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Cyclohexadienyl Niobium Complexes and Arene Hydrogenation Catalysis

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Hydrogenolysis of $^{R}[P_2N_2]NbCH_2SiMe_3$ (where $^{R}[P_2N_2] = RP(CH_2SiMe_2NSiMe_2CH_2)_2PR$; R = cyclohexyl, Cy, or phenyl, Ph) in benzene or toluene causes hydride addition to the aromatic solvent resulting in the formation of the π-bonded complexes $^{R}[P_2N_2]Nb(\eta^5\text{-}C_6H_7)$ (R = Cy, **1**; R = Ph, **2**) and $^{R}[P_2N_2]Nb(\eta^5\text{-}C_7H_9)$ (R = Cy, **3**; R = Ph, **4**) in benzene and toluene, respectively. Performing the hydrogenation at a higher pressure of 29 atm at room temperature causes the catalytic hydrogenation of benzene to cyclohexane as determined by NMR spectroscopy and GC−MS analysis. The hydrogenation of toluene to methylcyclohexane can also be performed, but the turnover frequency is considerably lower. Examination of the solid residues from the high-pressure hydrogenations indicates the formation of the π-bonded complexes **1** and **2**. The addition of 29 atm of H_2 to these cyclohexadienyl derivatives in benzene or toluene, however, shows no hydrogenation products, indicating these species are not catalytically active.

Introduction

While there are numerous examples of soluble transition metal complexes that can catalyze the homogeneous hydrogenation of alkenes and alkynes, there is a paucity of systems that will hydrogenate aromatic substrates such as benzene.[1−3] Of the soluble complexes that do show activity in arene hydrogenation, some are limited to polycyclic aromatic hydrocarbons, and for others there is some question as to whether they are truly homogeneous.[3−12]

A particularly impressive class of arene hydrogenation catalysts is based on niobium and tantalum complexes stabilized by bulky aryloxide ancillary ligands.[13−17] These systems have been shown to hydrogenate aromatic substrates with good chemoselectivity and stereoselectivity. Attempts at isolating intermediates in these group 5 systems have resulted in the formation of phosphine-stabilized hydride derivatives. While these isolated species demonstrate mild capability as arene hydrogenation catalysts, phosphine-free derivatives show much higher reactivity.

We have previously reported the synthesis and characterization of a series of paramagnetic niobium(III) chloride and hydrocarbyl derivatives stabilized by the $[P_2N_2]$ macrocyclic ligand.[18] Here we report the attempted isolation of niobium hydrides via hydrogenolysis of these alkyl species. Although discrete niobium hydride complexes were not isolated, there is indirect evidence for their formation since the resulting species display reactivity toward the hydrogenation of aromatic substrates.

Results and Discussion

Synthesis of Cyclohexadienyl Complexes of Niobium. The addition of 1 atm of H_2 to deep blue benzene solutions of $^{R}[P_2N_2]NbCH_2SiMe_3$ results in the formation of olive green solutions within 1 h. Besides the typical resonances attributed to diamagnetic complexes of the $[P_2N_2]$ ligand, a striking feature of the ^1H NMR spectrum is the presence of three multiplet resonances

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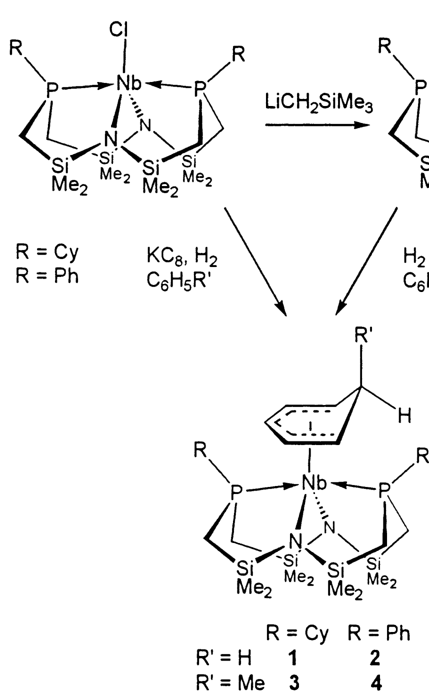
Scheme 1



at 2.51, 4.14, and 5.71 ppm for R = Cy (**1**), and at 2.45, 4.23, and 5.42 ppm for R = Ph (**2**), in a 2:2:1 integration ratio. This is consistent with a π-coordinated arene-type ligand. Complexes **1** and **2** each display four sets of silyl methyl resonances as well as four sets of methylene resonances. The $^{31}P\{^{1}H\}$ NMR spectra display two broad peaks at 30.08 and 26.52 ppm for **2** at room temperature, while only one broad resonance at 32.36 ppm for **1**. Performing the hydrogenation in an NMR tube sealed under H_2 reveals that $SiMe_4$ is eliminated by hydrogenolysis as anticipated. However, rather than generating the expected $^{R}[P_2N_2]NbH_n$ (n = 1 or 3), diamagnetic species possessing cyclohexadienyl ligands were formed. On the basis of NMR spectral data, elemental analysis, and mass spectrometry, the resulting products can be formulated as $^{R}[P_2N_2]Nb(\eta^5\text{-}C_6H_7)$ (R = Cy, **1**; R = Ph, **2**) (Scheme 1).

Hydrogenation of $^{R}[P_2N_2]NbCH_2SiMe_3$ in toluene produces ^{1}H NMR spectra resembling those of complexes **1** and **2**, with upfield shifted π-type resonances indicative of a similarly bound arene-type ligand. In this case, however, the ^{1}H NMR spectrum of the initially formed product shows a mixture of isomers. There appear to be at least two sets of resonances arising from the coordinated arene ligand, suggesting hydride addition at different sites within the toluene molecule. Over time, these isomers apparently undergo rearrangement that ultimately leads to one thermodynamically preferred species in solution. After several hours the ^{1}H NMR spectrum shows one series of π-type resonances at 2.82, 4.04, and 5.72 ppm for R = Cy (**3**) and at 2.85, 4.21, and 5.51 ppm for R = Ph (**4**) (Figure 1). Additionally, doublets at 0.64 ppm corresponding to a methyl resonance coupled to a single proton are observed for both **3** and **4**. As in **1** and **2** above, **3** and **4** display four sets of silyl methyl resonances as well as four sets of methylene resonances. No exchange of the methylcyclohexadienyl ligand with C_6D_6 solvent is observed, thus suggesting the conversion of isomers in the C_7H_9 fragment is intramolecular. Reaction of the niobium alkyl complexes with deuterium gas in benzene or toluene leads to simplified *ortho*-H resonances as well as to loss of coupling in the cyclohexadienyl C*H*H(Me) peak. The endo addition of the deuterium was confirmed by loss of the resonance at 2.10 ppm (H_d) for **3** and **4**. The endo hydrogen atoms in **1** and **2** are obscured by the methylene resonances of the $[P_2N_2]$ ligand. Microanalysis and mass spectrometry support the formulation of these products as $^{R}[P_2N_2]Nb(\eta^5\text{-}C_7H_9)$ (R = Cy, **3**; R = Ph, **4**) (Scheme 1). The $^{31}P\{^{1}H\}$ NMR spectra of **3** and **4** are analogous to those of **1** and **2**; namely, the phenyl-substituted complex **4** shows two broad resonances at 29.32 and 26.36 ppm, while cyclohexyl-substituted **3** displays a single broad resonance at 24.29 ppm.

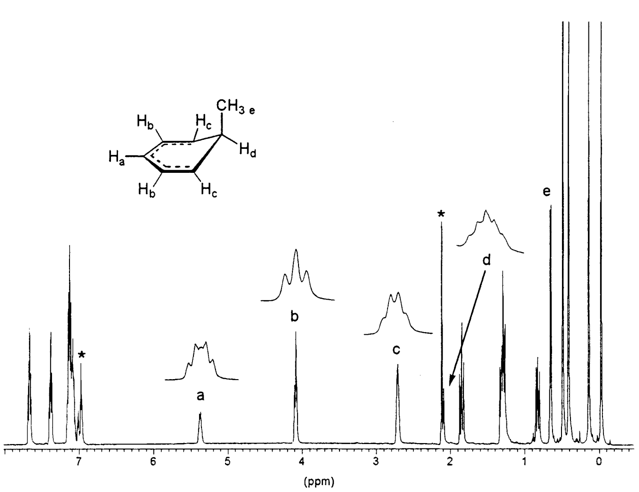


Figure 1. ^{1}H NMR spectrum (500 MHz) of $^{Ph}[P_2N_2]Nb(\eta^5\text{-}C_7H_9)$ (**4**) in toluene-d_8 (*) and assignment of methylcyclohexadienyl resonances.

An alternate route to generating niobium hydrides was explored. It has been shown that in addition to hydrogenolysis of vanadium alkyl complexes, reduction of a vanadium(III) chloride complex by KC_8 under H_2 is also an effective route to vanadium hydride species.[19] Reacting solutions of $^{R}[P_2N_2]NbCl$ with KC_8 under H_2 in benzene or toluene also results in the hydrogenation of the respective aromatic solvent to generate complexes **1** through **4** in good yield (Scheme 1).

The reactivity of other simple arenes to form similarly bound species was also explored. The addition of H_2 to hexanes solutions of $^{R}[P_2N_2]NbCH_2SiMe_3$ and naphthalene or anthracene did show the presence of coordinated arene moieties determined spectroscopically. However, these products could not be fully characterized as a result of the difficulty in their isolation from paramagnetic impurities that were consistently observed.

Solid State Characterization. Evaporation of hexanes solutions of **1** and **2** allowed isolation of light green crystals; the solid state molecular structure of **1** is shown in Figure 2. Crystallographic data appear in Table 1, and selected bond lengths and angles are shown in Table 2. The structure unequivocally reveals that a benzene molecule has been partially hydrogenated to form a cyclohexadienyl moiety. The C(25)−C(26) and C(25)−C(30) single bond lengths of 1.511(3) and

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Table 1. Crystallographic Data[a]

	$^{Cy}[P_2N_2]Nb(\eta^5\text{-}C_6H_7)$ (**1**)	$^{Cy}[P_2N_2]Nb(\eta^5\text{-}C_7H_9)$ (**3**)	$^{Ph}[P_2N_2]Nb(\eta^5\text{-}C_7H_9)$ (**4**)
formula	$C_{30}H_{61}N_2Si_4P_2Nb$	$C_{31}H_{63}N_2Si_4P_2Nb$	$C_{31}H_{51}N_2P_2Si_4Nb\bullet C_3H_7$
fw	717.02	731.05	762.04
color, habit	green, chip	green, chip	green, chip
cryst size, mm	0.35 × 0.20 × 0.20	0.20 × 0.20 × 0.20	0.25 × 0.20 × 0.20
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)
a, Å	11.4451(4)	10.613(2)	11.0005(4)
b, Å	12.218(1)	11.2703(7)	12.4477(8)
c, Å	14.2486(5)	17.031(1)	15.7988(7)
α, deg	89.522(2)	89.197(2)	74.735(2)
β, deg	67.759(2)	85.949(2)	82.464(2)
γ, deg	89.131(2)	67.378(3)	73.092(3)
V, Å^3	1844.0(2)	1875.5(3)	1993.3(2)
Z	2	2	2
T, °C	-100 ± 1	-100 ± 1	-100 ± 1
ρ_{calc}, g/cm^3	1.291	1.294	1.270
$F(000)$	764.00	780.00	806.00
μ(Mo Kα), cm^{-1}	5.65	5.57	5.27
transmn factors	0.8302−1.0000	0.8123−1.0000	0.7747−1.0000
$2\theta_{max}$, deg	57.5	55.8	55.9
total no. of reflns	16 404	16 246	16 647
no. of unique reflns	7358	7533	7548
R_{merge}	0.024	0.052	0.046
no. reflns with $I \geq 3\sigma(I)$	6671	5237	6069
no. of variables	352	393	408
R (F^2, all data)	0.049	0.065	0.059
R_w (F^2, all data)	0.105	0.102	0.098
R (F, $I > 3\sigma(I)$)	0.030	0.035	0.034
R_w (F, $I > 3\sigma(I)$)	0.053	0.043	0.0449
gof	1.82	1.16	1.32

[a] Rigaku/ADSC CCD diffractometer, $R = \sum||F_o^2| - |F_c^2||/\sum|F_o^2|$; $R_w = (\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2)^{1/2}$.

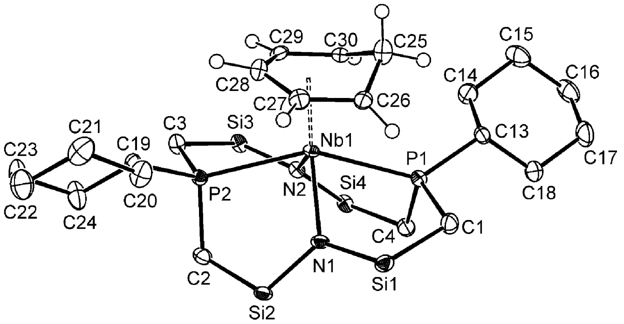

Figure 2. Molecular structure (ORTEP) of $^{Cy}[P_2N_2]Nb(\eta^5\text{-}C_6H_7)$ (**1**). Silyl methyl groups omitted for clarity.

1.499(3) Å, respectively, are longer than those of the planar fragment. The average bond distance of 1.420 Å for C(26)−C(27), C(27)−C(28), C(28)−C(29), and C(29)−C(30) is consistent with slightly elongated C=C double bonds. All of these derivatives that possess η^5-ligands are diamagnetic and can be considered 16-electron complexes ($[P_2N_2]$ can be formally considered a six-electron ligand). Assuming the cyclohexadienyl ligand occupies a single coordination site, **1** possesses a distorted trigonal bipyramidal geometry around niobium. The phosphine-donor groups occupy axial positions slightly bent back from 180°. The two amido-donor N atoms and the cyclohexadienyl ligand reside in the equatorial positions. Alternatively, as for cyclopentadienyl ligands, the cyclohexadienyl ligand can be regarded as being three-coordinate, resulting in a seven-coordinate niobium center. The increased steric bulk of the cyclohexadienyl ligand over the previously described alkyl and halide substituents is apparent in the more acute P(1)−Nb(1)−P(2) and N(1)−Nb(1)−N(2) bond angles of 148.95(2)° and 99.06(6)°, respectively, found in **1**. The Nb−P bond lengths of 2.5417(8) and 2.5760(8) Å are comparable to those found in previously reported $[P_2N_2]$ complexes of Nb(III).[40]

Dark green crystals of **3** and **4** were also obtained by slow evaporation of hexanes solutions, and their structures were characterized by single-crystal X-ray diffraction. The molecular structure of **3** is shown in Figure 3, with selected bond lengths and angles listed in Table 3. The structure of **4** is shown in Figure 4, with selected bond lengths and angles listed in Table 4. Crystal-

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Table 2. Selected Bond Lengths (Å) and Angles (deg) in $^{Cy}[P_2N_2]Nb(\eta^5\text{-}C_6H_7)$ (1)

Distances			
Nb(1)−P(1)	2.6194(5)	Nb(1)−P(2)	2.6231(5)
Nb(1)−N(1)	2.178(2)	Nb(1)−N(2)	2.164(2)
Nb(1)−C_M	1.926	C(25)−C(26)	1.511(3)
C(26)−C(27)	1.430(3)	C(27)−C(28)	1.415(3)
C(28)−C(29)	1.408(3)	C(29)−C(30)	1.426(3)
C(30)−C(25)	1.499(3)		
Angles			
P(1)−Nb(1)−P(2)	148.95(2)	N(1)−Nb(1)−N(2)	99.06(6)
P(1)−Nb(1)−C_M	110.48	N(1)−Nb(1)−C_M	130.48
P(2)−Nb(1)−C_M	100.57	N(2)−Nb(1)−C_M	130.08
P(1)−Nb(1)−N(1)	76.19(5)	P(1)−Nb(1)−N(2)	84.03(5)
P(2)−Nb(1)−N(1)	83.23(5)	P(2)−Nb(1)−N(2)	76.47(5)
Nb(1)−P(1)−C(13)	133.12(7)	Nb(1)−P(2)−C(19)	132.12(7)
Angles			
C(25)−C(30)−C(29)−C(28)	−22.3(3)	C(27)−C(28)−C(29)−C(30)	−11.7(3)

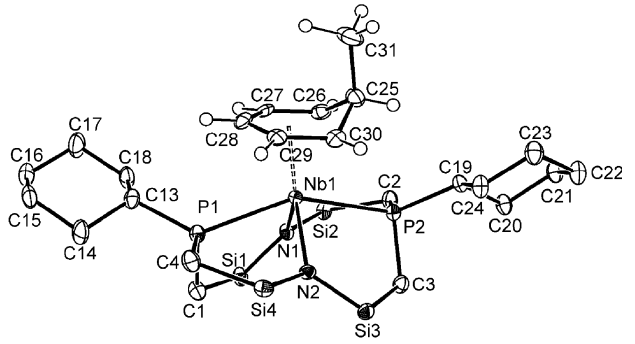


Figure 3. Molecular structure (ORTEP) of $^{Cy}[P_2N_2]Nb(\eta^5\text{-}C_7H_9)$ (**3**). Silyl methyl groups omitted for clarity.

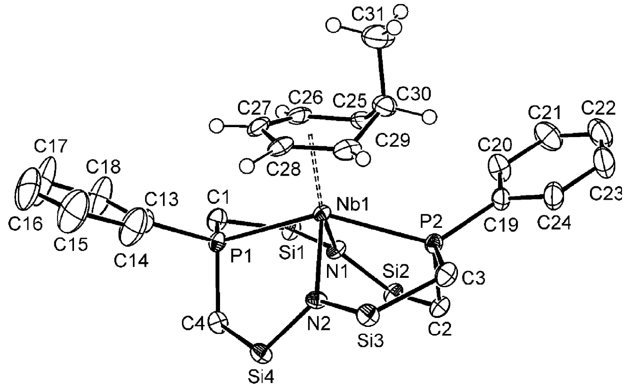
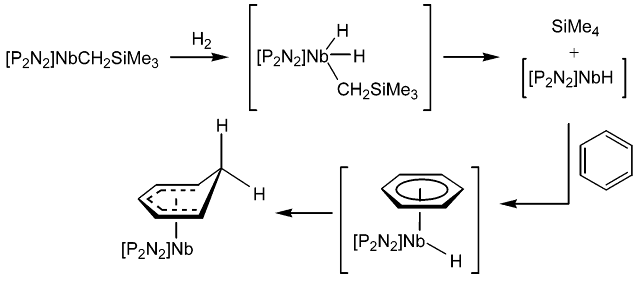


Figure 4. Molecular structure (ORTEP) of $^{Ph}[P_2N_2]Nb(\eta^5\text{-}C_7H_9)$ (**4**). Silyl methyl groups are omitted for clarity.

Scheme 2



lographic data for **3** and **4** appear in Table 1. It is immediately apparent that the toluene fragment has been hydrogenated in an endo fashion, thus forcing the methyl group into an axial orientation, and can be best described as a methylcyclohexadienyl moiety. As mentioned above, this is likely the thermodynamically preferred orientation, as this arrangement minimizes steric interaction of the toluene methyl group with the phosphorus substituents. The resulting C−C and Nb−C bond lengths of this fragment in both **3** and **4** confirm an η^5-coordination mode. In **4**, the bond distances for C(25)−C(30) and C(29)−C(30) are identical at 1.519(4) Å, and the methyl carbon bond distance, C(30)−C(31), is 1.535(4) Å. All are typical C−C single bond lengths. Similarly, **3** possesses C(25)−C(26) and C(25)−C(30) bond lengths of 1.517(5) and 1.527(5) Å, respectively, and a methyl carbon bond distance of 1.547(5) Å for C(25)−C(31).

Formation of complexes **1**−**4** can be rationalized by the mechanism presented in Scheme 2. Oxidative addition of H_2 to the niobium(III) alkyl species allows formation of a niobium(V) dihydride. Reductive elimination of the alkyl ligand and a hydride forms the stable tetramethylsilane molecule and the coordinatively unsaturated niobium(III) hydride. The Lewis acidity of the resulting d^2 metal hydride allows π-coordination of the aromatic solvent molecule.[17,20−22] Endo addition of the hydride onto the coordinated arene (as demonstrated by deuterium labeling studies, above) results in the formation of an anionic cyclohexadienyl moiety; this route to cyclohexadienyl ligand formation has also been exhibited by cobalt hydride species stabilized by phosphine ligands.[23−26] Transition metal cyclohexadienyl compounds are typically prepared by hydrogen abstraction from cyclohexadiene compounds[27−29] or nucleophilic addition to arene complexes.[30,31] In the latter case, the arene becomes activated toward nucleophilic attack by virtue of its coordination to the metal, and the nucleophile enters an exo position on the ring.

The coordination of the cyclohexadienyl ligand to the niobium center is inert to exchange with other aromatic moieties. Cyclohexadienyl ligands on cobalt phosphine systems, on the other hand, exhibit a much more weakly bound arene. Whereas the cobalt cyclohexadienyl complexes $(Cy_2P(CH_2)_nPCy_2)Co(\eta^5\text{-}C_6H_7)$ (n = 1−3) show ligand exchange with other aromatic species,[23−26] the niobium cyclohexadienyl complexes **1**−**4** are robust.

Variable-Temperature NMR Studies. In the solid state, the cyclohexadienyl and methycyclohexadienyl fragments in **1**−**4** align themselves such that the methylene CH_2 or methine CHMe fragment resides over one of the phosphorus atoms, resulting in inequivalent phosphine environments. The ^1H NMR spectra reflect this by the presence of four silyl methyl and four

Table 3. Selected Bond Lengths (Å) and Angles (deg) in $^{Cy}[P_2N_2]Nb(\eta^5\text{-}C_7H_9)$ (3)

Distances			
Nb(1)−P(1)	2.6077(9)	Nb(1)−P(2)	2.6264(9)
Nb(1)−N(1)	2.187(2)	Nb(1)−N(2)	2.164(3)
Nb(1)−C_M	1.912	C(25)−C(26)	1.517(5)
C(26)−C(27)	1.412(5)	C(27)−C(28)	1.407(5)
C(28)−C(29)	1.404(5)	C(29)−C(30)	1.430(5)
C(30)−C(25)	1.527(5)	C(25)−C(31)	1.547(5)
Angles			
P(1)−Nb(1)−P(2)	149.63(3)	N(1)−Nb(1)−N(2)	98.6(1)
P(1)−Nb(1)−C_M	101.76	N(1)−Nb(1)−C_M	130.94
P(2)−Nb(1)−C_M	108.59	N(2)−Nb(1)−C_M	130.17
P(1)−Nb(1)−N(1)	82.76(7)	P(1)−Nb(1)−N(2)	76.57(7)
P(2)−Nb(1)−N(1)	76.33(7)	P(2)−Nb(1)−N(2)	84.99(7)
Nb(1)−P(1)−C(13)	130.0(1)	Nb(1)−P(2)−C(19)	134.1(1)
Angles			
C(25)−C(30)−C(29)−C(28)	29.4(4)	C(29)−C(30)−C(25)−C(31)	66.2(4)

Table 4. Selected Bond Lengths (Å) and Angles (deg) in $^{Ph}[P_2N_2]Nb(\eta^5\text{-}C_7H_9)$ (4)

Distances			
Nb(1)−P(1)	2.5696(7)	Nb(1)−P(2)	2.5677(7)
Nb(1)−N(1)	2.179(2)	Nb(1)−N(2)	2.190(2)
Nb(1)−C_M	1.909	C(25)−C(26)	1.426(4)
C(26)−C(27)	1.401(4)	C(27)−C(28)	1.418(4)
C(28)−C(29)	1.426(4)	C(29)−C(30)	1.519(4)
C(30)−C(25)	1.519(4)	C(30)−C(31)	1.535(4)
Angles			
P(1)−Nb(1)−P(2)	148.71(2)	N(1)−Nb(1)−N(2)	98.39(8)
P(1)−Nb(1)−C_M	101.59	N(1)−Nb(1)−C_M	131.94
P(2)−Nb(1)−C_M	114.45	N(2)−Nb(1)−C_M	129.48
P(1)−Nb(1)−N(1)	76.17(6)	P(1)−Nb(1)−N(2)	83.90(6)
P(2)−Nb(1)−N(1)	83.21(6)	P(2)−Nb(1)−N(2)	76.04(6)
Nb(1)−P(1)−C(13)	126.7(1)	Nb(1)−P(2)−C(19)	128.34(9)
Angles			
C(25)−C(26)−C(27)−C(28)	−3.9(4)	C(28)−C(29)−C(30)−C(31)	69.5(3)

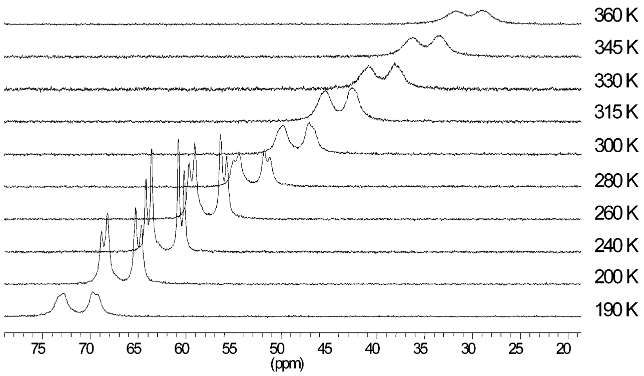


Figure 5. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of $^{Ph}[P_2N_2]Nb(\eta^5\text{-}C_7H_9)$ (**4**).

methylene environments. The cyclohexadienyl ligand, however, is fluxional and experiences a rotation about the Nb−centroid axis. This process is most easily detected by variable-temperature $^{31}P\{^1H\}$ NMR spectroscopy. The cyclohexyl-phosphine systems **1** and **3** possess a single broad resonance in the $^{31}P\{^1H\}$ spectrum at room temperature. As the temperature is lowered, the resonance broadens until decoalescence at 260 K. At 200 K, a pair of doublet resonances is observed with a coupling constant of 112 Hz. At this temperature, the rotation of the arene ligand is slowed, resulting in the resolution of the two phosphorus environments. The phenyl-phosphine-substituted systems, on the other hand, show two broad resonances at 300 K (Figure 5). No coalescence of the peaks is observed even at 360 K. Lowering the temperature results in a pair of doublets being resolved at 280 K and sharpening at 240 K with a coupling constant of 125 Hz. Lowering the temperature further causes line broadening and loss of coupling information. This results from the effects of the quadrupolar niobium nucleus being enhanced at lower temperatures. Similar effects on line width in low-temperature ^{31}P NMR spectroscopy were observed in other diamagnetic $[P_2N_2]$ niobium complexes.[32]

The rate of arene ligand rotation does not appear to depend on the nature of the arene, that is, whether the cyclohexadienyl or methylcyclohexadienyl species is studied. The variable-temperature $^{31}P\{^1H\}$ NMR spectra of $^{Ph}[P_2N_2]Nb(\eta^5\text{-}C_6H_7)$, **2**, and $^{Ph}[P_2N_2]Nb(\eta^5\text{-}C_7H_9)$, **4**, display the same properties. Likewise, the cyclohexadienyl- and methylcyclohexadienyl-niobium complexes supported by the $^{Cy}[P_2N_2]$ ligand show similar behavior. The nature of the phosphorus-donor atom appears to dictate the rate of arene rotation. For **2** and **4**, where phenyl phosphine donors were utilized, the rate of rotation of the arene is slow relative to the cyclohexyl-substituted ligand, and even at high temperature a relatively sharp single ^{31}P resonance is unobservable. Cyclohexyl phosphine-substituted complexes **1** and **3**, however, show equivalent ^{31}P environments at room temperature. A depiction of the fluxional process is shown in Figure 6. The rotation of the cyclohexadienyl ligand proceeds through an arrangement where the methylene CH_2 group resides over one of the amide ligands, producing equivalent phosphorus environments.

The different fluxional behavior observed between the cyclohexyl- and phenyl-substituted complexes may be

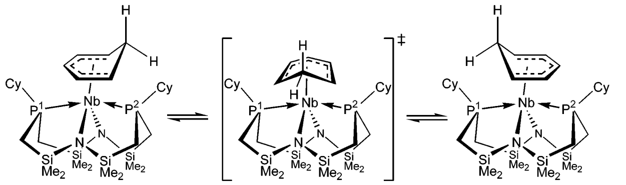


Figure 6. Depiction of fluxional behavior in complexes **1** and **3** via cyclohexadienyl ligand rotation and resultant phosphorus environment exchange between P^1 and P^2.

correlated to the degree of congestion imposed upon the cyclohexadienyl ligand. An examination of the Nb−P bond lengths and Nb−P−C_{ipso} angles shows the cyclohexyl group is positioned further away than the phenyl substituent from the cyclohexadienyl moiety. For example, the Nb−P bond lengths in **1** average 2.6213 and 2.6171 Å in **3** and 2.5687 Å in **4**. The average Nb−P−C_{ipso} bond angles are 132.62° in **1**, 132.1° in **3**, and 127.5° in **4**. As a result, the more constricted cyclohexadienyl ligand in the phenyl-substituted complex **4** experiences a hindered rotation about the metal−centroid axis.

Catalytic Arene Hydrogenation Studies. In a number of catalytic systems, the hydrogenation of benzene is proposed to proceed via a cyclohexadienyl intermediate before the eventual formation of cyclohexane.[23,33] Cyclohexadienyl complexes **1** and **2** were therefore examined for benzene hydrogenation activity.

The catalytic hydrogenation of aromatic substrates by mixed hydrido aryloxide derivatives of niobium studied by Rothwell and co-workers requires high-pressure hydrogenolysis of mixed alkyl/aryloxides, typically in the presence of phosphine donors, to generate d^0 niobium hydrides. A drawback of these precursors is that hydrogenolysis of certain alkyl groups is slow. The resulting hydride complexes were found to effectively hydrogenate benzene to cyclohexane at 1200 psi H_2 and 100 °C. A suggested mechanistic pathway involves the formation of a cyclohexadienylmetal hydride intermediate. We therefore decided to explore whether complexes **1**−**4** would display catalytic arene hydrogenation.

Solutions of the niobium alkyl complexes $^{R}[P_2N_2]NbCH_2SiMe_3$ (R = Ph, Cy) (0.025 mmol) in benzene (4 g, 51.3 mmol) were exposed to 500 psi of H_2 at room temperature for 20 h. Approximately 5 mmol of cyclohexane was produced as shown by NMR (calculated from the integration ratio of the benzene to cyclohexane resonances) and GC−MS analysis yielding a turnover number (TON = mol product per mol catalyst) of 225. No partially hydrogenated substrate (cyclohexadiene or cyclohexene) was apparent. Examination of the solid residues after removal of all solvents showed the cyclohexadienyl complexes **1** and **2** had formed for their respective cyclohexyl- and phenyl phosphine-substituted niobium alkyl precursors. Hydrogenation of toluene to methylcyclohexane can also be performed, but the percent conversion is much poorer than for benzene, yielding only 2% C_7H_{14} after 20 h.

For $^{Ph}[P_2N_2]NbCH_2SiMe_3$, no hydrogenation of the phosphorus phenyl group was observed. Examination of the catalyst residue by NMR spectroscopy shows the product to be purely **2**; no **1** was detected. This is likely due to the inability of the phenyl substituent of $[P_2N_2]$ to undergo intramolecular interaction with the metal center because of the geometric restrictions of the macrocycle. Although intramolecular coordination is not likely to occur in $^{Ph}[P_2N_2]$, a related intermolecular phosphorus phenyl activation between two $^{Ph}[P_2N_2]Nb$ fragments has been observed.[34]

The possibility that cyclohexadienyl complexes **1** and **2** may be intermediates in the catalytic hydrogenation of benzene by these systems was examined. Benzene solutions of **1** and **2** were exposed to 500 psi H_2 at room temperature for 20 h. No cyclohexane or partially hydrogenated substrate was observed in the resulting solution, indicating that **1** and **2** are not catalytically active species. Even at 80 °C no benzene hydrogenation was observed in solutions of the cyclohexadienyl species, **1** and **2**.

That **1** and **2** show no hydrogenation activity may not be surprising. As discussed above, they are coordinatively and electronically saturated species. The mechanistic details of benzene hydrogenation by these systems, although likely related to those of the niobium aryloxide systems, suggest that the formation of a niobium η^5-cyclohexadienyl complex is a catalytic dead-end. Although it is highly likely that the catalytically active species is a niobium hydride complex, we have as yet been unable to isolate such a product. Performing the reactions in nonaromatic solvents such as THF or hexanes even in the presence of stabilizing phosphine donors yields intractable products. A remarkably stable dimeric Ta(IV)-hydride $(^{Ph}[P_2N_2]Ta)_2(\mu\text{-}H)_4$ has recently been synthesized in our group.[35] Exposure of this dinuclear tantalum hydride to ethylene, carbon monoxide, and even oxygen results in no reaction. A related mononuclear tantalum(V) trihydride, $^{Ph}[P_2N_2]TaH_3(PMe_3)$,[36] has also been prepared, but again this complex does not react with arenes. A large number of transition metal hydrides are stable in aromatic solvents. If reactivity does occur, C−H bond activation is commonly involved either by oxidative addition pathways or by σ-bond metathesis with highly electrophilic d^0 metal hydrides.[3]

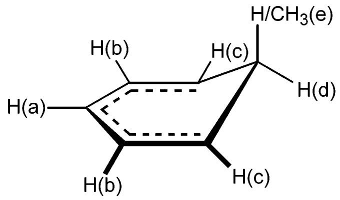
Benzene and pyridine have been shown to undergo η^2-coordination to coordinatively unsaturated Ta(III) d^2 centers.[20−22,37] Concentrated benzene solutions of $(^{t}Bu_3SiO)_3Ta$ spontaneously form a bridging benzene adduct $[(^{t}Bu_3SiO)_3Ta]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_6H_6)$, which decomposes via cyclometalation to generate a Ta(V) hydride species.[37] This suggests the possibility of a pathway whereby an η^2-arene adduct forms with a Nb(III) hydride. Homogeneous arene hydrogenation catalysts are commonly believed to begin their catalytic cycle with an η^6 π-bonded arene species (it should be noted that this paradigm has been challenged by examples where such coordination is unnecessary in catalytic hydrogenation).[10] What becomes apparent from our observations is that an η^6-arene species must be avoided in order for hydrogenation to proceed in the niobium $[P_2N_2]$ system. It seems that an η^2- or at most an η^4-coordination of the arene may be required. It has been shown that cyclohexa-1,3-diene strongly binds to Nb(III) aryloxide centers, and the resulting robust η^4-cyclohexadiene complex reacts with hydrogen to produce cyclohexane.[38] Although an η^4-benzene adduct is possible, it is likely that migratory insertion into such a moiety would also lead to the η^5-cyclohexadienyl ligand and terminate the catalytic cycle.

Conclusion

Attempts at isolating niobium hydride derivatives by hydrogenolysis of the alkyl complexes $^R[P_2N_2]NbCH_2SiMe_3$ (R = Cy or Ph) result in the activation of aromatic solvent molecules. The addition of 1− 4 atm H_2 to benzene or toluene solutions of $^R[P_2N_2]NbCH_2SiMe_3$ leads to hydride addition to the arene moiety, forming the cyclohexadienyl or methylcyclohexadienyl complexes $^R[P_2N_2]Nb(\eta^5\text{-}C_6H_7)$ (R = Cy, **1**; R = Ph, **2**) and $^R[P_2N_2]Nb(\eta^5\text{-}C_7H_9)$ (R = Cy, **2**; R = Ph, **4**) in benzene and toluene, respectively. Although niobium hydride species could not be isolated, formation of complexes **1**−**4** likely proceeds via migratory insertion of a hydride onto the arene fragment. While the niobium alkyl complexes act as precursors for the catalytic hydrogenation of benzene under higher pressures of H_2, their activity is short-lived. Formation of the stable 16 e^- cyclohexadienyl complexes (**1** and **2**) terminates the catalytic cycle. Regardless of the shortcomings of niobium(III) alkyl complexes as good arene hydrogenation catalysts, the formation of niobium cyclohexadienyl complexes from partial hydrogenation of benzene and toluene is significant to understanding related group 5 transition metal arene hydrogenation catalysts.[13−17] Although such metal-bonded η^5-C_6H_7 species are considered to be possible intermediates in the catalytic hydrogenation of benzene, complexes **1**−**4** are catalytically inactive. However, the reduction of benzene to cyclohexane by $^R[P_2N_2]NbCH_2SiMe_3$ in 30 atm of H_2 suggests that alternate intermediates exist for this system.

Experimental Section

Unless otherwise stated, all manipulations were performed under an atmosphere of dry oxygen-free nitrogen or argon by means of standard Schlenk or glovebox techniques (Vacuum Atmospheres HE-553-2 glovebox equipped with a MO-40-2H purification system and a −40 °C freezer). Hexanes and toluene were purchased anhydrous from Aldrich and further dried by passage through a tower of alumina and degassed by passage through a tower of Q-5 catalyst under positive pressure of nitrogen.[39] Anhydrous THF was stored over sieves and distilled from sodium benzophenone ketyl under argon. Nitrogen and argon were dried and deoxygenated by passing the gases through a column containing molecular sieves and MnO. Deuterated benzene and toluene were dried by refluxing over sodium and potassium alloy, and THF-d_8 was dried over sodium, in a sealed vessel under partial pressure, and then trap-to-trap distilled. They were degassed under three freeze−pump−thaw cycles. Unless otherwise stated, all NMR spectra were recorded on a Bruker AMX-500 instrument operating at 500.132 MHz. ^1H NMR spectra were referenced to residual protons in the deuterated solvent. ^{31}P NMR spectra were referenced to external $P(OMe)_3$ at 141 ppm relative to 85% H_3PO_4 in D_2O at 0 ppm. Elemental analyses were performed by Mr. P. Borda of this department. Mass spectrometry was performed on a Kratos MS 50 by Mr. M. Lapawa, also of this department. The compounds $^R[P_2N_2]NbCl$ (R = Ph, Cy), $^R[P_2N_2]NbCH_2SiMe_3$ (R = Ph, Cy),[18] and KC_{840} were prepared according to literature procedures. KC_{840} was prepared according to literature procedures. Hydrogen gas was used as received from Praxair without further purification. NMR assignments of the cyclohexadienyl ligands are made using the following convention:



$^R[P_2N_2]Nb(\eta^5\text{-}C_6H_7)$ (R = Cy, 1; R = Ph, 2). Method A: A benzene solution (60 mL) of $^R[P_2N_2]NbCH_2SiMe_3$ (500 mg, 0.690 mmol, R = Cy; 0.702 mmol, R = Ph) was loaded into a thick walled glass reactor fitted with a Teflon Kontes valve and degassed by three freeze−pump−thaw cycles. Hydrogen gas was added to the frozen solution at −196 °C, and the sealed reactor was allowed to warm to room temperature. The resulting olive-green colored solution was stirred for a further 4 h. All volatiles were removed in vacuo, leaving an olive green solid. Extraction of the solid with minimal hexanes and slow cooling to −40 °C allows isolation of diamagnetic $^R[P_2N_2]Nb(\eta^5\text{-}C_6H_7)$ as green crystals. For **1**: Yield: 400 mg (80%). For **2**: Yield: 410 mg (83%).

Method B: $^R[P_2N_2]NbCl$ (500 mg, 0.758 mmol) and KC_8 (113 mg, 0.830 mmol) were loaded into a thick walled glass reactor flask fitted with a Teflon Kontes valve and degassed by three freeze−pump−thaw cycles. Hydrogen gas was added to the frozen solution at −196 °C, and the sealed reactor was allowed to warm to room temperature. The flask was gently stirred for 24 h, during which the solution changed from green to dark brown. The contents of the flask were then filtered through Celite and solvents removed in vacuo, leaving a dark green-brown solid. Extraction of the solid with minimal hexanes and slow cooling to −40 °C allows isolation of diamagnetic $^R[P_2N_2]Nb(\eta^5\text{-}C_6H_7)$ as green crystals. For **1**: Yield: 350 mg (70%). For **2**: Yield: 375 mg (76%).

For **1**: ^1H NMR (C_6D_6, 400.13 MHz, 300 K): δ −0.08, 0.0, 0.40, 0.52 (s, 6H each, $SiCH_3$), 0.80 to 1.90 (m's, overlapping cyclohexyl-CH_2's and macrocycle PCHH), 2.50 (m, 2H, arene-H(c)) 4.21 (m, 2H, arene-H(b)), 5.70 (m, 1H, arene-H(a)). Arene-H(e) and -H(d) obscured by methylene region. $^{31}P\{^1H\}$ (C_6D_6, 202.46 MHz, 300 K): δ 32.36 (s, $w_{1/2}$ = 330 Hz). MS (EI) m/z (%): 716, (80) $[M]^+$. Anal. Calcd for $C_{30}H_{61}N_2NbP_2Si_4$: C, 50.25; H, 8.58; N, 3.91. Found: C, 50.65; H, 7.74; N, 3.73. For **2**: ^1H NMR (C_6D_6, 400.13 MHz, 300 K): δ 0.03, 0.21, 0.47, 0.55 (s, 6H each, $SiCH_3$), 0.91 (ABX m, 2H, PCHH), 1.36 (ABX m, 4H, PCHH), 1.36 (obscured, 1H, arene-CHH(d)) 1.51 (m, 1H, arene-CHH(e)), 1.90 (ABX m, 2H, PCHH), 2.51 (m, 2H, arene-H(c)) 4.29 (m, 2H, arene-H(b)), 5.48 (m, 1H, arene-H(a)), 7.19 (t, 2H, p-H phenyl), 7.45 (dd, 4H, o-H phenyl), 7.74 (dd, 4H, m-H phenyl). $^{31}P\{^1H\}$ (C_6D_6, 202.46 MHz, 300 K): δ 30.08 and 26.52 ($w_{1/2}$ = 330 Hz). MS (EI) m/z (%): 704, (80) $[M]^+$. Anal. Calcd for $C_{30}H_{49}N_2NbP_2Si_4$: C, 51.12; H, 7.01; N, 3.97. Found: C, 51.48; H, 7.34; N, 4.23.

$^R[P_2N_2]Nb(\eta^5\text{-}C_7H_9)$ (R = Cy, 3; R = Ph, 4). Using toluene in lieu of benzene in both of the above methods allows isolation of $^R[P_2N_2]Nb(\eta^5\text{-}C_7H_9)$ as green crystals grown from slow evaporation of a saturated hexanes solution. For **3**: Yield: 390 mg (78%). ^1H NMR (C_6D_6, 400.13 MHz, 300 K): δ −0.06, 0.05, 0.42, 0.55 (s, 6H each, $SiCH_3$), 0.64 (d, $^3J_{HH}$ = 6.09 Hz, 3H, arene-CH_3(e)), 0.80 to 1.90 (m's, overlapping cyclohexyl-CH_2's and macrocycle PCHH), 2.82 (m, 2H, arene-H(c)) 4.04 (m, 2H, arene-H(b)), 5.72 (m, 1H, arene-H(a)). H(d) obscured by methylene region. $^{31}P\{^1H\}$ (C_6D_6, 161.98 MHz, 300 K): δ 32.82 (s, $w_{1/2}$ = 300 Hz) MS (EI) m/z, (%) 730, (80) $[M]^+$. Anal. Calcd for $C_{31}H_{63}N_2NbP_2Si_4$: C C, 50.93; H, 8.69; N, 3.83. Found: C, 50.86; H, 8.74; N, 3.93. For **4**: Yield: 380 mg (75%). ^1H NMR (C_6D_6, 400.13 MHz, 300 K): δ 0.08, 0.25, 0.51, 0.59 (s, 6H each, $SiCH_3$), 0.64 (d, $^3J_{HH}$ = 6.09 Hz, 3H, arene-CH_3(e)), 0.94 (ABX m, 2H, PCHH), 1.37 (ABX m, 4H, PCHH), 1.94 (ABX m, 2H, PCH*H*), 2.10 (m, ^{1}H, arene-H(d)), 2.85 (m, 2H, arene-H(c)), 4.21 (m, 2H, arene-H(b)), 5.51 (m, 1H, arene-H(a)), 7.41 (t, 2H, *p*-H phenyl), 7.47 (dd, 4H, *o*-H phenyl), 7.65 (dd, 4H, *m*-H phenyl). ^{31}P{^{1}H} (C_6D_6, 161.98 MHz, 300 K): δ 29.32 (s, $w_{1/2} = 420$ Hz), 26.36 (s, $w_{1/2} = 420$ Hz). MS (EI) *m*/*z* (%): 718, (80) [M]$^+$. Anal. Calcd for $C_{31}H_{51}N_2NbP_2Si_4$: C, 51.79; H, 7.15; N, 3.90. Found: C, 52.09; H, 7.44; N, 4.23.

High-Pressure Hydrogenation. $^R[P_2N_2]NbCH_2SiMe_3$ (0.0253 mmol) was dissolved in benzene (4.0 g, 51.3 mmol) (ca. 2030 mol benzene per mol Nb) and loaded into a glass vessel within a Parr Minireactor. The reactor was purged three times by pressurization to 500 psi H_2 and venting before final repressurization to 500 psi H_2. The solution was stirred for 20 h before depressurization. All volatile products were vacuum transferred before analysis by NMR spectroscopy and GC−MS. ^{1}H NMR (neat, 300.13 MHz, 300 K): δ 3.18 (s, 12H, C_6H_{12}), 7.15 (s, 6H, C_6H_6). Integral ratio = 1 C_6H_{12}:8 C_6H_6 corresponds to 5.7 mmol yield of cyclohexane. TON = 225. Nonvolatile residues were characterized as **1** and **2**.

X-ray Crystallographic Analyses of 1, 3, and 4. In all cases, suitable crystals were selected and mounted on a glass fiber using Paratone-N oil and freezing to −100 °C. All measurements were made on a Rigaku/ADSC CCD area detector with graphite-monochromated Mo Kα radiation. Crystallographic data appear in Table 1. In each case the data were processed[41] and corrected for Lorentz and polarization effects and absorption. Neutral atom scattering factors for all non-hydrogen atoms were taken from the *International Tables for X-ray Crystallography*.[42,43] All structures were solved by direct methods[44] and expanded using Fourier techniques.[45] Complex **4** contains one-half molecule of hexane in the asymmetric unit. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on cyclohexadienyl and methylcyclohexadienyl fragments were refined isotropically. Other hydrogen atoms were fixed in calculated positions with C−H = 0.98 Å.

Acknowledgment. We thank the NSERC of Canada for funding in the form of research grants.

Supporting Information Available: Complete crystallographic data including ORTEP diagrams, bond lengths and angles, final atomic coordinates and equivalent isotropic thermal parameters, anisotropic thermal parameters, intermolecular contacts, and least squares planes are available for complexes **1**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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