDE LIGATION: SELECTIVITY DIFFERENCES IN THE HYDROGENATION OF 1,3-CYCLOHEXADIENE†

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Abstract—The sodium amalgam reduction (2 Na per M) of hydrocarbon solutions of $[M(OAr)_3Cl_2]$ (M = Nb, Ta) or $[Nb(OAr)_2Cl_3]_2$ (OAr = 2,6-di-isopropylphenoxide) in the presence of either 1,3- or 1,4-cyclohexadiene yielded the complexes $[M(OAr)_3(\eta^4\text{-}C_6H_8)]$ (**1a**: M = Nb; **1b**: M = Ta) and $[Nb(OAr)_2Cl(\eta^4\text{-}C_6H_8)]$, **2**, respectively. The solid state structures of **1a**, isomorphous **1b** and **2** showed the 1,3-cyclohexadiene strongly bound to the metal. The ligand is not symmetrically bound to the metal in **1** but in **2** there is a crystallographic mirror plane. The solution NMR spectra of **1a** and **1b** show only one set of aryloxide ligand signals and only four proton and three carbon resonances for the C_6H_8 group. The hydrolysis of **1** or **2** yielded 2,6-di-isopropylphenol and one equivalent of cyclohexane (^{1}H NMR). The niobium compounds **1a** and **2** will catalyse the disproportionation and hydrogenation of 1,3-cyclohexadiene with differing selectivity.

Recent work by our group has shown that mixed hydrido, aryloxide derivatives of the Group 5 metals Nb and Ta will catalyse the regio- and stereoselective hydrogenation of a variety of arene substrates.[1,2] As an extension of this work we have attempted to isolate and study the chemistry of organometallic compounds that may be intermediates within the catalytic cycle. We wish to report here the characterization and reactivity of a series of 1,3-cyclohexadiene complexes of these metals.

The sodium amalgam (2 Na per M) reduction of benzene solutions of the di-chlorides $[M(OAr)_3Cl_2]$ (M = Nb, Ta; OAr = 2,6-di-isopropylphenoxide)[3,4] or $[Nb(OAr)_2Cl_3]_2$ in the presence of either 1,3- or 1,4-cyclohexadiene leads to the compounds $[M(OAr)_3(\eta^4\text{-}C_6H_8)]$ (M = Nb, **1a**; Ta, **1b**) and $[Nb(OAr)_2Cl(\eta^4\text{-}C_6H_8)]$, **2** in moderate yield (Scheme 1).‡ The solid state structures of **1a** (Fig. 1), isomorphous **1b** and **2** (Fig. 2) show the 1,3-cyclohexa

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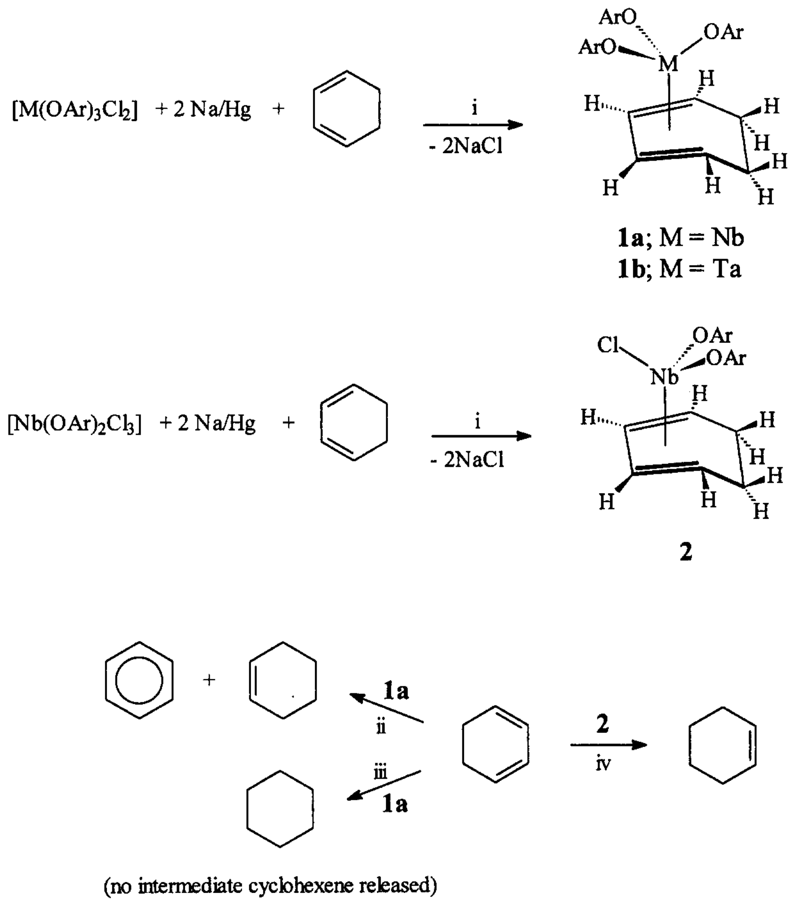
† Dedicated to Professor Malcolm Chisholm on the occasion of his 50th birthday.

‡ *Selected spectroscopic data.* For **1a**: ^{1}H NMR (C_6D_6, 30°C): δ 1.25 (d, CH*Me*$_2$); 3.61 (septet, C*H*Me$_2$); 2.22 (d), 2.51 (d, 8.7 Hz, C*H*$_2$); 3.98 (m, CH$_2$-C*H*); 5.92 (m, CH$_2$CH-C*H*); 6.9–7.2 (m, aromatics). ^{13}C NMR (C_6D_6, 30°C): δ 24.2 (CH*Me*$_2$); 27.6 (*C*HMe$_2$); 30.2 (*C*H$_2$); 92.4 (CH$_2$-*C*H); 122.3 (CH$_2$CH-*C*H); 159.9 (Nb-O-*C*). For **1b**: ^{1}H NMR (C_6D_6, 30°C): δ 1.25 (d, CH*Me*$_2$); 3.65 (septet, C*H*Me$_2$); 2.72 (m, C*H*$_2$); 3.48 (m, CH$_2$-C*H*); 6.28 (m, CH$_2$CH-C*H*); 6.9–7.2 (m, aromatics). ^{13}C NMR (C_6D_6, 30°C): δ 24.3 (CH*Me*$_2$); 27.3 (*C*HMe$_2$); 31.9 (*C*H$_2$); 84.0 (CH$_2$-*C*H); 125.8 (CH$_2$CH-*C*H); 156.8 (Ta-O-*C*). For **2**. ^{1}H NMR (C_6D_6, 30°C): δ 1.25 (d), 1.28 (d, 8.8 Hz, CH*Me*$_2$); 3.60 (septet, C*H*Me$_2$); 2.40 (d), 2.66 (d, C*H*$_2$); 3.87 (m, CH$_2$-C*H*); 5.73 (dd, CH$_2$CH-C*H*); 7.04–7.17 (m, aromatics). ^{13}C NMR (C_6D_6, 30°C): δ 24.2, 24.5 (CH*Me*$_2$); 27.8 (*C*HMe$_2$); 33.0 (*C*H$_2$); 99.1 (CH$_2$-*C*H); 124.9 (CH$_2$CH-*C*H); 159.2 (Nb-O-*C*).



Scheme 1. *Reagents and conditions*: i, metal chloride (1.4 mmol), Na/Hg (4 mmol/5 mL), 1,3-cyclohexadiene (2.8 mmol), hexane (10 mL), 15 h; ii, **1a** (0.085 M in C_6D_6), 1,3-cyclohexadiene (50 per Nb), 110°C, 18 h; iii, **1a** (0.1 mmol), 1,3-cyclohexadiene (5.0 mmol), H_2 (900 psi), C_6H_6 (3 mL), 25°C, 5 h; iv, **2** (0.1 mmol), 1,3-cyclohexadiene (2.5 mmol), H_2 (100 psi), C_6H_6 (3 mL), 25°C, 15 h.

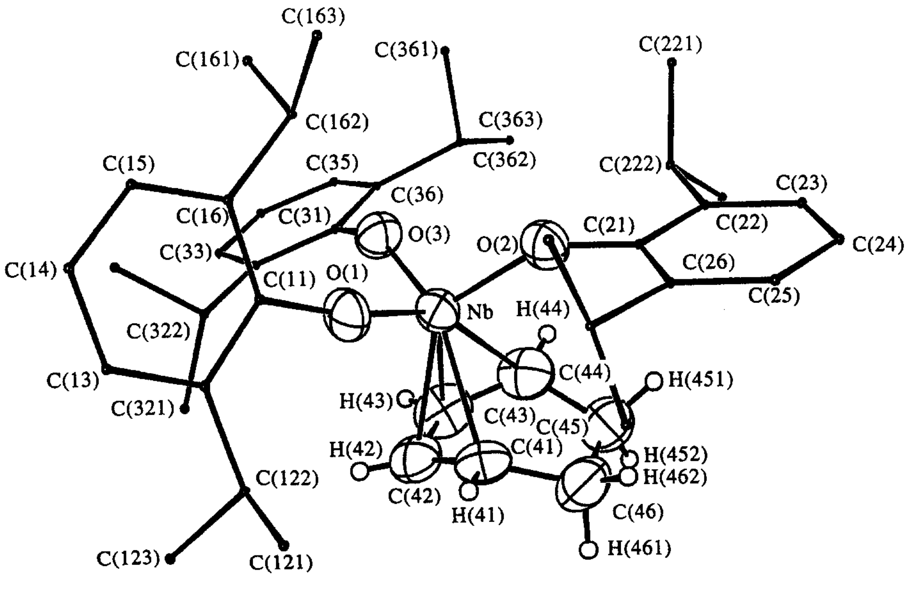


Fig. 1. Molecular structure of **1a**. Selected interatomic distances (Å) and angles (°) for **1a**, isomorphous **1b**: M—O(1) 1.886(6), 1.888(3); M—O(2) 1.906(6), 1.889(3); M—O(3) 1.898(7), 1.902(3); M—C(41) 2.25(1), 2.243(5); M—C(42) 2.27(1), 2.310(5); M—C(43) 2.34(1), 2.366(4); M—C(44) 2.40(1), 2.337(5); C(41)—C(42) 1.42(1), 1.433(7); C(42)—C(43) 1.37(2), 1.375(7); C(43)—C(44) 1.38(2), 1.413(7); M—O(1)—C(11) 162.5(6), 164.8(3); M—O(2)—C(21) 150.8(6), 149.5(3); M—O(3)—C(31) 149.8(6), 150.9(3)

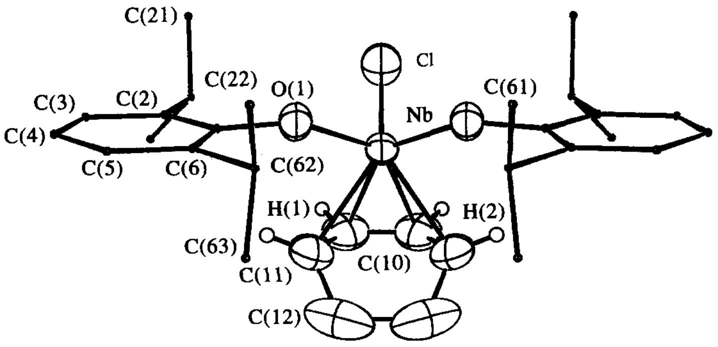


Fig. 2. Molecular structure of **2**. Selected interatomic distance (Å) and angles (°): Nb—Cl 2.367(1), Nb—O(1) 1.897(2), Nb—C(10) 2.344(4), Nb—C(11) 2.326(5), C(10)—C(10)′ 1.37(1), C(10)—C(11) 1.388(7), Nb—O(1)—C(1) 151.9(2).

diene strongly bound to the metal.* The ligand is not symmetrically bound to the metal in **1** (Fig. 1) but in **2** there is a crystallographic mirror plane (Fig. 2). The solution NMR spectra of **1a** and **1b** show only one set of aryloxide ligand signals and only four proton and three carbon resonances for the C_6H_8 group. Hence, rapid rotation of the bound cyclohexadiene about the metal centre must be occurring on the NMR time scale. The hydrolysis of **1** or **2** yields 2,6-di-isopropylphenol and one equivalent of cyclohexene (^{1}H NMR).

Thermolysis of compounds **1** and **2** (110°C, C_6D_6, sealed 5 mm NMR tube) leads to the formation of benzene, cyclohexene and cyclohexane along with unidentified metal products. Solutions of **1a** catalyse the disproportionation of 1,3-cyclohexadiene to cyclohexene and benzene (1 : 1 ratio) with only trace amounts of cyclohexane being formed. A 0.085 M solution of **1a** in C_6D_6 completely disproportionates 50 equivalents of 1,3-cyclohexadiene in 18 h at 110°C, with less than 3% (^{1}H NMR) cyclohexane being formed. In contrast the tantalum compounds **1b** and niobium monochloride **2** will disproportionate <5 equivalents under the same conditions.

Both cyclohexene and 1,3-cyclohexadiene undergo hydrogenation catalysed by **1a** and **2** but with differing selectivities. Hydrogenation (benzene solvent, 900 psi of H_2) of 50 equivalents of cyclohexene or 1,3-cyclohexadiene by **1a** is complete after 5 h at 25°C. Analysis (NMR and GC) of the reaction mixture during hydrogenation of 1,3-cyclohexadiene failed to detect significant amounts of cyclohexene. Carrying out the reaction in C_6D_6 under only 1 atm of H_2 in a 5 mm NMR tube showed the slow conversion of 1,3-cyclohexadiene to cyclohexane with only trace amounts of cyclohexene detected. This result implies that either cyclohexene is not released from the metal during hydrogenation of 1,3-cyclohexadiene by **1a** or else cyclohexene is hydrogenated at a much faster rate than 1,3-cyclohexadiene. This reactivity was further interrogated by carrying out the partial hydrogenation of a 50 : 50 mixture of cyclohexene and 1,3-cyclohexadiene in C_6D_6 solvent by **1a** using D_2 as reagent gas. Analysis of the product mixture by GC/MS after 20% reaction showed that the cyclohexane originated entirely from the 1,3-cyclohexadiene with none of the initial cyclohexene undergoing hydrogenation. The lack of any detectable deuterium incorporation into either the unreacted cyclohexene or 1,3-cyclohexadiene indicates that 1,3-cyclohexadiene is irreversibly hydrogenated to cyclohexane by solutions of **1a** without release of any intermediate cyclohexene.

In contrast, the hydrogenation of 1,3-cyclohexadiene by **2** was found to produce cyclohexene. Only when all of the 1,3-cyclohexadiene was converted

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* *Crystal data.* For **1a** at 20°C: $NbO_3C_{42}H_{59}$. $M = 704.84$, space group $P2_1/c$ (No. 14), $a = 11.562(1)$, $b = 16.117(2)$, $c = 21.914(3)$ Å, $\beta = 103.69(1)°$, $V = 3967(2)$ Å^3, $D_c = 1.180$ g cm^{-3}, $Z = 4$. Of the 5409 unique reflections collected ($4.0° \leqslant 2\theta \leqslant 45.0°$) with Mo-$K_\alpha$ ($\lambda = 0.71073$ Å) the 2161 with $I > 3\sigma(I)$ were used in the final least squares refinement to yield $R = 0.045$ and $R_w = 0.051$. For **1b** at -57°C: $TaO_3C_{42}H_{59}$. $M = 792.88$, space group $P2_1/c$ (No. 14), $a = 11.452(2)$, $b = 16.175(3)$, $c = 21.765(3)$ Å, $\beta = 103.52(1)°$, $V = 3919(2)$ Å^3, $D_c = 1.343$ g cm^{-3}, $Z = 4$. Of the 5324 unique reflections collected ($4.0° \leqslant 2\theta \leqslant 45.0°$) with Mo-$K_\alpha$ ($\lambda = 0.71073$ Å) the 4076 with $I > 3\sigma(I)$ were used in the final least-squares refinement to yield $R = 0.022$ and $R_w = 0.027$. For **2** at 20°C: $NbClO_2C_{30}H_{42}$. $M = 563.03$, space group P_{nma} (No. 62), $a = 12.237(1)$, $b = 21.633(1)$, $c = 10.883(2)$ Å, $V = 2881.0(9)$ Å^3, $D_c = 1.298$ g cm^{-3}, $Z = 4$. Of the 4690 unique reflections collected ($4.0° \leqslant 2\theta \leqslant 60°$) with Mo-$K_\alpha$ ($\lambda = 0.71073$ Å) the 2050 with $I > 3\sigma(I)$ were used in the final least-squares refinement to yield $R = 0.037$ and $R_w = 0.043$.

to cyclohexene was the latter slowly hydrogenated to cyclohexane. This selectivity difference may be attributable to the chemistry of the as yet unisolated intermediate cyclohexene complexes [Nb(OAr)$_3$(η^2-C_6H_{10})] and [Nb(OAr)$_2$Cl(η^2-C_6H_{10})]. The tris-phenoxide complex apparently undergoes hydrogenation at a rate faster than exchange with either free cyclohexene or 1,3-cyclohexadiene, while the mono-chloride complex must undergo substitution by 1,3-cyclohexadiene to regenerate **2** at a rate faster than hydrogenation.

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