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A Cationic Iridium Complex Bearing an Imidazol-2-ylidene Ligand as Alkene Hydrogenation Catalyst

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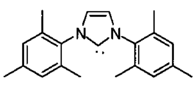
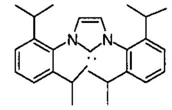
*Summary: The new cationic iridium carbene complex [Ir(cod)(py)(SIMes)]PF$_6$ (**2**) has been synthesized by reaction of [Ir(cod)(py)$_2$]PF$_6$ with SIMes. Complex **2** is an active hydrogenation catalyst capable of hydrogenating simple olefins at room temperature and atmospheric pressure of hydrogen.*

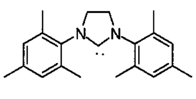
Introduction

Among homogeneous hydrogenation catalysts, the most widely used are RhCl(PPh$_3$)$_3$ (Wilkinson's catalyst)[1] and [Ir(cod)(py)(PCy$_3$)]PF$_6$ [py = pyridine; cod = cyclooctadiene] (**1**, Crabtree's catalyst).[2] The latter complex is an efficient catalyst for polysubstituted olefins lacking coordinating functionalities and is particularly useful in directed hydrogenation processes.[3] Despite having such remarkable catalytic activity, **1** has been shown to be susceptible to deactivation through the formation of the inactive hydride-bridged trimer [(Ir(py)(PCy$_3$)(H$_2$))$_3$(μ_3-H)]PF$_6$ and has also been demonstrated as thermally unstable.[2a,c]

Nucleophilic *N*-heterocyclic carbenes, or so-called "phosphine mimics", have attracted considerable attention as possible alternatives for the widely used phosphine ligands in homogeneous catalysis.[4] Indeed, we and others have found that the replacement of bulky phosphines with sterically demanding *N*-heterocyclic carbenes IPr (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) or IMes (IMes = bis(1,3-(2,4,6-trimethylphenyl)imidazol-2-ylidene) can result in significant catalytic performance in olefin metathesis,[5] C−C bond formation reactions,[6] amination of aryl chlorides,[7] hydrogenation,[8] and hydroformylation.[9]


IMes

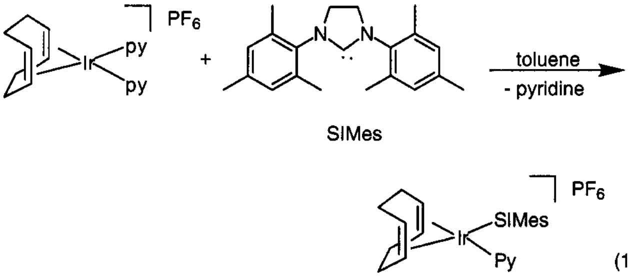

IPr


SIMes

In view of these findings and in our continued search for more efficient and stable catalysts, we turned our attention to the Crabtree-type iridium hydrogenation catalyst. We wished to examine whether the replacement of PCy$_3$ with SIMes (1,3-dimesityl-4,5-dihydroimidazol-2-ylidene, which we trivially call saturated IMes or SIMes) in **1** could lead to the generation of a more active and more thermally tolerant hydrogenation catalyst. We now report the synthesis of a new iridium carbene complex [Ir(cod)(py)(SIMes)]PF$_6$ (**2**) and its catalytic behavior in the hydrogenation of simple olefins.

Results and Discussion

Synthesis and Characterization of [Ir(cod)(py)(SIMes)]PF$_6$ (2). Complex **2** was prepared by a simple ligand exchange reaction of [Ir(cod)(py)$_2$]PF$_6$ with SIMes in toluene (eq 1). Due to the steric bulk of SIMes, this ligand could be used in slight excess to accelerate the kinetics of ligand substitution without fear of obtaining



(1)

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[1] Herrmann, W. A.; Cornils, B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1049−1067.

[2] (a) Crabtree, R. H.; Felkin, H.; Morris, G. E. *J. Organomet. Chem.* **1977**, *135*, 205−215. (b) Crabtree, R. H.; Morris, G. E. *J. Organomet. Chem.* **1977**, *135*, 395−403. (c) Crabtree, R. H. *Acc. Chem. Res.* **1979**, *12*, 331−338. (d) Crabtree, R. H.; Felkin, H.; Fillebeen-Khan, T.; Morris, G. E. *J. Organomet. Chem.* **1979**, *168*, 183−195.

[3] (a) Stork, G.; Kahne, D. E. *J. Am. Chem. Soc.* **1983**, *105*, 1072−1073. (b) Evans, D. A.; Morrissey, M. M. *Tetrahedron Lett.* **1984**, *25*, 4637−4640. (c) Schultz, A. G.; McCloskey, P. J. *J. Org. Chem.* **1985**, *50*, 5905−5907. (c) Crabtree, R. H.; Davis, M. W. *J. Org. Chem.* **1986**, *51*, 2655−2661. (d) Hoveyda, A.; Evans, D. A.; Fu, G. C. *Chem. Rev.* **1993**, *93*, 1307−1370. (e) Wender, P. A.; Badham, N. F.; Conway, S. P.; Floreancig, P. E.; Glass, T. E.; Gränicher, C.; Houze, J. B.; Jänichen, J.; Lee, D.; Marquess, D. G.; McGrane, P. L.; Meng, W.; Mucciaro, T. P.; Mühlebach, M. *J. Am. Chem. Soc.* **1997**, *119*, 2755−2756.

[4] (a) Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 725−728. (b) Hermann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162−2187. (c) Arduengo, A. J., III; Krafczyk, R. *Chem. Z.* **1998**, *32*, 6−14. (d) Dullius, J. E. L.; Suarez, P. A. Z.; Einloft, S.; de Souza, R. F.; Dupont, J.; Fischer, J.; De Cian, A. *Organometallics* **1998**, *17*, 815−819. (e) Arduengo, A. J., III. *Acc. Chem. Res.* **1999**, *32*, 913−921.

[5] (a) Huang, J.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674−2678. (b) Huang, J.; Schanz, H. J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 5375−5380. (c) Jafarpour, L.; Schanz, H. J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 5416−5419. (d) Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 336. (e) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953−956. (f) Chatterjee, A. K.; Grubbs, R. H. *Org. Lett.* **2000**, *1*, 1751−1753. (g) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39−91, and references therein.

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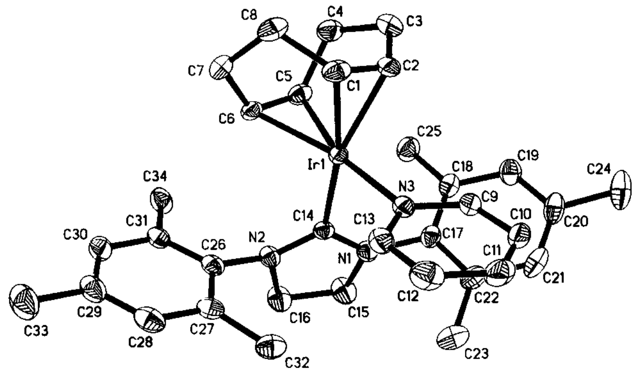

Figure 1. ORTEP of [Ir(cod)(py)(SIMes)]PF$_6$ (**2**) with ellipsoids drawn at 50% probability. Hydrogens and PF$_6$ are omitted for clarity.

a dicarbene iridium complex. Since the free carbene SIMes is relatively unstable, it was not isolated but prepared and used in situ by the reaction of SIMes·HCl with KOBu^t in THF. The free carbene was subsequently extracted with toluene and treated with [Ir(cod)(py)$_2$]PF$_6$ directly. After stirring at room temperature for 2 days, **2** was isolated as a yellow-orange solid in 80% yield. A similar methodology has been used by Grubbs to prepare a SIMes-bearing ruthenium olefin metathesis catalyst.[5e]

The ^{1}H NMR spectrum of **2** showed two multiplets at δ 3.15 and 3.80 for the vinyl protons of the cod ligand. It has been previously demonstrated for [Ir(cod)(Cl)(L)]PF$_6$ (L = monophosphine) that the downfield signal can be assigned to the vinyl resonance trans to L (δ(H$_A$)). By analogy, the signal at δ 3.80 can be assigned to the vinyl protons trans to the SIMes and that at δ 3.15 to the two vinyl protons trans to the pyridine ligand. Two multiplets at δ 3.78 and 3.96 were observed for the methylene protons of the SIMes ligand. To unequivocally establish the structure of **2**, a single-crystal X-ray diffraction study was performed on crystals grown from slow diffusion of diethyl ether into a saturated dichloromethane solution of **2**.

Single X-ray Analysis of 1 and 2. As shown in the ORTEP (Figure 1), **2** adopts a square-planar coordination geometry around the iridium center. The structure of **2** is very similar to that of **1**, which had not previously been reported and is presented here for comparative purposes (Figure 2).[10] Selected bond lengths and angles for **1** and **2** are given in Table 1. Consistent with the greater trans influences of SIMes and PCy$_3$ compared to pyridine, the Ir–C bond distances trans to the SIMes in **2** and PCy$_3$ in **1** are significantly longer than those trans to pyridine. This is also in accord with the vinyl proton assignments in the ^{1}H NMR spectrum (vide supra). Previously, we showed that IMes was a stronger σ-donor than PCy$_3$,[5a] so it is reasonable to assume that the saturated analogue would also have a strong σ-donating capability. Consistently, the Ir–N bond distance in **2** (2.1073 Å) was longer than that found in **1** (2.089 Å), and the C=C bond distance trans to the SIMes in **2** was slightly shorter than that trans to PCy$_3$ in **1** by 0.013 Å. A comparison of Figures 1 and 2 clearly illustrates the SIMes ligand in **2** occupying significantly more space around the iridium center than the PCy$_3$ ligand in **1**.

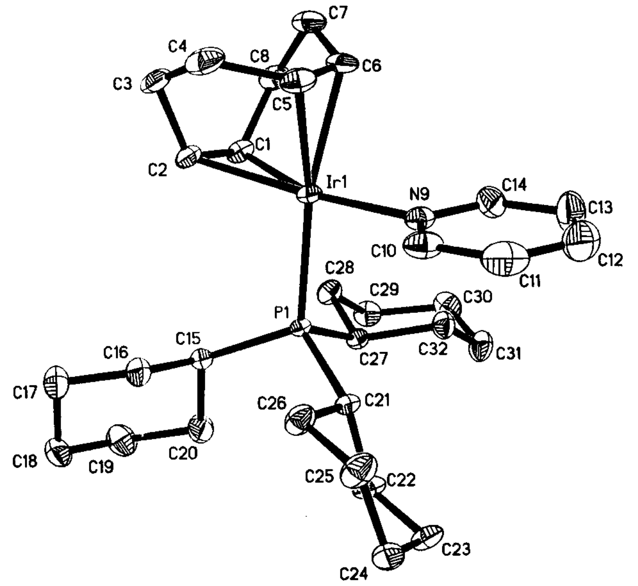

Figure 2. ORTEP of [Ir(cod)(py)(PCy$_3$)]PF$_6$ (**1**) with ellipsoids drawn at 50% probability. Hydrogens and PF$_6$ are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1 and 2

1		2	
	Bond Lengths		
Ir–P(1)	2.3676(6)	Ir–C(14)	2.0743(18)
Ir–N(9)	2.089(2)	Ir–N(3)	2.1073(16)
Ir–C(5)	2.176(3)	Ir–C(1)	2.215(2)
Ir–C(6)	2.195(3)	Ir–C(2)	2.1545(19)
Ir–C(1)	2.145(3)	Ir–C(5)	2.144(2)
Ir–C(2)	2.163(3)	Ir–C(6)	2.1349(18)
C(1)–C(2)	1.407(4)	C(5)–C(6)	1.408(3)
C(5)–C(6)	1.404(4)	C(1)–C(2)	1.391(3)
	Bond Angles		
N(9)–Ir–P(1)	92.17(7)	N(3)–Ir–C(14)	96.00(7)
C(1)–Ir–P(1)	92.46(8)	C(5)–Ir–C(14)	89.71(8)
C(2)–Ir–P(1)	97.70(8)	C(6)–Ir–C(14)	93.00(7)
C(5)–Ir–N(9)	85.67(11)	C(1)–Ir–N(3)	88.21(7)
C(6)–Ir–N(9)	86.90(11)	C(2)–Ir–N(3)	86.93(7)
C(1)–Ir–N(9)	156.23(10)	C(5)–Ir–N(3)	164.45(7)
C(2)–Ir–N(9)	162.39(10)	C(6)–Ir–N(3)	154.58(8)
C(5)–Ir–P(1)	160.95(8)	C(1)–Ir–C(14)	169.80(8)
C(6)–Ir–P(1)	161.43(9)	C(2)–Ir–C(14)	152.16(9)

Catalytic Hydrogenation. The catalytic performance of **2** in the hydrogenation of simple alkenes has been investigated. The catalytic activity of **1** was also studied for comparative purposes. Selected results are listed in Table 3. The catalytic reactions were performed with 1 mol % of catalyst in 5 mL of CH$_2$Cl$_2$. At ambient temperature and pressure of hydrogen, **2** was an efficient catalyst in the hydrogenation of cyclohexene, although displaying a lower activity than **1** (entries 1, 2). It is generally significantly more difficult to hydrogenate highly substituted alkenes. As shown in entries

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(6) (a) Zhang, C.; Huang, J.; Trudell, M. L.; Nolan, S. P. *J. Org. Chem.* **1999**, *64*, 3804–3805. (b) Böhm, V. P. W.; Gstöttmayr, C. W. K.; Weskamp, T.; Hermann, W. A. *J. Organomet. Chem.* **2000**, *595*, 186–190. (c) Huang, J.; Nolan, S. P. *J. Am. Chem. Soc.* **1999**, *121*, 9889–9890. (d) Lee, H. M.; Nolan, S. P. *Org. Lett.* **2000**, *2*, 2053–2055. (e) Grasa, G. A.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 119–122.

(7) Huang, J.; Grasa, G.; Nolan, S. P. *Org. Lett.* **1999**, *1*, 1307–1309.

(8) Lee, H. M.; Smith, D. C., Jr.; He, Z.; Stevens, E. D.; Yi, C. S.; Nolan, S. P. *Organometallics*, manuscript accepted for publication.

(9) Chen, A. C.; Ren, L.; Decken, A.; Crudden, C. M. *Organometallics* **2000**, *19*, 3459–3461.

(10) Orange crystals suitable for X-ray measurements were obtained by slow diffusion of ether into a dichloromethane solution of **1**.

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Table 2. Crystallographic Data for Complexes 1 and 2

	1	**2**
formula	$[C_{31}H_{50}IrPN]^+PF_6^-$	$[C_{34}H_{43}IrN_3]^+PF_6^-$
fw	804.86	830.88
cryst syst	triclinic	triclinic
space group	$P1$	$P\bar{1}$
a, Å	9.5882(3)	10.1394(2)
b, Å	16.2726(4)	12.4885(3)
c, Å	10.3721(3)	13.8435(3)
α, deg	90.0000(10)	81.1310(10)
β, deg	103.2130(10)	74.43
γ, deg	90.0000(10)	80.4040(10)
V, Å^3	1575.46(8)	1653.94(6)
Z	2	2
D_{calcd}, Mg/m^3	1.697	1.668
R	0.0246	0.0231
R_w	0.0267	0.0328
no. of refined params	571	513
no. of data collected	30 173	32 308
no. of unique data, $I > 3\sigma$	11 317	11 895
R_{merge}	0.0318	0.0333

Table 3. Catalytic Hydrogenation of Olefins with Complexes 1 and 2[a]

entry	cat	substrate	time, h	yield,[b] %
1	**1**	cyclohexene	<0.5	100
2	**2**	cyclohexene	2	100
3	**1**	1-methyl-1-cyclohexene	2	65
			28	77
4	**2**	1-methyl-1-cyclohexene	3.5	42
			16	44
5	**1**	1-methyl-1,4-cyclohexadiene	1	100 (63:0:35)
			2	100 (76:0:24)
			13	100 (84:0:16)
6	**2**	1-methyl-1,4-cyclohexadiene	1	40 (3:12:25)
				93 (12:45:36)
			4	100 (40:23:37)
			7	100 (57: 4:39)
			18	
7	**1**	1-methyl-1-cyclohexene	7	34[c]
8	**2**	1-methyl-1-cyclohexene	7	100[c]

[a] cat, 0.01 mmol; olefin, 1.0 mmol; CH_2Cl_2, 5 mL; H_2, 15 psi; temp, 25 °C. [b] The ratios in parentheses = (methylcyclohexane: 1-methyl-4-cyclohexene:1-methyl-1-cyclohexene). Yields are average of two runs. [c] H_2, 60 psi; temp, 50 °C; time not optimized.

3 and 4, Crabtree's catalyst gave a final 77% conversion of 1-methyl-1-cyclohexene, while a modest yield of 44% was obtained when using **2**. The catalytic reaction did not proceed to completion even after prolonged stirring when either **1** or **2** was employed. It had been shown that **1** undergoes an irreversible deactivation process over time involving the formation of the catalytic inactive hydrogen-bridged cluster (vide supra).

Interestingly, **1** and **2** displayed different catalytic behaviors in the hydrogenation of 1-methyl-1,4-cyclohexadiene, which contains both a trisubstituted and a disubstituted nonconjugated double bond. Complex **1** gave a mixture of methylcyclohexane and 1-methyl-1-cyclohexene within 1 h (entry 5). The ratio of the fully hydrogenated to the partially hydrogenated product increased slowly over time until a final ratio of 84:16 was obtained. The isomeric, partially hydrogenated product, 1-methyl-4-cyclohexene, was not observed. Presumably, **1** catalyzes a simple two-step process in which the first hydrogenation occurs at the less hindered double bond to form 1-methyl-1-cyclohexene, which is then converted to the fully hydrogenated methylcyclohexane in the subsequent step. Surprisingly, **2** gave a mixture of products, methylcyclohexane, 1-methyl-4-cyclohexene, and 1-methyl-1-cyclohexene in a ratio of 3:12:25 after 1 h (entry 6). The amount of 1-methyl-4-cyclohexene increased to a maximum after 4 h and then gradually decreased with time. The yield of the fully hydrogenated product increased slowly to a final 57% yield. These results showed that, in contrast to **1**, the relative kinetics of hydrogenation of the least substituted and more substituted olefins are similar. Efforts directed at understanding the relative kinetics and mechanism involved in these hydrogenation reactions are underway.

In an effort to determine the factors leading to an increase of the yield of the fully hydrogenated product for hindered substrates, we conducted catalytic hydrogenations of 1-methyl-1-cyclohexene under 60 psi of H_2 at 50 °C. Since Crabtree's catalyst is not very thermally stable, it may not be surprising that its activity was drastically decreased when the catalytic reaction was conducted under 60 psi at 50 °C. Catalyst degradation is presumably favored at elevated temperatures, and conversion into a catalytically inactive species results in poor or no olefin hydrogenation. A poor 34% yield of methylcyclohexane was obtained after 7 h (entry 7) when using **1**. In contrast, the activity of **2** is significantly improved under these conditions. In fact, a complete conversion to the fully hydrogenated product was obtained within 7 h (entry 8).

In summary, a new cationic iridium carbene complex **2** has been prepared and found to be effective in the hydrogenation of simple olefins. Although it is less efficient than Crabtree's catalyst at room temperature and atmospheric pressure of hydrogen (which may be related to the larger steric bulk of SIMes in **2** compared to that of PCy_3 in **1**), it displayed a higher activity under a mild pressure of hydrogen at 50 °C. This is in contrast to the catalytic property of **1**, which is significantly less active under the same conditions. The difference in activity can be attributed to the presence of the bulky *N*-heterocyclic carbene ligand in **2**, which also results in an improved thermal stability of the complex. Investigations into the use of the new catalyst with a variety of substrates and synthesis of a family of nucleophilic carbene-bearing iridium complexes are ongoing.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of dry argon with standard Schlenk tube techniques or in a MBraun glovebox containing less than 1 ppm of oxygen and water. Anhydrous hexane was purchased from Aldrich and used as received. Toluene, THF, and CH_2Cl_2 were dried through activated alumina columns.[11] The NMR solvents were dried from activated molecular sieves (4 Å). Olefins were dried by stirring over Na/K alloy followed by vacuum transfer under reduced pressure. Complex **1** was purchased from Strem and used as received. $[Ir(cod)(py)_2]PF_6$[3a] and SIMes·HCl[12] were prepared according to the literature procedures. NMR spectra were recorded using a Varian 400 MHz spectrometer. Elemental analyses were performed by

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[11] Pangborn, A. B.; Giardello, M. A.; Grubbs R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518−1520.

[12] Arduengo, A. J., III; Krafczyk, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523−14534.

Desert Analysis, Tucson, AZ. Gas chromatographic analyses were performed on a Hewlett-Packard HP 5890 II equipped with a FID and a HP-5 column.

Synthesis of [Ir(cod)(py)(SIMes)]PF$_6$ (2). A mixture of 423 mg of SIMes·HCl (1.24 mmol) and 139 mg of potassium *tert*-butoxide (1.24 mmol) in 20 mL of THF was stirred at room temperature for 1 h. The solvent was then removed completely under vacuum. The residue was extracted with 20 mL of toluene. The solution was filtered and charged with 500 mg of [Ir(cod)(py)$_2$]PF$_6$ (0.828 mmol). The suspension was then stirred at room temperature for 2 days. The orange precipitate was filtered on a collection frit, washed with hexane, and dried under vacuum. Yield: 550 mg (80%). Anal. Calcd for $C_{34}H_{43}F_6IrN_3P$: C, 49.15; H, 5.22; N, 5.60. Found: C, 49.35; H, 5.31; N, 5.80. ^{1}H NMR (399.95 MHz, CD_2Cl_2): δ 1.60 (m, 4 H, CH$_2$ of cod), 1.90 (m, 4 H, CH$_2$ of cod), 2.33 (s, 3 H, CH$_3$), 2.36 (s, 6 H CH$_3$), 2.39 (s, 6 H, CH$_3$), 2.50 (s, 3 H, CH$_3$), 3.15 (m, 2 H, CH of cod trans to py), 3.78 (m, 2 H, NCH$_2$CH$_2$N), 3.80 (m, 2 H, CH of cod trans to SIMes), 3.96 (m, NCH$_2$CH$_2$N), 6.93−7.26 (m, 6H, aromatic H), 7.70−7.77 (m, 3 H, aromatic H). Crystals suitable for X-ray measurements were obtained by slow diffusion of ether into a dichloromethane solution of **2**.

The Hydrogenation Experiments. A solution of 0.01 mmol of catalyst and 1.0 mmol of olefin in 5 mL of dichloromethane was loaded into a 50 mL scintillation vial equipped with a screw cap and septum inside a glovebox. The vial was then purged with hydrogen from a Schlenk line for 1 min. The reaction was allowed to stir under atmospheric pressure of hydrogen, and the product ratio was monitored by GC. In some cases, the catalytic solution was loaded into a 100 mL Fisher-Porter pressure bottle, which was purged with hydrogen three times and then pressurized with 60 psi of hydrogen. The reaction was allowed to stir in an oil bath at 50 °C for 7 h. The reaction flask was cooled to room temperature. The pressure was then carefully discharged, and product ratios were determined by gas chromatography. Reported experimental yields are the average of two runs.

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Supporting Information Available: Tables of crystal data and structure refinement details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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