Syntheses, Characterizations, and Reactivities of 4,5-Diazafluorenide Complexes of Palladium(II) and Rhodium(I)

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Received April 7, 2008

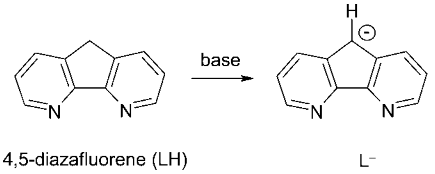
The reaction of 4,5-diazafluorene (LH) and NaH generates NaL, which reacts with $Pd(PPh_3)_2Cl_2$ and $[Rh(COD)Cl]_2$ to afford $[Pd(PPh_3)ClL]_2$ (**1**) and Rh(COD)L (**2**), respectively. Both **1** and **2** were fully characterized by NMR, elemental, and single-crystal X-ray diffraction analyses. Compound **2** can promote the hydrogenation of a variety of terminal olefins, without affecting the carbonyl groups in the substrates. Attempts to crystallize NaL results in the formation of a partially protonated species, $Na_2(LH)_2L_2$, whose structure is confirmed by X-ray crystallography.

Introduction

4,5-Diazafluorene (LH), reported over three decades ago,[1] has attracted a lot of research interest. Being viewed as a 3,3′-annealed 2,2′-bipyridine (bpy) derivative, LH has been studied as a dinitrogen chelating ligand and a photon harvesting unit to populate the excited states in its ruthenium complexes,[2] because of the extensive interest in the photochemical water-splitting processes sensitized by $[Ru(bpy)_3]^{2+}$ and its analogues. Marx and Lees have studied the photochemistry of group 6 carbonyl complexes with the LH ligand.[3]

Alternatively, the structure of LH can be viewed as two pyridine rings fused onto the middle cyclopentadiene (CpH) ring in a *syn* fashion (Scheme 1). Therefore, it is conceivable that if LH is deprotonated at the 9-position, the resulting 4,5-diazafluorenide (L^-) has two types of metal binding sites: the pyridine nitrogen donors and Cp^- carbon donors. Despite such interesting structural features displayed by L^-, metal complexes of the L^- ligand are barely known. In fact, even complexes with the charge neutral LH ligand are still very limited.[1–4] One possible reason for the limited number of complexes is the restrained geometry of the ligand backbone. Schröder's study has suggested that the coordinating ability of the neutral LH ligand to Mn(II) is weaker than that of 1,10-phenanthroline (phen), but stronger than that of bpy,[5] while Cherry's study has suggested that LH is a weaker ligand than bpy.[2a] Compared to the two pyridine moieties of phen, those of LH are tied back by a methylene group, which presumably undermines the chelating ability of LH. However, such restrained geometry gives rise to the ability to bridge over two metal centers through the two nitrogen donor atoms of the LH ligand.[6]

Scheme 1



The intriguing structural features of L^- have prompted us to examine its coordination chemistry, because both Cp^- and pyridine are versatile ligands for a large variety of metals. In addition, the distinct electronic properties of pyridine and Cp^- may give L^- the possibility of accommodating two metal centers with different properties. Although the two pyridine nitrogen donors in LH are tied back by the methylene group, undermining its coordinating ability, when the ligand is deprotonated, the negative charge may change coordinating capability dramatically.

The charge neutral α- and β-diimine ligands and the −1 charged β-diiminate ligands have been widely used to form complexes with different metal ions. Some of these complexes show interesting reactivities toward C−H activation,[7] polymerization,[8] dinitrogen activation,[9] and dioxygen activation.[10] In contrast, the −1 charged α-diimine ligands are relatively underdeveloped. The L^- ligand falls into this category. Recently, we have studied the coordination chemistry of L^- with late transition metals. Indeed, the L^- ligand shows novel coordination modes and the corresponding complexes show interesting reactivities. The palladium and rhodium chemistry of the L^- ligand is reported herein.

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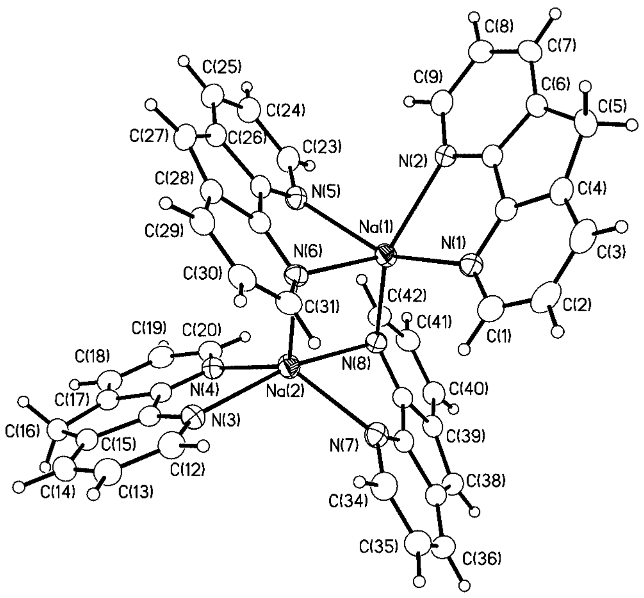


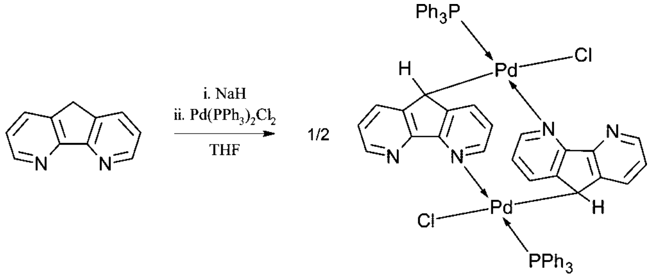
Figure 1. Molecular structure of $Na_2(LH)_2L_2$ with thermal ellipsoids plotted at 30% probability.

Results and Discussions

Synthesis and Structure of LH Sodium Salt. The reaction of a pale yellow solution of LH in THF and NaH generates a purple solution of NaL cleanly at ambient temperature with visible gas evolution. The NMR tube reaction in THF-d_8 indicates that the deprotonation of the LH ligand reaches completion within half an hour. Thus, the chemical shift of the protons at the 9-position changes from 3.85 to 5.91 ppm, and the integration changes from 2H to 1H against the aromatic protons. The significant downfield shift is consistent with the increased aromatic character. Other proton signals are also downfield shifted to different extents, although not as significant. The resulting NaL is extremely air- and moisture-sensitive. Attempts to obtain X-ray quality crystals through slow diffusion of hexanes into the THF solution of NaL resulted in the partially protonated product $Na_2(LH)_2L_2$, whose molecular structure has been confirmed by X-ray crystallography. The partial protonation is possibly due to the adventitious acidic solvent vapor, such as alcohol and acetonitrile, in the atmosphere of the glovebox.

As shown in Figure 1, each Na(I) center is coordinated by five nitrogen donor atoms from one LH and two L^- ligands. Each L^- ligand bridges over two metal centers with one nitrogen donor atom and dedicates the other nitrogen donor atom to only one metal center, with the Na−N bonds off the direction of the nitrogen lone pairs, showing the highly electrostatic nature of the bonding. Each LH ligand coordinates to one Na(I) center in the chelating mode, and the five-membered chelate ring has a planar geometry, with Na−N bonds along the nitrogen lone-pair directions, suggesting a higher level of covalence. The Na−N bond length range is 2.447(2)−2.566(2) Å, where the longest bonds are formed by the bridging nitrogen atoms N(8) and N(6). These bond lengths are comparable to the literature values.[11] The Na−Na separation is 3.129(1) Å. The 9-positions of the LH ligands (C(5) and C(16) in Figure 1) have the typical sp^3 characters with the average CC bond length of 1.504(3) Å, while those of the L^- ligands (C(27) and C(38) in Figure 1) are sp^2 like, with the average CC bond length of 1.410(3) Å. The average C−C−C angles around the 9-positions of the LH and L^- ligands are 103.1(2)° and 107.6(2)°, respectively.

Scheme 2. Synthesis of Compound 1



Because of its reactive nature, NaL is always generated freshly and used in situ for further coordination chemistry with transition metals in the sections below. Nevertheless, $Na_2(LH)_2L_2$ is an interesting compound with both the neutral LH ligand and its deprotonated version in the same molecule. The bond lengths and angles are useful handles for structural comparison of the coordinating LH and L^- ligands.

Synthesis and Structure of $[Pd(PPh_3)ClL]_2$, 1. The reaction of in situ generated NaL and $Pd(PPh_3)_2Cl_2$ produces compound **1** as an orange solid in good yield (Scheme 2). Compound **1** is insoluble in THF and slightly soluble in CH_2Cl_2. It reacts with $CHCl_3$ to generate a mixture of HL, $Pd(PPh_3)_2Cl_2$, and some unidentified species. Compound **1** is air-stable in the solid state, but air-sensitive in solution.

Compound **1** crystallizes as a CH_2Cl_2 solvate in the triclinic space group $P\bar{1}$. The molecular structure of **1** in the solid state has been confirmed by X-ray crystallography and is shown in Figure 2. Compound **1** has a dimeric structure with a crystallographically imposed center of inversion in the middle. Each Pd(II) center has a typical square-planar coordination geometry with a carbon donor atom from an L^- ligand and a chloride *trans* to each other, and a phosphine ligand and a nitrogen donor atom from the other L^- ligand *trans* to each other. Such a spatial arrangement is probably favored because the phosphine and carbon donor ligands with strong *trans* influence are *cis* to each other. Each L^- ligand adopts a unique bridging mode, coordinating through one nitrogen donor atom to one Pd(II) center and one carbon donor atom of the Cp^- moiety (C(5) in Figure 2) to the other, leaving one pyridine nitrogen atom dangling. The distance between the dangling nitrogen atom and the Pd(II) center is ~3.27 Å. This coordination mode is related to that observed in Pd-nacnac compounds, where the nitrogen donor atoms coordinate to one Pd center and the carbon donor atom of the nacnac backbone coordinates to another Pd center.[12] The Pd(1)−C(5) bond length in **1** is 2.141(5) Å, also similar to the values found in the Pd-nacnac compounds.[12] Because of the strong *trans* influence of the carbon donor ligand, the Pd(1)−Cl(1) bond (2.362(2) Å) is longer than the previously reported Pd−Cl bonds that are *trans* to a chloride or a nitrogen donor ligand[13] and similar to the reported Pd−Cl bonds that are *trans* to carbon donor ligands.[14] Interestingly, the geometry around the 9-position of the L^- ligand (C(5) in Figure 2) is similar to that of the

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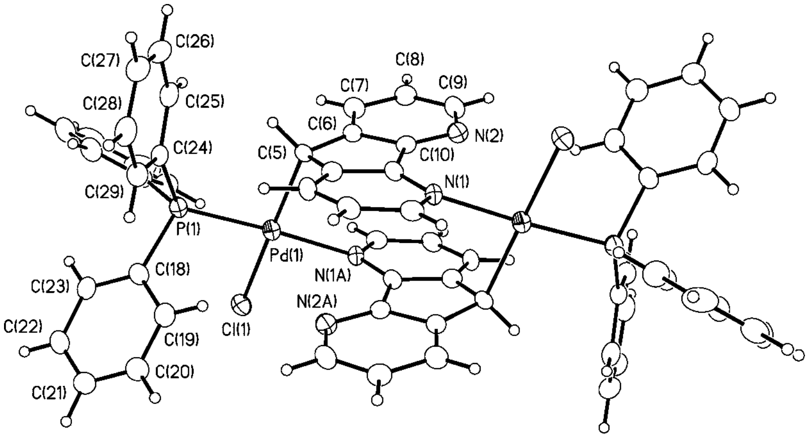
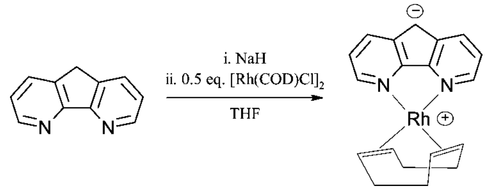


Figure 2. Molecular structure of **1** with thermal ellipsoids plotted at 30% probability.

Scheme 3. Synthesis of 2



LH ligand in $Na_2(LH)_2L_2$ and best described as a distorted tetrahedron. Thus, the C(6)−C(5)−C(4) angle is 103.9(5)°. The bond lengths of C(4)−C(5) and C(5)−C(6) are 1.491(8) and 1.478(7) Å, respectively, close to the length of a typical C−C single bond, showing little delocalization of the negative charge over the ring system. The C(3A)−N(1A)−Pd(1) angle is ~165°, ~15° off the ideal value, 180°, presumably due to steric effects. Because of the inversion center symmetry, the two planes defined by the L^- ligands are parallel to each other, with an interplane distance of ~2.95 Å, indicating the existence of strong $\pi-\pi$ stacking interactions between the two L^- ligands.

In the ^{1}H NMR spectrum in CD_2Cl_2, the proton on the coordinating carbon shows a resonance at 4.29 ppm as a doublet, with a $^3J_{P-H}$ coupling constant of 12 Hz, indicating that the Pd−C linkage in **1** is retained in solution. The Pd−N linkage appears to be retained in solution as well, as evidenced by the asymmetry displayed by the signals from the L^- ligand in the ^{1}H NMR spectrum. The proton-decoupled ^{31}P NMR spectrum of **1** shows the only resonance at 38.36 ppm.

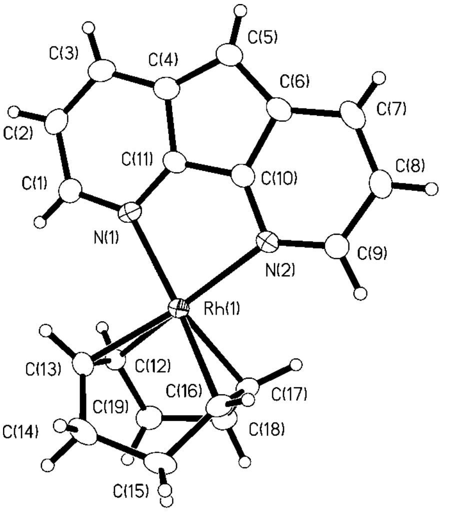
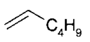
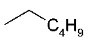
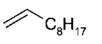
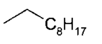
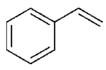
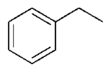
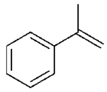
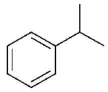
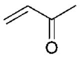
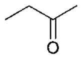
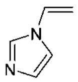
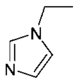
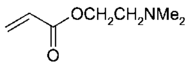
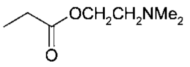


Figure 3. Molecular structure of **2** with thermal ellipsoids plotted at 50% probability.

Table 1. Olefin Hydrogenation Catalyzed by 2

Entry	Substrate[a]	Product[b]	Time (h)[c]	TOF[d] (h^{-1})
1			4	500
2			10	200
3			9	222
4			12	167
5			10	200
6			21	95
7			36	56

[a]7 M in benzene, 0.05 mol % of **2**, ~4 atm H_2, ambient temperature. [b]Products in entries 1,[18] 2,[18] 3,[19] 4,[20] 5,[19] 6,[21] and 7[22] were identified by ^{1}H NMR. [c]Time required for 100% conversion monitored by NMR. [d]Turnover frequency.

Synthesis and Structure of Rh(COD)L, 2. The reaction of in situ generated NaL and $[Rh(COD)Cl]_2$ gives **2** in good yield (Scheme 3). The dark green compound **2** is soluble in most common organic solvents, except for the nonpolar hexanes and pentane. It is air-stable in the solid state, but air-sensitive in solution.

The NMR spectra of **2** are consistent with the proposed structure in Scheme 3. Thus, the protons and carbons of the two pyridine rings show only one set of signals in the ^{1}H and ^{13}C NMR spectra, respectively. The proton of the Cp^- moiety shows a singlet at 6.72 ppm, integrated for one proton against the protons from the two pyridine rings. The corresponding carbon resonates at 116.7 ppm. The carbon donor atoms of the COD ligand show a doublet at 79.5 ppm in the ^{13}C NMR spectrum, with the $^1J_{Rh-C}$ coupling constant of 12 Hz, which is greater than the reported $^1J_{Rh-C}$ coupling constant for Rh and an η^5 Cp-carbon (4 Hz), but smaller than the Rh−*C*O coupling constants (46 and 84 Hz).[15]

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Table 2. Crystallographic Data

	$Na_2(LH)_2L_2$	**1**$\cdot 2CH_2Cl_2$	**2**
formula	$C_{44}H_{30}N_8Na_2$	$C_{58}H_{44}Cl_2N_4P_2Pd_2 \cdot 2CH_2Cl_2$	$C_{19}H_{19}N_2Rh$
fw	716.74	1312.46	378.27
T (K)	150(2)	150(2)	150(2)
λ (Å)	0.71073	0.71073	0.71073
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a (Å)	14.4180(6)	9.9317(6)	10.0544(4)
b (Å)	15.3044(7)	11.7023(6)	11.1105(5)
c (Å)	16.7139(8)	13.2396(8)	12.8356(3)
α (deg)	90	79.655(3)	90
β (deg)	109.206(2)	87.484(3)	97.249(2)
γ (deg)	90	65.604(3)	90
V (Å^3)	3482.8(3)	1377.80(14)	1422.40(9)
Z	4	1	4
D_c (g$\cdot$cm^{-3})	1.367	1.582	1.766
μ (mm^{-1})	0.105	1.046	1.198
no. of reflns collected	20 477	12 069	9719
no. of indept reflns	7921	4791	3221
GOF on F^2	0.986	1.011	1.056
R indices [$I > 2\sigma (I)$]	$R_1 = 0.0518$ $wR_2 = 0.1139$	$R_1 = 0.0567$ $wR_2 = 0.1311$	$R_1 = 0.0272$ $wR_2 = 0.0646$
R indices (all data)	$R_1 = 0.1307$ $wR_2 = 0.1490$	$R_1 = 0.0813$ $wR_2 = 0.1488$	$R_1 = 0.0345$ $wR_2 = 0.0686$

Compound **2** has crystallized in the monoclinic space group $P2_1/c$, and its structure in the solid state has been confirmed by X-ray crystallography. As shown in Figure 3, the Rh(I) center has a typical square-planar coordination geometry, with two nitrogen donor atoms from the L^- ligand and two CC double bonds from the COD ligand occupying the four coordination sites. In contrast to the coordination mode found in compound **1**, the L^- ligand coordinates to the Rh(I) center through both nitrogen donor atoms in a chelating fashion, leaving the carbon donor atom of the Cp^- moiety dangling. The Rh−N (av 2.147(2) Å) bonds are longer than those of $[Rh(COD)(phen)]^+$ (2.103 Å)[16] and $[Rh(COD)(bipy)]^+$ (2.095 Å)[17] species, while the Rh−C (av 2.108(2) Å) bonds are shorter than those of $[Rh(COD)(phen)]^+$ (2.146 Å)[16] and $[Rh(COD)(bipy)]^+$ (2.135 Å)[17] species. The bite angle of the L^- ligand is 83.25(7)°, greater than those of the $[Rh(COD)(phen)]^+$ (av 79.80°)[16] and $[Rh(COD)(bipy)]^+$ (78.61°)[17] species. The local geometry around the 9-position of the L^- ligand (C(5) in Figure 3) is similar to that of the L^- ligand found in $Na_2(LH)_2L_2$, showing typical sp^2 character. The C(5)−C(4) and C(5)−C(6) bond lengths are 1.423(4) and 1.432(3) Å, respectively, shorter than the counterparts in the structure of **1**, indicating a higher level of delocalization of the negative charge in the C_5 ring in **2**. The C(4)−C(5)−C(6) angle is 107.9(2)°, close to the angle of a regular pentagon and greater than that found in compound **1** (103.9(5)°).

Olefin Hydrogenation Catalyzed by 2. Compound **2** is capable of promoting the hydrogenation of olefins. As shown in Table 1, various terminal and 1,1-disubstituted olefins can be hydrogenated under mild conditions with low catalyst loading, leaving the polar CO double bonds intact. Comparison experiments show that hydrogenation of styrene promoted by **2** is not as fast as that promoted by $Rh(PPh_3)Cl$ or $Ru(PPh_3)_3Cl_2$. Thus, under otherwise identical conditions (i.e., ambient temperature, 1 atm of H_2, 0.05 mol % catalyst loading, 7 M of styrene in benzene, 24 h) the hydrogenation reactions catalyzed by **2**, $Rh(PPh_3)_3Cl$, and $Ru(PPh_3)_3Cl_2$ give 55%, 86%, and 88% conversion, respectively. The corresponding TOFs for **2**, $Rh(PPh_3)_3Cl$, and $Ru(PPh_3)_3Cl_2$ are 46, 72, and 73 h^{-1}, respectively.

Compound **2** does not seem to catalyze the hydrogenation of 1,5-cyclooctadiene (COD) or 2-methylstyrene under the conditions shown in Table 1. Unlike $Rh(PPh_3)_3Cl$, which dissociates in solution and reacts with H_2 to produce the hydrido species, when the solution of **2** is under ~4 atm of H_2, no observable amount of the corresponding hydrido species is produced according to the ^{1}H NMR spectrum, which shows only the signals from the unchanged **2** and the dissolved free H_2. These findings suggest that the hydrogenation reactions might follow a different mechanism compared to Wilkinson's catalyst. Further mechanistic study is being conducted in our laboratory to reveal the nature of the hydrogenation process.

Conclusions

We have demonstrated that L^- is a versatile ligand that forms interesting complexes with various metal ions. In the dimeric Pd(II) complex, **1**, the L^- ligand displays the bridging mode, using nitrogen and carbon donor atoms, leaving the remaining nitrogen donor atom dangling, while in the monomeric Rh(I) complex, **2**, the L^- ligand chelates to the metal center through both nitrogen donor atoms. The π-coordination through the Cp^- moiety has not been observed, although such a coordination mode has been claimed in a patent without any structural information.[23] Compound **2** shows catalytic reactivity toward olefin hydrogenation. Although not as active as $Rh(PPh_3)_3Cl$, **2** is stable in solution under inert atmosphere. The mechanism of the hydrogenation process is being investigated and will be published in due course.

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As a −1 charged α-diimine ligand, L^- shows analogies to the *β*-diketiminate ligand (also known as nacnac), e.g., overall −1 charge, nitrogen donor set, and noninnocent carbon backbone. Furthermore, L^- can potentially be modified by introducing bulky groups on the *ortho* positions of the nitrogen donor atoms, which might mimic the bulky nacnac ligands. From this perspective, the coordination chemistry of the L^- ligand and its bulky derivatives with other metals, especially the first-row transition metals, is being investigated in our laboratory. The L^- ligand and its complexes are also being investigated in comparison with the charge neutral α-diimine ligands and the corresponding complexes in our laboratory.

Experimental Section

General Procedures. All reactions were handled under argon using standard Schlenk techniques or in a nitrogen-atmosphere glovebox from MBraun. Unless otherwise stated, all chemicals were purchased from commercial sources and used without further purification. Benzene was distilled over sodium/benzophenone under argon and stored over activated 4 Å sieves in the glovebox. THF and pentane were purified using the solvent purification system from Vacuum Atmospheres Company. 4,5-Diazafluorene (LH) was prepared according to the literature procedure.[24] CD_2Cl_2 and C_6D_6 purchased from Cambridge Isotope Laboratories, Inc. were degassed and dried over activated 4 Å sieves prior to use. Anhydrous THF-d_8 (in ampules and packed under nitrogen) was purchased from Cambridge Isotope Laboratories, Inc. and used without further purification. NMR spectra were recorded on a Mercury 300 spectrometer working at 300 MHz for ^1H, 121 MHz for ^{31}P, and 75 MHz for ^{13}C or a Varian 400 spectrometer working at 400 MHz for ^1H and 100 MHz for ^{13}C. Elemental analyses were performed at our Chemistry Department using a PE 2400 C/H/N/S analyzer.

Preparation of NaL. To a suspension of NaH (60%, 8 mg, 0.2 mmol) in THF-d_8 (0.5 mL) was added dropwise a clear, pale yellow solution of LH (32 mg, 0.2 mmol) in THF-d_8 (0.5 mL), during which gas evolution was observed. The reaction mixture was stirred for 0.5 h to afford a clear, purple solution of NaL. ^1H NMR (THF-d_8, 400 MHz) δ: 7.84 (2H, d, $^3J = 4$ Hz), 7.73 (2H, d, $^3J = 8$ Hz), 6.83 (2H, dd, $^3J_1 = 8$ Hz, $^3J_2 = 4$ Hz), 5.91 (1H, s). ^{13}C NMR (THF-d_8, 100 MHz) δ: 139.45, 133.67, 131.56, 125.69, 117.36, 80.30. For comparison purposes, the ^1H NMR data of LH in THF-d_8 are provided: (400 MHz) δ 8.63 (2H, d, $^3J = 4$ Hz), 7.88 (2H, d, $^3J = 8$ Hz), 7.25 (2H, dd, $^3J_1 = 8$ Hz, $^3J_2 = 4$ Hz), 3.85 (2H, s).

Synthesis of $[PdCl(PPh_3)L]_2$, 1. A purple solution of NaL prepared in situ from LH (50 mg, 0.3 mmol) and NaH (60%, 20 mg, 0.5 mmol) in THF (3 mL) was cannulated dropwise to a solution of $Pd(PPh_3)_2Cl_2$ (0.21 g, 0.3 mmol) in THF (5 mL) with stirring to afford an orange precipitate. The mixture was further stirred for 3 h. The precipitate was collected by filtration, washed with THF (10 mL), and dried under vacuum to yield an orange solid of **1** (0.147 g, 86%). Crystals suitable for X-ray crystallographic analysis were obtained from slow diffusion of hexanes into a concentrated solution of **2** in CH_2Cl_2. ^1H NMR (CD_2Cl_2, 300 MHz) δ: 8.16−8.10 (12H, m, Ph), 7.52−7.49 (18H, m, Ph), 7.69−7.61 (2H, m, L), 7.47−7.33 (4H, m, L), 7.15−7.10 (2H, m, L), 7.07−7.01 (4H, m, L), 4.29 (2H, d, $^3J_{P-H} = 12$ Hz, Pd−*CH*). ^{31}P NMR (CD_2Cl_2, 121 MHz) δ: 38.36 (s). ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 147.5, 135.8, 135.5, 131.4, 131.12, 131.08, 128.8, 128.6, 67.95. Anal. Calcd for $C_{58}H_{44}Cl_2N_4P_2Pd_2 \cdot CH_2Cl_2$: C, 53.73; H, 3.78; N, 4.56. Found: C, 53.98; H, 3.49; N, 4.67.

Table 3. Selected Bond Lengths (Å) and Angles (deg)

	$Na_2(LH)_2L_2$		
Na(1)−N(1)	2.448(2)	N(1)−Na(1)−N(5)	148.25(7)
Na(1)−N(8)	2.464(2)	N(8)−Na(1)−N(5)	95.75(7)
Na(1)−N(2)	2.479(2)	N(2)−Na(1)−N(5)	87.24(7)
Na(1)−N(5)	2.483(2)	N(1)−Na(1)−N(6)	92.00(7)
Na(1)−N(6)	2.519(2)	N(8)−Na(1)−N(6)	103.03(7)
Na(2)−N(7)	2.447(2)	N(2)−Na(1)−N(6)	123.77(7)
Na(2)−N(6)	2.452(2)	N(5)−Na(1)−N(6)	75.61(7)
Na(2)−N(4)	2.460(2)	N(7)−Na(2)−N(6)	100.86(7)
Na(2)−N(3)	2.469(2)	N(7)−Na(2)−N(4)	137.13(7)
Na(2)−N(8)	2.566(2)	N(6)−Na(2)−N(4)	122.00(7)
C(4)−C(5)	1.497(3)	N(7)−Na(2)−N(3)	102.54(7)
C(5)−C(6)	1.506(3)	N(6)−Na(2)−N(3)	95.42(7)
C(15)−C(16)	1.511(3)	N(4)−Na(2)−N(3)	75.64(6)
C(16)−C(17)	1.501(3)	N(7)−Na(2)−N(8)	76.06(7)
C(26)−C(27)	1.415(3)	N(6)−Na(2)−N(8)	102.01(7)
C(27)−C(28)	1.402(3)	N(4)−Na(2)−N(8)	93.39(7)
C(37)−C(38)	1.413(3)	N(3)−Na(2)−N(8)	162.48(7)
C(38)−C(39)	1.410(3)	C(4)−C(5)−C(6)	103.0(2)
N(1)−Na(1)−N(8)	115.65(7)	C(17)−C(16)−C(15)	103.2(2)
N(1)−Na(1)−N(2)	75.44(6)	C(28)−C(27)−C(26)	107.8(2)
N(8)−Na(1)−N(2)	132.10(7)	C(39)−C(38)−C(37)	107.4(2)
	1		
Pd(1)−N(1A)	2.124(4)	C(5)−Pd(1)−P(1)	92.80(15)
Pd(1)−C(5)	2.141(5)	N(1A)−Pd(1)−Cl(1)	87.75(12)
Pd(1)−P(1)	2.2527(15)	C(5)−Pd(1)−Cl(1)	171.83(15)
Pd(1)−Cl(1)	2.362(2)	P(1)−Pd(1)−Cl(1)	89.77(5)
C(4)−C(5)	1.491(8)	C(6)−C(5)−C(4)	103.9(5)
C(5)−C(6)	1.478(7)	C(6)−C(5)−Pd(1)	108.2(4)
N(1A)−Pd(1)−C(5)	89.90(19)	C(4)−C(5)−Pd(1)	105.7(3)
N(1A)−Pd(1)−P(1)	176.98(12)		
	2		
Rh(1)−C(17)	2.103(2)	C(13)−Rh(1)−C(16)	83.24(10)
Rh(1)−C(13)	2.105(2)	C(12)−Rh(1)−C(16)	91.69(10)
Rh(1)−C(12)	2.111(2)	C(17)−Rh(1)−N(2)	90.18(8)
Rh(1)−C(16)	2.113(2)	C(13)−Rh(1)−N(2)	166.32(8)
Rh(1)−N(2)	2.147(2)	C(12)−Rh(1)−N(2)	154.23(8)
Rh(1)−N(1)	2.147(2)	C(16)−Rh(1)−N(2)	97.80(9)
C(4)−C(5)	1.423(4)	C(17)−Rh(1)−N(1)	150.70(9)
C(5)−C(6)	1.432(3)	C(13)−Rh(1)−N(1)	93.45(9)
C(17)−Rh(1)−C(13)	98.92(9)	C(12)−Rh(1)−N(1)	91.46(8)
C(17)−Rh(1)−C(12)	82.17(9)	C(16)−Rh(1)−N(1)	170.15(9)
C(13)−Rh(1)−C(12)	38.63(9)	N(2)−Rh(1)−N(1)	83.25(7)
C(17)−Rh(1)−C(16)	39.12(10)	C(4)−C(5)−C(6)	107.9(2)

Synthesis of Rh(COD)L, 2. A purple solution of NaL prepared in situ from LH (50 mg, 0.3 mmol) and NaH (60%, 20 mg, 0.5 mmol) in THF (3 mL) was cannulated dropwise to a solution of $[Rh(COD)Cl]_2$ (74 mg, 0.15 mmol) in THF (3 mL) with stirring. After the resulting dark green solution was stirred overnight (∼12 h), the solvent was removed under reduced pressure. The residue was dissolved in benzene (2 mL) and filtered through a pad of Celite. The filtrate was dried under vacuum to afford a dark green solid of **2** (81 mg, 72%). Crystals suitable for X-ray crystallographic analysis were obtained from slow diffusion of hexanes into a concentrated solution of **2** in benzene. ^1H NMR (C_6D_6, 300 MHz) δ: 7.98 (2H, d, $^3J = 9$ Hz, L), 6.92 (2H, d, $^3J = 6$ Hz, L), 6.78 (2H, dd, $^3J_1 = 9$, $^3J_2 = 6$ Hz, L), 6.72 (1H, s, L), 4.28 (4H, s, COD), 1.87−1.84 (4H, m, COD), 1.27−1.22 (4H, COD). ^{13}C NMR (C_6D_6, 75 MHz) δ: 129.2, 128.4, 128.0, 127.7, 127.3, 116.7, 79.5 (d, $^1J_{Rh-C} = 12$ Hz), 30.5. Anal. Calcd for $C_{19}H_{19}N_2Rh$: C, 60.33; H, 5.06; N, 7.40. Found: C, 60.73; H, 4.84; N, 7.30.

Olefin Hydrogenation: General Procedure. A glass vessel was charged with 2 mg (0.007 mmol) of **2**, an olefin substrate (14 mmol), benzene (to reach a total volume of 2 mL), and a magnetic stir bar, submerged in liquid nitrogen, and purged under vacuum. After the introduction of 1 atm of H_2, the vessel was sealed and then warmed to ambient temperature (∼4 atm). The mixture was stirred at ambient temperature and the progress of the reaction was monitored by ^1H NMR (compared with the spectra reported in the literature). The results are summarized in Table 1.

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Comparison of 2 and Wilkinson's Catalysts for the Hydrogenation of Styrene. At ambient temperature under 1 atm of hydrogen a glass vessel was charged with 0.007 mmol of a catalyst, 14 mmol of styrene, and an appropriate amount of benzene to reach a total volume of 2 mL. The mixture was stirred for 24 h and the conversion was determined by ^{1}H NMR. When $Rh(PPh_3)_3Cl$ was used, the conversion was 86%. When $Ru(PPh_3)_3Cl_2$ was used, the conversion was 88%. When **2** was used, the conversion was 55%.

X-ray Diffraction Analysis. Single crystals suitable for X-ray crystallographic analysis of $Na_2(LH)_2L_2$, **1**, and **2** were obtained as described above. All crystals were mounted on the tip of a MiTeGen MicroMount. All single-crystal X-ray diffraction data were collected on a Nonius Kappa-CCD diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å), operating at 50 kV and 30 mA, at 150 K controlled by an Oxford Cryostream 700 series low-temperature system. The diffraction data were processed with the DENZO-SMN package.[25] All structures were solved by the direct methods and refined using SHELXTL V6.10.[26] All non-hydrogen atoms were refined anisotropically. The positions for hydrogen atoms were either calculated or directly located from a difference Fourier map, and their contributions were included in the structure factor calculations. The crystallographic data are summarized in Table 2, while selected bond lengths and angles are listed in Table 3.

Acknowledgment. This research is supported by grants to D.S. from the Natural Science and Engineering Research Council (NSERC) of Canada, the Canadian Foundation for Innovation, the Ontario Research Fund (ORF), and the University of Toronto (Connaught Foundation). Dr. Alen Hadzovic is thanked for some preliminary work.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800312D

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