Coordination and Hydrogenation of 1,3-Cyclohexadiene by Niobium and Tantalum Aryl Oxide Compounds: Relevance to Catalytic Arene Hydrogenation

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Received November 25, 1996[⊗]

Abstract: The sodium amalgam (2 Na per M) reduction of hydrocarbon solutions of the chloro, aryl oxide compounds $[M(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_3]_2$ (**1**) and $[M(OC_6H_3Pr^i_2\text{-}2,6)_3Cl_2]$ (**2**) (**a**, M = Nb; **b**, M = Ta) in the presence of 1,3-cyclohexadiene leads to formation of the η^4-cyclohexadiene derivatives $[M(OC_6H_3Pr^i_2\text{-}2,6)_2Cl(\eta^4\text{-}C_6H_8)]$ (**3**) and $[M(OC_6H_3Pr^i_2\text{-}2,6)_3(\eta^4\text{-}C_6H_8)]$ (**4**). Spectroscopic studies of compounds **3** and **4** show in all cases a strongly bound cyclohexadiene ligand which does not readily undergo displacement (NMR) with added reagents such as PMe_2Ph and cyclohexene. Single crystal X-ray diffraction analyses of **3a** and the isomorphous pair **4a** and **4b** show in all three cases a geometry about the metal center best described as three-legged piano stool. Compound **4a** will catalyze the disproportionation of 1,3-cyclohexadiene into cyclohexene and benzene as well as the hydrogenation of 1,3-cyclohexadiene and cyclohexene into cyclohexane. Mechanistic studies clearly show that cyclohexene is not released during the conversion of 1,3-cyclohexadiene to cyclohexane catalyzed by **4a**. In contrast, solutions of **3a** will convert 1,3-cyclohexadiene slowly to cyclohexene prior to conversion to cyclohexane. The addition of 1,3-cyclohexadiene to the trihydride compounds $[Ta(OC_6H_3Cy_2\text{-}2,6)_2(H)_3(PMe_2Ph)_2]$ and $[Ta(OC_6HPh_2\text{-}3,5\text{-}Cy_2\text{-}2,6)_2(H)_3(PMe_2Ph)_2]$ leads to the interesting products $[Ta(OC_6H_3Cy_2\text{-}2,6)_2(\eta^1\text{-}C_6H_{10}\text{-}\eta^4\text{-}C_6H_7)]$ (**5**) and $[Ta(OC_6HPh_2\text{-}3,5\text{-}Cy_2\text{-}2,6)_2(\eta^1\text{-}C_6H_{10}\text{-}\eta^4\text{-}C_6H_7)]$ (**6**) which, based upon structural studies of **5** contain a partially hydrogenated non-Diels−Alder dimer of 1,3-cyclohexadiene. The addition of 1,3-cyclohexadiene to the dihydride compounds $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(Cl)(H)_2(PMe_2Ph)_2]$ and $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2(Cl)(H)_2(PMe_2Ph)]$ leads to the dehydrogenation product $[Ta(OC_6H_3\text{-}Pr^i\text{-}\eta^2\text{-}CMe=CH_2)(OC_6H_3Pr^i_2\text{-}2,6)(Cl)(PMe_2Ph)_2]$ (**7**) and the cyclohexyl compound $[Ta(OC_6H_3Bu^t\text{-}CMe_2CH_2)(OC_6H_3\text{-}Bu^t_2\text{-}2,6)(Cl)(C_6H_{11})]$ (**8**), respectively. The mechanistic implications of these stoichiometric and catalytic reactions are discussed. Crystal data for **3a** 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}, $Z = 4$; for **4a** 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}, $Z = 4$; for **4b** 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}, $Z = 4$; for **5** at 20 °C: $TaO_2C_{48}H_{67}$. $M = 857.02$, space group $P2_1$ (no. 4), $a = 10.559(9)$, $b = 15.828(10)$, $c = 13.266(12)$ Å, $V = 2095(6)$ Å^3, $D_c = 1.358$ g cm^{-3}, $Z = 2$.

Introduction

The demonstrated ability of various aryl oxide derivatives of niobium and tantalum to carry out the regio- and stereoselective hydrogenation of aromatic substrates[1,2] raises many mechanistic questions. During the hydrogenation of simple aromatic hydrocarbons[3] as well as aryl-phosphine ligands[4] by catalysts of this type no products containing partially hydrogenated aryl rings have been detected. Furthermore, in a number of cases that have been studied a predominantly all-*cis* stereochemistry has been established for the H(D) atoms introduced to saturate the arene substrate.[1,3a] It is difficult to envisage any reasonable mechanistic pathway for the hydrogenation of a benzene ring that does not proceed via intermediate cyclohexadiene and cyclohexene fragments. The above observations, therefore, strongly imply that metal-bound cyclohexadiene and cyclohexene species should exhibit displacement/dissociation rates slower than subsequent reaction with H$_2$ under the conditions of catalysis. In this paper we report the synthesis and chemistry of a series of new η^4-cyclohexadiene derivatives of niobium and tantalum containing aryl oxide ligation.[5] This

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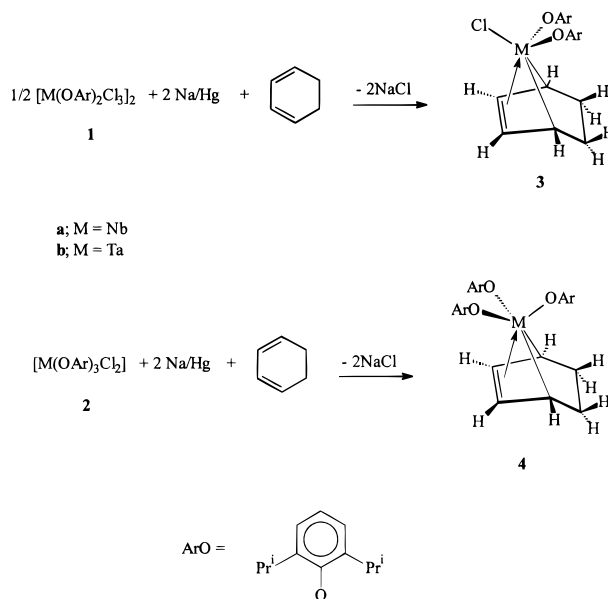
Scheme 1
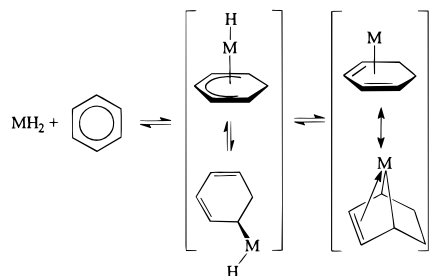
synthetic work is complemented by an investigation of the reactivity of previously isolated tantalum hydride compounds[6] as well as related niobium catalysts toward 1,3-cyclohexadiene and cyclohexene. The studies reported here focus on gaining a better insight into the overall mechanism of arene hydrogenation by this specific pedigree of catalyst.

Results and Discussion

Synthesis and Spectroscopic Characterization. The hydrogenation of an arene substrate can be catalyzed either using discrete tantalum hydride compounds $[Ta(OAr)_{5-x}(H)_x(PR_3)_n]$ ($x = 2, 3$; $n = 1$ or 2)[6] or via the hydrogenolysis of niobium alkyl precursors $[Nb(OAr)_2R_3]$.[1] The tantalum reagents exhibit low reactivity and are inhibited by trace amounts of free phosphine ligand. The niobium compounds require initial hydrogenolysis of the Nb−alkyl bonds, typically slow at temperatures below 80 °C, in order to generate the active catalyst. A recent development has been the use of niobium chloride precursors $[Nb(OAr)_2Cl_3]$ and $[Nb(OAr)_3Cl_2]$ "activated" by addition of Bu^{n}Li in the presence of the arene substrate prior to pressurization with H_2.[4b] This method generates a catalyst active even at ambient temperatures.

The initial attack of a catalyst containing at least two hydride ligands on a benzene ring would be expected to proceed via an intermediate η^1-, η^3-, or potentially η^5-cyclohexadienyl, hydride prior to formation of a cyclohexadiene complex (Scheme 1). We have previously isolated just such a cyclohexadiene complex formed via a stoichiometric intramolecular hydrogenation of one of the *o*-phenyl substituents of a 2,6-diphenylphenoxide ligand attached to niobium.[7] We have, however, yet to detect the intermolecular reaction of isolated hydrido, aryl oxide compounds of tantalum with arene substrates; these molecules exhibit considerable thermal stability, for instance, in benzene solvent. We have found that an alternative synthetic route to cyclohexadiene derivatives of these metals involves reduction of mixed chloro, aryl oxides in the presence of 1,3-cyclohexadiene. Previous work has shown that low valent aryl oxide[8] and related siloxide[9] derivatives of Nb and Ta are highly reactive species able to coordinate and activate a variety of unsaturated substrates. The sodium (2 Na per M) amalgam reduction of benzene solutions of the compounds $[M(OC_6H_3Pr^i_2-2,6)_2Cl_3]_2$ (**1**) and $[M(OC_6H_3Pr^i_2-2,6)_3Cl_2]$ (**2**) (**a**, M = Nb; **b**, M = Ta)[10] in the presence of 1,3-cyclohexadiene leads to formation of the η^4-cyclohexadiene derivatives $[M(OC_6H_3Pr^i_2-2,6)_2Cl(\eta^4-C_6H_8)]$

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Scheme 2

(**3**) and $[M(OC_6H_3Pr^i_2-2,6)_3(\eta^4-C_6H_8)]$ (**4**) (Scheme 2). Although **3b** could be observed in solution by ^{1}H NMR spectroscopy, it was found to convert to mixtures of **4b** and other unidentified products presumably via ligand exchange processes. The other three compounds **3a**, **4a**, and **4b** were found to be stable in C_6D_6 solution for weeks without any noticeable change in their ^{1}H NMR spectra.

The ^{1}H NMR spectra (C_6D_6 solution) of **3** and **4** show well resolved resonances for the aryl oxide and cyclohexadiene ligands (Figure 1). In **3** the lack of a plane of symmetry through the aryl oxide ligands leads to diastereotopic CH*Me*$_2$ doublets. In all cases four separate, equal intensity multiplets can be readily assigned to the nonequivalent protons in the η^4-C_6H_8 ligand. In the ^{13}C NMR spectra the three carbon atoms of this ligand are also easily detected.

We have also investigated the reaction of various tantalum hydride compounds toward 1,3-cyclohexadiene. The colorless trihydride compounds $[Ta(OC_6H_3Cy_2-2,6)_2(H)_3(PMe_2Ph)_2]$ and $[Ta(OC_6HPh_2-3,5-Cy_2-2,6)_2(H)_3(PMe_2Ph)_2]$[6] react slowly over days with 1,3-cyclohexadiene in C_6D_6 solution to produce bright yellow solutions of new organometallic compounds **5** and **6** (Scheme 3). The ^{1}H NMR spectra of these compounds is extremely complicated, containing a large number of multiplets in the δ 1−7 ppm region. A single crystal X-ray analysis of **5** (*vide infra*) shows it to contain, besides two terminal aryl oxide groups, a new ligand derived by coupling and partial reduction of 2 equiv of 1,3-cyclohexadiene. At first sight the exact regio- and stereochemistry adopted by the organic fragment in this molecule appears haphazard. This particular product can, however, be rationalized by consideration of results recently obtained by our group on the extremely rapid regio- and stereoselective dimerization of 1,3-cyclohexadiene catalyzed by titanium aryl oxides (Scheme 4).[11] By analogy with this chemistry we propose dimerization of 1,3-cyclohexadiene occurs at tantalum yielding *threo*-5-(3-cyclohexenyl)-1,3-cyclohexadiene. This occurs by initial loss of H_2 (observed in solution by ^{1}H NMR) yielding a monohydride species. The coupling of 2 equiv of 1,3-cyclohexadiene at the resulting d^2-metal center can produce six isomeric 9-tantalaoctahydrofluorene complexes. The *cis-anti-cis*- and *cis-syn-cis*-3,4,5,6,1a,4a,5a,8a-octahydro derivatives (Scheme 5) have the potential for stabilization via

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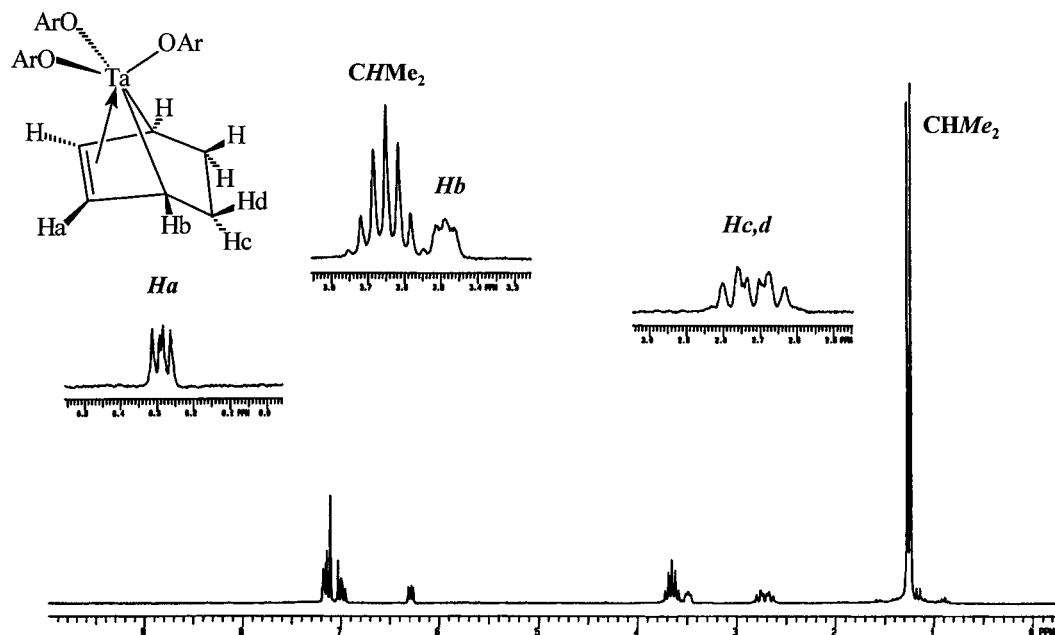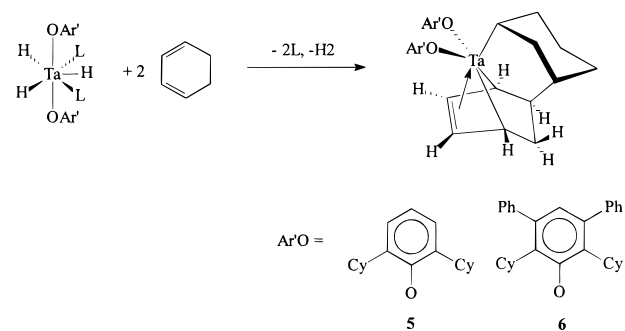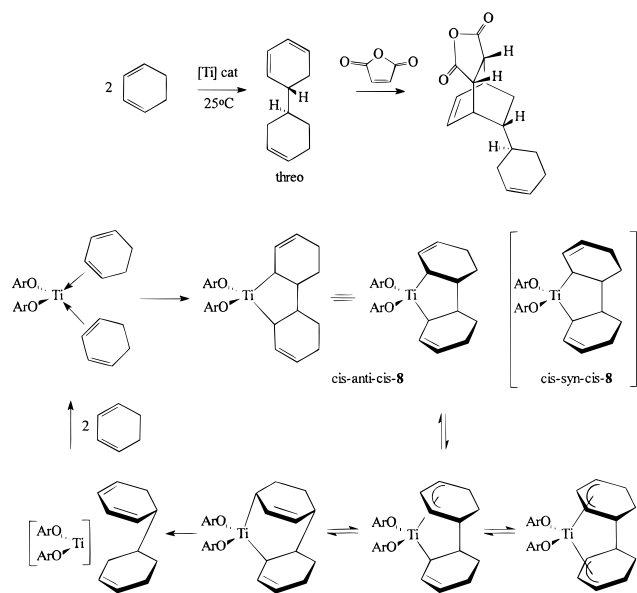
Figure 1. 200 MHz (C_6D_6) ^1H NMR spectrum of [Ta(OC$_6$H$_3$Pr$^i_2$-2,6)$_3$(η^4-C$_6$H$_8$)], **4b**.
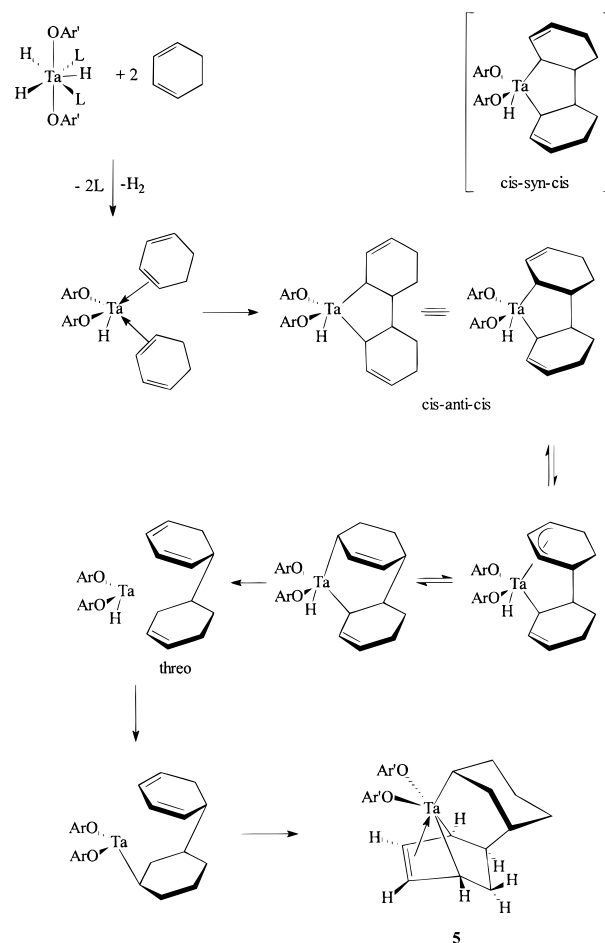
Scheme 3

Scheme 4

Scheme 5

formation of π-allyllic interactions. Direct elimination from either of these intermediates is disallowed as both central β-hydrogens are *trans* to the metal center. The intermediate 5-(3-cyclohexenyl)-1,3-cyclohexadiene can be generated by abstraction of a hydrogen atom from the 4-position of one of the rings. This hydrogen can be made accessible to the metal center via a 1,3-shift. The final product is then obtained by
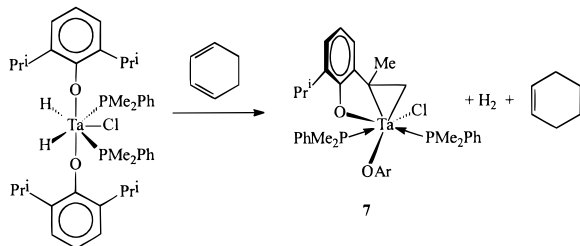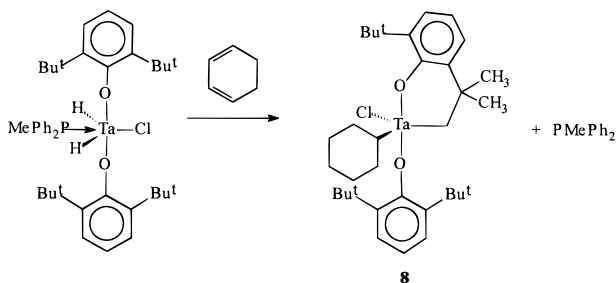
transfer of the remaining hydride ligand to the 3-cyclohexenyl ring (Scheme 5). The regio- and stereochemistry observed in **5** can only arise via the *cis-anti-cis* intermediate, the *cis-syn-cis* producing an erythro stereochemistry.

The stoichiometric reaction of the tantalum dihydride compound [Ta(OC$_6$H$_3$Pr$^i_2$-2,6)$_2$(Cl)(H)$_2$(PMe$_2$Ph)$_2$] with 1,3-cyclohexadiene and cyclohexene is also slow at room temperature and leads to the dehydrogenation product [Ta(OC$_6$H$_3$Pr^i-η^2-

Scheme 6

Scheme 7

Table 1. Selected Spectroscopic Data on the Tantalum-Cyclohexyl Ligand in **8**

	δ (ppm)	coupling constants (Hz)	
H1	1.05 m		
H2e, H2e′	3.07 d, 3.42 d	$2J$(1H2a−1H2e)	12.8
H2a, H2a′	2.05 m, 1.84 m		
H3e, H3e′	1.40−1.50 m		
H3a, H3a′	1.25−1.35 m		
H4e	1.58 m		
H4a	1.20 m		
C1	131.3	$1J$(13C1−1H1)	102.3
C2, C2′	43.0, 41.6	$1J$(13C2−1H2)	124.8, 129.1
C3, C3′	33.2, 32.9	$1J$(13C3−1H3)	*a*
C4	27.3	$1J$(13C4−1H4)	131.8

a Not resolved.

CMe=CH$_2$)(OC$_6$H$_3$Pr$^i_2$-2,6)(Cl)(PMe$_2$Ph)$_2$] (**7**) and cyclohexene or cyclohexane, respectively (Scheme 6). Previous studies have shown that **7** is formed when the seven coordinate dihydride is reacted with styrene.[3d] The dihydride reacts much faster with 1,3-cyclohexadiene than with cyclohexene as monitored by ^{1}H and ^{31}P NMR (*vide infra*).

The reaction of the six-coordinate dihydride [Ta(OC$_6$H$_3$Bu$^t_2$-2,6)$_2$(Cl)(H)$_2$(PMePh$_2$)] with 1,3-cyclohexadiene produces the cyclohexyl compound [Ta(OC$_6$H$_3$Bu^t-CMe$_2$CH$_2$)(OC$_6$H$_3$Bu$^t_2$-2,6)(Cl)(C$_6$H$_{11}$)] (**8**) (Scheme 7). Compound **8** has also been obtained by reacting the trichloride [Ta(OC$_6$H$_3$Bu$^t_2$-2,6)$_2$(Cl)$_3$][12] with either a mixture of [(Bu^n)$_3$SnH]/1,3-cyclohexadiene or [Mg-(c-C$_6$H$_{11}$)]. The ^{1}H and ^{13}C NMR spectra clearly show the presence of the cyclometalated 2,6-di-*tert*-butylphenoxide ligand.[13] Based upon previously isolated cyclometalated compounds we assign a pseudotrigonalbipyramidal structure to **8** with the aryl oxide oxygen atoms mutually *trans*. The solution NMR spectroscopic properties of the cyclohexyl group in **8** are of some interest. The lack of a plane of symmetry leads to six nonequivalent carbon atoms and 11 nonequivalent protons for the Ta-C$_6$H$_{11}$ unit. Using COSY and HETCOR experiments most of these resonances and certain coupling constants could be assigned (Table 1).

The chemical shift for the α-carbon C1 is significantly downfield of the region typical for tantalum alkyl groups. Furthermore, the ^1J(^{13}C1−^{1}H1) coupling of 102.3 Hz is low. We interpret these spectroscopic data as possible indications of an agostic interaction between the α-CH bond and the tantalum metal center.[14]

Solid State Structures. In order to gain a better understanding of the interaction of 1,3-cyclohexadiene ligands with these particular metal systems, the solid state molecular structures of **3a**, the isomorphous pair **4a** and **4b**, and the dimerization product **5** were determined. The molecular structures are shown in Figures 2−4, while selected structural parameters are contained in Tables 2−4. It can be seen that these four compounds adopt structures that can best be described as three-legged piano stools, the legs consisting of two aryl oxides and a chloride (**3a**), three aryl oxides (**4a**, **4b**), or two aryl oxides

Figure 2. Molecular structure of [NbCl(OC$_6$H$_3$Pr$^i_2$-2,6)$_2$(η^4-C$_6$H$_8$)], **3a**.
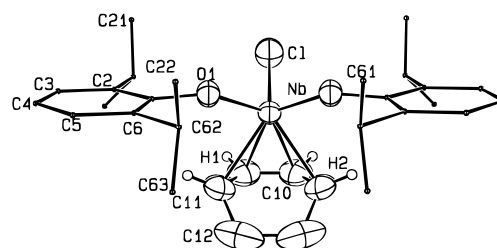
Figure 3. Molecular structure of [Nb(OC$_6$H$_3$Pr$^i_2$-2,6)$_3$(η^4-C$_6$H$_8$)], **4a**. An identical numbering scheme is used for isomorphous [Ta(OC$_6$H$_3$-Pr$^i_2$-2,6)$_3$(η^4-C$_6$H$_8$)], **4b**.

and a chelated alkyl group (**5**). Due to the complexity, a view of the central coordination sphere of **5** is given in Figure 5. A series of molecules [M(η^4-C$_6$H$_8$)(PMe$_3$)$_2$Cl$_2$] (M = Zr, Hf) has been reported by Green et. al.[15] The M-O(aryl oxide) distances in the new compounds lie in the very narrow range of 1.886-(6)−1.916(5) Å. The most interesting structural feature of these molecules concerns the bonding of the cyclohexadiene fragment to the metal center. In Figure 6 the most important features are highlighted. In compound **3a** there is a crystallographically imposed mirror-plane which indicates a totally symmetric interaction of the metal center with both sides of the cyclohexadiene ring (Figure 6). In contrast, in the other three structures there is a pronounced asymmetry to the structural parameters arising from a slightly closer contact of the metal

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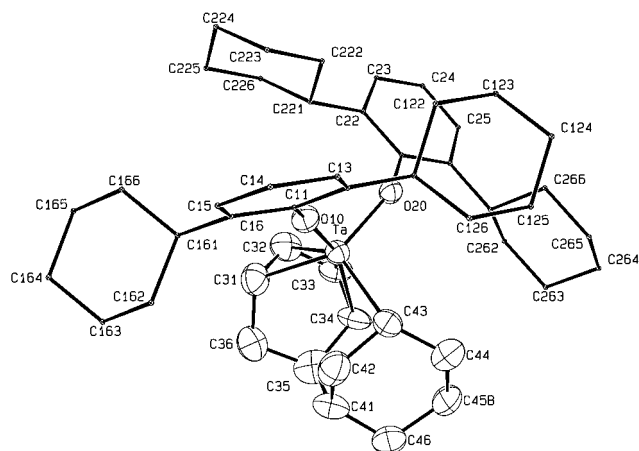**Figure 4.** Molecular structure of $[Ta(OC_6H_3Cy_2\text{-}2,6)_2(\eta^1\text{-}C_6H_{10}\text{-}\eta^4\text{-}C_6H_7)]$, **5**.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[NbCl(OC_6H_3Pr^i_2\text{-}2,6)_2(\eta^4\text{-}C_6H_8)]$, **3a**

Nb−O(1)	1.897(2)	Nb−C(10)	2.344(4)
Nb−Cl	2.367(1)	Nb−C(11)	2.326(5)
C(10)−C(10)′	1.37(1)	C(10)−C(11)	1.388(7)
C(11)−C(12)	1.496(9)	C(12)−C(12)′	1.52(2)
Cl−Nb−O(1)	105.24(8)	C(10)−Nb−C(10)	33.9(2)
Cl−Nb−C(10)	87.4(1)	C(10)−Nb−C(11)	34.6(2)
Cl−Nb−C(11)	115.6(2)	C(10)−Nb−C(11)	59.9(2)
O(1)−Nb−O(1)′	102.3(1)	C(11)−Nb−C(11)	66.8(3)
O(1)−Nb−C(10)	109.2(1)	O(1)−Nb−C(11)	82.2(2)
O(1)−Nb−C(10)	141.6(1)	O(1)−Nb−C(11)	136.3(2)
Nb−O(1)−C(1)	151.9(2)		

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[M(OC_6H_3Pr^i_2\text{-}2,6)_3(\eta^4\text{-}C_6H_8)]$ (M = Nb, **4a**; Ta, **4b**)

	Nb	Ta
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(41)−C(46)	1.50(1)	1.515(7)
C(42)−C(43)	1.37(1)	1.375(7)
C(43)−C(44)	1.38(2)	1.413(7)
C(44)−C(45)	1.50(2)	1.516(7)
C(45)−C(46)	1.52(2)	1.504(8)
O(1)−M−O(2)	103.6(3)	102.9(1)
O(1)−M−O(3)	103.0(3)	100.6(1)
O(2)−M−O(3)	109.9(3)	108.3(1)
O(1)−M−C(41)	91.5(3)	91.7(2)
O(1)−M−C(42)	95.4(4)	95.9(2)
O(1)−M−C(43)	125.6(4)	125.6(1)
O(1)−M−C(44)	155.1(4)	156.2(2)
O(2)−M−C(41)	99.4(3)	103.6(1)
O(2)−M−C(42)	132.7(4)	136.9(1)
O(2)−M−C(43)	125.2(4)	127.7(1)
O(2)−M−C(44)	91.8(4)	92.9(1)
O(3)−M−C(41)	142.8(4)	142.0(1)
O(3)−M−C(42)	107.1(4)	105.8(1)
O(3)−M−C(43)	83.2(4)	82.9(1)
O(3)−M−C(44)	89.6(4)	91.0(2)
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)

center with one of the diene double bonds. This situation is not detected in solution for **4a** and **4b** where the proton multiplicities indicate either a symmetric interaction is present, or else the molecules are fluxional.

Table 4. Selected Bond Distances (Å) and Angles (deg) for $[Ta(OC_6H_3Cy_2\text{-}2,6)_2(\eta^1\text{-}C_6H_{10}\text{-}\eta^4\text{-}C_6H_7)]$, **5**

Ta−O(10)	1.915(6)	C(31)−C(32)	1.44(2)
Ta−O(20)	1.916(5)	C(32)−C(33)	1.40(2)
Ta−C(43)	2.166(10)	C(33)−C(34)	1.40(2)
Ta−C(31)	2.218(10)	C(34)−C(35)	1.53(2)
Ta−C(32)	2.297(11)	C(35)−C(36)	1.56(1)
Ta−C(33)	2.438(10)	C(31)−C(36)	1.55(1)
Ta−C(34)	2.374(10)		
O(10)−Ta−O(20)	98.5(3)	O(20)−Ta−C(33)	84.6(3)
O(10)−Ta−C(43)	108.1(3)	O(20)−Ta−C(34)	101.8(3)
O(10)−Ta−C(31)	98.7(3)	C(43)−Ta−C(31)	115.9(4)
O(10)−Ta−C(32)	120.0(3)	C(43)−Ta−C(32)	135.7(4)
O(10)−Ta−C(33)	153.9(3)	C(43)−Ta−C(33)	110.5(4)
O(10)−Ta−C(34)	159.5(3)	C(43)−Ta−C(34)	77.5(4)
O(20)−Ta−C(43)	108.1(3)	Ta−O(10)−C(11)	160.3(5)
O(20)−Ta−C(31)	131.3(3)	Ta−O(20)−C(21)	141.6(5)
O(20)−Ta−C(32)	95.7(4)		
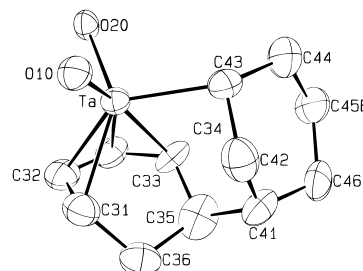
Figure 5. View of the central coordination sphere of $[Ta(OC_6H_3Cy_2\text{-}2,6)_2(\eta^1\text{-}C_6H_{10}\text{-}\eta^4\text{-}C_6H_7)]$, **5**.
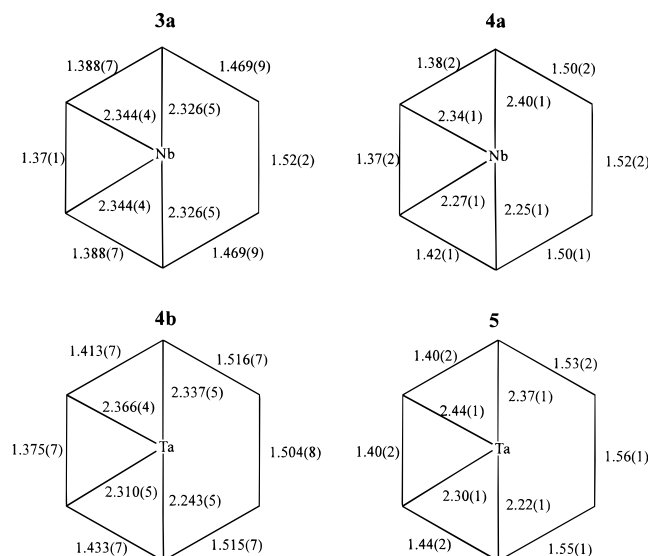
Figure 6. Structural parameters (Å) for the η^4-bound cyclohexadiene ligands in **3a**, **4a**, **4b**, and **5**.

The literature now contains a large number of transition metal compounds containing η^4-bound 1,3-cyclohexadiene to which the compounds obtained in this study can be compared. Directly related are the even larger set of transition metal derivatives of 1,3-butadiene.[16] In these acyclic species there is the potential for formation of η^4-s-*trans*-1,3-diene structures. In the case of the η^4-s-*cis*-1,3-butadiene complexes, Nakamura and Yasuda have carried out an extensive analysis of the determined solid state structures.[16a] They have focused upon three key parameters for discussing the bonding in these molecules. The first is the dihedral angle (θ) subtended by the C1−M−C4 and C1−C2−

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Scheme 8
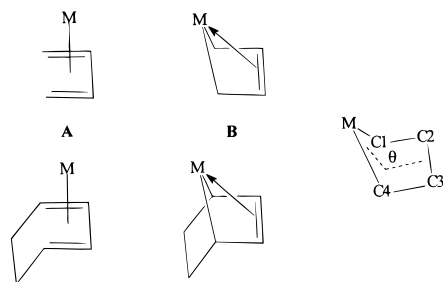
C3−C4 best fit planes. This is also a key parameter in discussing related heteroatom containing five-membered metallacycles, although in these cases the "fold" angle $(180-\theta)$ is normally quoted to highlight distortions from planarity. The other two parameters are differences in metal−carbon and carbon−carbon bond lengths defined as follows:

$$\Delta d = [d(M-C1) + d(M-C4)]/2 -$$
$$[d(M-C2) + d(M-C3)]/2$$

$$\Delta l = [l(C1-C2) + l(C3-C4)]/2 - l(C2-C3)$$

For transition metal derivatives of 1,3-butadiene, there was a distinct trend involving a larger value of θ for early d-block metal complexes compared to later transition metals. This correlated well with values of Δd (the two being geometrically tied) while there was a less pronounced trend involving Δl. These trends were interpreted in terms of two limiting resonance bonding pictures; a "conventional" η^4-s-*cis*-1,3-butadiene structure (**A**) adopted by later transition metals and a $(\sigma^2,\pi$-bonded) metallacyclopent-3-ene structure (**B**) found for the Group 5 and in particular by the Group 4 metals (Scheme 8).[16] By direct analogy we can evaluate the structural parameters for 1,3-cyclohexadiene complexes to asses the importance of η^4-1,3-cyclohexadiene and $(\sigma^2,\pi$-bonded) metallanorbornene bonding pictures (Scheme 8). In Table 5 are collected the values of θ, Δd, and Δl for the compounds obtained in this study and for other derivatives of 1,3-cyclohexadiene contained in the Cambridge Crystallographic Database.[17−43] It can be seen that the new Group 5 metal compounds have the largest values for θ

Table 5. Structural Parameters for 1,3-Cyclohexadiene Complexes

compd	Δd	θ	Δl	ref
3a	−0.018	85.1	0.018	*a*
4a	0.020	83.7	0.030	*a*
4b	−0.048	86.0	0.048	*a*
5	−0.075	89.6	0.020	*a*
[CpCr(η^4-C$_6$H$_8$){P(OMe)$_3$}]	0.113	78.5	−0.003	17
[CpMo(η^4-C$_6$H$_8$)(dppe)][PF$_6$]	0.006	85.6	0.027	18
[(Cp-CH$_2$CH$_2$NMe$_2$)Mo (η^4-C$_6$H$_8$)(CO)][PF$_6$]	0.116	79.0	0.027	19
[W(η^4-C$_6$H$_8$)(CO)$_3$(C$_6$H$_{10}$F$_4$Si$_2$)]	0.145	77.4	−0.093	20
[Mn(η^4-C$_6$H$_8$)$_2$(CO)]	0.083	80.0	0.011	21
	0.080	80.3	−0.036	
[Re(η^4-C$_6$H$_8$)(η^6-C$_6$H$_6$)(H)]	0.032	81.6	0.026	22
[Re(η^4-C$_6$H$_8$)(H)$_3$(PPh$_3$)]	0.153	81.4	0.002	23
[Fe(η^4-C$_6$H$_8$)$_2$(CO)]	0.083	80.4	−0.008	24
	0.088	80.0	−0.044	
[Fe(η^4-C$_6$H$_8$)(CO)$_3$]	0.071	80.1	0.017	25
[Fe(η^4-C$_6$H$_8$)(CO)$_2$(PPh$_3$)]	0.052	81.1	−0.008	26
[Fe(η^4-C$_6$H$_8$)(CO)$_2${P(*o*-tol)$_3$}]	0.085	80.0	0.011	27
[Fe(η^4-C$_6$H$_8$)(CO)$_2$(CNEt)]	0.033	81.1	−0.028	28
[Fe(η^4-C$_6$H$_8$)(CO)$_2${C(OEt)(*o*-tol)}]	0.165	75.9	0.102	29
[Fe(η^4-C$_6$H$_8$)(CO)$_2$(C$_6$H$_{10}$F$_4$Si$_2$)]	0.159	74.5	−0.053	30
[Fe$_2$(η^4-C$_6$H$_8$)(PHPh)$_2$(CO)$_4$]	0.111	78.6	0.027	31
[FeRe(η^4-C$_6$H$_8$)(η^4-C$_7$H$_9$)(CO)$_6$]	0.073	80.9	0.004	32
[Fe$_3$(η^4-C$_6$H$_8$)(NPη)(CO)$_8$]	0.095	79.4	−0.003	33
[Fe$_3$(η^4-C$_6$H$_8$)(S)(CO)$_8$]	0.077	79.5	0.006	34
[Ru(η^4-C$_6$H$_8$)(acac)$_2$]	0.114	79.5	−0.047	35
	0.111	80.3	−0.036	
[CpRu(η^4-C$_6$H$_8$)(CO)][BF$_4$]	0.124	79.7	−0.032	36
[Ru$_3$(CO)8(η^4-C$_6$H$_8$)(H)$_2$(COMe)]	0.042	82.2	−0.007	37
[Ru$_4$(η^4-C$_6$H$_8$)(cyclophane)(CO)$_9$]	0.070	81.1	−0.017	38
[Ru$_5$(η^4-C$_6$H$_8$)$_2$(C)(CO)$_{11}$]	0.059	81.4	0.002	39
[Os$_3$(η^4-C$_6$H$_8$)(CO)$_{10}$]	0.049	80.5	0.050	40
[Os$_4$(η^4-C$_6$H$_8$)(η^6-C$_6$H$_6$)(H)$_4$(CO)$_{10}$]	0.006	83.2	−0.089	41
	0.059	81.0	0.046	
[Co$_2$(η^4-C$_6$H$_8$)$_2$(CO)$_4$]	0.086	81.0	−0.028	42
[Ir(η^4-C$_6$H$_8$)$_2$(2-furyl)]	0.038	82.3	−0.014	43

a This study.

(most negative value of Δd Figure 7) implying that these molecules may best be represented by the $(\sigma^2, \pi$-bonded) metallanorbornene bonding model (**B**). A study of related Group 5 metal η^6-arene complexes has identified a metallanorbonadiene bonding description as reasonable.[44]

Reactivity Studies. Solutions of the η^4-1,3-cyclohexadiene complexes **3a**, **4a**, and **4b** in C$_6$D$_6$ solvent are stable for weeks at ambient temperatures when monitored by ^{1}H NMR. As discussed above, **3b** slowly is converted to **4b**. When these solutions are heated at 110 °C, thermal decomposition occurs to produce benzene, cyclohexene, and cyclohexane (typically a 50:40:10 mixture by ^{1}H NMR and GC) along with unidentified

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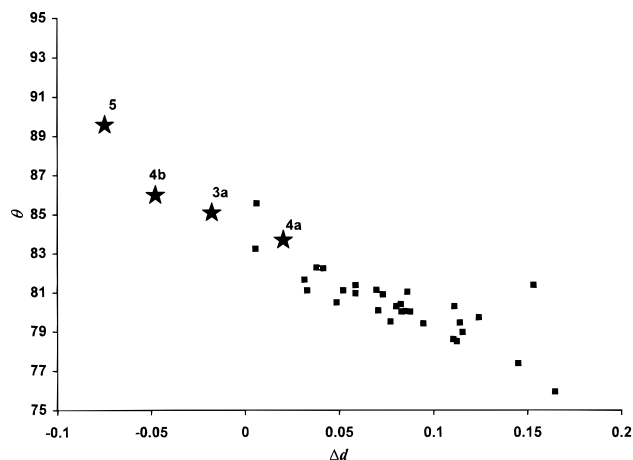(44) Wexler, P. A.; Wigley, D. E.; Koerner J. B.; Albright, T. A. *Organometallics* **1991**, *10*, 2319.

Figure 7. A plot of θ vs Δd for the η^4-cyclohexadiene metal compounds contained in Table 5.
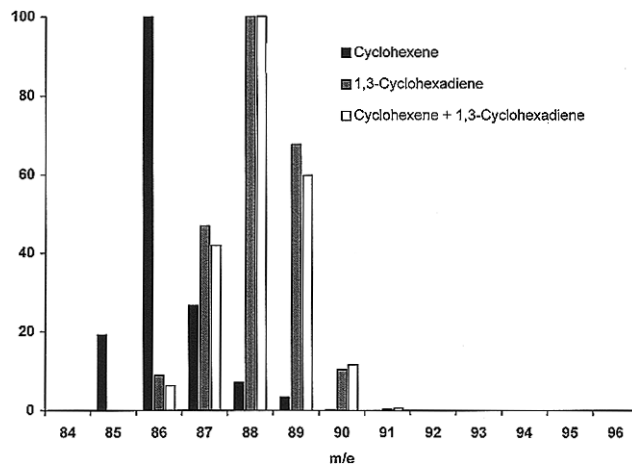

Figure 8. Parent molecular ions of cyclohexane produced from the reaction of cyclohexene, 1,3-cyclohexadiene, and a mixture of cyclohexene and 1,3-cyclohexadiene with D_2 catalyzed by **4a** (see Table 6).

metal products. The niobium monochloride **3a** and the tantalum compound **4b** appear to be thermally more robust than **4a**. Solutions of **4a** catalyze the disproportionation of 1,3-cyclohexadiene into benzene and cyclohexene.[45] When a 0.085 M solution of **4a** in C_6D_6 in the presence of 50 equiv of 1,3-cyclohexadiene is heated at 110 °C and monitored by ^{1}H NMR complete conversion to a 50:50 mixture of benzene and cyclohexene occurs over 18 h with less than 3% cyclohexane being produced.
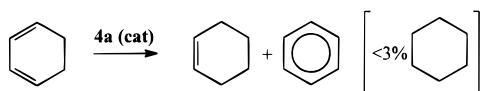
The 1,3-cyclohexadiene complex **4a** will catalyze the hydrogenation of cyclohexene and 1,3-cyclohexadiene under conditions (ambient temperatures and H_2 pressures of 15−1000 psi) which are mild compared to those required for benzene hydrogenation. At pressures of 900 psi of H_2, **4a** will hydrogenate 50 equiv of cyclohexene or 1,3-cyclohexadiene in less than 5 h at 25 °C. When a mixture of **4a** and 1,3-cyclohexadiene in C_6D_6 is exposed to 1 atm of H_2 in a sealed 5 mm NMR tube, slow conversion to cyclohexane is observed with no detection by ^{1}H NMR of cyclohexene.

We have further probed this hydrogenation reactivity utilizing D_2 as reagent gas. The reaction of 25 equiv of cyclohexene or 25 equiv of 1,3-cyclohexadiene in C_6D_6 solvent with D_2 (900 psi) catalyzed by **4a** produced cyclohexane which was analyzed by mass spectrometry (Figure 8). Correcting for the ^{13}C natural abundance gives the distribution of isotopologs (Table 6).

It can be seen that the major products are cyclohexane-d_2 and cyclohexane-d_4, respectively. There are, however, molecules in both samples that are enriched in D-label as well as molecules that contain lower amounts of deuterium. The incorporation of excess deuterium can be rationalized in terms of scrambling processes (*vide infra*). The source of the hydrogen atoms for formation of molecules such as $C_6H_{11}D$ from C_6H_{10} and $C_6H_9D_3$ from C_6H_8 appears to be the aryl oxide ligands. Related work has shown that during the hydrogenation of arene substrates with D_2 gas, incorporation of deuterium label into the Pr^i substituents of 2,6-diisopropylphenoxide ligands occurs.[7] We have also shown that low valent niobium derivatives of this ligand can undergo facile dehydrogenation of an

o-isopropyl substituent to generate chelated η^2-vinyl groups.[46] Furthermore, the stoichiometric reaction of the tantalum dihydride compound $[Ta(OC_6H_3Pr^i_2-2,6)_2(Cl)(H)_2(PMe_2Ph)_2]$ with 1,3-cyclohexadiene and cyclohexene leads to the dehydrogenation product $[Ta(OC_6H_3Pr^i-\eta^2-CMe{=}CH_2)(OC_6H_3Pr^i_2-2,6)(Cl)(PMe_2Ph)_2]$ (**7**)[3d] and cyclohexene or cyclohexane, respectively. The formation of cyclohexyl compound **8** (Scheme 7) presumably arises via initial formation of a cyclohexene intermediate which then undergoes intramolecular CH bond activation. It is hence possible that cyclometalation processes can lead to simultaneous incorporation of excess H into the product cyclohexane and incorporation of D label into the aryl oxide ligands (e.g., the process outlined in Scheme 9). When a mixture of 25 equiv each of cyclohexene and 1,3-cyclohexadiene is partially hydrogenated in C_6D_6 using D_2 and catalyst **4a**, the mass spectrum of the product cyclohexane has essentially the same isotopic distribution as that obtained in the absence of cyclohexene (Figure 8, Table 6). This experiment is of particular mechanistic significance. We can conclude that this catalyst preferentially hydrogenates 1,3-cyclohexadiene over cyclohexene. During the course of hydrogenation of 1,3-cyclohexadiene no intermediate cyclohexene is released by catalyst precursor **4a**.

The niobium monochloride species $[Nb(OC_6H_3Pr^i_2-2,6)_2Cl-(\eta^4-C_6H_8)]$ (**3a**) will also catalyze the hydrogenation of cyclohexene and 1,3-cyclohexadiene. In this case the reactivity at 25 °C is much lower than that of **4a**. Furthermore, the reaction with 1,3-cyclohexadiene is found to proceed entirely via intermediate cyclohexene. Only upon exhaustion of all 1,3-cyclohexadiene is cyclohexene converted by **3a** to cyclohexane. Hence, in this case intermediate cyclohexene is released into solution by the catalyst and does not compete with 1,3-cyclohexadiene as a substrate.

The preferential hydrogenation of 1,3-cyclohexadiene over cyclohexene is also observed in the stoichiometric reactivity of $[Ta(OC_6H_3Pr^i_2-2,6)_2(Cl)(H)_2(PMe_2Ph)_2]$. This compound reacts with an excess of an equimolar mixture of cyclohexene and 1,3-cyclohexadiene to produce compound **7** along with only trace amounts of cyclohexane. When the labeled compound $[Ta(OC_6H_3Pr^i_2-2,6)_2(Cl)(D)_2(PMe_2Ph)_2]$ is reacted with 1,3-cyclohexadiene under mild conditions in C_6H_6 solvent, the ^{2}H NMR spectrum of the reaction mixture shows deuterium present in equal amounts in both methylene groups of cyclohexene. This is consistent with the reaction occurring by preferential 1,2-

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Coordination/Hydrogenation of 1,3-Cyclohexadiene

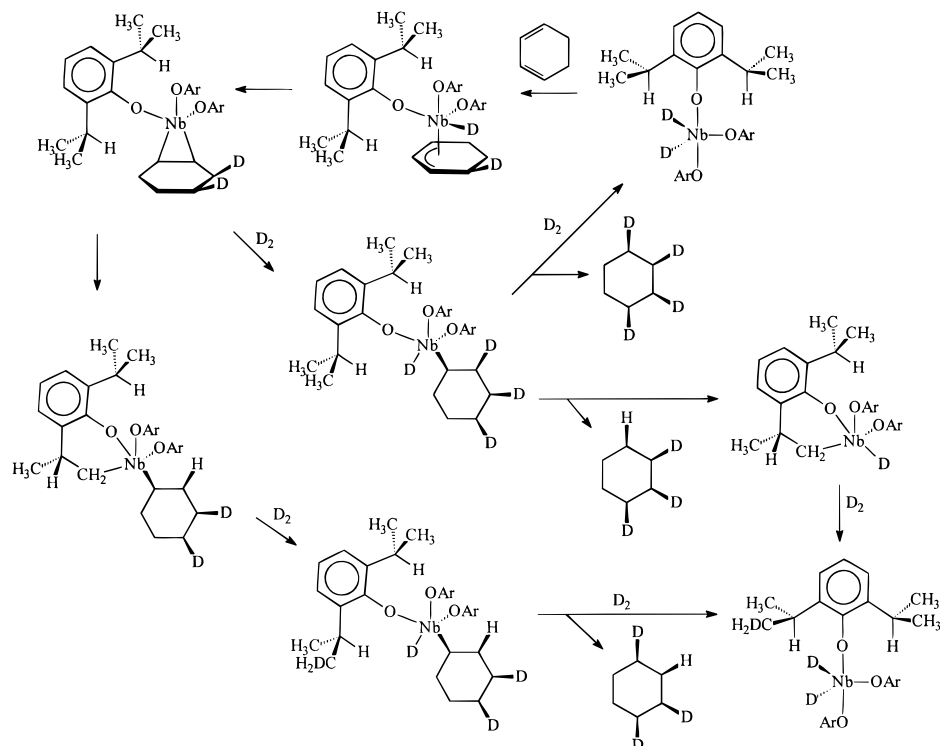*J. Am. Chem. Soc., Vol. 119, No. 15, 1997* 3497

Scheme 9

Table 6. Product Distribution from the Reaction of Cyclohexene, 1,3-Cyclohexadiene, and a Mixture of Cyclohexene and 1,3-Cyclohexadiene with D_2 Catalyzed by **4a**[a]
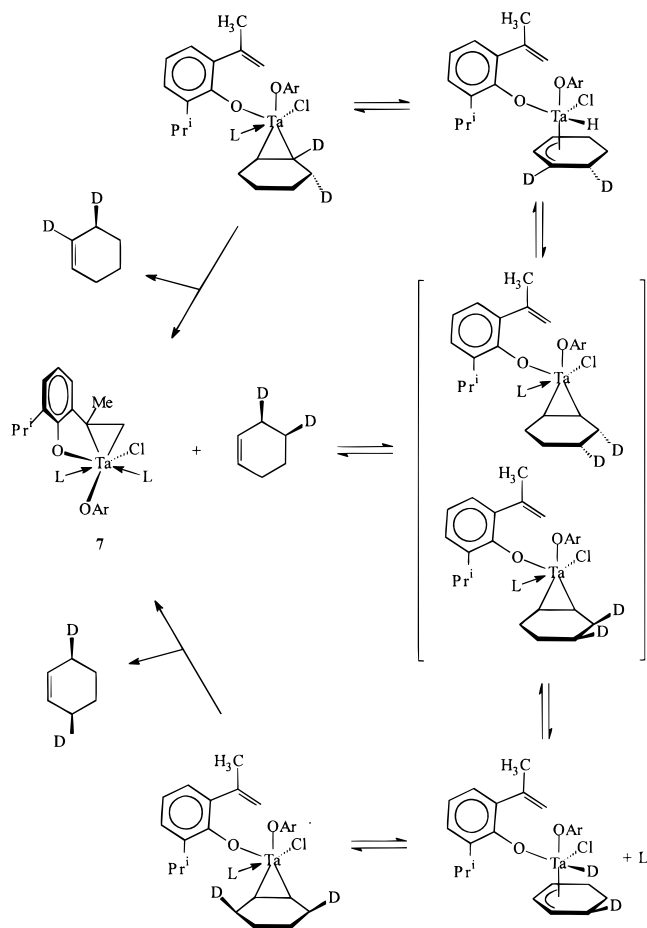
product cyclohexane	substrates		
	C_6H_{10},[b] %	C_6H_8,[b] %	$[C_6H_8 + C_6H_{10}]$,[c] %
C_6H_{12}	0	0	0
$C_6H_{11}D$	13	0	0
$C_6H_{10}D_2$	67	4	3
$C_6H_9D_3$	14	21	20
$C_6H_8D_4$	4	44	47
$C_6H_7D_5$	2	28	26
$C_6H_6D_6$	0	3	4
$C_6H_5D_7$	0	0	0

[a] **4a**, 0.085 mmol; substrate(s), 2.25 mmol (25 per Nb); C_6D_6, 0.8 mL; D_2, 900 psi; 25 °C. [b] 24 h, 100% conversion. [c] 5 h, 20% conversion.

hydrogenation. Interestingly, when this reaction mixture is heated further, scrambling of the deuterium label occurs to produce a statistical distribution over all three sites within the cyclohexene molecule (^{2}H NMR). We propose that this scrambling process is being catalyzed by the organometallic product **7**. Low valent early d-block metal compounds can catalyze olefin isomerization via the formation of allyl, hydride intermediates.[47,48] Applying this process to cyclohexene-3,4-D_2 can account for the statistical distribution of D over the molecule (Scheme 10). It should also be pointed out that this process will ultimately lead to the loss of any stereochemistry of the labels within the product cyclohexene.

Mechanistic Discussion. The above results can be accommodated into an overall reaction scheme for the hydrogenation of benzene, 1,3-cyclohexadiene, and cyclohexene by a metal dihydride species (Scheme 11). The η^4-cyclohexadiene species formed by transfer of the two hydrides to benzene has been shown in this study to be a robust species which reacts readily with hydrogen. The disproportionation of 1,3-cyclohexadiene

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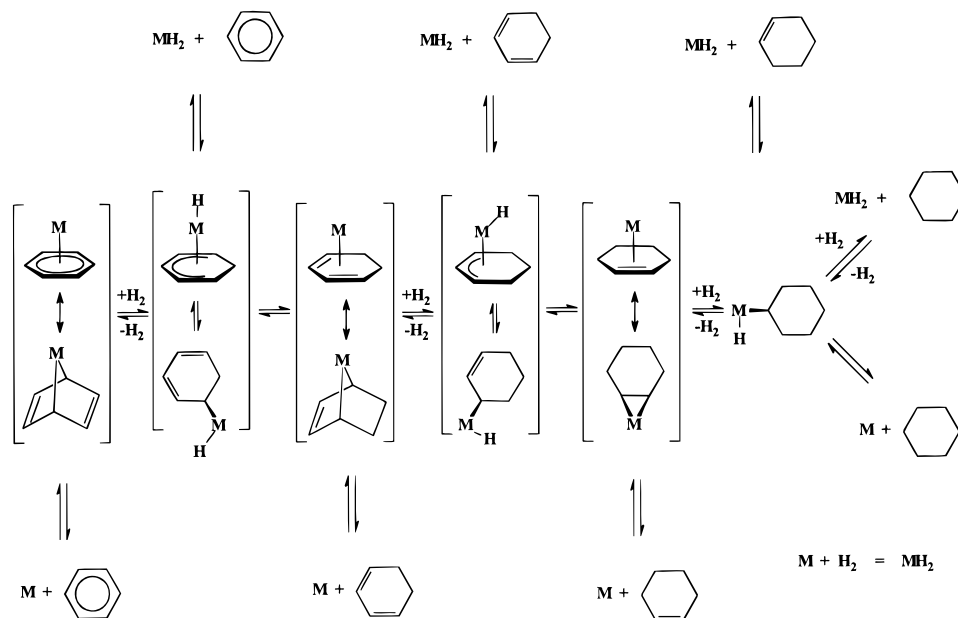
Scheme 10

catalyzed by **4a** cleanly produces cyclohexene and benzene. A reasonable pathway for this disproportionation reaction involves initial loss of benzene and formation of a dihydride which attacks 1,3-cyclohexadiene to produce a cyclohexene complex.

Scheme 11

Displacement by 1,3-cyclohexadiene regenerates **4a**. In the case of the hydrogenation of 1,3-cyclohexadiene by **3a** and **4a** some of the elementary steps are identical to those in the disproportionation sequence. The differing selectivities observed for catalysts **3a** and **4a** can be ascribed to the reactivity of the cyclohexene intermediate $[Nb(OC_6H_3Pr^i_2-2,6)_2(X)(\eta^2-C_6H_{10})]$. In the case of X = $OC_6H_3Pr^i_2-2,6$ (catalyst **4a**) the intermediate undergoes reaction with H_2 faster than displacement by 1,3-cyclohexadiene and vice versa for X = Cl (catalyst **3a**). A cohesive picture of a much faster reaction of metal-hydride species with 1,3-cyclohexadiene over cyclohexene is also present. Toward the end of the disproportionation reaction there are many more equivalents of cyclohexene in solution than 1,3-cyclohexadiene. Despite this only traces of cyclohexane are produced, indicating that the intermediate dihydride selectively attacks the 1,3-cyclohexadiene. The labeling experiments involving **4a** as hydrogenation catalyst (Table 6) as well as the reactivity of tantalum dihydrides with cyclohexene and 1,3-cyclohexadiene echo this hypothesis.

Conclusions

Stable η^4-cyclohexadiene complexes of niobium and tantalum containing ancillary aryl oxide ligation have been isolated. Studies show that the cyclohexadiene molecule is strongly bound to the metal center with structural parameters consistent with a metallanorbornene bonding description. The molecule [Nb-$(OC_6H_3Pr^i_2-2,6)_3(\eta^4-C_6H_8)]$ (**4a**) catalyzes the disproportionation of 1,3-cyclohexadiene into a mixture of cyclohexene and benzene. Compound **4a** also hydrogenates 1,3-cyclohexadiene selectively over cyclohexene to produce cyclohexane with no intermediate cyclohexene being released. The much higher reactivity of isolated tantalum hydride compounds towards 1,3-cyclohexadiene compared to cyclohexene indicates the possible origin of this selectivity.

Experimental Section

All operations were carried out under a dry nitrogen atmosphere or *in vacuo* either in a Vacuum Atmosphere Dri-Lab or by standard Schlenk techniques. Hydrocarbon solvents were dried by distillation from sodium/benzophenone and stored under dry nitrogen. 1,3-Cyclohexadiene was purchased from Aldrich Chemical Co. and was dried over 3Å molecular sieves prior to use. The compounds

$[M(OC_6H_3Pr^i_2-2,6)_3Cl_2]$ (**1**), $[M(OC_6H_3Pr^i_2-2,6)_2Cl_3]_2$ (**2**) (**a**, M = Nb; **b**, M = Ta), $[Ta(OC_6H_3Cy_2-2,6)_2(H)_3(PMe_2Ph)_2]$, $[Ta(OC_6HPh_2-3,5-Cy_2-2,6)_2(H)_3(PMe_2Ph)_2]$, and $[Ta(OC_6H_3Bu^t-2,6)_2(Cl)(H)_2(PMe_2Ph)]$ were prepared by reported procedures.[6,10] The spectroscopic data on $[Ta(OC_6H_3Pr^i-\eta^2-CMe=CH_2)(OC_6H_3Pr^i_2-2,6)(Cl)(PMe_2Ph)_2]$ (**7**) has been reported.[3d] The ^1H and ^{13}C NMR spectra were recorded on a Varian Associates Gemini 200 and a General Electric QE-300 spectrometer and were referenced using protio impurities of commercial benzene-d_6 as an internal standard. The ^2H NMR spectra were recorded on a Varian VXR500 spectrometer. Microanalytical data was obtained in-house at Purdue. All high pressure reactions were performed in a Parr Model 4561, 300 mL internal volume minireactor.

$[Nb(OC_6H_3Pr^i_2-2,6)_2Cl(\eta^4-C_6H_8)]$ (3a). To a sodium amalgam (0.18 g Na/5 mL Hg) was added $[Nb(OC_6H_3Pr^i_2-2,6)_2Cl_3]_2$ (**1a**) (2.0 g, 3.6 mmol) dissolved in hexane (25 mL) and 1,3-cyclohexadiene (0.58 g, 7.2 mmol) was then added to the system. The mixture was stirred vigorously for 20 h resulting in the formation of a dark red suspension. The red solution was filtered from the mixture and dried *in vacuo*. The crude product was dissolved in pentane, and slow cooling of the solution gave **3a** as red crystals. Yield 1.50 g (74%). Anal. Calcd for $NbClO_2C_{30}H_{42}$: C, 64.00; H, 7.52; Cl, 6.30. Found: C, 63.44; H, 7.51; Cl, 6.55. ^1H NMR (C_6D_6, 30 °C): δ 7.04−7.17 (m, 6H, aromatics); 5.73 (m, 2H, CH_2CH-C*H*); 3.87 (m, 2H, CH_2-C*H*); 2.66 (d, 2H), 2.40 (d, 2H, C*H$_2$*) ^2J (^1H−^1H) = 9.2 Hz; 3.60 (septet, 4H, C*H*Me$_2$); 1.28 (d, 12H, CH*Me$_2$*); 1.25 (d, 12H, CH*Me$_2$*). ^{13}C NMR (C_6D_6, 30 °C): δ 159.2 (Nb-O-*C*); 124.9 (CH_2CH-*C*H); 99.1 (CH_2-*C*H); 33.0 (*C*H$_2$); 27.8 (*C*HMe$_2$); 24.5, 24.2 (CH*Me$_2$*); 119.2−123.9 (aromatics).

$[Ta(OC_6H_3Pr^i_2-2,6)_2Cl(\eta^4-C_6H_8)]$ (3b). To a sodium amalgam (0.15 g Na/5 mL Hg) was added $[Ta(OC_6H_3Pr^i_2-2,6)_2Cl_3]_2$ (**1b**) (2.0 g, 3.1 mmol) in benzene (25 mL), and 1,3-cyclohexadiene (1.25 g, 15.5 mmol) was then added to the system. The mixture was stirred vigorously for 20 h resulting in the formation of a dark orange suspension. The orange solution was filtered from the mixture and dried *in vacuo*. Analysis of the crude product by NMR showed the presence of **3b** contaminated with **4b**. Over time the **3b** present was converted to **4b** and another unidentified tantalum component. ^1H NMR (C_6D_6, 30 °C): δ 6.90−7.12 (m, 6H, aromatics); 6.31 (m, 2H, CH_2CH-C*H*); 3.33 (m, 2H, CH_2-C*H*); 2.91 (d, 2H), 2.65 (d, 2H, C*H$_2$*) ^2J(^1H−^1H) = 7.8 Hz; 3.61 (septet, 4H, C*H*Me$_2$); 1.26 (d, 12H, CH*Me$_2$*); 1.23 (d, 12H, CH*Me$_2$*).

$[Nb(OC_6H_3Pr^i_2-2,6)_3(\eta^4-C_6H_8)]$ (4a). To a sodium amalgam (0.1 g Na/5 mL Hg) was added $[Nb(OC_6H_3Pr^i_2-2,6)_3Cl_2]$ (**2a**) (1 g, 1.4 mmol) in hexane (10 mL) and 1,3-cyclohexadiene (0.23 g, 2.8 mmol) was then added to the system. The mixture was stirred vigorously for 15 h resulting in the formation of a dark red suspension. The red solution was filtered from the mixture and dried *in vacuo*. The crude product

was then dissolved in pentane, and slow cooling of the solution gave **4a** as red crystals. Yield 0.73 g (72%). Anal. Calcd for $NbO_3C_{42}H_{59}$: C, 71.57; H, 8.44. Found: C, 71.46; H, 8.48. ^{1}H NMR (C_6D_6, 30 °C): δ 6.9–7.2 (m, 9H, aromatics); 5.92 (m, 2H, CH$_2$CH-C*H*); 3.98 (m, 2H, CH$_2$-C*H*); 2.51 (d, 2H), 2.22 (d, 2H, C*H*$_2$) $^2J(^1H-^1H)$ = 8.7 Hz; 3.61 (septet, 6H, C*H*Me$_2$); 1.25 (d, 36H, CHM*e*$_2$);. ^{13}C NMR (C_6D_6, 30 °C): δ 159.9 (Nb-O-*C*); 138.5–123.9 (aromatics); 122.3 (CH$_2$CH-*C*H); 92.4 (*C*H$_2$-CH); 30.2 (*C*H$_2$); 27.6 (*C*HMe$_2$); 24.2 (CHM*e*$_2$).

[Ta(OC$_6$H$_3$Pr^i$_2$-2,6)$_3$($η^4$-C$_6$H$_8$)] (4b). To a sodium amalgam (0.1 g Na/5 mL Hg) was added [Ta(OC$_6$H$_3$Pr^i$_2$-2,6)$_3$Cl$_2$] (**2b**) (1 g, 1.3 mmol) in hexane (10 mL), and 1,3-cyclohexadiene (0.23 g, 2.8 mmol) was then added to the system. The mixture was stirred vigorously for 15 h resulting in the formation of an orange-yellow suspension. The orange solution was filtered from the mixture and dried *in vacuo*. The crude product was then dissolved in pentane, and slow cooling of the solution gave **4b** as orange-yellow crystals. Yield 0.72 g (71%). Anal. Calcd for $TaO_3C_{42}H_{59}$: C, 63.62; H, 7.50. Found: C, 63.39; H, 7.30. ^{1}H NMR (C_6D_6, 30 °C): δ 6.9–7.2 (m, 9H, aromatics); 6.28 (m, 2H, CH$_2$CH-C*H*); 3.48 (m, 2H, CH$_2$-C*H*); 2.72 (m, 4H, unresolved C*H*$_2$); 3.65 (septet, 6H, C*H*Me$_2$); 1.25 (d, 36H, CHM*e*$_2$);. ^{13}C NMR (C_6D_6, 30 °C): δ 156.8 (Ta-O-*C*); 138.9–124.0 (aromatics); 125.8 (CH$_2$CH-*C*H); 84.0 (*C*H$_2$-CH); 31.9 (*C*H$_2$); 27.3 (*C*HMe$_2$); 24.3 (CHM*e*$_2$).

[Ta(OC$_6$H$_3$Cy$_2$-2,6)$_2$(C$_{12}$H$_{17}$)] (5). To a suspension of [Ta(OC$_6$H$_3$-Cy$_2$-2,6)$_2$(H)$_3$(PMe$_2$Ph)$_2$] (0.1 g, 0.11 mmol) in benzene (1 mL) was added 1,3-cyclohexadiene (0.04 g, 0.55 mmol). The reaction was warmed at 60 °C for 3 h until the trihydride was completely dissolved. The resulting orange solution was layered with hexane to produce orange crystals of **5** which were washed with hexane and dried *in vacuo*. Anal. Calcd for $TaO_2C_{48}H_{67}$: C, 67.27; H, 7.88. Found: C, 66.98; H, 7.87. ^{1}H NMR (C_6D_6, 30 °C): δ 7.58–6.56 (m); 6.43 (t); 6.13 (t); 5.22 (s, br); 4.74 (d, br); 3.42 (m); 3.21 (m); 3.15 (m); 2.96 (d); 2.8 (m); 2.27–1.11 (m).

[Ta(OC$_6$HPh$_2$-3,5-Cy$_2$-2,6)$_2$(C$_{12}$H$_{17}$)] (6). To a suspension of [Ta(OC$_6$HPh$_2$-3,5-Cy$_2$-2,6)$_2$(H)$_3$(PMe$_2$Ph)$_2$] (0.1 g, 0.08 mmol) in benzene (1 mL) was added 1,3-cyclohexadiene (0.04 g, 0.55 mmol). The reaction was warmed at 60 °C for 3 h until the trihydride was dissolved. The solvent was removed *in vacuo* to yield the crude **6** as an orange oil. ^{1}H NMR (C_6D_6, 30 °C): δ 7.36–6.87 (m); 6.70 (s); 6.30 (t); 5.55 (t); 4.88 (d); 4.08 (t, br); 3.84 (t, br); 3.75 (s, br); 3.38 (m); 3.37 (m); 3.27 (t, br); 3.05 (m); 2.99 (s, br); 2.17 (m); 2.07 (m); 1.95–0.85 (m).

Reactivity of [Ta(OC$_6$H$_3$Pr^i$_2$-2,6)$_2$(Cl)(H)$_2$(PMe$_2$Ph)$_2$]. A suspension of the dihydride compound [Ta(OC$_6$H$_3$Pr^i$_2$-2,6)$_2$(Cl)(H)$_2$(PMe$_2$Ph)$_2$] in C_6D_6 was treated with cyclohexene or 1,3-cyclohexadiene, and the reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy. The slow build up of the organometallic species [Ta(OC$_6$H$_3$Pr^i-$η^2$-CMe=CH$_2$)-(OC$_6$H$_3$Pr^i$_2$-2,6)(Cl)(PMe$_2$Ph)$_2$] (**7**)[3d] and cyclohexene or cyclohexane,

respectively was observed over the course of several hours. The reaction was complete after 1 h when heated at 100 °C. Reactions between the labeled compound [Ta(OC$_6$H$_3$Pr^i$_2$-2,6)(Cl)(D)$_2$(PMe$_2$Ph)$_2$] and 1,3-cyclohexadiene were carried out in C_6H_6 and monitored by ^{2}H NMR.

[Ta(OC$_6$H$_3$Bu^t-CMe$_2$CH$_2$)(OC$_6$H$_3$Bu^t$_2$-2,6)(Cl)(C$_6$H$_{11}$)] (8). Method 1. To a suspension of [Ta(OC$_6$H$_3$Bu^t$_2$-2,6)$_2$Cl$_3$] (0.5 g, 0.71 mmol) in hexane (5 mL) was added 1,3-cyclohexadiene (0.29 g, 3.62 mmol) followed by (Bu^n)$_3$SnH (0.63 g, 2.16 mmol), and the resulting mixture was allowed to stand for 20 h. Removal of the solvent *in vacuo* left the crude product as a yellow oil contaminated with (Bu^n)$_3$SnCl. Layering the oil with hexane (5 mL) precipitated the product as a crystalline yellow solid which was washed with hexane and dried *in vacuo*. Anal. Calcd for $C_{34}H_{54}ClO_2Ta$: C, 57.60; H, 7.40; Cl, 4.94. Found: C, 57.14; H, 7.71; Cl, 5.43. ^{1}H NMR (C_6D_6, 30 °C): δ 6.81–7.26 (m, 11H, aromatics); 3.08 (d, 1H), 2.55 (d, 1H, Ta-C*H$_2$*, $^2J(^1H-^1H)$ = 15.3 Hz); 1.45 (s), 1.47 (s, CH$_2$CM*e*$_2$); 1.24 (s, CM*e*$_3$). Selected ^{13}C NMR (C_6D_6, 30 °C): 162.6 (Ta-O-*C*); 155.6 (Ta-O-*C*); 99.4 (Ta-*C*H$_2$CMe$_2$).

Method 2. Addition of an excess 1,3-cyclohexadiene to a C_6D_6 solution of [Ta(OC$_6$H$_3$Bu^t$_2$-2,6)$_2$(Cl)(H)$_2$(PMe$_2$Ph)] was found upon standing for several hours to produce **8** identified by ^{1}H NMR.

Method 3. When a solution of [Ta(OC$_6$H$_3$Bu^t$_2$-2,6)$_2$Cl$_3$] in C_6D_6 is reacted with [Mg(c-C$_6$H$_{11}$)$_2$], the pale yellow mixture was shown by ^{1}H NMR to contain **8** along with other unidentified tantalum species.

Hydrogenation Reactions. Similar procedures were used for all hydrogenation reactions. A representative example is given for the hydrogenation of 1,3-cyclohexadiene by **4a**. In the Dri-Lab a sample of **4a** (60 mg, 0.085 mmol) was dissolved in C_6D_6 (0.8 mL) in a 25 mL round bottom flask. To this solution was added 1,3-cyclohexadiene (215 μL, 2.25 mmol, 25 per Nb), and the flask containing the mixture was placed inside the pressure reactor which was sealed. After removing from the Dri-Lab the reactor was "flushed" with 200 psi of D$_2$, pressurized to 900 psi, and allowed to stand for 3 days. The reactor was depressurized and taken into the Dri-Lab. The reaction mixture was initially analyzed by ^{1}H NMR spectroscopy (complete conversion to cyclohexane) and by GC/MS.

Supporting Information Available: Description of the experimental procedures for X-ray diffraction studies and tables of thermal parameters, bond distances and angles, intensity data, torsion angles, and multiplicities (87 pages). See any current masthead page for ordering and Internet access instructions.