# Annulated N-Heterocyclic Carbene Ligands Derived from 2-Methylaminopiperidine: Their Complexes and Catalytic Applications

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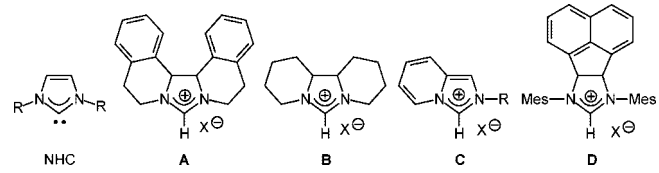
A new type of carbene precursor, 1,5,6,7,8,8a-hexahydroimidazo[1,5-*a*]pyridine (**1**), has been prepared from 2-(aminomethyl)piperidine and *N,N*-dimethylformamide dimethylacetal. The reactions of three imidazolidinium salts with [Rh(acac)(COD)] and [Ir($\mu$-OMe)(COD)]$_2$ were found to afford rhodium and iridium complexes of N-heterocyclic carbenes, respectively. These complexes have been tested as catalysts in the transfer hydrogenation of cyclohexanone and acetophenone using 2-propanol as hydrogen source.

## Introduction

Over the past decade, metal complexes of N-heterocyclic carbenes (NHCs), in particular imidazolin-2-ylidenes, have attracted much interest because of the unique coordination chemistry of NHC ligands and the application of such complexes as catalysts in various catalytic processes. These catalysts display much higher stability and activity compared to the parent tertiary phosphine-based complexes.[1] In order to modify the ligand properties, various annulated imidazolin-2-ylidenes and imidazolidin-2-ylidenes such as the ones derived from **A**, **B**, and **C** have been studied in detail.[2–4] Within the framework of our recent interest in the development of new types of NHCs we have reported on the synthesis of **D** and its metal complexes.[5] As an extension of these investigations, we now wish to report on the synthesis, molecular structure, and catalytic performance in the catalytic transfer hydrogenations of $Rh^I$ and $Ir^I$ complexes (**3** or **4**, Scheme 1) containing piperidoimidazolidin-2-ylidenes as novel carbene ligands.

The preparation of alcohols has become an important field of activity for transition metal catalyzed reactions.[6] Compared to other catalytic approaches developed such as addition of organometallic reagents to carbonyl compounds, hydroxylation of olefins, and functionalization reactions of epoxides, the hydrogenation of ketones or aldehydes is the most




powerful tool with respect to industrial applications. In partıcular, transfer hydrogenation represents a potent strategy, because of high atom efficiency, no need of pressure, and economic as well as environmental advantages.[7] In more detail, a broad scope of alcohols is accessible by transfer hydrogenation using nontoxic hydrogen donors under mild reaction conditions in the presence of various metal catalysts, such as Ir, Rh, or Ru.[8]

## Results and Discussion

**Synthesis of Ligands.** Unsymmetrical imidazolidinium salts **2a**−**c** were synthesized in two steps. Initially, racemic 1,5,6,7,8,8a-hexahydroimidazo[1,5-*a*]pyridine (**1**) was prepared according to the previously reported procedure, by a condensation reaction of commercially available 2-(aminomethyl)piperidine with *N,N*-dimethylformamide dimethylacetal.[9] In the second step, the

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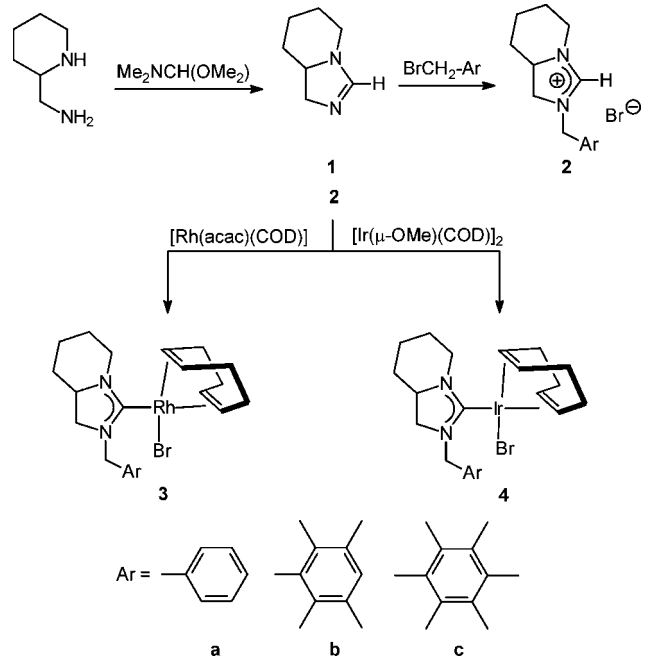
**Scheme 1. Synthesis of Imidazolidinium Salts 2 and Their Rhodium- and Iridium−NHC Complexes 3 and 4**




benzyl groups were introduced by stirring **1** with benzyl, 2,3,5,6-tetramethylbenzyl or pentamethylbenzyl bromides (Scheme 1).

Compound **1** was obtained as a colorless liquid. The $^1$H NMR spectrum of **1** exhibits the NCHN resonance at $\delta$ 6.70 ppm. The formation of **1** is also supported by a signal at $\delta$ 155.4 ppm in the $^{13}$C NMR spectrum for the NCN carbon atom. The addition of 1 equiv of benzyl halide to give the unsymmetrically substituted imidazolidinium salts **2** was achieved in refluxing toluene. The salts of type **2**, which precipitate from the reaction mixture, could be purified by recrystallization from hot methanol either by cooling or by addition of diethyl ether. The salts **2a**−**c** were found to be hygroscopic and soluble in chlorinated solvents, alcohols, and water. The NMR spectroscopic data of **2a**−**c** agree with the proposed structures. In the $^1$H NMR spectra of **2a**−**c**, the imidazolidinium protons appear at $\delta$ 9.99, 9.46, and 9.34 ppm, respectively. The $^{13}$C NMR shift of the NCN sp$^2$ carbon atoms in **2a**−**c** appear between $\delta$ 155.7 and 154.9 ppm, respectively. Signals at $\delta$ 3.5–53.3 ppm correspond to the benzylic methylene carbon resonances for **2a**−**c**.

**Synthesis of Rhodium and Iridium Complexes.** We prepared rhodium(I) and iridium(I) complexes from salts of type **2** by deprotonation. Reaction of the imidazolidinium precursors with [Rh(acac)(COD)] in toluene at 110 °C gave the rhodium complexes **3a**−**c**. The iridium complexes **4a**−**c** were prepared by reaction of the iridium dimer [Ir($\mu$-OMe)(COD)]$_2$ with 2 equiv of the imidazolidinium salts **2a**−**c**. The complexes were purified by chromatography on silica gel. Solutions of complexes **3** and **4** in acetone or chlorinated solvents were observed to be stable toward air and moisture. The identity of the compounds was confirmed by $^1$H and $^{13}$C NMR spectroscopy and elemental analysis. Both iridium(I) and rhodium(I) complexes exhibit characteristic $^{13}$C chemical shifts which provide a useful diagnostic tool for this type of metal carbene complexes. The chemical shifts for the carbene carbon atom fall in the range $\delta$ 210.9–210.2 ppm for rhodium complexes and $\delta$ 207.7–204.8 ppm for iridium complexes. Coupling constants $J$($^{103}$Rh−$^{13}$C) for the new rhodium complexes **3a**−**c** are comparable to those found for rhodium−NHC complexes, which have been described previously.[10]

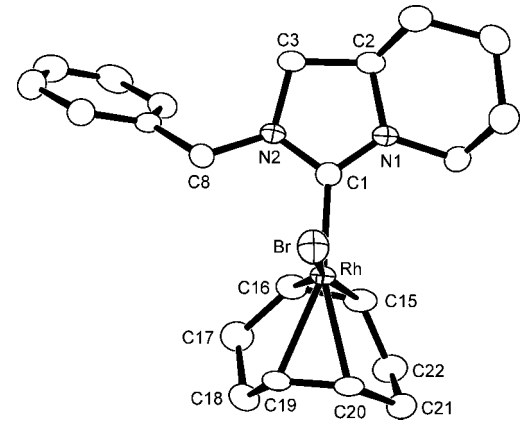



**Figure 1.** Molecular structure of complex **3a** with the crystallographic numbering scheme.

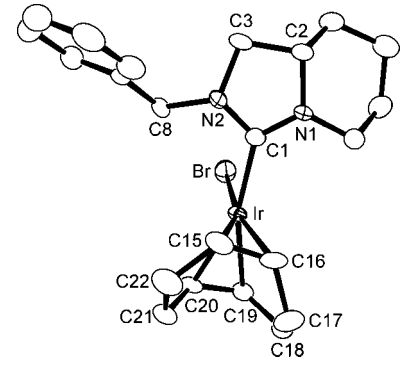



**Figure 2.** Molecular structure of complex **4a** with the crystallographic numbering scheme.

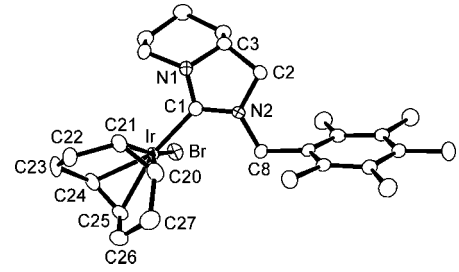



**Figure 3.** Molecular structure of complex **4c** with the crystallographic numbering scheme.

**Structural Studies.** The molecular structures of the complexes **3a**, **4a**, and **4c** in the solid state are depicted in Figures 1, 2, 3. Selected bond lengths and angles are given in Tables 1 and 2, respectively. Crystal data and details of the structure determination of the three crystal structures are presented in Table 3.

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**Table 1. Selected Bond Lengths [Å] and Angles [deg] for 3a and 4a**

| | **3a** (M = Rh) | **4a** (M = Ir) |
|---|---|---|
| | Bond Lengths | |
| M−Br | 2.4942(5) | 2.4801(8) |
| M−C1 | 2.009(3) | 2.027(6) |
| M−C15 | 2.121(3) | 2.091(7) |
| M−C16 | 2.103(4) | 2.114(6) |
| M−C19 | 2.213(3) | 2.186(6) |
| M−C20 | 2.207(3) | 2.197(6) |
| C1−N1 | 1.325(4) | 1.321(8) |
| C1−N2 | 1.349(4) | 1.347(8) |
| C15−C16 | 1.402(5) | 1.395(10) |
| C19−C20 | 1.375(5) | 1.395(9) |
| | Bond Angles | |
| Br−M−C1 | 85.30(10) | 86.2(2) |
| C1−M−C15 | 96.22(14) | 90.6(3) |
| C1−M−C16 | 90.51(14) | 96.0(2) |
| C1−M−C19 | 159.93(13) | 162.8(3) |
| C1−M−C20 | 163.71(13) | 160.0(3) |
| N1−C1−N2 | 107.9(3) | 109.9(5) |
| M−C1−N1 | 127.6(3) | 127.1(5) |
| M−C1−N2 | 124.1(2) | 123.6(4) |

**Table 2. Selected Bond Lengths [Å] and Angles [deg] for 4c**

| | | | |
|---|---|---|---|
| | Bond Lengths | | |
| Ir−Br | 2.4909(6) | Ir−C25 | 2.207(5) |
| Ir−C1 | 2.011(5) | C1−N1 | 1.350(6) |
| Ir−C20 | 2.108(5) | C1−N2 | 1.337(6) |
| Ir−C21 | 2.120(5) | C20−C21 | 1.422(7) |
| Ir−C24 | 2.181(5) | C24−C25 | 1.379(7) |
| | Bond Angles | | |
| Br−Ir−C1 | 86.33(12) | C1−Ir−C25 | 165.6(2) |
| C1−Ir−C20 | 91.8(2) | N1−C1−N2 | 108.2(4) |
| C1−Ir−C21 | 93.6(2) | Ir−C1−N1 | 125.3(3) |
| C1−Ir−C24 | 157.8(2) | Ir−C1−N2 | 126.4(3) |

As shown in the ORTEP plot (Figure 1), complex **3a** adopts a square-planar coordination geometry around the rhodium center. The Rh−C1 bond distance of 2.009(3) Å is typical for this type of carbene coordination.[2,3] The difference in the *trans*-influences of the carbene and the bromo ligands leads to different C=C bond lengths in the coordinated COD ligand (C19−C20 1.375(5) Å and C15−C16 1.402(5) Å).

The molecular structures of **4a** and **4c** (Figures 2 and 3) are very similar. Selected bond lengths and angles are given in Tables 2 (**4a**) and 3 (**4c**). Complexes **4a** and **4c** also exhibit a square-planar geometry at the iridium atom taking the cyclooctadiene C=C midpoints as vertexes. The Ir−$C_{carbene}$ distance in **4c** (2.011(5) Å) is slightly shorter than in **4a** (2.027(6) Å), presumably due to a combination of steric and electronic effects that favor a stronger Ir−$C_{carbene}$ interaction for **4c**. While complex **4a** displays effectively the same bond distances for the C=C bonds *trans* to carbene and to bromide, complex **4c** showes different bond distances for the C=C bonds *trans* to carbene and *trans* to bromide. Thus, the Ir−Br bond distance in **4a** (2.4801(8) Å) is shorter than that found in **4c** (2.4909(6) Å), and the C=C bond distance *trans* to the carbene in **4c** (1.379(7) Å) is slightly shorter than that *trans* to the carbene in **4a** (1.395(9) Å) by 0.016 Å. A similar structural situation, which has been discussed controversially, has been reported for complexes of type $[Ir(NHC)(COD)(L)]^{n+}$ (L = Br, $n = 0, 1$;[10a] L = Cl, $n = 0$;[10b] L = pyridine, $n = 1$;[10c] L = $PPh_3$, $n = 1$[10d]), where the differences in the Ir−C distances (*trans* to carbene vs *trans* to L) are smaller for complexes with L = $PR_3$ owing to the more similar *trans* influences of NHCs and phosphines.

**Catalytic Studies.** Rhodium− and iridium−NHC complexes of types **3** and **4** are efficient catalytic precursors for the transfer hydrogenation of ketones to alcohols with 2-propanol as hydrogen donor in the presence of base. In order to improve the reactivity of our catalytic system, we examined the influence of the base. With the organic base triethylamine and pyridine we observed only poor yields. Using the inorganic bases $Cs_2CO_3$, $K_2CO_3$, KOH, NaOH, and *t*BuOK the conversion showed a dependency upon the base strength. The stronger the base, the higher the conversion rate ($Cs_2CO_3$ < $K_2CO_3$ < NaOH < *t*BuOK < KOH).

In order to evaluate the differences between the various carbene complexes, we applied a low catalyst loading (0.02 mol %) at 80 °C. The yield for transfer hydrogenation of acetophenone and cyclohexanone (reaction time 160 min) was studied (Figures 4 and 5). As shown in the diagram, the reaction is faster for acetophenone than for cyclohexanone, and among the complexes the iridium derivatives **4b**,**c** are more active, giving more than 90% conversion after 60 min (Figure 4). When cyclohexanone was used in the transfer hydrogenation, more than 60% conversion was observed with 0.02 mmol of rhodium and iridium complexes after 100 min. The rhodium complexes **3a**−**c** are generally less active than the iridium complexes **4a**−**c**. Among the tested complexes, the complex **4c** is highly efficient in the transfer hydrogenation of acetophenone to 1-phenylethanol and cyclohexanone to cyclohexanol (Figure 4 and 5). The data indicate clearly the superiority of the complexes with pentamethyl benzyl substituents at the ring nitrogen atom (type **c**, Scheme 1). Additional transfer hydrogenation experiments with different ketones are in progress.

In conclusion, tetrahydropyridoimidazolidin-2-ylidenes have been generated as new NHC ligands for rhodium and iridium complexes of types **3** and **4**. These complexes are active in the transfer hydrogenation of ketones. High yields, up to 90%, in the catalytic transfer hydrogenation of cyclohexanone have been achieved with catalytic systems containing **3** or **4** in the presence of KOH and isopropanol.

## Experimental Section

All reactions for the preparation of **3** and **4** were carried out under argon in flame-dried glassware using standard Schlenk-type flasks. Anhydrous solvents were either distilled from appropriate drying agents or purchased from Merck and degassed prior to use by purging with dry argon and kept over molecular sieves. All other reagents were commercially available and used as received. NMR spectra were recorded at 297 K on a Varian Mercury AS 400 at 400 MHz ($^1$H) and 100.56 MHz ($^{13}$C). Elemental analyses were carried out by the analytical service of TUBITAK with a Carlo Erba Instrumentazione model 1106 apparatus.

**General Procedure for the Preparation of 1.** A mixture of (2-methylamino)piperidine (2.00 g, 17.64 mmol) and *N,N*-dimethylformamide dimethylacetal (2.6 mL, 19.22 mmol) was heated on a steam bath (90–95 °C) for 2 h in order to remove MeOH and $HNMe_2$. The mixture was then heated with an oil bath (120 °C) for 1 h. Volatiles were removed under vacuum, and the remaining yellow viscous liquid was distilled under vacuum (58–60 °C/0.001 mm Hg) to give a colorless liquid. Yield: 2.1 g, 95%. $^1$H NMR ($CDCl_3$): $\delta$ 6.70 (s, 1H, NCHN), 3.81–3.67 (m, 1H, piperidine-H), 3.52–3.45 (m, 2H, $NCH_2CH$), 3.40–3.29 (m, 2H, piperidine-H), 3.04–2.90 (m, 2H, piperidine-H), 1.78–1.73 (m, 2H, piperidine-H), 1.58–1.21 (m, 2H, piperidine-H). $^{13}$C NMR ($CDCl_3$): $\delta$ 155.4 (NCN), 60.8 (piperidine-C), 57.6 ($NCH_2CH$), 43.9, 29.9, 26.2, 23.3 (piperidine-C). Anal. Calcd for $C_7H_{12}N_2$ (124.18): C, 67.70; H, 9.74; N, 22.56. Found: C, 67.81; H, 9.78; N, 22.49.

**General Procedure for the Preparation of 2.** Different benzyl bromides (15 mmol) and compound **1** (1.86 g, 15 mmol) were refluxed in toluene (15 mL) for 3–4 h. The volume of the solution was reduced to 5 mL, and diethyl ether was added to the remaining solution, which was vigorously shaken and then decantated. The

**Table 3. Summary of Crystallographic Data for 3a, 4a, and 4c**

| | 3a | 4a | 4c |
|---|---|---|---|
| formula | $C_{22}H_{30}N_2BrRh$ | $C_{22}H_{30}N_2BrIr$ | $C_{27}H_{40}N_2BrIr$ |
| $M_r$ | 505.30 | 594.59 | 664.72 |
| cryst size [mm$^3$] | 0.10 × 0.08 × 0.06 | 0.11 × 0.07 × 0.05 | 0.15 × 0.07 × 0.04 |
| $a$ [Å] | 10.339(2) | 10.364(2) | 17.867(2) |
| $b$ [Å] | 13.433(2) | 13.438(3) | 8.7314(10) |
| $c$ [Å] | 14.932(3) | 14.932(3) | 15.988(2) |
| $\beta$ [deg] | 96.477(3) | 96.208(4) | 96.694(2) |
| $V$ [Å$^3$] | 2060.6(6) | 2067.5(8) | 2477.2(5) |
| $Z$ | 4 | 4 | 4 |
| space group | $P2_1/n$ | $P2_1/n$ | $P2_1/c$ |
| $\rho_{calcd}$ [g cm$^{-3}$] | 1.629 | 1.910 | 1.782 |
| $\mu$ [mm$^{-1}$] | 2.776 | 8.399 | 7.020 |
| $2\theta$ range [deg] | 4.1–60.1 | 4.1–60.1 | 2.3–60.1 |
| no. of data collected | 23 253 | 23 033 | 27 827 |
| no. of unique data, $R_{int}$ | 5975, 0.0496 | 6010, 0.0601 | 7215, 0.0535 |
| obsd data [$I \geq 2\sigma(I)$] | 4669 | 4700 | 6322 |
| $R$ (all data) | 0.0667 | 0.0692 | 0.0556 |
| $wR$ (all data) | 0.0984 | 0.0888 | 0.0855 |
| no. of variables | 235 | 235 | 285 |
| peak/hole [e Å$^{-3}$] | 1.11/−0.72 | 2.21/−1.71 | 1.94/−1.86 |

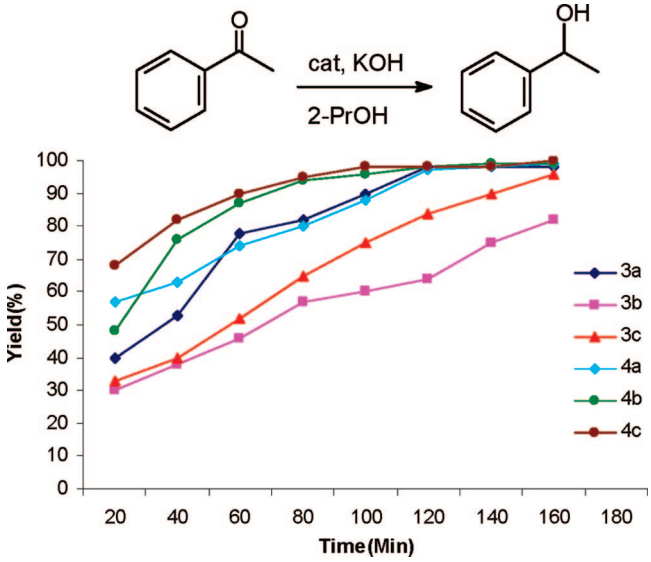


**Figure 4.** Time dependence of the catalytic transfer hydrogenation of acetophenone; 0.02 mmol of cat. (**3a**−**c**, **4a**−**c**) and KOH, 4 mmol of acetophenone, solvent 2-propanol (20 mL), $T$ = 353 K.

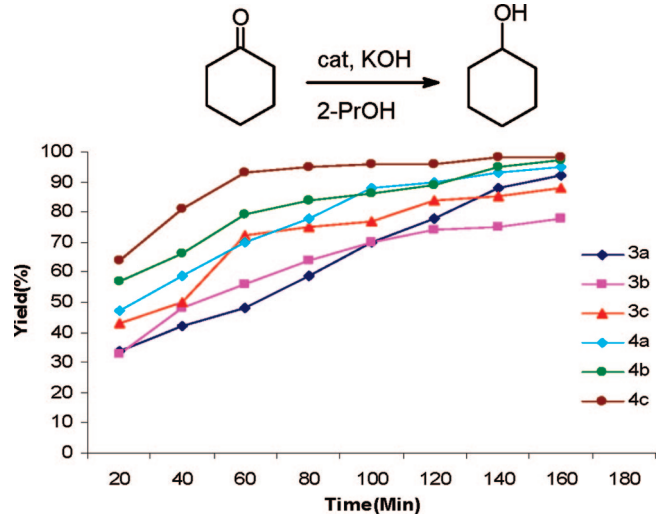


**Figure 5.** Time dependence of the catalytic transfer hydrogenation of cyclohexanone; 0.02 mmol of cat. (**3a**−**c**, **4a**−**c**) and KOH, 4 mmol of cyclohexanone, solvent 2-propanol (20 mL), $T$ = 353 K.

solid residue was washed with diethyl ether (3 × 20 mL) to obtain an orange solid, which was recrystallized from methanol/diethyl ether (3 mL/20 mL).

**Compound 2a.** Yield: 4.1 g, 93%. $^1$H NMR ($CDCl_3$): $\delta$ 9.99 (s, 1H, NCHN), 7.34 (m, 5H, $CH_2C_6H_5$), 4.83 (s, 2H, $CH_2C_6H_5$), 3.96 (m, 1H, piperidine-H), 3.91 (m, 2H, $NCH_2CH$), 3.31 (m, 3H, piperidine-H), 1.91–1.50 (m, 5H, piperidine-H). $^{13}$C NMR ($CDCl_3$): $\delta$ 155.7 (NCHN), 132.5, 129.1, 128.8, 128.6 ($CH_2C_6H_5$), 59.3 ($NCH_2CH$), 53.3 ($CH_2C_6H_5$), 51.9, 45.7, 31.4, 25.2, 22.0 (piperidine-C). Anal. Calcd for $C_{14}H_{19}N_2Br$ (295.21): C, 56.96; H, 6.49; N, 9.49. Found: C, 56.89; H, 6.55; N, 9.44.

**Compound 2b.** Yield: 5.1 g, 96%. $^1$H NMR ($CDCl_3$): $\delta$ 9.46 (s, 1H, NCHN), 6.93 (s, 1H, $NCH_2C_5H(CH_3)_4$), 4.87 (s, 2H, $NCH_2C_5H(CH_3)_4$), 4.20 (m, 2H, piperidine-H), 4.15 (m, 1H, piperidine-H), 3.29 (s, 2H, $NCH_2CH$), 2.20 (s, 6H, $C_6H(CH_3)_4$-*m*-$CH_3$), 2.17 (s, 6H, $C_6H(CH_3)_4$-*o*-$CH_3$), 1.89 (m, 3H, piperidine-H), 1.49 (m, 3H, piperidine-H). $^{13}$C NMR ($CDCl_3$): $\delta$ 154.9 (NCHN), 134.5, 133.6, 132.5, 127.8 ($C_6H(CH_3)_4$), 59.0 ($NCH_2CH$), 53.5 ($NCH_2C_6H(CH_3)_4$), 46.5, 45.7, 31.5, 25.4, 25.2 (piperidine-C), 21.9 ($C_6H(CH_3)_4$-*m*-$CH_3$), 20.3 ($C_6H(CH_3)_4$-*o*-$CH_3$). Anal. Calcd for $C_{18}H_{27}N_2Br$ (351.32): C, 61.54; H, 7.75; N, 7.97. Found: C, 61.53; H, 7.71; N, 8.04%.

**Compound 2c.** Yield: 4.9 g, 91%. $^1$H NMR ($CDCl_3$): $\delta$ 9.34 (s, 1H, NCHN), 4.89 (s, 2H, $NCH_2C_6(CH_3)_5$), 4.28 (m, 2H, piperidine-H), 3.90 (m, 1H, piperidine-H), 3.67 (s, 2H, $NCH_2CH$), 3.26 (m, 1H, piperidine-H), 2.27 (s, 6H, $C_6(CH_3)_5$-*m*-$CH_3$), 2.19 (s, 3H, $C_6(CH_3)_5$-*p*-$CH_3$), 2.17 (s, 6H, $C_6(CH_3)_5$-*o*-$CH_3$), 1.91 (m, 2H, piperidine-H), 1.55 (m, 3H, piperidine-H). $^{13}$C NMR ($CDCl_3$): $\delta$ 154.9 (NCHN), 133.4, 133.3, 133.3, 125.5 ($C_6(CH_3)_5$), 59.1 ($NCH_2CH$), 53.3 ($NCH_2C_6(CH_3)_5$), 50.3, 45.8, 31.5, 25.4, 22.2 (piperidine-C), 17.0 ($C_6(CH_3)_5$-*o*-$CH_3$), 16.9 ($C_6(CH_3)_5$-*m*-$CH_3$), 16.7 ($C_6(CH_3)_5$-*p*-$CH_3$). Anal. Calcd for $C_{14}H_{19}N_2Br$ (365.35): C, 62.46; H, 8.00; N, 7.67. Found: C, 62.33; H, 8.05; N, 7.72.

**General Procedure for the Preparation of Complexes 3.** A sample of [Rh(acac)(COD)] (194 mg, 0.4 mmol) was stirred with one of the compounds of type **2** (0.4 mmol) in toluene (15 mL) for 12 h. The solvent was removed in vacuo, and the remaining yellow precipitate was then dissolved in dichloromethane (5 mL). The product was purified by column chromatography on silica gel. Removal of the solvent and crystallization from $CH_2Cl_2$/pentane afforded the yellow complexes of type **3**.

**Complex 3a.** Yield: 0.14 g, 67%. $^1$H NMR ($CDCl_3$): $\delta$ 7.37 (s, 5H, $NCH_2C_6H_5$), 5.48 (s, 1H, $NCHHC_6H_5$), 5.41 (s, 1H, $NCHHC_6H_5$), 5.12–4.96 (br, 4H, COD-C*H*=C*H*, piperidine-H), 3.62–3.55 (br, 2H, COD-C*H*=C*H*), 3.48 (m, 2H, $NCH_2CH$),

3.36–3.26 (m, 1H, piperidine-H), 3.22–3.10 (m, 2H, piperidine-H), 2.87–2.79 (m, 2H, piperidine-H), 2.36–2.18 (m, 2H, piperidine-H), 1.95–1.86 (m, 4H, COD-C$H_2$), 1.52–1.44 (m, 4H, COD-C$H_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ 210.7 (d, $^1J_{Rh\text{-}C}$ = 44.4 Hz, Rh-$C_{carbene}$), 134.2, 132.7, 131.3, 128.4, ($CH_2C_6H_5$), 98.8, 98.5, 98.4, 98.2 (COD-CH), 69.6, 69.4, 67.6, 67.3 (COD-CH), 59.2 (N$CH_2$CH), 54.3 (N$CH_2C_6H_5$), 48.0, 33.4, 32.4, 31.9, 31.8, 29.2, 28.5, 26.7, 26.5 (piperidine-C, COD-$CH_2$). Anal. Calcd for $C_{22}H_{30}BrN_2Rh$ (505.29): C, 52.29; H, 5.98; N, 5.54. Found: C, 52.33; H, 5.94; N, 5.51.

**Complex 3b.** Yield: 0.14 g, 63%. $^1$H NMR ($CDCl_3$): $\delta$ 6.94 (s, 1H, $NCH_2C_6H(CH_3)_4$), 5.50, 5.43 (s, 2H, $NCH_2C_6H(CH_3)_4$), 5.11–4.89 (br, 3H, COD-C$H$=C$H$, piperidine-H), 3.55–3.41 (br, 2H, COD-C$H$=C$H$), 3.11 (m, 2H, N$CH_2$CH), 2.58 (m, 2H, piperidine-H), 2.38 (m, 2H, piperidine-H), 2.33 (m, 2H, piperidine-H), 2.28 (s, 6H, $C_6H(CH_3)_4$-*m*-C$H_3$), 2.27 (s, 6H, $C_6H(CH_3)_4$-*o*-C$H_3$), 1.98–1.65 (m, 4H, COD-$CH_2$), 1.72 (m, 2H, piperidine-H), 1.49–1.26 (m, 4H, COD-$CH_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ 210.9 (d, $^1J_{Rh\text{-}C}$ = 44.5 Hz, Rh-$C_{carbene}$), 134.2, 131.9, 131.4, 128.4, ($CH_2C_6H(CH_3)_4$), 98.5, 98.3, 98.2, 98.0 (COD-CH), 69.7, 69.5, 67.8, 67.4 (COD-CH), 59.1 (N$CH_2$CH), 54.3 (N$CH_2C_6H(CH_3)_4$), 48.3, 33.0, 32.1, 31.9, 31.7, 29.2, 28.3, 26.4, 26.0 (piperidine-C, COD-$CH_2$), 21.7 ($C_6H(CH_3)_4$-*m*-C$H_3$), 20.1 ($C_6H(CH_3)_4$-*o*-C$H_3$). Anal. Calcd for $C_{26}H_{38}BrN_2Rh$ (561.4): C, 55.62; H, 6.82; N, 4.99. Found: C, 55.57; H, 6.87; N, 5.01.

**Complex 3c.** Yield: 0.15 g, 63%. $^1$H NMR ($CDCl_3$): $\delta$ 5.50 (s, 1H, NC$H$$HC_6(CH_3)_5$), 5.44 (s, 1H, NCH$H$$C_6(CH_3)_5$), 5.11–4.92 (br, 3H, COD-C$H$=C$H$, piperidine-H), 3.55–3.42 (br, 2H, COD-C$H$=C$H$), 3.14 (m, 2H, N$CH_2$CH), 2.62 (m, 2H, piperidine-H), 2.37 (m, 8H, piperidine-H, $C_6(CH_3)_5$-*m*-C$H_3$), 2.24 (s, 3H, $C_6(CH_3)_5$-*p*-C$H_3$), 2.22 (s, 6H, $C_6(CH_3)_5$-*o*-C$H_3$), 1.93–1.72 (m, 8H, piperidine-H, COD-$CH_2$), 1.46–1.25 (m, 4H, COD-$CH_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ 210.2 (d, $^1J_{Rh\text{-}C}$ = 45.6 Hz, Rh-$C_{carbene}$), 134.9, 134.4, 133.8, 129.3, ($CH_2(C_6(CH_3)_5$), 98.5, 98.4, 98.0, 97.9 (COD-CH), 59.2 (N$CH_2$CH), 54.2 (N$CH_2C_6H(CH_3)_5$), 48.7, 33.1, 32.2, 31.8, 29.3, 28.7, 28.4, 26.0, 23.4 (piperidine-C, COD-$CH_2$), 17.5 ($C_6H(CH_3)_4$-*p*-C$H_3$), 17.2 ($C_6H(CH_3)_4$-*m*-C$H_3$), 16.6 ($C_6H(CH_3)_4$-*o*-C$H_3$). Anal. Calcd for $C_{27}H_{40}BrN_2Rh$ (575.43): C, 56.36; H, 7.01; N, 4.87. Found: C, 56.41; H, 7.07; N, 4.87.

**Complex 4a.** [Ir($\mu$-OMe)(COD)]$_2$ (200 mg, 0.3 mmol) was strirred together with an azolium salt of type **2** (0.6 mmol) in toluene (15 mL) for 8 h. Workup proceeded as described for complexes of type **3**. Yield: 0.22 g, 63%. $^1$H NMR ($CDCl_3$): $\delta$ 7.28 (m, 5H, $CH_2C_6H_5$), 5.46 (s, 1H, NC$H$$HC_6H_5$), 5.37 (s, 1H, NCH$H$$C_6H_5$), 4.95 (m, 1H, piperidine-H), 4.87 (m, 1H, COD-C$H$=C$H$), 4.59 (m, 1H, COD-C$H$=C$H$), 4.57 (m, 2H, COD-C$H$ = C$H$), 3.66 (m, 2H, N$CH_2$CH), 3.49 (m, 2H, piperidine-H), 3.39 (m, 2H, piperidine-H), 3.07 (m, 1H, piperidine-H), 2.86 (m, 1H, piperidine-H), 2.21–2.01 (m, 4H, COD-$CH_2$), 2.00 (m, 2H, piperidine-H), 1.83–1.23 (m, 4H, COD-$CH_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ 204.8 (Ir-$C_{carbene}$), 136.3, 128.4, 127.5, 127.4 ($CH_2C_6H_5$), 84.2, 84.0 (COD-CH), 59.2 (N$CH_2$CH), 54.1, 53.9, 52.6 (NH$CH_2C_6H_5$, COD-CH), 47.5, 33.4, 32.8, 29.7, 29.4, 26.5, 23.2 (piperidine-C, COD-$CH_2$). Anal.Calcd for $C_{22}H_{30}BrN_2Ir$ (594.61): C, 44.44; H, 5.09; N, 4.71. Found: C, 44.47; H, 5.14; N, 4.77%.

**Complex 4b.** Yield: 0.21 g, 53%. $^1$H NMR ($CDCl_3$): $\delta$ 6.95 (s, 1H, $NCH_2C_6H(CH_3)_4$), 5.41 (s, 1H, NC$H$$HC_6H(CH_3)_4$), 5.34 (s, 1H, NCH$H$$C_6H(CH_3)_4$), 4.88 (m, 1H, piperidine-H), 4.81 (s, br, 2H, COD-C$H$ = C$H$), 4.60 (s, br, 2H, COD-C$H$=C$H$), 3.48 (m, 2H, N$CH_2$CH), 3.15 (m, 2H, piperidine-H), 2.64 (m, 2H, piperidine-H), 2.27 (m, 8H, piperidine-H, $C_6H(CH_3)_4$-*m*-C$H_3$), 2.23 (s, 6H, $C_6H(CH_3)_4$-*o*-C$H_3$), 1.84–1.71 (m, 6H, piperidine-H, COD-$CH_2$), 1.58–1.25 (m, 4H, COD-$CH_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ 206.3 (Ir-$C_{carbene}$), 134.2, 133.8, 131.8, 131.4, ($CH_2C_6H(CH_3)_4$), 84.4, 84.3, 83.7, 83.4 (COD-CH), 59.3 (N$CH_2$CH), 54.2, 53.9, 53.5, 52.9, 51.1 (N$CH_2C_6H(CH_3)_4$, COD-CH), 48.1, 33.7, 32.8, 32.0, 31.9, 30.0, 28.9, 26.6, 26.1 (piperidine-C, COD-$CH_2$), 20.5 ($C_6H(CH_3)_4$-*m*-C$H_3$), 16.4 ($C_6H(CH_3)_4$-*o*-C$H_3$). Anal.Calcd for $C_{26}H_{38}BrN_2Ir$ (650.71): C, 47.99; H, 5. 89; N, 4.31. Found: C, 47.97; H, 5.93; N, 4.33.

**Complex 4c.** Yield: 0.21 g, 53%. $^1$H NMR ($CDCl_3$): $\delta$ 5.42 (s, 1H, NC$H$$HC_6(CH_3)_5$), 4.94 (s, 1H, NCH$H$$C_6(CH_3)_5$), 4.88 (m, 1H, piperidine-H), 4.66 (s, br, 2H, COD-C$H$=C$H$), 4.56 (s, br, 2H, COD-C$H$=C$H$), 3.53 (m, 2H, N$CH_2$CH), 3.22 (m, 2H, piperidine-H), 2.65 (m, 2H, piperidine-H), 2.31 (m, 8H, piperidine-H, $C_6(CH_3)_5$-*m*-C$H_3$), 2.28 (s, 3H, $C_6(CH_3)_5$-*p*-C$H_3$), 2.25 (s, 6H, $C_6(CH_3)_5$-*o*-C$H_3$), 1.83–1.71 (m, 6H, piperidine-H, COD-$CH_2$), 1.51–1.26 (m, 4H, COD-$CH_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ 207.7 (Ir-$C_{carbene}$), 134.8, 133.7, 132.6, 129.2, ($CH_2C_6(CH_3)_5$), 84.3, 84.2 (COD-CH), 59.3 (N$CH_2$CH), 54.2 (N$CH_2C_6(CH_3)_5$), 53.9, 52.9 (COD-CH), 48.5, 33.6, 32.8, 31.9, 30.0, 29.8, 28.9, 26.6, 26.1 (piperidine-C, COD-$CH_2$), 17.4 ($C_6(CH_3)_5$-*m*-C$H_3$), 17.2 ($C_6(CH_3)_5$-*p*-C$H_3$), 16.7 ($C_6H(CH_3)_4$-*o*-C$H_3$). Anal. Calcd for $C_{27}H_{40}BrN_2Ir$ (664.74): C, 48.78; H, 6.07; N, 4.21. Found: C, 48.82; H, 6.13; N, 4.22.

**Catalytic Hydrogen Transfer Experiments.** The tested complex (0.02 mmol) was dissolved in a solution of KOH (0.2 mmol) and isopropanol (20 mL) in a Schlenk tube. The solution was heated to 80 °C for 30 min. Subsequently, cyclohexanone (413 $\mu$L, 4 mmol) was added with an Eppendorf pipet. The reaction progress was monitored by GC analysis.

**Crystal Structure Determinations.** Diffraction data for **3a**, **4a**, and **4c** were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 153(2) K using graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å). Diffraction data were collected over the full sphere and were corrected for absorption. The data reduction was performed with the Bruker SMART[11] program package. For further crystal and data collection details see Table 3. Structure solutions were found with the SHELXS-97[12] package using the heavy-atom method and were refined with SHELXL-97[13] against $F^2$ using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions.

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**Note Added after ASAP Publication.** The version of this paper published on February 1, 2008, was missing the Supporting Information paragraph. The version published on February 18, 2008, has the correct information.

**Supporting Information Available:** This material is available free of charge via the Internet at http://pubs.acs.org.

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