Iridium Complexes with *N*-Allyl-Substituted Benzimidazol-2-ylidene Ligands and Their Application in Catalytic Transfer Hydrogenation

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The reactions of $[Ir(\mu\text{-OMe})(cod)]_2$ with the *N*-allyl-substituted benzimidazolium salts 1-methyl-3-(2-propenyl)benzimidazolium iodide (**2**) and 1,3-di(2-propenyl)benzimidazolium bromide (**3**) have been found to afford the five-coordinated Ir(I) complexes [IrX(cod)(η^2-*C*-NHC)] (X = I, NHC = 1-methyl-3-(2-propenyl)benzimidazol-2-ylidene, **4**; X = Br, NHC = 1,3-di(2-propenyl)benzimidazol-2-ylidene, **5**), respectively. The cationic derivative [Ir(cod)(η^2:η^2-*C*-NHC)]BF_4 (NHC = 1,3-di(2-propenyl)benzimidazol-2-ylidene, **6**), which contains an iridium center exclusively coordinated by sp^2 carbon atoms, has been prepared by treatment of **5** with $AgBF_4$. The reaction between $[Ir(\mu\text{-Cl})(cod)]_2$ and **3** in ethanol, in the presence of excess NaOEt, has allowed the synthesis of the four-coordinate complex [IrBr(cod)(*C*-NHC)] (NHC = 1,3-di(propyl)benzimidazol-2-ylidene, **7**) after deprotonation of **3** and hydrogenation of both *N*-allyl substituents. The compounds **5**, **6**, and **7** have been characterized by X-ray diffraction. The neutral complexes **4**, **5**, and **7** have been tested as catalysts in the transfer hydrogenation of cyclohexanone using 2-propanol as hydrogen source. The catalytic reactions using **4** and **5** have been observed to progress without hydrogenation of the allyl substituents.

Introduction

Complexes with *N*-heterocyclic carbene (NHC) ligands exhibit desirable catalytic properties particularly when a phosphine ligand in an established system is substituted for an NHC.[1] For example, substitution of a tricyclohexylphosphine by imidazol-2-ylidene in the ruthenium catalyst developed by Grubbs[2] leads to novel, highly active and functional group tolerant olefin metathesis catalysts.[3] The introduction of NHC ligands instead of phosphines into iridium complexes generates catalysts for various hydrogenation reactions. Based on Crabtrees's catalyst $[Ir(cod)(py)(PCy_3)]PF_6$ (py = pyridine, cod = η^2:η^2-1,5-cyclooctadiene),[4] Nolan et al. synthesized complexes of type $[Ir(cod)(py)(NHC)]PF_6$, which show high activities in transfer hydrogenations of C=C, C=O, and N=O double bonds.[5] These latter complexes, and the closely related $[Ir(cod)(PR_3)(NHC)]PF_6$, also show activity in catalytic olefin hydrogenation.[6] Parent iridium(III) complexes with chelating imidazol-2-ylidene ligands, $(NHC)_2CH_2$, are capable of transfer hydrogenation of aldehydes under basic conditions while protecting the catalyst from formation of inactive L_nIr-CO species.[7]

N-Functionalization of the NHC ligands with N- or O-donor groups may lead to hemilabile chelating ligands that stabilize free coordination sites at catalytically active metal centers.[8] As an alternative to achieve such desirable vacancy stabilization, we became interested in NHC ligands bearing *N*-allyl substituents. The use of this type of ligands also meets challenges from the synthetic point of view, since, even though different

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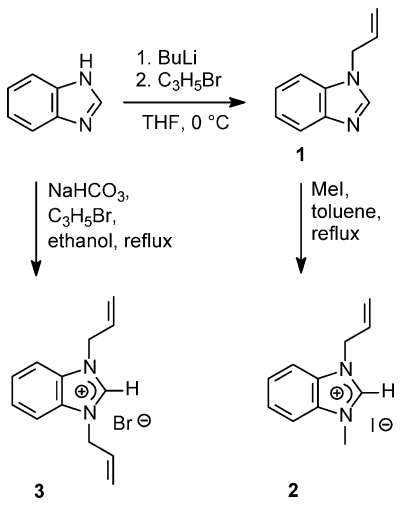
Scheme 1



procedures for their preparation have been reported,[9] it has been so far impossible to isolate such a carbene or its electron-rich dimeric enetetramine, which shows a high tendency to rearrange. Nevertheless, some preceding work has shown that either the *N*-alkylation of a previously coordinated NHC ligand[10] or the in situ deprotonation of an azolium salt followed by fast ligand trapping with a suitable metal center[9a,11] constitutes a feasible route to this type of carbene complex. In this paper, we report on the application of this latter methodology to *N*-allyl-substituted benzimidazolium salts, using iridium complexes $[Ir(\mu\text{-OR})(cod)]_2$ as both the base and the source of trapping metal fragments. The new carbene complexes so obtained exhibit coordination of one or two allyl groups to the iridium atom and are catalysts for the transfer hydrogenation of ketones.

Results and Discussion

***N*-Allyl-Substituted Benzimidazolium Salts.** The synthesis of 1-methyl-3-(2-propenyl)benzimidazolium iodide (**2**) and 1,3-di(2-propenyl)benzimidazolium bromide (**3**) from commercially available benzimidazole is summarized in Scheme 1. The selective introduction of one allyl substituent has been found to proceed in THF, after deprotonation of the benzimidazole with *n*-BuLi and reaction with 1 equiv of allyl bromide. This procedure has led to the intermediate compound 1-(2-propenyl)benzimidazole (**1**), which has been isolated as a hygroscopic brown oil soluble in most organic solvents. The addition of a second equivalent of alkyl halide to give the unsymmetrically substituted benzimidazolium salt **2** has been achieved in refluxing toluene.[12] The salt, which precipitates from the reaction mixture, could be purified by recrystallization from hot ethanol, either by cooling or by addition of diethyl ether. The symmetrically substituted bis-allyl derivative **3** has been prepared in a one-step reaction by heating of benzimidazole and allyl bromide in ethanol, in the presence of $NaHCO_3$ as a base.[13] The benzimidazolium salts **2** and **3** have been observed to be hygroscopic and soluble in chlorinated solvents, hot alcohols, and water.

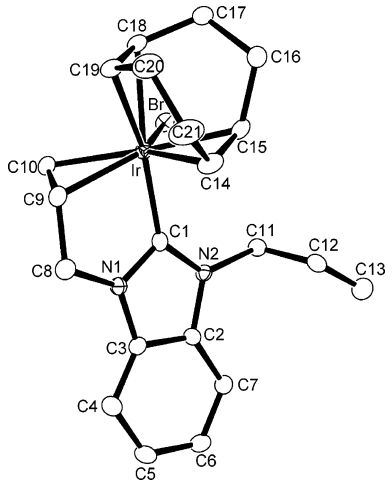


Figure 1. Molecular structure of complex **5**.

The NMR spectroscopic data of **1**−**3** agree with the proposed structures. The ^1H NMR spectrum of **1** displays signals for the terminal hydrogen atoms of the allyl group at δ 4.58 and 4.46 ppm with typical J_{HH} coupling constants ($^3J_{HH} = 11.4$ Hz, *cis* and $^3J_{HH} = 17.0$ Hz, *trans*). This characteristic coupling scheme can be found in each molecule described below bearing an allyl group. The NCHN hydrogen atom of the neutral compound **1** gives rise to a singlet at δ 7.29 ppm, while the corresponding signal in the salts **2** and **3** (δ 10.55 and 10.97 ppm, respectively) shows a characteristic downfield shift attributable to the positive charge.

Iridium Carbene Complexes. The five-coordinate Ir(I) complexes $[IrX(cod)(\eta^2\text{-}C\text{-NHC})]$ (X = I, NHC = 1-methyl-3-(2-propenyl)benzimidazol-2-ylidene, **4**; X = Br, NHC = 1,3-di(2-propenyl)benzimidazol-2-ylidene, **5**) have been prepared by reaction of the iridium dimer $[Ir(\mu\text{-OMe})(cod)]_2$ with 2 equiv of the benzimidazolium salts **2** and **3**, respectively. The reactions have been carried out in acetone, and the complexes could be isolated in good yield by precipitation in methanol or diethyl ether. The solutions of **4** and **5** in acetone or chlorinated solvents have been observed to be stable toward air and moisture.

The molecular structure of complex **5** determined by X-ray diffraction is shown in Figure 1. Most relevant distances and angles of this structure are collected in Table 1. This structural analysis confirms both the five-coordinate nature of the complex and the η^2-*C* coordination mode of the *N*-allyl-substituted carbene ligand. The overall molecular geometry of **5** is best described as trigonal bipyramidal, taking the midpoints of the coordinated C=C bonds as vertexes. One cyclooctadiene and one allyl C=C bond together with the bromide form the equatorial plane, with the other cyclooctadiene C=C bond and the carbene carbon atom in the axial positions. The Ir−C distances to the axial C=C double bond, *trans*

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for 5, 6·2CHCl$_3$, and 7·C$_7$H$_8$

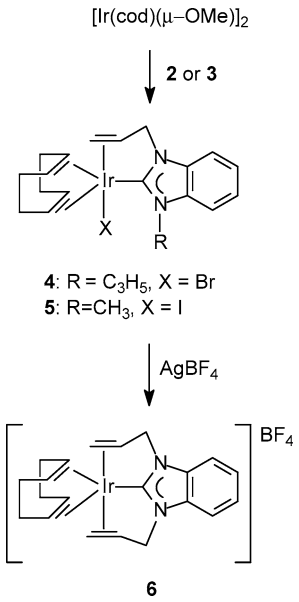
	5	**6**·2CHCl$_3$	**7**·C$_7$H$_8$
Ir−Br	2.6355(4)		2.4908(5)
Ir−C1	2.015(3)	1.942(2)	2.005(4)
Ir−C9	2.151(3)	2.203(3)	
Ir−C10	2.138(3)	2.203(3)	
Ir−C12		2.295(3)	
Ir−C13		2.279(3)	
Ir−C14	2.129(3)	2.183(3)	2.108(4)
Ir−C15	2.144(3)	2.211(3)	2.103(4)
Ir−C18	2.246(3)	2.272(3)	2.207(4)
Ir−C19	2.237(3)	2.274(3)	2.183(4)
N1−C1	1.358(4)	1.337(3)	1.363(5)
N1−C3	1.385(4)	1.400(3)	1.395(5)
N1−C8	1.456(4)	1.467(3)	1.459(5)
N2−C1	1.359(4)	1.336(3)	1.361(5)
N2−C2	1.400(3)	1.399(3)	1.386(5)
N2−C11	1.473(4)	1.465(3)	1.466(5)
C9−C10	1.407(5)	1.398(4)	1.519(6)
C12−C13	1.311(5)	1.387(4)	1.529(6)
Br−Ir−C1	89.08(8)		90.19(10)
Br−Ir−C9	126.69(10)		
Br−Ir−C10	90.44(10)		
Br−Ir−C12			
Br−Ir−C13			
Br−Ir−C14	130.03(10)		162.54(13)
Br−Ir−C15	92.66(9)		158.14(13)
Br−Ir−C18	81.72(8)		93.13(13)
Br−Ir−C19	116.32(8)		90.88(12)
C1−Ir−C9	78.77(12)	75.99(11)	
C1−Ir−C10	88.58(13)	84.95(11)	
C1−Ir−C12		74.75(11)	
C1−Ir−C13		82.24(11)	
C1−Ir−C14	87.06(12)	92.36(10)	91.5(2)
C1−Ir−C15	95.85(12)	96.97(11)	90.8(2)
C1−Ir−C18	169.64(12)	164.33(12)	165.6(2)
C1−Ir−C19	154.33(12)	160.47(12)	157.5(2)

to the carbene carbon atom, are clearly longer (2.237(3) and (2.246(3) Å) than the four equatorial ones, which lie within the range 2.129(3)−2.151(3) Å.

The spectroscopic data of **5** indicate the η^2-*C* coordination mode of the NHC ligand to be retained in solution. The ^{1}H and ^{13}C{^{1}H} NMR spectra of **5** exhibit resonances for two different allyl groups, one of them at chemical shifts very similar to those found for the benzimidazolium salt **3** and therefore attributable to an uncoordinated allyl, but the other significantly shifted toward lower field. For example, one of the CH_2−CH=*C*H$_2$ resonances of **5**, at δ 116.3 ppm, is close to the signal observed for **3** (δ 113.5 ppm), while that attributable to this carbon atom in the coordinated allyl group appears at δ 51.5 ppm. Similar observations can be pointed out for the CH_2−*C*H=CH$_2$ resonance (δ 141.3 ppm for **3**, δ 133.9 ppm for the uncoordinated allyl in **5**, and δ 46.9 ppm for the coordinated allyl in **5**) and also for the ^{1}H NMR signals due to the allylic hydrogens. Following these considerations, a η^2-*C* coordination mode can also be deduced for the 1-methyl-3-(2-propenyl)benzimidazol-2-ylidene ligand of complex **4**, which shows the ^{13}C NMR resonances attributable to the allylic carbons CH_2−*C*H=*C*H$_2$ at δ 45.4 and 59.2 ppm, respectively.

Removal of the bromide ligand of **5** by reaction with $AgBF_4$ in THF has been found to afford the cationic complex [Ir(cod)(η^2:η^2-*C*-NHC)]BF_4 (NHC = 1,3-di(2-propenyl)benzimidazol-2-ylidene, **6**) (Scheme 2). The compound is air stable both in solid state and in solution (chlorinated solvents or methanol). Figure 2 shows the structure of the cation of **6** as determined by X-ray

Scheme 2



diffraction; selected bond lengths and angles can be found in Table 1. The structure displays an iridium center exclusively coordinated by sp^2 carbon atoms, which are of three different types: alkene, allyl, and carbene. It resembles an armchair with the coordinated allyl groups functioning as armrests and the carbene plane as backrest. We would therefore like to call the cation of **6** an armchair complex.

The geometry around the Ir atom of **6** can be described as distorted trigonal-bipyramidal, with three C=C double bonds (two allyl and one from cod) arranged in the equatorial plane and the carbene carbon atom together with the remaining cod C=C moiety in the axial positions. As seen previously, the Ir−C distances to the cod double bond *trans* to carbene, Ir−C18 and Ir−C19, are longer than those in the equatorial plane, Ir−C14 and Ir−C15. Noteworthy, the Ir−carbene distance in **6** (1.942(2) Å) is significantly shorter than that of **5**. This effect could be attributed to the attempt of the positively charged iridium center to compensate its electron deficiency through a stronger bond with the only remaining σ-donor atom. Nevertheless, steric con-

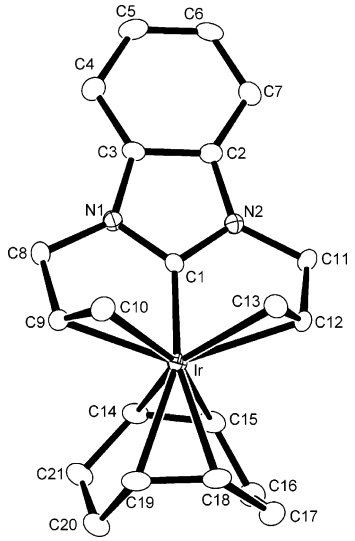
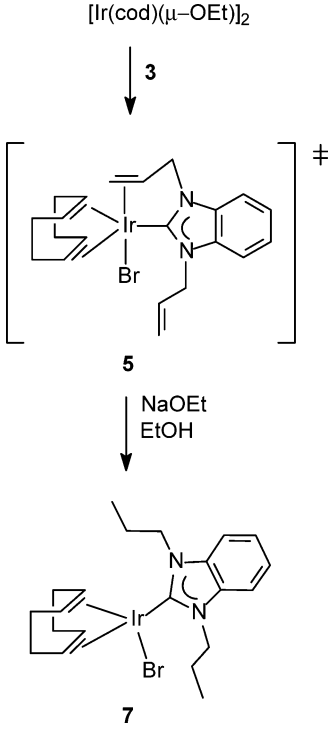


Figure 2. Molecular structure of the cation of complex **6**.

Scheme 3



straints resulting from the simultaneous coordination of both allyl arms could also be invoked to rationalize not only the shortening of this distance but also the significant differences between the two sets of Ir−C distances involving the allylic carbons. The NMR data of the compound are fully consistent with this solid-state structure, being indicative of a C_s symmetric structure in solution.

The synthetic protocol followed in the preparation of complexes **4** and **5** differs only slightly from a more general one, originally described by Köcher and Herrmann,[14] which implies the in situ generation of an alkoxyde iridium precursor by treatment of [Ir(μ-Cl)(cod)]$_2$ with NaOEt in ethanol. However, despite the close similarities, this latter procedure has been found to be inconvenient for the synthesis of **4** and **5**, since the presence of alkoxide excess seems to favor the slow hydrogenation of the carbene ligand allyl substituents. In fact, after 48 h under these conditions, the reaction between [Ir(μ-Cl)(cod)]$_2$ and the benzimidazolium salt **3** has been found to afford the four-coordinate complex [IrBr(cod)(*C*-NHC)] (NHC = 1,3-di(propyl)benzimidazol-2-ylidene, **7**) (Scheme 3). The compound has been isolated as yellow crystals in 55% yield after purification of the reaction outcome by column chromatography on silica gel. This unsaturated complex has also been found to be stable against air and moisture, even in ethanol solution.

The molecular structure of **7** in Figure 3 confirms the hydrogenation of both allylic arms of the carbene ligand. Selected bond lengths and angles of the structure are listed in Table 1. The complex contains an iridium atom coordinated in a distorted square-planar fashion by a bromide, a carbene, and two cod C=C moieties. All Ir−C bond distances to the olefinic carbons are shorter than

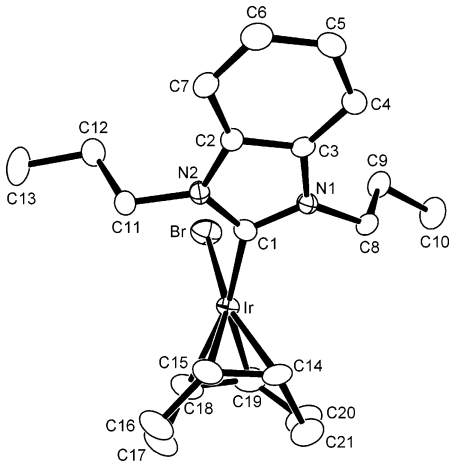


Figure 3. Molecular structure of complex **7**.

the equivalent ones in compounds **5** and **6**, a likely consequence of the decrease in the coordination number. As has been noted in the previously described structures, the Ir−C bond distances to the olefinic carbons *trans* to the carbene carbon atom are long. In this case, the significant differences found between these distances and those *trans* to bromide can be straightforwardly attributed to the larger *trans* influence of the carbene ligand, which results from its strong donating capability. Regarding the cod double bonds predominantly as donor ligands does explain this observation. The larger *trans* influence of the carbene weakens the olefin−Ir donor interaction. Consistently with the differences found in the Ir−C distances, the C=C bond distances within the cod ligand are shorter for the double bond *trans* to the carbene ligand (C18−C19 1.380(7) Å) than for that *trans* to bromide (C14−C15 1.414(6) Å). A similar structural situation, which has been discussed controversially,[5,15] has been reported for complexes of type [Ir(cod)(NHC)(L)]$^{n+}$ (L = Cl, n = 0;[15] L = pyridine, n = 1;[5] L = PR_3, n = 1[16]), where the differences in Ir−C distances (*trans* to carbene vs *trans* to L) are smaller for the complexes with L = PR_3 owing to the more similar *trans* influences of NHCs and phosphines.

The ^{1}H NMR spectrum of **7** displays four multiplets at δ 4.65, 4.53, 2.15, and 1.89 ppm corresponding to diastereotopic protons of the four *N*-propyl methylene groups. This indicates that free rotation around the Ir−CN_2 bond is hindered at room temperature, a fact already described for related imidazol-2-ylidene complexes.[15] All other spectroscopic features of the complex are consistent with the structure found in the solid state and do not deserve further comment.

Catalytic Transfer Hydrogenation. The aforementioned hydrogenation of the NHC allyl substituents leading to **7** strongly suggests the potential application of these carbene complexes in catalytic transfer reductions of unsaturated organic substrates using alcohols as hydrogen source. This possibility has been tested for the neutral complexes [Ir(X)(cod)(NHC)] **4**, **5**, and **7** in the transfer hydrogenation of cyclohexanone to cyclohexanol using 2-propanol as hydrogen source and KOH

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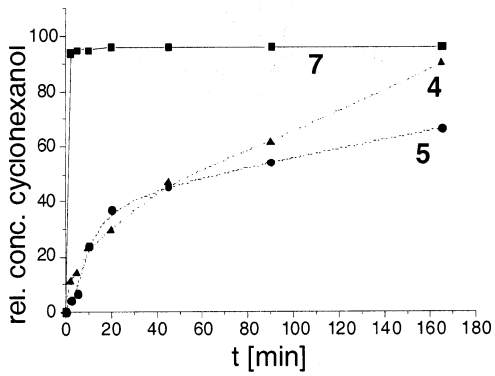

Figure 4. Time dependence of the catalytic transfer hydrogenation of cyclohexanone with complexes **4**, **5**, and **7**. Conditions: [catalyst] = [KOH] = 0.2 mmol, [cyclohexanone] = 4 mmol. Solvent: 2-propanol (20 mL), T = 353 K.

as cocatalyst. Representative results of these reactions are shown in Figure 4.

Among the tested precursors, the four-coordinate complex **7** clearly shows the higher activity, achieving turnover frequencies above 6000 h^{-1}. This is in the same order of magnitude found by Nolan et al. under similar conditions with the cationic catalyst precursor [Ir(cod)(py)(NHC)]PF_6, which contains an imidazol-2-ylidene ligand.[5] The five-coordinate precursors **4** and **5** display initial turnover frequencies much lower than that of **7** (ca. 70 and 50 h^{-1}, respectively), a fact that can be readily rationalized taking into account that the additional η^2 allyl coordination is likely to reduce the availability of the vacant coordination sites necessary for substrate coordination and activation. These catalytic activities are maintained below that shown by **7** until the end of the reactions, indicating that allyl substituents remain essentially unaffected despite the progress of ketone hydrogenation. This observation is consistent with the selectivity commonly observed in competitive hydrogen transfer reductions of mixtures of alkenes and ketones or aldehydes, which most often implies the selective reduction of the C=O bonds over the C=C ones.[17] Such preference for the C=O bonds becomes more apparent in our systems when considering the intramolecular character of the less favored C=C reduction.

These latter observations could be significant in the context of most recent mechanistic interpretations of catalytic reductions of polar C=O functions, which support the preponderance of hydrogen transfer steps of ionic type (proton and hydride transfers) over concerted routes involving C=O coordination and subsequent insertion into metal−hydride bonds.[18] Actually, the observation of a selective intermolecular reduction of ketone under conditions that also allow an alternative intramolecular C=C hydrogenation seems hardly compatible with a catalytic cycle involving hydride intermediates and concerted insertion elementary steps.

Experimental Section

If not noted otherwise, all manipulations were carried out in an atmosphere of purified argon using Schlenk flasks. Solvents were dried over Na/benzophenone (THF) or CaH_2 ($CHCl_2$). The iridium precursors [Ir(μ-OMe)(cod)]$_2$ and [Ir(μ-Cl)(cod)]$_2$ have been prepared by reported methods.[19,20] Elemental analyses (C, H, N) were performed on a Vario EL elemental analyzer at the Department of Chemistry, WWU Münster.

1-(2-Propenyl)benzimidazole (1). Benzimidazole (5.9 g, 50 mmol) is dissolved in THF (50 mL). The solution is cooled to 195 K and *n*-BuLi (20 mL of a 2.5 mM solution in hexane, 50 mmol) is added to give a white slurry. The reaction mixture is stirred at this temperature for 2 h. Then, allyl bromide (7.3 g, 5.1 mL, 60 mmol) is added and stirring is continued at room temperature for 16 h. The solvents are removed under reduced pressure und the residue is suspended in dichloromethane (30 mL). The suspension is washed three times with water (30 mL). The organic layer is separated and dried over $MgSO_4$, and the solvent is removed to yield **1** as a brown oil. Yield: 6.6 g (83%). ^{1}H NMR (200.1 MHz, $CDCl_3$): δ 7.38 (m, 1H, Ar−H), 7.29 (s, 1H, NCHN), 6.69 (m, 3H, Ar−H), 5.24 (m, 1H, CH_2CH=CH_2), 4.58 (dd, 1H, $^2J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 11.4 Hz, CH_2CH=CH_{cis}), 4.46 (dd, 1H, $^2J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 17.0 Hz, CH_2CH=CH_{trans}), 3.94 (m, 2H, CH_2CH=CH_2). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 142.5 (CH_2CH=CH_2), 141.7 (NCN), 130.7, 132.5 (Ar−C_{ipso}), 121.4, 120.6 (Ar−C_{meta}), 119.7, 116.6 (Ar−C_{ortho}), 108.8 (CH_2CH=CH_2), 45.6 (CH_2CH=CH_2).

1-Methyl-3-(2-propenyl)benzimidazolium iodide (2). 1-(2-Propenyl)benzimidazole **1** (1.58 g, 10 mmol) is refluxed with methyl iodide (1.42 g, 10 mmol) in toluene (40 mL) for 4 h. The reaction mixture is allowed to cool to room temperatue, and the crude product is colleted by filtration and recrystallized from ethanol. Yield: 2.46 g (82%). ^{1}H NMR (200.1 MHz, $CDCl_3$): δ 10.55 (s, 1H, NCHN), 7.68 (m, 2H, Ar−H_{ortho}), 7.54 (m, 2H, Ar−H_{meta}), 6.03 (m, 1H, CH_2CH=CH_2), 5.48 (dm, 1H, $^3J_{HH}$ = 17.0 Hz, CH_2CH=CH_{trans}), 5.46 (dm, 1H, $^3J_{HH}$ = 9.8 Hz, CH_2CH=CH_{cis}), 5.18 (d, 2H, CH_2CH=CH_2), 4.19 (s, 3H, CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 141.5 (CH_2CH=CH_2), 130.9 (NCN), 129.7 (2 × Ar−C_{ipso}), 126.9 (2 × Ar−C_{meta}), 121.6 (2 × Ar−C_{ortho}), 112.2 (CH_2CH=CH_2), 49.8 (CH_2CH=CH_2), 34.2 (CH_3). Anal. Calcd for $C_{11}H_{13}N_2I$: C, 44.02; H, 4.37; N, 9.33. Found: C, 44.18; H, 4.23; N, 9.11.

1,3-Di(2-propenyl)benzimidazolium Bromide (3). Benzimidazole (7 g, 60 mmol) is refluxed together with $NaHCO_3$ (5.04 g, 60 mmol) and allylbromine (21.8 g, 180 mmol) in ethanol (100 mL) for 24 h. The volume of the solutions is reduced to 20 mL, and the precipitated NaBr is removed by filtration from the hot solution. The product crystallizes as white needles after cooling of the filtrate to 277 K. Yield: 11.0 g (39 mmol, 65%). ^{1}H NMR (200.1 MHz, $CDCl_3$): δ 10.97 (s, 1H, NCHN), 7.65 (m, 2H, Ar−H_{ortho}), 7.48 (m, 2H, Ar−H_{meta}), 5.97 (m, 2H, CH_2CH=CH_2), 5.29 (dm, 2H, $^3J_{HH}$ = 17.2 Hz, CH_2CH=CH_{trans}), 5.23 (dm, 2H, $^3J_{HH}$ = 10.2 Hz, CH_2CH=CH_{cis}), 5.15 (dm, 4H, $^3J_{HH}$ = 6.01 Hz, CH_2CH=CH_2). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 141.3 (CH_2CH=CH_2), 130.9 (NCN), 129.7 (Ar−C_{ioso}), 126.9 (Ar−C_{meta}), 121.6 (Ar−C_{ortho}), 113.5 (CH_2CH=CH_2), 49.7 (CH_2CH=CH_2). Anal. Calcd for $C_{13}H_{15}N_2Br$: C, 55.93; H, 5.42; N, 10.03. Found: C, 55.65; H, 5.12; N, 9.87.

Synthesis of Cyclooctadiene-[1-methyl-3-(2-propenyl)-benzimidazol-2-ylidene]iridium Iodide (4). [Ir(μ-OMe)(cod)]$_2$ (200 mg, 0.3 mmol) is stirred with 1-methyl-3-(2-propenyl)benzimidazolium iodide (**2**) (179 mg, 0.6 mmol) in acetone (20 mL) for 3 h. The volume of the resulting pale yellow suspension is reduced to 3 mL. The solvent is decanted and the remaining white precipitate is washed three times with diethyl ether (5 mL each). After drying the residue under vacuum, complex **4** is obtained as a white powder. Yield: 229

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Table 2. Summary of Crystallographic Data for for 5, 6·2CHCl$_3$, and 7·C$_7$H$_8$

	5	**6**·2CHCl$_3$	**7**·C$_7$H$_8$
formula	$C_{21}H_{26}N_2BrIr$	$C_{23}H_{28}N_2BCl_6F_4Ir$	$C_{28}H_{34}N_2BrIr$
M_r	578.55	824.18	670.68
cryst size [mm]	0.20 × 0.18 × 0.10	0.14 × 0.14 × 0.12	0.22 × 0.03 × 0.02
a [Å]	8.6482(8)	29.6219(12)	34.958(3)
b [Å]	10.7943(10)	10.7321(4)	7.5715(6)
c [Å]	11.8122(11)	17.8342(7)	17.7650(14)
α [deg]	64.4420(10)	90.0	90.0
β [deg]	75.631(2)	97.5890(10)	98.403(2)
γ [deg]	88.124(2)	90.0	90.0
V [Å^3]	960.17(15)	5619.9(4)	4651.6(6)
Z	2	8	8
space group	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)	$C2/c$ (no. 15)
ρ_{calcd} [g cm^{-3}]	2.001	1.948	1.915
μ (Mo Kα) [mm^{-1}]	9.039	5.367	7.478
λ [Å]	0.71073	0.71073	0.71073
2θ range [deg]	$4.0 \le 2\theta \le 57.5$	$2.8 \le 2\theta \le 57.7$	$2.4 \le 2\theta \le 60.0$
unique data	4562	6932	6760
obsd data [$I \ge 2\sigma(I)$]	4148	5696	5587
R (all)	0.0227	0.0312	0.0453
wR^2 (all)	0.0380	0.0367	0.0771
no. of variables	275	364	272
peak/hole [e Å^{-3}]	1.40/−0.72	1.59/−0.85	1.48/−1.92

mg (64%). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.23 (m, 4H, Ar−H), 4.93 (m, 1H, NCH_2CH=CH_2), 4.31 (m, 1H, $^3J_{HH}$ = 5.7 Hz, NCH_2CH=CH_{cis}), 4.15 (m, 1H, cod-CH), 4.08 (s, 3H, NCH_3), 3.96 (d, 1H, $^3J_{HH}$ = 11.7 Hz, NCH_2CH=CH_{trans}), 3.76 (m, 1H, cod-CH), 3.44 (m, 1H, cod-CH), 3.31 (m, 1H, cod-CH), 3.13 (m, 1H, cod-CH_2), 2.79 (m, 2H, cod-CH_2), 2.64 (m, 1H, cod-CH_2), 2.49 (m, 1H, cod-CH_2), 2.40 (m, 1H, cod-CH_2), 2.18 (m, 3H, NCH_2CH=CH_2 and cod-CH_2), 1.79 (m, 1H, cod-CH_2). ^{13}C NMR (75.0 MHz, $CDCl_3$): δ 170.6 (NCN), 135.7 (Ar−C_{ipso}), 132.4 (Ar−C_{ipso}), 123.5 (Ar−C_{meta}), 122.8 (Ar−C_{meta}), 110.3 (2 × Ar−C_{ortho}), 96.8 (cod-CH), 93.9 (cod-CH), 57.7 (cod-CH), 55.5 (cod-CH), 59.2 (NCH_2CH=CH_2), 45.4 (NCH_2CH=CH_2), 39.3 (cod-CH_2), 37.3 (NCH_2CH=CH_2), 35.1 (NCH_3), 34.1 (cod-CH_2), 31.3 (cod-CH_2), 26.5 (cod-CH_2).

Synthesis of Cyclooctadiene-[1,3-di(2-propenyl)benzimidazol-2-ylidene]iridium Bromide (5). [Ir(μ-OMe)(cod)]$_2$ (200 mg, 0.3 mmol) is stirred with 1,3-di(2-propenyl)benzimidazolium bromide (**3**) (169 mg, 0.6 mmol) in acetone (20 mL) for 3 h. Workup is as described for **4**. Yield: 260 mg (74%) of a white powder. Crystals suitable for X-ray diffraction experiments were grown for a saturated solution of **5** in acetone at 277 K. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.21 (m, 4H, Ar−H), 6.08 (d, 1H, $^3J_{HH}$ = 16.8 Hz, NCH_2CH=CH_{trans}, coordinated), 5.94 (m, 1H, NCH_2CH=CH_2, uncoordinated), 5.14 (d, 1H, $^3J_{HH}$ = 9.6 Hz, NCH_2CH=CH_{cis}, uncoordinated), 4.85 (m, 3H, NCH_2CH=CH_{trans}, uncoordinated, and NCH_2CH=CH_{cis}, coordinated and cod-CH), 4.31 (m, 2H, NCH_2CH=CH_2, coordinated, and $NCH'HCH$=CH_2, uncoordinated), 3.96 (d, 1H, $NCHH'CH$=CH_2, uncoordinated), 3.68 (m, 1H, cod-CH), 3.56 (m, 1H, cod-CH), 3.48 (m, 1H, cod-CH), 3.08 (m, 1H, cod-CH_2), 2.79 (m, 1H, cod-CH_2), 2.64 (m, 1H, cod-CH_2), 2.56 (m, 1H, cod-CH_2), 2.46 (m, 1H, cod-CH_2), 2.16 (m, 4H, cod-CH_2 and NCH_2CH=CH_2, coordinated), 1.27 (m, 1H, cod-CH_2). ^{13}C NMR (75.0 MHz, $CDCl_3$): δ 172.3 (NCN), 135.1 (Ar−C_{ipso}), 133.9 (NCH_2CH=CH_2, uncoordinated), 133.1 (Ar−C_{ipso}), 123.3 (Ar−C_{meta}), 122.6 (Ar−C_{meta}), 116.3 (NCH_2CH=CH_2, uncoordinated), 111.7 (Ar−C_{ortho}), 110.3 (Ar−C_{ortho}), 99.2 (cod-CH), 97.8 (cod-CH), 59.2 (cod-CH), 55.5 (cod-CH), 51.1 (NCH_2CH=CH_2, coordinated), 49.5 (NCH_2CH=CH_2, uncoordinated), 46.9 (NCH_2CH=CH_2, coordinated), 40.3 (cod-CH_2), 36.5 (NCH_2CH=CH_2, coordinated), 33.2 (cod-CH_2), 29.7 (cod-CH_2), 27.0 (cod-CH_2).

Synthesis of Cyclooctadiene-[1,3-di(2-propenyl)benzimidazol-2-ylidene]iridium Tetrafluoroborate (6). Complex **5** (242 mg, 0.42 mmol) is stirred with $AgBF_4$ (82 mg, 0.42 mmol) in THF (20 mL) for 4 h. The solvent is evaporated and the gray residue is suspended in dichloromethane (20 mL) and filtered over Celite. The volume of the solution is reduced to 2 mL, and the crude product is precipitated by addition of diethyl ether (5 mL). A brown oil separates and is dissolved again by addition of dichloromethane. From this solution complex **6** is isolated as a pale gray powder by dropwise addition of diethyl ether. Yield: 215 mg (87%). Crystals suitable for X-ray diffraction studies were grown from a saturated solution of **7** in chloroform at 277 K. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.21 (m, 2H, Ar−H_{ortho}), 7.12 (m, 2H, Ar−H_{meta}), 5.33 (m, 2H, NCH_2CH=CH_2), 4.69 (m, 2H, cod-CH), 4.63 (m, 2H, $^3J_{HH}$ = 4.5 Hz, NCH_2CH=CH_{cis}), 4.48 (d, 2H, $^3J_{HH}$ = 13.2 Hz, NCH_2CH=CH_{trans}), 3.68 (m, 2H, cod-CH), 3.53 (m, 2H, cod-CH_2), 2.79 (m, 2H, cod-CH_2), 2.67 (m, 4H, NCH_2CH=CH_2), 2.35 (m, 2H, cod-CH_2), 2.23 (m, 2H, cod-CH_2). ^{13}C NMR (75.0 MHz, $CDCl_3$): δ 173.3 (NCN), 133.8 (Ar−C_{ipso}), 124.1 (Ar−C_{meta}), 111.6 (Ar−C_{ortho}), 95.7 (cod-CH), 74.5 (NCH_2CH=CH_2), 64.3 (cod-CH), 49.1 (NCH_2CH=CH_2), 42.6 (NCH_2CH=CH_2), 32.4 (cod-CH_2), 30.9 (cod-CH_2).

Synthesis of Cyclooctadiene-[1,3-di(propyl)benzimidazol-2-ylidene]iridium Bromide (7). A sample of [Ir(μ-Cl)(cod)]$_2$ (0.56 g, 0.83 mmol) is stirred with sodium ethoxyde (33 mL of an 1 M solution in ethanol) for 10 min. When the color of the initially orange suspension changes to bright yellow, 1,3-di(2-propenyl)-benzimidazolium bromide (**3**) (0.47 g, 1.68 mmol) is added and the reaction mixture is stirred for 2 day at 333 K. The solvent is removed and the resulting brown powder is purified by column chromatography (SiO_2, eluent dichloromethane:acetone, 8:1) to yield yellow crystals. Yield: 0.54 g (55%). Crystals suitable for an X-ray diffraction study were grown from a saturated solution of **7** in dichloromethane/toluene. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.28 (m, 2H, Ar−H_{ortho}), 7.18 (m, 2H, Ar−H_{meta}), 4.78 (t, 2H, cod-CH *trans* to carbene), 4.65 (m, 2H, $NCHH'CH_2CH_3$), 4.53 (m, 2H, $NCHH'CH_2CH_3$), 2.97 (m, 2H, cod-CH *trans* to bromide), 2.23 (m, 4H, cod-CH_2), 2.15 (m, 2H, $NCH_2CHH'CH_3$), 1.89 (m, 2H, $NCH_2CHH'CH_3$), 1.84 (m, 2H, cod-CH_2), 1.57 (m, 2H, cod-CH_2), 1.08 (t, 6H, $NCH_2CH_2CH_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 191.2 (NCN), 134.9 (Ar−C_{ipso}), 122.1 (Ar−C_{meta}), 110.0 (Ar−C_{ortho}), 85.4 (cod-CH *trans* to carbene), 53.0 (cod-CH *trans* to bromide), 49.9 ($CH_2CH_2CH_3$), 33.2 (cod-CH_2), 29.6 (cod-CH_2), 22.8 ($CH_2CH_2CH_3$), 11.7 ($CH_2CH_2CH_3$).

Hydrogen Transfer Catalytic Experiments. The tested complex (0.2 mmol, 0.5 mol %) was dissolved in a solution of KOH (0.2 mmol) in 2-propanol (20 mL) in a Schlenk tube. The solution was heated to 353 K for 30 min. Subsequently, cyclohexanone (413 μL, 4 mmol) was added with an Eppendorf pipet. The reaction progress was monitored by GC-MS analysis. Products were identified by comparison of GC retention times with those of authentic samples and by GC-MS.

X-ray Diffraction Studies. Diffraction data for **5**, **6**·2$CHCl_3$, and **7**·C_7H_8 were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 173(2) K (for **7**·C_7H_8) or a Bruker SMART APEX CCD diffractometer at 100(2) K (for **5** and **6**·2$CHCl_3$) using graphite-monochromated Mo Kα radiation. Data were collected over the full sphere and were corrrected for absorption. Structure solutions were found by the Patterson method. Structure refinement was carried out by full-matrix least squares on F^2 using SHELXL-97[21] using first isotropic and later anisotropic displacement parameters for all non-hydrogen atoms. The asymmetric unit of **7**·C_7H_8 contains two half-molecules of toluene, which are both disordered. Hydrogen atom positions were observed or calculated and refined riding on carbon atoms. No hydrogen positions were determined for the disordered solvent molecules in **7**·C_7H_8. The highest electronic residuals for all three structure determinations were found in close vicinity to the iridium atoms and make no chemical sense. Additional data collection and refinement parameters can be found in Table 2.

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Supporting Information Available: X-ray crystallographic file for the complexes **5**, **6**·2$CHCl_3$, and **7**·C_7H_8 in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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