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Efficient Transfer Hydrogenation Using Iridium and Rhodium Complexes of Benzannulated N-Heterocyclic Carbenes

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Benzimidazol-2-ylidene(NHC) derivatives of iridium(I) and rhodium(I) bearing electron-rich and/or functional substituents R and R′ at the nitrogen atoms of the heterocycle [IrBr(cod)(NHC)] (**a**) or [RhBr(cod)(NHC)] (**b**) (R = 2,3,5,6-tetramethylbenzyl; R′ = methoxyethyl, **1a**,**b**; R = R′ = 2,3,5,6-tetramethylbenzyl, **2a**,**b**; R = pentamethylbenzyl, R′ = methoxyethyl, **3a**,**b**; R = R′ = pentamethylbenzyl, **4a**,**b**) were prepared. All compounds were fully characterized by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry (MALDI), and elemental analysis. In addition, the molecular structures of **1a**, **2a**, and **3a** were determined by single-crystal X-ray diffraction studies. All of the new benzimidazol-2-ylidene iridium(I) and rhodium(I) complexes were found to be effective catalysts for transfer hydrogenation with iridium(I) derivative **1a** showing the highest catalytic activity.

Introduction

Asymmetric catalytic transfer hydrogenation of C=O or C=N bonds by using 2-propanol as a source of hydrogen is an attractive method for the preparation of chiral alcohols and amines.[1] In particular, transfer hydrogenation of ketones or aldehydes represents a potent strategy for the generation of alcohols because of high atom efficiency, no need for elevated pressure, and economic as well as environmental advantages.[2] Today, a broad scope of alcohols have become accessible by transfer hydrogenation by using nontoxic hydrogen donors under mild reaction conditions in the presence of various homogeneous Ir, Rh, or Ru catalysts.[3]

Homogeneous catalysis offers the possibility of finetuning the properties of the catalyst to enhance its selectivity, because the activity of homogeneous transition-metal catalysts can be controlled by steric and electronic effects exerted by the ligands. Thus, in the past, phosphane complexes have been used as transfer hydrogenation catalysts,[2,3] where the electronic and steric parameters of the phosphane ligands are easily modified.[4]

Derived from Crabtree's catalyst $[Ir(cod)(py)(PCy_3)]PF_6$ (py = pyridine, cod = η^2:η^2-1,5-cyclooctadiene),[5] iridium complexes $[Ir(cod)(py)(NHC)]PF_6$ with N-heterocyclic carbene (NHC) ligands[6] have recently been introduced.[7] These complexes show high activities in the transfer hydrogenation reactions of C=C, C=O, and N=O bonds.[7] In addition, neutral iridium(III) complexes with bidentate chelating bis(NHC) ligands are capable of transfer hydrogenation of aldehydes under basic conditions.[8]

In previous work, we introduced iridium(I) complexes with *N*-allyl-substituted benzimidazol-2-ylidene[9] and annulated saturated NHC ligands[10] and studied their activity in catalytic transfer hydrogenation reactions. Here we report the preparation of some neutral rhodium(I) and iridium(I) complexes [MBr(cod)(NHC)] (M = Rh^I, Ir^I) with sterically demanding *N*,*N*′-substituted benzimidazol-2-ylidene ligands. We also report their activity in catalytic transfer hydrogenation reactions.

Results and Discussion

Synthesis and Characterization of Iridium and Rhodium Carbene Complexes

Complexes with benzimidazol-2-ylidene ligands can be prepared from the free carbene ligands.[11] However, the free carbene ligands are normally highly reactive species that are difficult to handle. Alternative methods for the synthesis of NHC complexes are the cleavage of electron-rich enetetraamine by transition-metal complexes[12] and the template-controlled intramolecular cyclization of metal-coordinated β-functionalized isocyanides.[13] The most convenient methods, however, are the carbene transfer reactions from easily accessible silver carbene complexes to other transition metals[14] and the in situ deprotonation of azolium salts by complexes with basic ligands or counterions like OAc^-[15] or OR^-.[9,10]

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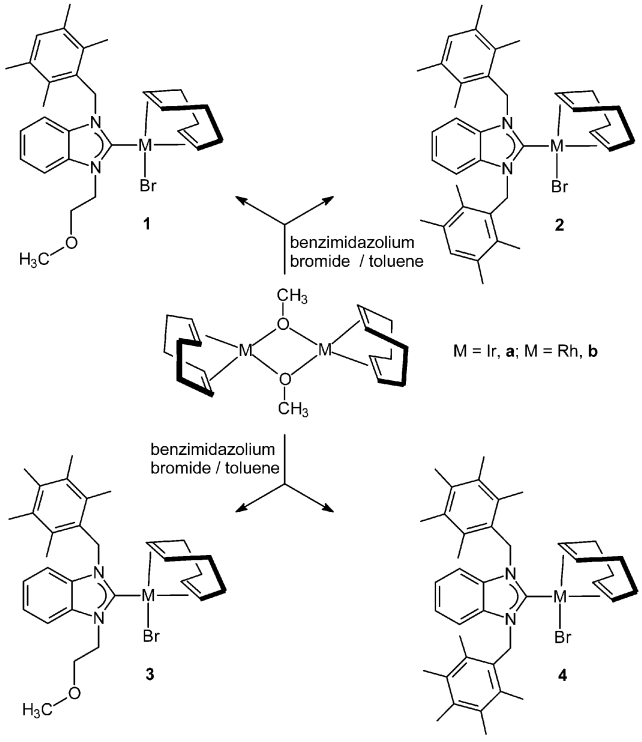
This latter method was used for the preparation of complexes **1**–**4** from dinuclear complexes of the type [M(OMe)(cod)]$_2$, (M = Rh, Ir) and a benzimidazolium salt (2 equiv.; Scheme 1). All reactions were carried out in toluene, and the complexes could be isolated in good yields (73–88%) by precipitation with diethyl ether from the reaction mixture. Solutions of **1**–**4** in chlorinated solvents were observed to be stable towards air and moisture. The identities of the compounds were confirmed by ^{1}H and ^{13}C NMR spectroscopy, MALDI mass spectrometry, and elemental analysis.



Scheme 1. Preparation of Rh^{I}and Ir^{I} complexes **1**–**4**.

The ^{1}H NMR spectra of complexes **1a**, **1b**, **3a**, and **3b** exhibit resonances for the O–CH_3 groups at δ = 3.36, 3.27, 3.39, and 3.32 ppm, respectively. The ^{13}C NMR spectra show the characteristic resonances for the benzimidazol-2-ylidene carbene carbon atom in the range δ = 192.7–193.5 ppm (for iridium complexes **1a**–**4a**) and δ = 196.2–198.0 ppm (for rhodium complexes **1b**–**4b**). These values, as well as the Rh,$C_{carbene}$ coupling constants observed for rhodium complexes **1b**–**4b** [^1J(Rh,C) = 49.6–50.2 Hz], fall in the range observed previously for iridium[9] and rhodium[12e] complexes with benzimidazol-2-ylidene ligands.

The molecular structures of iridium complexes **1a** (Figure 1), **2a** (Figure 2), and **3a** (Figure 3) were determined by single-crystal X-ray diffraction. The iridium atom in the complexes is coordinated in a distorted square-planar fashion by taking the midpoints of the C=C bonds as vertices. The Ir–C bond lengths to the C=C bond *trans* to the carbene carbon atom [Ir–C34 2.195(5) Å, Ir–C35 2.192(5) Å for **2a**], are clearly longer than those to the C=C bond *trans* to the bromide ligand [Ir–C30 2.109(5) Å, Ir–C31 2.117(5) Å for **2a**]. Similar observations were made for **1a** and **3a** and for additional complexes of the type [IrBr(cod)(benzimidazolin-2-ylidene)].[9]

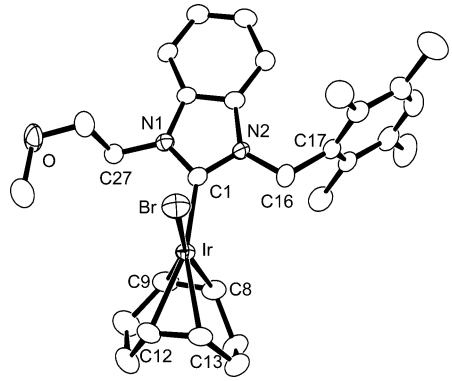


Figure 1. Molecular structure of complex **1a** (hydrogen atoms have been omitted). Selected bond lengths [Å] and angles [°]: Ir–Br 2.4920(6), Ir–C1 2.008(4), Ir–C8 2.103(5), Ir–C9 2.114(5), Ir–C12 2.213(5), Ir–C13 2.193(4), N1–C1 1.351(5), N2–C1 1.362(6), C8–C9 1.392(7), C12–C13 1.396(7); Br–Ir–C1, 87.81(12), Br–Ir–C8 162.54(14), Br–Ir–C9 158.9(2), Br–Ir–C12 93.63(14), Br–Ir–C13 91.46(13), C1–Ir–C8 93.1(2), C1–Ir–C9 92.4(2), C1–Ir–C12 163.4(2), C1–Ir–C13 159.7(2), C8–Ir–C9 38.6(2), C8–Ir–C12 90.4(2), C8–Ir–C13 81.6(2), C9–Ir–C12 80.4(2), C9–Ir–C13 95.5(2), C12–Ir–C13 36.9(2), N1–C1–N2 106.4(4).

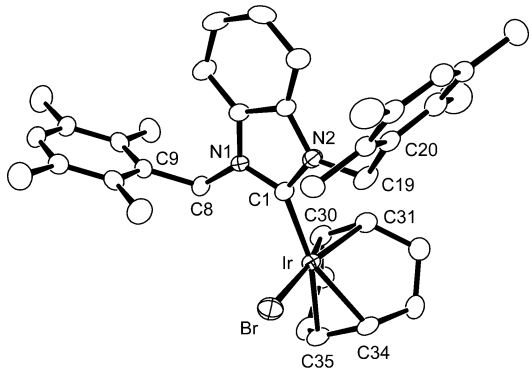


Figure 2. Molecular structure of complex **2a** in **2a**·CH_2Cl_2 (hydrogen atoms have been omitted). Selected bond lengths [Å] and angles [°]: Ir–Br 2.4803(6), Ir–C1 2.010(4), Ir–C30 2.109(5), Ir–C31 2.117(5), Ir–C34 2.195(5), Ir–C35 2.192(5), N1–C1 1.363(6), N2–C1 1.361(6), C30–C31 1.406(7), C34–C35 1.390(7); Br–Ir–C1, 90.75(13), Br–Ir–C30 161.58(14), Br–Ir–C31 159.42(14), Br–Ir–C34 93.12(14), Br–Ir–C35 89.61(14), C1–Ir–C30 93.3(2), C1–Ir–C31 88.1(2), C1–Ir–C34 158.4(2), C1–Ir–C35 164.5(2), C30–Ir–C31 38.9(2), C30–Ir–C34 89.7(2), C30–Ir–C35 81.7(2), C31–Ir–C34 80.9(2), C31–Ir–C35 96.9(2), C34–Ir–C35 36.9(2), N1–C1–N2 105.9(4).

The Ir–$C_{carbene}$ bond lengths are identical within experimental error for **1a**, **2a**, and **3a** and fall in the range previously observed for square-planar Ir^{I} complexes with benzimidazol-2-ylidene ligands.[9] The different N^1,N^2-substitution pattern of the benzimidazol-2-ylidene ligands in **1a**, **2a**, and **3a** does not lead to significantly different geometric parameters for the three complexes. No interaction of the ether donor in **1a** and **3a** with the metal center was observed.

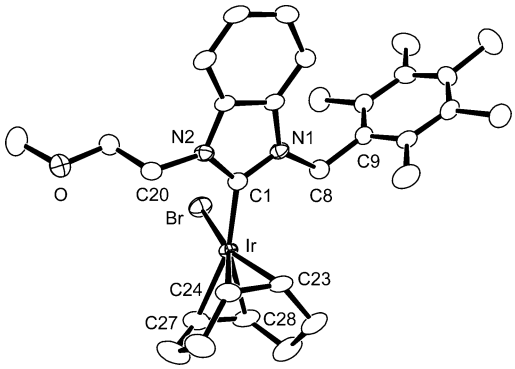


Figure 3. Molecular structure of complex **3a** (hydrogen atoms have been omitted). Selected bond lengths [Å] and angles [°]: Ir–Br 2.4907(5), Ir–C1 1.999(4), Ir–C23 2.110(4), Ir–C23 2.118(4), Ir–C27 2.195(4), Ir–C28 2.197(4), N1–C1 1.367(5), N2–C1 1.361(4), C23–C24 1.422(6), C27–C28 1.385(6); Br–Ir–C1, 87.46(10), Br–Ir–C23 158.70(11), Br–Ir–C24 161.96(12), Br–Ir–C27 91.12(12), Br–Ir–C28 93.48(11), C1–Ir–C23 90.78(14), C1–Ir–C24 94.85(15), C1–Ir–C27 163.4(2), C1–Ir–C28 159.9(2), C23–Ir–C24 39.33(15), C23–Ir–C27 96.4(2), C23–Ir–C28 81.07(15), C24–Ir–C27 81.6(2), C24–Ir–C28 90.5(2), C27–Ir–C28 36.8(2), N1–C1–N2 105.7(3).

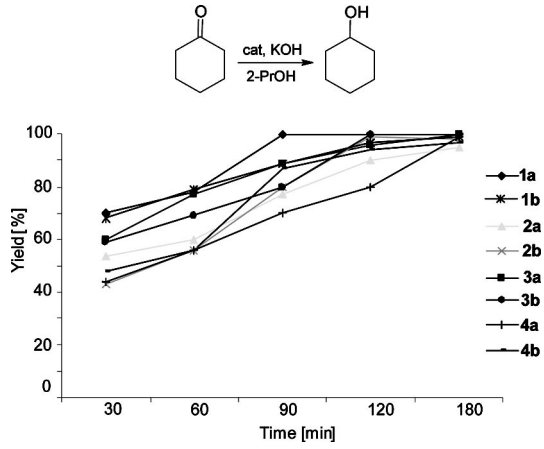


Figure 5. Time dependence of the catalytic transfer hydrogenation of cyclohexanone; catalyst (**1a**–**4b**; 0.02 mmol), KOH (0.2 mmol), cyclohexanone (4 mmol), and 2-propanol (20 mL), T = 353 K.

Catalytic Studies

We reported that the activities of NHC complexes are influenced by the steric bulk and electronegativities of *para* substituents.[10,16] So we have devoted efforts to the study of the sterically similar *N*-benzylic substituents on the common benzimidazolylidene framework. Both rhodium– and iridium–NHC complexes **1**–**4** are efficient precursors for the catalytic transfer hydrogenation of ketones to alcohols by using 2-propanol as a hydrogen donor in the presence of a suitable base. The yields for transfer hydrogenation of acetophenone and cyclohexanone (reaction time 180 min) were studied (Figures 4 and 5). The highest catalytic activity was observed with iridium complex **1a** bearing the sterically least encumbered, unsymmetrically *N*,*N*′-substituted benzimidazol-2-ylidene ligand.

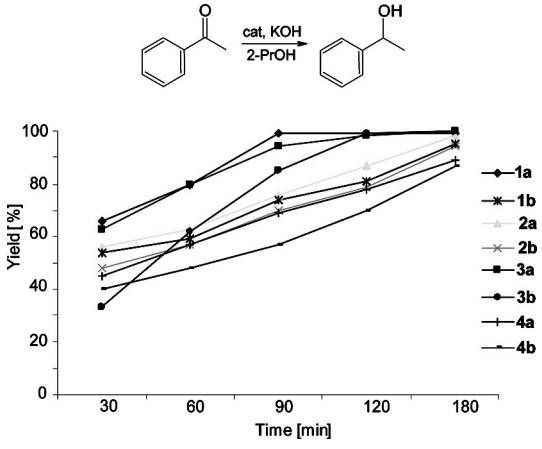


Figure 4. Time dependence of the catalytic transfer hydrogenation of acetophenone; catalyst (**1a**–**4b**, 0.02 mmol), KOH (0.2 mmol), acetophenone (4 mmol), and 2-propanol (20 mL), T = 353 K.

In order to estimate the differences in the catalytic activities of complexes **1**–**4** we applied a low catalyst loading (0.2 mmol, at 353 K) in the transfer hydrogenation of acetophenone and cyclohexanone (Figures 4 and 5). After 90 min, a 99% yield was achieved for the preparation of 1-phenyethanol by using complex **1a**. A difference in catalytic activity was, however, observed in the case of the symmetrical ligands (*N*,*N*′-disubstituted by identical benzylic groups: **4a** < **2a**; **4b** < **2b**). Our results indicate that complexes **1a** and **3a** are highly efficient in the transfer hydrogenation of acetophenone to 1-phenyethanol and cyclohexanone to cyclohexanol. By far the most efficient catalyst is unsymmetrically *N*,*N*′-substituted complex **1a**, which transfer hydrogenates benzophenone to >68% conversion of 13600 h^{-1} in only 30 min. This activity is significantly higher than those of related iridium(I) monocarbene complexes[7] and compares well with those of the most active transfer hydrogenation catalysts previously described.[17] The data indicate clearly the superiority of complexes **1** and **3** containing a 2-methoxyethyl substituent on the N^3 atom. This may be due to the hemilabile functionality of the OMe group.[16a,18]

In order to improve the reactivity of our catalytic system, we examined the influence of base. The reduction of acetophenone, taken as a model ketone, was carried out in 2-propanol by using iridium complex **1a**. The reactions were studied at 353 K over 90 min. Typically, to solutions containing acetophenone and catalyst **1a**, different bases were added and the yields obtained are shown in Figure 6. With the organic bases triethylamine and pyridine poor yields were observed. By using the inorganic bases Cs_2CO_3, K_2CO_3, KOH, NaOH and *t*BuOK the conversion was strongly dependent upon the base strength with the stronger bases giving higher yields (K_2CO_3 < Cs_2CO_3 < *t*BuOK < NaOH < KOH). As in the previous study,[10] the best results were obtained with KOH and other bases required longer reaction times.

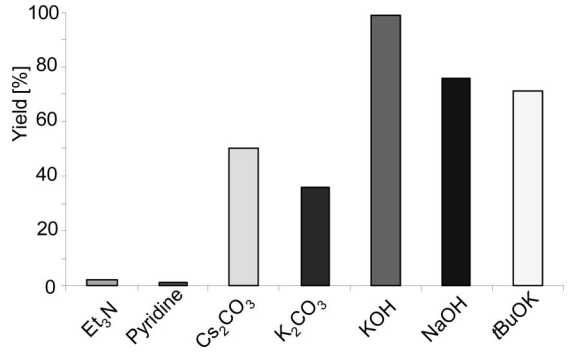


Figure 6. Influence of the base on the transfer hydrogenation of acetophenone by using catalyst **1a** (0.02 mmol), acetophenone (4 mmol), and 2-propanol (20 mL), T = 353 K, t = 90 min.

Conclusions

Iridium(I) and rhodium(I) complexes bearing electron-rich benzimidazol-2-ylidene ligands were prepared by the reaction of suitable benzimidazolium salts with $[M(OMe)(cod)]_2$ (M = Ir, Rh). The complexes show high activity in the catalytic transfer hydrogenation of acetophenone and cyclohexanone in 2-propanol. The iridium complex with the sterically least encumbered unsymmetrically *N*,*N*′-substituted benzimidazol-2-ylidene ligands shows the highest catalytic activity, which is further influenced by the type of base used.

Experimental Section

General Procedure for the Preparation of Complexes [IrBr(η⁴-cod)(NHC)] (complex type a) and [RhBr(η⁴-cod)(NHC)] (complex type b): The salts were prepared according to known methods.[9,16] A sample of 1,3-alkylbenzimidazolium bromide (0.64 mmol) and $[Ir(\mu\text{-}OMe)cod]_2$ or $[Rh(\mu\text{-}OMe)cod]_2$ (0.32 mmol) were suspended in toluene (8 mL) in a Schlenk tube. The reaction mixture was heated under reflux overnight. Insoluble reaction products were separated by filtration and diethyl ether was added to the solution causing precipitation of the metal complexes. They were separated by filtration and dried under reduced pressure. The solid complexes can be recrystallized from CH_2Cl_2/EtOH.

Bromo(η⁴-1,5-cylooctadiene)[1-(2,3,5,6-tetramethylbenzyl)-3-(2-methoxyethyl)benzimidazol-2-ylidene]iridium(I) (1a): Yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, J = 2.2 Hz, 2 H, Ar-H NHC), 7.06 [s, 1 H, Ar-H $C_6H(CH_3)_4$], 6.26 [d, J = 2.2 Hz, 1 H, N-CH*H*-$C_6H(CH_3)_4$], 6.03 (d, J = 2.2 Hz, 2 H, Ar-H NHC), 5.79 [d, J = 2.2 Hz, 1 H, N-CH*H*-$C_6H(CH_3)_4$], 5.12 (m, 1 H, cod-C*H*=C*H*), 4.76 (m, 3 H, cod-C*H*=C*H* and $NCH_2CH_2OCH_3$), 3.96 (m, 2 H, $NCH_2CH_2OCH_3$), 3.36 (s, 3 H, $NCH_2CH_2OCH_3$), 3.16 (m, 1 H, cod-C*H*=C*H*), 3.03 (m, 1 H, cod-C*H*=C*H*), 2.25 [s, 6 H, $C_6H(CH_3)_4$-*o*-CH_3], 2.20 [s, 6 H, $C_6H(CH_3)_4$-*m*-CH_3], 1.82 (m, 4 H, cod-CH_2), 1.59 (m, 4 H, cod-CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.9 ($C_{carbene}$), 135.6, 135.0, 134.8, 134.0, 132.3, 122.3, 121.7, 110.9, 110.7, 110.5 (Ar-C), 85.9, 85.8 (cod-CH), 71.4 ($NCH_2CH_2OCH_3$), 59.1 ($NCH_2CH_2OCH_3$), 53.7, 52.7 (cod-CH), 50.6 [$NCH_2C_6H(CH_3)_4$], 47.9 ($NCH_2CH_2OCH_3$), 33.3, 33.1, 29.6, 29.4 (cod-CH_2), 20.5 [$C_6H(CH_3)_4$-*m*-CH_3], 16.3 [$C_6H(CH_3)_4$-*o*-CH_3] ppm. $C_{29}H_{38}BrIrN_2O$ (702.74): calcd. C 49.56, H 5.45, N 3.99; found C 49.57, H 5.42, N 4.01.

Bromo(η⁴-1,5-cylooctadiene)[1-(2,3,5,6-tetramethylbenzyl)-3-(2-methoxyethyl)benzimidazol-2-ylidene]rhodium(I) (1b): Yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (d, J = 2.1 Hz, 1 H, Ar-H NHC), 7.01 [s, 1 H, Ar-H $C_6H(CH_3)_4$], 6.97 (t, J = 2.1 Hz, 1 H, Ar-H NHC), 6.71 (t, J = 2.1 Hz, 1 H, Ar-H NHC), 6.27 [d, J = 4.1 Hz, 1 H, N-CH*H*-$C_6H(CH_3)_4$], 5.9 (d, J = 2.1 Hz, 1 H, Ar-H NHC), 5.88 [d, J = 4.1 Hz, 1 H, N-CH*H*-$C_6H(CH_3)_4$], 5.17 (m, 3 H, cod-C*H*=C*H* and $NCH_2CH_2OCH_3$), 4.84 (m, 2 H, $NCH_2CH_2OCH_3$), 4.01, 3.51, 3.43 (s, 3 H, cod-C*H*=C*H*), 3.32 (s, 3 H, $NCH_2CH_2OCH_3$), 2.33 (m, 4 H, cod-CH_2), 2.25 [s, 6 H, $C_6H(CH_3)_4$-*o*-CH_3], 2.19 [s, 6 H, $C_6H(CH_3)_4$-*m*-CH_3], 1.94 (m, 4 H, cod-CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.2 (d, J = 50.2 Hz, $C_{carbene}$), 134.5, 134.2, 133.9, 131.4, 129.9, 121.2, 120.7, 109.5, 109.3 (Ar-C), 99.5, (d, J = 6.1 Hz, cod-CH), 98.4 (d, J = 4.2 Hz, cod-CH), 70.4 ($NCH_2CH_2OCH_3$), 69.4 (d, J = 14.5 Hz, cod-*C*H), 68.2 (d, J = 13.7 Hz, cod-*C*H), 58.1 ($NCH_2CH_2OCH_3$), 50.0 [$NCH_2C_6H(CH_3)_4$], 47.6 ($NCH_2CH_2OCH_3$), 31.9, 31.5, 28.1, 27.9 (cod-CH_2), 19.5 [$C_6H(CH_3)_4$-*m*-CH_3], 15.4 [$C_6H(CH_3)_4$-*o*-CH_3] ppm. $C_{29}H_{38}BrN_2ORh$ (613.43): calcd. C 56.78, H 6.24, N 4.57; found C 56.77, H 6.32, N 4.71. MS (MALDI): m/z = 533 $[M - Br]^+$.

Bromo(η⁴-1,5-cylooctadiene)[1,3-bis(2,3,5,6-tetramethylbenzyl)-benzimidazol-2-ylidene]iridium(I) (2a): Yield: 87%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.05 [s, 2 H, Ar-H $C_6H(CH_3)_4$], 6.70 (m, 2 H, Ar-H NHC), 6.52 [d, J = 4.0 Hz, 2 H, N-CH*H*-$C_6H(CH_3)_4$], 6.10 (m, 2 H, Ar-H NHC), 5.84 [d, J = 4.0 Hz, 2 H, N-CH*H*-$C_6H(CH_3)_4$], 4.94 (br., 2 H, cod-C*H*=C*H*), 3.24 (br., 2 H, cod-C*H*=C*H*), 2.26 [s, 12 H, $C_6H(CH_3)_4$-*o*-CH_3], 2.24 [s, 12 H, $C_6H(CH_3)_4$-*m*-CH_3], 1.87 (m, 4 H, cod-CH_2), 1.61 (m, 4 H, cod-CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.5 ($C_{carbene}$), 135.3, 134.6, 134.0, 132.3, 130.7, 121.7, 110.8 (Ar-C), 85.6, 53.0 (cod-CH), 50.8 [$NCH_2C_6H(CH_3)_4$], 33.2, 29.4 (cod-CH_2), 20.5 [$C_6H(CH_3)_4$-*m*-CH_3], 16.5 [$C_6H(CH_3)_4$-*o*-CH_3] ppm. $C_{37}H_{46}BrIrN_2$ (790.89): calcd. C 56.19, H 5.86, N 3.54; found C 56.23, H 5.94, N 3.57. MS (MALDI): m/z = 710 $[M - Br]^+$.

Bromo(η⁴-1,5-cylooctadiene)[1,3-bis(2,3,5,6-tetramethylbenzyl)-benzimidazol-2-ylidene]rhodium(I) (2b): Yield: 73%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.06 [s, 2 H, Ar-H $C_6H(CH_3)_4$], 6.64 (m, 2 H, Ar-H NHC), 6.08 (m, 2 H, Ar-H NHC), 6.03, 5.99 [d, J = 4.1 Hz, 4 H, N-CH*H*-$C_6H(CH_3)_4$], 5.27 (s, 2 H, cod-C*H*=C*H*), 3.66 (s, 2 H, cod-C*H*=C*H*), 2.44 (m, 4 H, cod-CH_2), 2.30 [s, 12 H, $C_6H(CH_3)_4$-*o*-CH_3], 2.24 [s, 12 H, $C_6H(CH_3)_4$-*m*-CH_3], 2.00 (m, 4 H, cod-CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.9 (d, J = 49.6 Hz, $C_{carbene}$), 135.6, 135.0, 134.4, 132.6, 131.3, 121.8, 110.8 (Ar-C), 99.8 (d, J = 6.1 Hz, cod-CH), 70.0 (d, J = 14.5 Hz, cod-CH), 51.5 [$NCH_2C_6H(CH_3)_4$], 29.2, 33.0 (cod-CH_2), 20.8 [$C_6H(CH_3)_4$-*m*-CH_3], 16.4 [$C_6H(CH_3)_4$-*o*-CH_3] ppm. $C_{37}H_{46}BrN_2Rh$ (701.58): calcd. C 63.34, H 6.61, N 3.99; found C 63.51, H 6.73, N 4.01. MS (MALDI): m/z = 622 $[M - Br]^+$.

Bromo(η⁴-1,5-cylooctadiene)[(1-pentamethylbenzyl)-3-(2-methoxyethyl)benzimidazol-2-ylidene]iridium(I) (3a): Yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, J = 2.0 Hz, 1 H, Ar-H NHC), 7.06 (t, J = 2.0 Hz, 1 H, Ar-H NHC), 6.80 (t, J = 2.0 Hz, 1 H, Ar-H NHC), 6.26 [d, J = 4.1 Hz, 1 H, N-CH*H*-$C_6(CH_3)_5$], 6.09 (d, J = 2.1 Hz, 1 H, Ar-H NHC), 5.78 [d, J = 4.1 Hz, 1 H, N-CH*H*-$C_6(CH_3)_5$], 5.12 (m, 1 H, cod-C*H*=C*H*), 4.78 (m, 3 H, cod-C*H*=C*H* and $NCH_2CH_2OCH_3$), 3.99 (m, 2 H, $NCH_2CH_2OCH_3$), 3.39 (s, 3 H, $NCH_2CH_2OCH_3$), 3.21 (m, 1 H, cod-C*H*=C*H*), 3.06 (m, 1 H, cod-C*H*=C*H*), 2.32 [s, 3 H, $C_6(CH_3)_5$-*p*-CH_3], 2.27 [s, 6 H, $C_6(CH_3)_5$-*m*-CH_3], 2.25 (s, 6 H, $C_6(CH_3)_5$-*o*-CH_3), 1.84 (m, 4 H, cod-CH_2), 1.60 (m, 4 H, cod-CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.7 ($C_{carbene}$), 135.5, 135.1, 134.3, 132.8, 127.9, 122.2, 121.6,

111.1, 110.4 (Ar-C), 85.7, 85.6 (cod-CH), 71.3 ($NCH_2CH_2OCH_3$), 59.0 ($NCH_2CH_2OCH_3$), 53.6, 52.6 (cod-CH), 51.1 [$NCH_2C_6(CH_3)_5$], 47.9 ($NCH_2CH_2OCH_3$), 33.2, 33.0, 29.5, 29.4 (cod-CH_2), 17.9 [$C_6(CH_3)_5$-*o*-CH_3], 17.5 [$C_6(CH_3)_5$-*p*-CH_3], 17.0 [$C_6(CH_3)_5$-*m*-CH_3] ppm. $C_{30}H_{40}BrIrN_2O$ (716.77): calcd. C 50.27, H 5.62, N 3.91; found C 50.33, H 5.54, N 3.89. MS (MALDI): *m*/*z* = 637 $[M - Br]^+$.

Bromo(η⁴-1,5-cylooctadiene)[(1-pentamethylbenzyl)-3-(2-methoxyethyl)benzimidazol-2-ylidene]rhodium(I) (3b): Yield: 79%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 2.2 Hz, 1 H, Ar-H NHC), 6.96 (m, 1 H, Ar-H NHC), 6.70 (m, 1 H, Ar-H NHC), 6.27 [d, *J* = 4.0 Hz, 1 H, N-CH*H*-$C_6(CH_3)_5$], 5.99 (d, *J* = 2.2 Hz, 1 H, Ar-H NHC), 5.88 [d, *J* = 4.0 Hz, 1 H, N-CH*H*-$C_6(CH_3)_5$], 5.16 (m, 3 H, cod-C*H*=C*H* and $NCH_2CH_2OCH_3$), 5.27 (s, 1 H, cod-C*H*=C*H*), 4.02 (m, 1 H, $NCH_2CH_2OCH_3$), 3.94 (m, 1 H, $NCH_2CH_2OCH_3$), 3.52, 3.43 (s, 2 H, cod-C*H*=C*H*), 3.32 (s, 3 H, $NCH_2CH_2OCH_3$), 2.35 (m, 4 H, cod-CH_2), 2.30 [s, 6 H, $C_6(CH_3)_5$-*o*-CH_3], 2.19 [s, 6 H, $C_6(CH_3)_5$-*m*-CH_3], 2.18 [s, 3 H, $C_6(CH_3)_5$-*p*-CH_3], 1.92 (m, 4 H, cod-CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.3 (d, *J* = 49.6 Hz, $C_{carbene}$), 136.1, 135.7, 135.6, 134.7, 133.2, 128.5, 122.5, 121.8, 111.2, 110.6 (Ar-C), 99.7 (d, *J* = 6.1 Hz, cod-CH), 99.5 (d, *J* = 6.1 Hz, cod-CH), 71.7 ($NCH_2CH_2OCH_3$), 70.5 (d, *J* = 14.5 Hz, cod-CH), 69.4 (d, *J* = 14.0 Hz, cod-CH), 59.3 ($NCH_2CH_2OCH_3$), 51.8 [$NCH_2C_6(CH_3)_5$], 48.7 ($NCH_2CH_2OCH_3$), 29.1, 29.3, 32.7, 33.08 (cod-CH_2), 17.7 [$C_6(CH_3)_5$-*p*-CH_3], 17.5 [$C_6(CH_3)_5$-*m*-CH_3], 17.1 [$C_6(CH_3)_5$-*o*-CH_3] ppm. $C_{30}H_{40}BrN_2ORh$ (627.46): calcd. C 57.43, H 6.73, N 4.46; found C 57.57, H 6.82, N 4.61. MS (MALDI): *m*/*z* = 548 $[M - Br]^+$.

Bromo(η⁴-1,5-cylooctadiene)[1,3-bis(pentamethylbenzyl)benzimidazol-2-ylidene]iridium(I) (4a): Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.66 (m, 2 H, Ar-H NHC), 6.49, 6.41 [d, *J* = 4.0 Hz, 2 H, N-CH*H*-$C_6H(CH_3)_4$], 6.14 (m, 2 H, Ar-H NHC), 5.86, 5.78 [d, *J* = 4.1 Hz, 2 H, N-CH*H*-$C_6H(CH_3)_4$], 4.83 (br., 2 H, cod-C*H*=C*H*), 3.27 (m, 2 H, cod-C*H*=C*H*), 2.31 [s, 12 H, $C_6(CH_3)_5$-*p*-CH_3], 2.29 [s,12 H, $C_6(CH_3)_5$-*m*-CH_3], 2.25 [s, 6 H, $C_6(CH_3)_5$-*o*-CH_3], 1.84 (m, 4 H, cod-CH_2), 1.62 (m, 4 H, cod-CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.3 ($C_{carbene}$), 135.6, 135.4, 134.2, 132.8, 128.1, 121.5, 110.8 (Ar-C), 85.4, 52.9 (cod-CH), 51.3 [$NCH_2C_6(CH_3)_5$], 33.2, 29.5, (cod-CH_2), 17.4 [$C_6(CH_3)_5$-*o*-CH_3], 17.2 [$C_6(CH_3)_5$-*p*-CH_3], 16.8 [$C_6(CH_3)_5$-*m*-CH_3] ppm. $C_{39}H_{50}BrIrN_2$ (818.94): calcd. C 57.20, H 6.15, N 3.42; found C 57.27, H 6.22, N 3.39. MS (MALDI): *m*/*z* = 739 $[M - Br]^+$.

Bromo(η⁴-1,5-cylooctadiene)[1,3-bis(pentamethylbenzyl)benzimidazol-2-ylidene]rhodium(I) (4b): Yield: 73%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.64 (m, 2 H, Ar-H NHC), 6.57 [d, *J* = 4.0 Hz, 2 H, NCH*H*-$C_6(CH_3)_5$], 6.31 (m, 2 H, Ar-H NHC), 6.01 [d, *J* = 4.1 Hz, 2 H, NCH*H*-$C_6(CH_3)_5$], 5.24 (s, 2 H, cod-C*H*=C*H*), 3.60 (s, 2 H, cod-C*H*=C*H*), 2.38 (m, 4 H, cod-CH_2), 2.27 [s, 12 H, $C_6(CH_3)_5$-*o*-CH_3], 2.20 [s, 12 H, $C_6(CH_3)_5$-*m*-CH_3], 2.11 [s, 6 H, $C_6(CH_3)_5$-*p*-CH_3], 2.01 (m, 4 H, cod-CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.0 (d, *J* = 50.0 Hz, $C_{carbene}$), 135.8, 135.3, 134.1, 132.2, 131.0, 120.8, 111.7 (Ar-C), 99.4 (d, *J* = 6.1 Hz, cod-CH), 70.0 (d, *J* = 14.5 Hz, cod-CH), 51.2 [$NCH_2C_6(CH_3)_5$], 33.1, 29.1 (cod-CH_2), 21.3 [$C_6(CH_3)_5$-*p*-CH_3], 20.8 [$C_6(CH_3)_5$-*m*-CH_3], 16.4 [$C_6(CH_3)_5$-*o*-CH_3] ppm. $C_{39}H_{50}BrN_2Rh$ (729.63): calcd. C 64.20, H 6.91, N 3.84; found C 64.21, H 6.99, N 3.94. MS (MALDI): *m*/*z* = 649 $[M - Br]^+$.

Hydrogen Transfer Catalytic Experiments: The tested complex (0.02 mmol) was dissolved in a solution of KOH (0.2 mmol), diethyleneglycol-di-*n*-butyl ether (0.3 mmol, internal standard), and 2-propanol (20 mL) in a Schlenk tube. The solution was heated to 353 K for 30 min. Subsequently, acetophenone or cyclohexanone (4 mmol) was added with an Eppendorf pipet. The reaction progress was monitored by GC analysis.

X-ray Diffraction Studies: Diffraction data for **1a**, **2a**·CH_2Cl_2, and **3a** were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 153(2) K by using graphite monochromated Mo-K_α radiation (λ = 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[19] program package. Structure solutions were found with the SHELXS-97[20] package by using the heavy-atom method and were refined with SHELXL-97[21] against $|F^2|$ by using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions. CCDC-695451 (for **1a**), -691392 (for **2a**·CH_2Cl_2), and -691393 (for **3a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Data for 1a: $C_{29}H_{38}N_2BrOIr$, *M* = 702.72, μ = 6.521 mm^{-1}, ρ = 1.748 g cm^{-3}, monoclinic, $P2_1/n$, *Z* = 4, *a* = 15.618(3) Å, *b* = 7.4645(14) Å, *c* = 23.833(5) Å, β = 106.062(4)°, *V* = 2670.0(9) Å^3, 29904 measured reflections, 7773 unique reflections (R_{int} = 0.0539), *R* = 0.0392, *wR* = 0.0832 for 5907 contributing reflections [$I \geq 2\sigma(I)$], refinement against $|F^2|$ with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions. The asymmetric unit contains one molecule of **1a**.

Crystal Data for 2a·CH_2Cl_2: $C_{38}H_{48}N_2BrCl_2Ir$, *M* = 875.79, μ = 5.124 mm^{-1}, ρ = 1.657 g cm^{-3}, triclinic, $P\bar{1}$, *Z* = 2, *a* = 9.0824(14) Å, *b* = 11.968(2) Å, *c* = 17.802(3) Å, α = 83.499(3)°, β = 78.275(3)°, γ = 67.980(3)°, *V* = 1755.0(4) Å^3, 20486 measured reflections, 10123 unique reflections (R_{int} = 0.0417), *R* = 0.0438, *wR* = 0.0988 for 8496 contributing reflections [$I \geq 2\sigma(I)$], refinement against $|F^2|$ with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions. The asymmetric unit contains one molecule of **2a** and one molecule of CH_2Cl_2.

Crystal Data for 3a: $C_{30}H_{40}N_2BrIrO$, *M* = 716.75, μ = 6.250 mm^{-1}, ρ = 1.709 g cm^{-3}, monoclinic, $P2_1/c$, *Z* = 4, *a* = 15.460(3) Å, *b* = 7.4701(13) Å, *c* = 24.613(4) Å, β = 101.406(4)°, *V* = 2786.4(8) Å^3, 30953 measured reflections, 8110 unique reflections (R_{int} = 0.0530), *R* = 0.0333, *wR* = 0.0711 for 6716 contributing reflections [$I \geq 2\sigma(I)$], refinement against $|F^2|$ with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions. The asymmetric unit contains one molecule of **3a**.

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[18] As suggested by one reviewer, additional experiments aimed at the comparative study of the alcohol function of the N-substituent as an efficient catalyst precursor was carried out. [RhBr(cod)(NHC)] (R = 2,3,4,5-tetramethylbenzyl, R′ = CH_2CH_2OH) was prepared in a similar manner and characterized by NMR spectroscopy. Yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (d, J = 2.1 Hz, 1 H, Ar-H NHC), 7.26 (s, 1 H, Ar-H NHC), 7.17 (t, J = 2.1 Hz, 1 H, Ar-H NHC), 7.09–7.04 [m, 2 H, Ar-H NHC, $C_6H(CH_3)_4$], 6.80 (t, J = 2.1 Hz, 1 H, Ar-H NHC), 6.34 [d, J = 4.1 Hz, 1 H, N-CH*H*-$C_6H(CH_3)_4$], 6.04–6.00 [m, 2 H, N-CH*H*-$C_6H(CH_3)_4$ and NCH_2CH_2O*H* confirmed with D_2O exchange experiment], 5.31–5.25 (m, 3 H, cod-C*H*=C*H* and NCH_2CH_2OH), 4.68 (s, 2 H, $NCH_2CH_2OCH_3$), 4.22, 3.58, 3.50 (s, 3 H, cod-C*H*=C*H*), 2.51–2.42 (m, 4 H, cod-CH_2), 2.27 [s, 6 H, $C_6H(CH_3)_4$-*o*-CH_3], 2.22 [s, 6 H, $C_6H(CH_3)_4$-*m*-CH_3], 2.06–1.99 (m, 4 H, cod-CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.4 (d, J = 50.1 Hz, $C_{carbene}$), 135.6, 135.2, 134.4, 131.1, 129.2, 128.9, 125.5, 122.7, 122.1, 111.3, 109.9, 109.3 (Ar-C), 99.5, (d, J = 6.1 Hz, cod-CH), 96.4 (d, J = 4.2 Hz, cod-CH), 70.7 (d, J = 14.5 Hz, cod-*C*H), 69.8 (d, J = 13.7 Hz, cod-*C*H), 60.9 (NCH_2CH_2OH), 51.6 [$NCH_2C_6H(CH_3)_4$], 50.7 (NCH_2CH_2OH), 33.1, 32.7, 29.3, 28.2 (cod-CH_2), 20.7 [$C_6H(CH_3)_4$-*m*-CH_3], 16.7 [$C_6H(CH_3)_4$-*o*-CH_3] ppm. The above complex was tested as a catalyst in the transfer hydrogenation of acetophenone, but in comparison to **1b** (values in parentheses) only less efficiency was observed under the same conditions: 17 (56), 30 (61), 48 (73), 60 (82), and 68 (93)% after 30, 60, 90, 120, and 180 min, respectively.
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