Preparation of Novel Titanium Complexes Bearing *o*-Phosphinophenol Ligands

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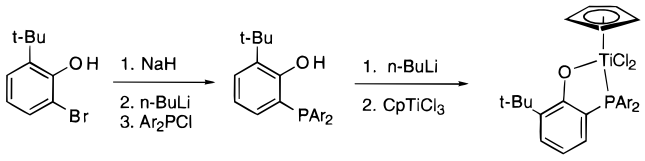
Summary: The preparation of novel titanium complexes bearing o-phosphinophenol ligands is reported. The feature of this ligand system is that its electronic and steric properties can be independently tuned. The complexes were found to be fluxional by ^1H NMR analysis at low temperature. An X-ray structural analysis showed that in the solid state the molecule is chiral at the metal center. These complexes were shown to be effective catalysts for olefin hydrogenation and imine hydrosilylation.

Introduction

The cyclopentadienyl ligand is one of the most widely used ligands in organometallic chemistry.[1] The application of bis(cyclopentadienyl) complexes of the group 4 transition metals to organic synthesis have been extensively studied.[2] We have previously reported the development of a bis(cyclopentadienyl)titanium complex that functions as a catalyst for the hydrogneation of imines.[3] For many reactions of transition metal complexes, ligand electronic effects can dramatically change the reactivity and/or selectivity.[4] One of the limitations of the cyclopentadienyl ligand is that its electronic properties are not easily modified without significantly changing the steric environment. We therefore sought to develop an electronically tunable ligand system in order to probe the electronic effects in the titanium-catalyzed reduction of organic substrates. To accomplish this goal we required a ligand that has similar electronic properties as a cyclopentadienyl ligand but allows a systematic variation of its electron-donating ability. The *o*-phosphinophenol[5] ligands appear to meet the desired criteria. Since titanium oxygen bonds are known to posses double-bond character, when bound to titanium,[6,7] the phosphinophenol ligand could act as a six electron, monoanionic ligand. An additional feature of the *o*-phosphinophenol ligand is that by changing the substituents on phosphorus the electronic properties can be easily varied without affecting steric properties of the metal complex. In addition the steric environment imposed by these ligands can also be modified. For example by placement of two different substituents on phosphorus the potential for a chiral ligand array exists. This paper reports the preparation and properties of novel titanium complexes bearing *o*-phosphinophenol ligands.[8]

Scheme 1. Synthesis of $CpTi(Cl)_2$(*o*-PPO) Complexes



1a; Ar = C_6H_5, 78 %
1b; Ar = p-C_6H_4Me, 26 %

2a; 63 %
2b; 45 %

Results and Discussion

Synthesis. The ligands were prepared in a one pot procedure by the reaction of 2-bromo-6-*tert*-butylphenol with sodium hydride in ether, followed by metal−halogen exchange with *n*-butyllithium to generate the dianion. Quenching this dianion with the requisite diarylchlorophosphine afforded the desired ligands in 78% and 26% yields for **1a**,**b**, respectively, after chromatography.

Reaction of **1a** or **1b** with *n*-butyllithium in THF followed by slow addition of the anion to a THF solution of $CpTiCl_3$ (Scheme 1)[9] afforded the desired titanium complexes in 45−63% isolated yields after recrystallization from toluene or toluene/hexane.

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1995.

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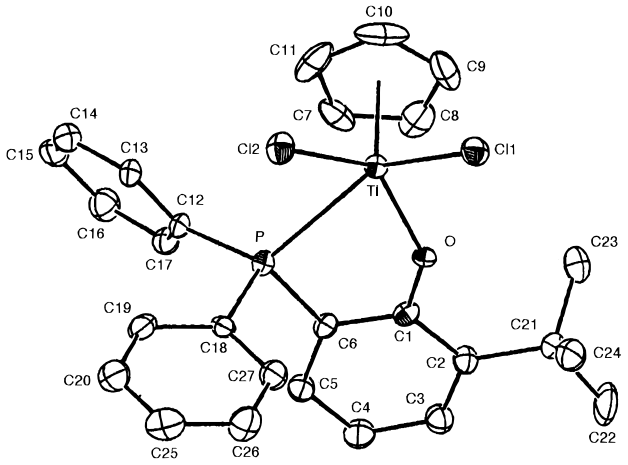


Figure 1. ORTEP diagram of complex **2a**.

The complexes are orange moisture sensitive crystalline solids. They are very soluble in halogenated solvents such as methylene chloride and slightly soluble in ethereal solvents. The compounds exhibit limited solubility in toluene or benzene. The ^{1}H NMR spectra of **2** (C_6D_6, rt) display a doublet for the Cp hydrogens (**2a**, δ 6.18 ppm, $J_{HP} = 2.7$ Hz; **2b**, δ 6.20 ppm, $J_{HP} = 2.4$ Hz) which indicates that the phosphorus is coordinated to titanium. Additionally the chemical shifts in the ^{31}P NMR spectra (**2a**, δ 28.4 ppm; **2b**, δ 27.6 ppm) are consistent with a triarylphosphine bound to a metal center. By ^{1}H NMR the two aryl groups bound to phosphorus are equivalent at room temperature. The protons on the two unsubstituted phenyl groups *ortho* to phosphorus (in complex **2a**) appear as a multiplet at 7.66 ppm integrating for 4 hydrogens. For complex **2b** the *para* methyl groups appear as a singlet at δ 1.91 ppm. The signals for the *ortho* and *meta* protons of the two equivalent aryl groups are split into doublets by coupling to phosphorus.

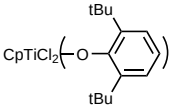
Since the solid-state structure indicates inequivalence of the two aromatic groups (*vide infra*), the molecule must be fluxional at room temperature. In order to support this hypothesis, a solution of **2a** in toluene-d_8 was examined by variable-temperature ^{1}H NMR spectroscopy. When the spectrum was acquired at temperatures above −30 °C, an apparent triplet at 7.60 ppm integrating for 4 hydrogens is observed. These are the hydrogens on the two unsubstituted phenyl groups *ortho* to the phosphorus. Upon cooling the sample to −35 °C this signal begins to broaden and at −40 °C is observed as a broad singlet. At −50 °C the signal begins to sharpen into two triplets. When the sample is cooled to −60 °C, complete resolution is observed; the two triplets appear at 7.61 and 7.54 ppm, and each signal integrates to two hydrogens. These data are most consistent with the suppositon that, of the two possible coordination geometries for a 5 coordinate complex (trigonal bipyramidal and square based pyramidal), the molecule is square pyramidal in solution. At temperatures above −40 °C the two nonequivalent phenyl groups are exchanging rapidly on the NMR time scale.

X-ray Structure. Crystals of **2a** suitable for single-crystal X-ray analysis were isolated by slow cooling of a saturated hot toluene solution. The ORTEP diagram is shown in Figure 1, and selected bond distances and angles are listed in Table 1. The crystals are triclinic in the *P*1 space group. In the solid state the molecule adopts a distorted square based pyramidal coordination geometry. The cyclopentadienyl ligand occupies the apical positon with the two chlorines, the oxygen, and the phosphorus atoms making up the base of the pyramid. In this geometry the molecule is chiral with the two phenyl groups on the phosphorus being diastereotopic. Both of the Ti−Cl bond lengths of 2.333(3) and 2.340(2) Å are in good agreement with those of Cp_2TiCl_2.[10] The Cl(1)−Ti−Cl(2) angles of 89.14(9)°, however, is smaller than that for Cp_2TiCl_2 which is 94.4°. The Ti−O bond length is 1.860(5) Å which is consistent with some degree of π bonding being present.[6,7] The Ti−O bond in $[CpTiCl_2]O$ is 1.74 Å,[9] while that in $Cp_2Ti(Cl)OEt$ is 1.855(2) Å.[6] The Ti−O−Cl(1) angle is 134.9(4)° and also indicates the presence of a π interaction between titanium and oxygen. The Ti−P distance of 2.624(3) Å is in good agreement with known Ti−P distances.[11] The Ti−P−C(6) angle is 97.2(2)°. Some strain in the ligand framework is evident from the O−C(1)−C(6) and the P−C(6)−C(1) angles (116.6(6) and 111.8(5)°, respectively) as these angles are significantly smaller than the expected value of 120°.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 2a

Bond Distances			
Ti−Cl(1)	2.333(3)	P−C(6)	1.794(7)
Ti−Cl(2)	2.340(2)	O−C(1)	1.367(8)
Ti−P	2.624(3)	Cp−Ti	2.13(2)
Ti−O	1.860(5)		
Bond Angles			
Cl(1)−Ti−Cl(2)	89.14(9)	P−Ti−O	72.4(2)
Cl(1)−Ti−P	142.09(9)	Ti−P−C(6)	97.2(2)
Cl(1)−Ti−O	89.2(2)	Ti−O−C(1)	134.9(4)
Cl(2)−Ti−P	78.77(8)	O−C(1)−C(6)	116.6(6)
Cl(2)−Ti−O	129.7(2)	P−C(6)−C(1)	111.8(5)

Table 2. Reduction Potentials of Titanium Complexes

complex	E_{red} vs SCE (V)
	−0.69 (±0.02)
Cp_2TiCl_2	−0.800[12]
2a	−0.79 (±0.02)
2b	−0.78 (±0.02)

Cyclic Voltammetry. Titanium compounds generally exhibit reversible redox behavior between the +3 and +4 oxidation states. For titanocene dichloride electrochemical measurements have shown that there is a reversible redox wave that appears at −0.800 V (vs SCE).[12] With this in mind the reduction potential of complexes **2** serve as a useful probe of the electron-donating capabilities of the *o*-phosphinophenol ligands. Thus the reduction potentials were measured by cyclic voltammetry for complexes **2** and some other related titanium complexes. The results are shown in Table 2. Complexes **2a**,**b** exhibited reversible redox waves at potentials of −0.79 (±0.02) V and −0.78 (±0.02) V (vs SCE). In comparison the $CpTiCl_2(O\text{-}2,6\text{-}di^tBuC_6H_3)$ complex has a reduction potential of −0.69 (±0.02) V. These results show that, as anticipated, **2a**,**b** are more

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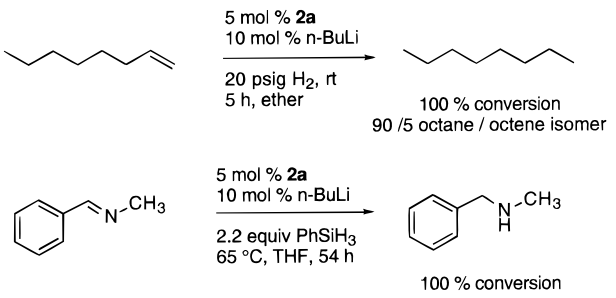
Scheme 2. Catalytic Activity of Complex 2a



electron rich than the related $CpTiCl_2(OAr)$ complex. The potentials of **2a**,**b** are comparable to that of Cp_2TiCl_2 at −0.800 V indicating that these ligands are electronically similar to the cyclopentadienyl ligand. However these measurements of the reduction potential are not sensitive enough to determine the subtle electronic differences between **2a**,**b**.

Catalytic Studies. A brief investigation of the catalytic activity of complex **2a** was also conducted. The results are shown in Scheme 2. Treatment of complex **2a** with *n*-butyllithium under a hydrogen atomosphere resulted in the formation of an active olefin hydrogenation catalyst. Hydrogenation of 1-octene proceeded under mild conditions (rt, 20 psig H_2) to give a mixture of octane and an unidentified octene isomer in a 90:5 ratio, respectively. Hydrogenation of an imine, however, was not successful with this complex. At 80 psig and 65 °C no reduction of *N*-benzylidenemethylamine was observed. Hydrosilylation of this imine was affected using **2a**. Treatment of **2a** with *n*-butyllithium in THF followed by addition of phenylsilane afforded an active hydrosilylation catalyst which converted the starting imine completely to product[13] in 54 h at 65 °C; no side products were observed in this reaction.

Conclusions

Two novel titanium complexes bearing the phosphinophenol ligand system have been prepared and studied. Electrochemical measurements indicate that the ligands are similar to the cyclopentadienyl ligand in their electron-donating properties. By the changing of substituents on phosphorus, the *o*-phosphinophenol ligands can be tailored both electronically and sterically making the *o*-phosphinophenol ligands well suited for further detailed reaction studies. A preliminary investigation of the catalytic activity of complex **2a** indicated that it is effective for the hydrogenation of an olefin and the hydrosilylation of an imine. However the reaction rates are rather slow. The reaction chemistry of these new titanium complexes remains largely unexplored; we are continuing to develop and study these and other novel titanium complexes for catalytic and stoichiometric transformations.

Experimental Section

General Considerations. All reactions were conducted under an atmosphere of prepurified argon or hydrogen using standard Schlenk and glovebox techniques. Handling of complexes **2** was conducted in a Vacuum Atmospheres glovebox under nitrogen. Hydrogenation reactions were conducted in a Fisher-Porter bottle (purchased from Aerosol Lab Equipment, Walton, NY) with Ultra High Purity hydrogen (grade 5). Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Unity-300, Varian XL-300, or Bruker AC-250 Fourier transform spectrometer. Variable-temperature NMR experiments were conducted using a Varian VXR-500 spectrometer. Elemental analyses were performed by E & R Microanalytical Laboratories (Corona, NY). Tetrahydrofuran (THF) and ether were dried and deoxygenated by refluxing and distilling from sodium/benzophenone ketyl under an argon atmosphere. All reagents are commercially available and were used as received unless otherwise stated.

2-Bromo-6-*tert*-butylphenol. The method of Pearson[14] was used to prepare 2-bromo-6-*tert*-butylphenol from 2-*tert*-butylphenol. The product was purified by column chromatography (silica, hexane) to give a colorless oil (61% yield). ^{1}H NMR (300 MHz, CDCl3, TMS): δ 7.34−7.31 (m, 1H), 7.22−7.19 (d, 1H, J = 7.8 Hz), 6.75−6.70 (t, 1H, J = 7.7 Hz), 5.79 (s, 1H), 1.39 (s, 9H).

2-(Diphenylphosphino)-6-*tert*-butylphenol, 1a. A dry Schlenk flask under argon was charged with NaH (0.4 g, 16.5 mmol) and 60 mL of ether. The suspension was cooled to 0 °C, and 2-bromo-6-*tert*-butylphenol (3.4 g, 15 mmol) was added dropwise *via* syringe. The mixture was allowed to stir for 3 h, and *n*-butyllithium (9.5 mL, 1.74 M in hexanes, 16.5 mmol) was added. After the mixture was stirred for 1 h, Ph_2PCl was added and the reaction mixture was warmed to room temperature and stirred for 16 h. Ether (100 mL) and saturated NH_4Cl (100 mL) were added, and the layers were separated. The organic portion was dried over $MgSO_4$ and concentrated to give the crude product. Column chromatography (silica, 100:1 hexane:EtOAc) afforded 3.92 g (78% yield) of the product as a viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.35−7.32 (m, 11H, 6.98−6.95 (d, 1H, J_{HP} = 11.3 Hz), 6.87−6.80 (m, 2H), 1.40 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.3 (d, J_{CP} = 19 Hz), 136.2, 135.0, 133.3 (d, J_{CP} = 18.7 Hz), 132.4, 128.9, 128.8, 128.5 (d, J_{CP} = 6.6 Hz), 120.9, 120.3, 34.8, 29.6. ^{31}P NMR (121 MHz, $CDCl_3$, 85% H_3PO_4): δ −31.3; HRMS: calc 334.1486, found 334.1488.

2-[Bis(4-methylphenyl)phosphino]-6-*tert*-butylphenol, 1b. This was prepared as above from 2-bromo-6-*tert*-butylphenol and bis(4-methylphenyl)chlorophosphine.[4b] Yield: 26%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.31−7.28 (d, 1H, J = 7.8 Hz), 7.24−7.17 (m, 8H), 6.97−6.91 (d, 1H, J_{HP} = 11.2 Hz), 6.90−6.78 (m, 2H), 2.36 (s, 6H), 1.40 (s, 9H). ^{31}P NMR (121 MHz, $CDCl_3$, 85% H_3PO_4): δ −32.7; HRMS: calc. 362.1799, found 362.1801.

Preparation of Cyclopentadienyltitanium Complexes. 2a. A dry Schlenk flask under an argon atmosphere was charged with **1a** (1.33 g, 4 mmol) and THF (20 mL). A solution of *n*-butyllithium (2.4 mL, 1.74 M in hexanes, 4.2 mmol) was added, and the mixture was allowed to stir for 1 h. The resulting solution was then added *via* cannula to a solution of $CpTiCl_3$ (0.877g, 4 mmol) in THF (20 mL) over a period of 10 min. The deep red solution was stirred overnight (12 h), and the solvent was removed *in vacuo* to give an orange solid. Toluene (40 mL) was added, and the mixture was heated to 100 °C and then filtered *via* cannula while hot. Slow cooling of the filtrate to −20 °C afforded orange crystals which were isolated by decanting the supernatant and washing with hexane. Removal of the residual solvents *in vacuo* afforded 1.3 g (63% yield) of the desired complex. ^{1}H NMR (300 MHz, CDCl3, TMS): δ 7.72−7.62 (m, 4H), 7.2−7.18 (d, 1H, J = 7.5 Hz), 7.0−6.9 (m, 7H), 6.67−6.60 (t, 1H, J = 7.5 Hz), 6.18 (d, J_{HP} = 2.7 Hz), 1.55 (s, 9H). ^{31}P NMR (121 MHz, C_6D_6, 85% H_3PO_4): δ 28.4. ^{13}C NMR (75 MHz, CD_2Cl_2): δ 171.3 (d, J_{CP} = 27.5 Hz), 138.6 (d, J_{CP} = 3.8 Hz), 132.6 (d, J_{CP} = 9.8 Hz), 131.4, 131.1 (d, J_{CP} = 11.3 Hz), 129.5 (d, J_{CP} = 9 Hz), 129.3,

(13) The initial product is assumed to be the silyl amine. However, the Si−N bond is very labile and is immediately hydrolyzed upon exposure to ambient atmosphere.

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128.5, 125.6, 122.4 (d, J_{CP} = 6 Hz), 121.5, 35.4, 29.7. Anal. Calc for $C_{27}H_{27}Cl_2OPTi$: C, 62.69; H, 5.26. Found: C, 62.94; H, 5.37.

2b. A dry Schlenk flask under an argon atmosphere was charged with **1b** (1.4 g, 3.8 mmol) and THF (20 mL). A solution of *n*-butyllithium (2.5 mL, 1.60 M in hexanes, 4.1 mmol) was added, and the mixture was allowed to stir for 1 h. The resulting solution was then added *via* cannula to a solution of $CpTiCl_3$ (0.847 g, 3.8 mmol) in THF (20 mL) over a period of 10 min. The deep red solution was stirred overnight (12 h), and the solvent was removed *in vacuo* to give an orange solid. Toluene (25 mL) and hexane (20 mL) were added, and the mixture was heated to 80 °C and filtered *via* cannula while hot. The filtrate was slowly cooled to −20 °C to give orange crystals. The crystals were washed with hexane and dried *in vacuo* to afford 0.54 g of product. The supernatant was concentrated and the resulting solid recrystallized in a similar manner to give an additional 0.4 g of product. Yield: 0.94 g (45%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.68−7.62 (m, 4H), 7.22−7.20 (d, 1H, J = 7.8 Hz), 7.12−7.09 (m, 1H), 6.81−6.78 (m, 4H), 6.68−6.63 (t, 1H, J = 7.8 Hz), 6.20 (d, J_{HP} = 2.4 Hz), 1.91 (s, 6H), 1.55 (s, 9H). ^{31}P NMR (121 MHz, C_6D_6, 85% H_3PO_4): δ 27.6. ^{13}C NMR (75 MHz, CD_2Cl_2): δ 171.1 (d, J_{CP} = 27.2 Hz), 142.0, 138.5 (d, J_{CP} = 4.5 Hz), 132.5 (d, J_{CP} = 9.5 Hz), 130.9 (d, J_{CP} = 14 Hz), 130.2 (d, J_{CP} = 9.9 Hz), 129.3, 128.5, 125.8, 122.3 (d, J_{CP} = 5.3 Hz), 121.5, 35.3, 29.7, 21.6. Anal. Calc for $C_{29}H_{31}Cl_2OPTi$: C, 63.87; H, 5.73. Found: C, 63.92; H, 5.96.

$CpTiCl_2$(O-2,6-di^{t}BuC_6H_3). A dry Schlenk flask under argon was changed with 2,6-di-*tert*-butylphenol (0.825 g, 4 mmol) and THF (15 mL). A solution of *n*-butyllithium (2.5 mL, 4 mmol, 1.6 M in hexanes) was added, and the reaction mixture was stirred for 30 min. The resulting solution was transferred *via* cannula to a solution of $CpTiCl_3$ (0.877 g, 4 mmol) in THF (15 mL). The mixture turned deep red and was allowed to stir at room temperature for 8 h. The solvent was removed *in vacuo*, and the resulting orange solid was extracted with hot hexane (60 mL). Cooling to −20 °C afforded 0.80 g of orange crystals (51% yield). ^{1}H NMR (250 MHz, C_6C_6): δ 7.2−7.25 (d, 2H, J = 6.8 Hz), 6.88−6.79 (dd, 1H, J = 6.8 Hz), 6.08 (s, 5H), 1.43 (s, 18 H).

X-ray Structure Determination of 2a. The X-ray structure determination of complex **2a** was conducted using a Rigaku-AFC6R diffractometer at 195 K. A total of 4016 reflections were collected. The crystals are triclinic, space group $P1$, with a = 10.009 Å, b = 14.590 Å, c = 9.889 Å, α = 92.95°, β = 98.56°, and γ = 77.72°. An empirical absorption correction, using the DIFABS[15] program, was applied. Anisotropic refinement was conducted using direct methods.[16] The final cycle was based on 2117 reflections and converged with an agreement factor of R = 0.052. Crystal data are shown in Table 3.

Cyclic Voltammetry. In a glovebox the titanium complex, Bu_4NPF_6, and ferrocene were dissolved in THF (5 mL). The measurements were conducted using a Pine RDE4 potentiostat with a glassy carbon working electrode, a Pt counter electrode, and a Ag reference electrode. The potential was scanned at a rate of 100 mV/s, and the voltammograms were recorded using a Kipp & Zonen BD90 X-Y recorder. The potentials were corrected vs the Cp_2Fe/Cp_2Fe^+ couple (+0.51 V vs SCE): Cp_2TiCl_2O(2,6-^{t}Bu$_6H_3$), −0.69 (±0.02) V; **2a**, −0.79 (±0.02) V; **2b**, −0.78 (±0.02) V.

Hydrogenation of 1-Octene with 2a. A dry Fisher-Porter bottle under nitrogen was charged with **2a** (52 mg, 0.1 mmol), and the vessel was evacuated and filled with hydrogen (3×).

Table 3. Crystal Data for Compound 2a

empirical formula	$C_{27}H_{27}OPCl_2Ti$
fw	517.295
cryst color, habit	orange, prismatic
cryst dimens	0.050 × 0.100 × 0.300 mm
cryst system	triclinic
lattice params	a = 10.009(3) Å
	b = 14.590(4) Å
	c = 9.889(3) Å
	α = 92.95(3)°
	β = 98.56(3)°
	γ = 77.72(2)°
	V = 1395.0(8) Å^3
space group	$P1$
Z value	2
D_{calc}	1.341 g/cm^3
diffractometer	Rigaku AFC6R
radiation	Mo Kα (0.710 69 Å)
temp	195 K
take-off angle	6.0°
scan rate	8.0°/min (in ω)
scan width	(1.15 + 0.3 tan φ)°
$2\theta_{max}$	0.0°
no. of reflcns measd	tot. 4016
	unique 3709
corrs	Lorentz−polarization
	abs (0.86−1.19)
no. of obsd reflcns	2117
no. of variables	334
R	0.052
R_w	0.057
max shift/error in final cycle	1.51

Ether (10 mL) and 1-octene (314 μL, 2 mmol) were added. A solution of *n*-butyllithium (123 μL, 1.63 M in hexanes, 0.2 mmol) was added, and the mixture turned a dark brown color. The vessel was charged to 20 psig, and the reaction mixture was stirred at room temperature for 5 h. At this point GC/MS analysis showed no 1-octene remaining. Two new products were present in a 90:5 ratio. These were identified by GC/MS; the major product was octane (MW = 114), and the minor product was an octene isomer (MW = 112).

Hydrosilylation of *N*-Benzylidenemethylamine with 2a. A dry Schlenk flask under argon was charged with **2a** (52 mg, 0.1 mmol) and THF (5 mL). The solution was cooled to 0 °C, and a solution of *n*-butyllithium (123 μL, 1.63 M in hexanes, 0.2 mmol) was added. After 1 min phenylsilane (271 μL, 2.2 mmol) was added followed by *N*-benzylidinemethylamine (250 μL, 2.0 mmol). The mixture was heated in an oil bath at 65 °C for 54 h. At this point GC analysis showed that no imine remained. The only product detected was *N*-methylbenzylamine.[13]

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Supporting Information Available: Tables of positional and thermal parameters, U values, and complete bond distances and angles for complex **2a** (21 pages). Ordering information is given on any current masthead page.

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