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Synthesis, Characterization, and H-Bonding Abilities of Ruthenium(II) Complexes Bearing Bidentate NR,NH-Carbene/Phosphine Ligands†

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Two new diphenylphosphine-substituted benzimidazoles featuring an ethylene (**2**) or a methylene linker (**5**) between the benzimidazole and the phosphine have been prepared. These precursors for bidentate carbene/phosphine ligands react with [RuCp*(μ^3-Cl)]$_4$ under tautomerization with formation of complexes of type [RuCp*Cl(L)] ([**6**] and [**7**], L = NR,NH-carbene/phosphine ligand). The crystal structures of [**6**] and [**7**] have been determined by X-ray diffraction. These studies revealed that the length of the bridge between the benzimidazol-2-ylidene and the phosphine determines the geometric parameters of the carbene/phosphine chelate ring and the donor properties of the phosphine. A ^{1}H NMR titration of complex [**6**] with DMPU revealed the formation of a (carbene)N−H···O(DMPU) hydrogen bond in solution.

Introduction

N-Heterocyclic diaminocarbenes and their metal complexes have found numerous applications in coordination chemistry,[1] in transition metal[2] and organocatalysis,[3] and most recently even in supramolecular chemistry.[4] The carbene center in N-heterocyclic diaminocarbenes **A** is normally stabilized by two trigonal-planar nitrogen atoms. Removal of the N,N′-substituents destabilized the carbenes, and stable NH,NH-functionalized diaminocarbenes of type **B** are consequently unknown. Such species have, however, been generated and stabilized at various transition metal centers. Complexes bearing NH,O- (**C**)[5] or NH,NH-functionalized cyclic carbene ligands (**D**)[6] can be obtained by the template-controlled cyclization of suitably functionalized isocyanide ligands. Alternatively, complexes bearing NR,NH-substituted NHC ligands (**F**) are accessible in selected cases by tautomerization of coordinated N-heterocycles starting from complexes of type **E** (Figure 1).[7]

The NH,NH-functionalized carbene ligands exhibit an interesting reactivity while coordinated to the metal center. For example, they can be N,N′-alkylated in a template-controlled reaction, which offers access to macrocyclic ligands featuring polycarbene or mixed carbene/phosphine donor functions.[8]

In addition to the facile alkylation, the N−H function in complexes bearing NR,NH-functionalized NHC ligands can function as a recognition unit by acting as a hydrogen bond donor.[9] Its close proximity to the metal center is particularly useful. In most related cases combining noncovalent substrate

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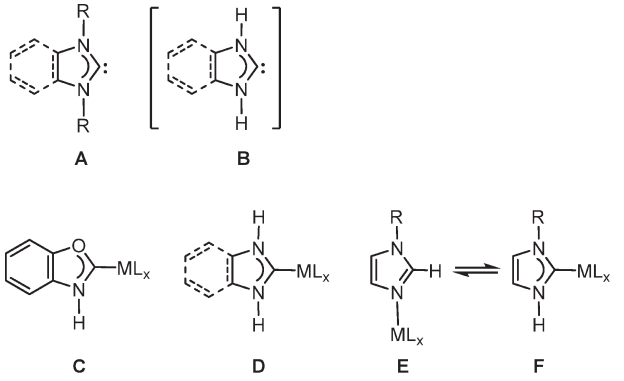


Figure 1. Heterocyclic carbenes and preparation of NHC complexes by tautomerization.

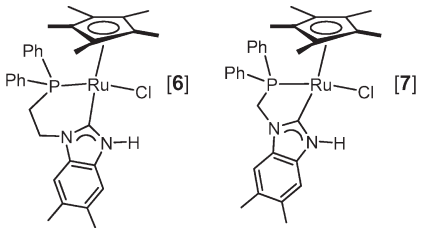


Figure 2. Complexes bearing donor-functionalized NR,NH-substituted NHC ligands.

binding and transition metal catalysis, the recognition unit is connected to the metal center by a flexible spacer, thereby causing entropic problems.[10]

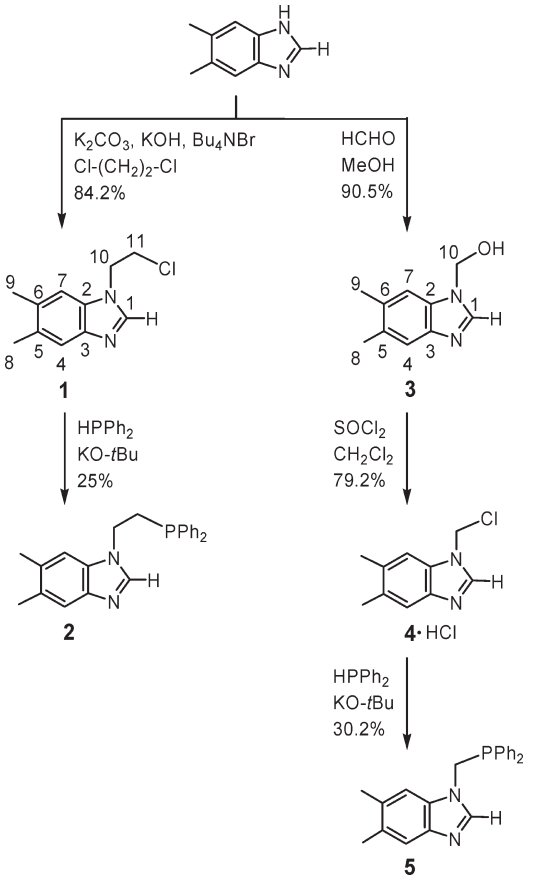
For example, a rhodium complex bearing an NR,NH-functionalized NHC ligand has been shown to form weak hydrogen bonds with hydrogen bond acceptors like DMPU in solution.[11] In a competitive hydrogenation experiment of 1-dococene and a 3-butenoic acid ester using this complex as hydrogenation catalyst, a preference for hydrogenation of the ester-containing substrate has been observed. It was proposed that the carbonyl-functionalized substrate will bind initially by a two-point interaction, while some attractive interactions will disappear after the catalytic transformation at the metal center, leading to the release of the hydrogenated substrate.[11]

In an effort to retain the potential interaction of the carbene N−H function with selected substrates while preventing tautomerization (see Figure 1, **F** → **E**) we have prepared donor-functionalized benzimidazoles and used these for the preparation of ruthenium complexes [**6**] and [**7**], containing bidentate NR,NH-substituted carbene/phosphine ligands, which after coordiantion of both donor groups cannot tautomerize (Figure 2).

Results and Discussion

Both diphenylphosphine-functionalized benzimidazoles **2** and **5**, featuring either an ethylene or a methylene spacer between the heterocycle and the phosphine donors, have been prepared from 5,6-dimethylbenzimidazole. For the preparation of **2**, alkylation of the benzimidazole[12] to give **1** was followed by reaction with potassium diphenylphosphite to yield *N*-(diphenylphosphinoethyl)benzimidazole ligand **2**. Synthesis of the methylene-bridged ligand proceeded via the alcohol derivative **3** and the chlorinated derivative **4**·HCl, which was finally reacted with potassium diphenylphosphite to give the ligand precursor **5** (Scheme 1).

Scheme 1. Synthesis of Donor-Functionalized Benzimidazoles[a]



[a] The numbering refers to the assignment of the NMR resonances.

Reaction of equimolar amounts of $[RuCp^*(\mu^3\text{-}Cl)]_4$ ($Cp^* = \eta^5\text{-}C_5(CH_3)_5$)[13] with **2** or **5** led to cleavage of the ruthenium tetramer and formal tautomerization of the benzimidazole under formation of the complexes [**6**] and [**7**], respectively, bearing donor-functionalized NR,NH-substituted NHC ligands (Scheme 2). Coordination of both the phosphine and carbene donors can be concluded from NMR spectra of the complexes. The $^{31}P\{^1H\}$ NMR spectra of the ligand precursors **2** and **5** showed resonances at δ −21.9 and −20.5 ppm, which shifted to lower field upon complex formation (δ 40.9 ppm for [**6**] and δ 79.3 ppm for [**7**]). Note the larger downfield shift of the phosphorus resonance in [**7**] arising from the superior donor properties of this atom in the five-membered chelate ring as compared to the six-membered chelate ring in [**6**]. The $^{13}C\{^1H\}$ NMR spectra of [**6**] and [**7**] exhibit the resonances for the carbene carbon atoms at δ 203.4 and 207.5 ppm. Coordination of the bidentate carbene/phosphine ligands

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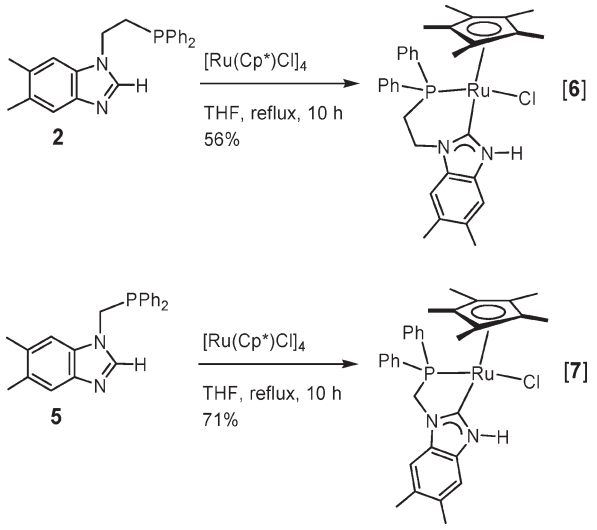
Scheme 2. Synthesis of Complexes [6] and [7]



renders the protons of the ethylene bridge in [**6**] and the methylene bridge in [**7**] diastereotopic. Compared to the free *N*-(diphenylphosphinoethyl)benzimidazole **2** (δ(H10) 4.23 and δ(H11) 2.61, see Scheme 1), for example, four resonances at δ 4.74, 4.07 ppm (H10) and 2.75, 2.28 ppm (H11) are observed for the ethylene protons in [**6**]. The resonance for the NH proton was observed at δ 10.60 ppm ([**6**]) and δ 10.91 ppm ([**7**]).

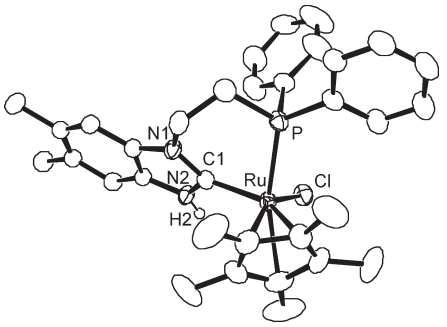


Figure 3. Molecular structure of [**6**] in [**6**]·THF·0.5CH_2Cl_2 (50% displacement ellipsoids, solvent molecules and hydrogen atoms have been omitted except for H2 bonded to N2). Selected bond lengths (Å) and angles (deg): Ru−Cl 2.4679(9), Ru−P 2.2726(10), Ru−C1 1.996(4), range Ru−C_{Cp} 2.184(4)−2.241(4); Cl−Ru−P 91.22(3), Cl−Ru−C1 91.69(10), P−Ru−C1 83.06(10).

Crystals of [**6**]·THF·0.5CH_2Cl_2 and [**7**] were investigated by X-ray diffraction. The molecular structure of [**6**] is depicted in Figure 3. The ruthenium atom is surrounded in a strongly distorted tetrahedral fashion by the midpoint of the Cp* ligand and the Cl, P, and C donor atoms. The bite angle of the chelate ligand P−Ru−Cl measures 83.06(10)°. Comparable metric parameters in [**6**] fall in the range reported for the related complex bearing an *N*-(2-pyridyl)benzimidazolin-2-ylidene ligand.[14] However, the bite angle of the *N*-(2-pyridyl)-benzimidazolin-2-ylidene ligand (C−Ru−N 76.1(2)° and 76.5(2)° for two molecules in the asymmetric unit)[14] is much smaller than the P−Ru−Cl angle in [**6**].

Complex [**7**] also features a distorted tetrahedrally coordinated ruthenium atom (Figure 4). However, selected geometric parameters differ strongly between [**6**] and [**7**]. Due to

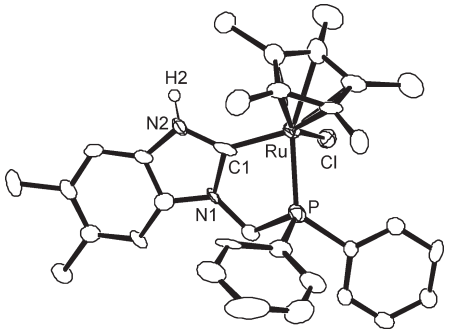
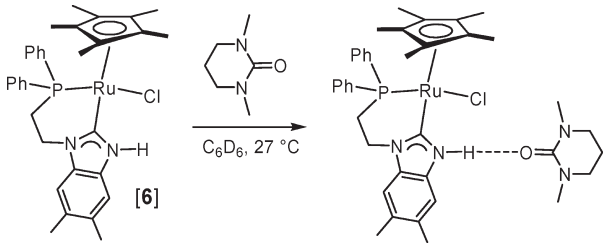


Figure 4. Molecular structure of [**7**] (50% displacement ellipsoids; solvent molecules and hydrogen atoms have been omitted except for H2 bonded to N2). Selected bond lengths (Å) and angles (deg): Ru−Cl 2.468(3), Ru−P 2.245(3), Ru−C1 1.979(14), range Ru−C_{Cp} 2.129(12)−2.211(13); Cl−Ru−P 86.86(11), Cl−Ru−C1 94.9(4), P−Ru−C1 79.6(4).

Scheme 3. Reaction of [6] with DMPU in C_6D_6



the shorter methylene bridge in [**7**], the bite angle of the carbene/phosphine ligand shrinks from 83.06(10)° in [**6**] to 79.6(4)° in [**7**]. As indicated by the $^{31}P\{^1H\}$ NMR data, the phosphine donor in the five-membered chelate ring of [**7**] is a more efficient donor than the phosphine donor in the six-membered chelate ring of [**6**]. This leads to a shortening of the Ru−P distances in [**7**] (2.245(3) Å) compared to the Ru−P distance in [**6**] (2.2726(10) Å). Additional molecular parameters of [**7**] resemble those of [**6**] and are largely unaffected by the shortening of the bridge between the carbene and phosphine donors.

The mechanism for the formation of complexes [**6**] and [**7**] has not been established unambigously yet. The related reaction of *N*-(diphenylphosphinoethyl)imidazole with $[IrCp^*(Cl)_2]_2$ leads to an initial breakup of the dinuclear iridium complex and coordination of the phosphine to the iridium atom in a mononuclear complex.[15] For the subsequent coordination of the imidazole, an oxidative addition[16] of the C2−H bond followed by reductive elimination/tautomerization is conceivable.[17] Alternatively, the imidazole tautomerizes to the NR, NH-substituted NHC, which then coordinates to the iridium center. Since the reaction starts with an Ir^{III} complex, the oxidative addition/reductive elimination sequence appears less likely. This situation is slightly different for the preparation of [**6**], [**7**], and the related complex with the *N*-(2-pyridyl)-benzimidazolin-2-ylidene ligand.[14] In these cases an oxidative addition of the C2−H bond to Ru^{II} followed by H-transfer

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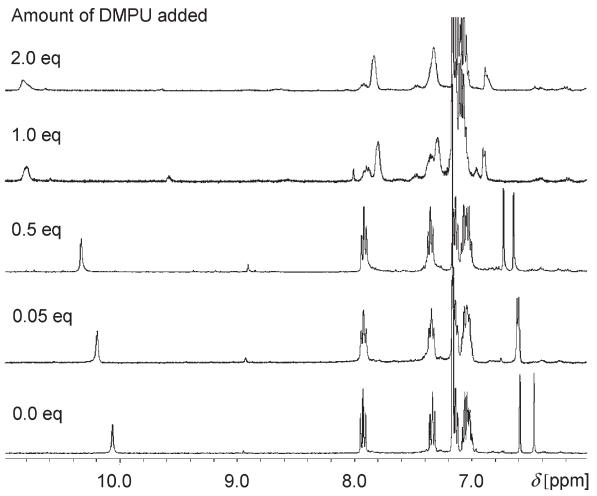

Figure 5. ^{1}H NMR titration of complex [**6**] with DMPU.

to the nitrogen atom of the heterocycle is more likely but has also not yet been confirmed experimentally.

Most complexes bearing NR,NH-functionalized NHC ligands exhibit hydrogen bonding of the N−H function to hydrogen bond acceptors in the solid state.[7b,9b,14,15] We became interested in utilizing this type of hydrogen bonding as a recognition unit for selected substrates in solution. As a proof of principle, complex [**6**] was therefore titrated with the strong hydrogen bond acceptor DMPU (DMPU = 1,3-dimethyltetrahydropyrimidin-2(1*H*)-one) as a model for substrates featuring hydrogen bond acceptors (Scheme 3).

The titration was carried out in C_6D_6 at ambient temperature and was monitored by ^{1}H NMR spectroscopy (Figure 5). The ^{1}H NMR spectrum showed a significant downfield shift of the resonance for the N−H proton upon addition of DMPU. Only broadening of the N−H resonances was observed upon addition of more than 1 equiv of DMPU. In addition, the ^{1}H resonance at δ 7.9 ppm (Ar−H_{ortho}) shifted upfield and the resonances around δ 6.5 ppm (H4 and H7) shifted downfield upon DMPU addition. These shifts are less significant than those observed for the N−H proton and can also be attributed to the DMPU hydrogen bonding to the ruthenium complex. From these data it can be concluded that complex [**6**] is capable of forming a (carbene)N−H···O hydrogen bond with DMPU in solution. Similar behavior is expected for complex [**7**] and has previously been noted for a tungsten complex bearing a related NEt,NH-functionalized benzimidazolinylidene ligand.[11]

Conclusion

We have prepared two novel diphenylphosphine-substituted benzimidazoles **2** and **5**. These precursors for bidentate NHC/phosphine ligands react with [RuCp*(μ^3-Cl)]$_4$ under formal tautomerization of the benzimidazole group and formation of complexes [**6**] and [**7**], bearing bidentate NHC/phosphine ligands. The NHC ligand in complexes [**6**] and [**7**] is NR,NH-substituted. A ^{1}H NMR titration of complex [**6**] with the strong hydrogen bond acceptor DMPU reveals the formation of an (NHC)N−H···O(DMPU) hydrogen bond in solution. Potentially, such hydrogen bonds can function as recognition units for substrates, and corresponding investigations of selected catalytic transformations using metal complexes with NR,NH-substituted NHC ligands are underway.

Experimental Section

General Comments. All preparations were carried out under an argon atmosphere using conventional Schlenk techniques. Solvents were dried and degassed by standard methods prior to use. 5,6-Dimethyl-1*H*-benzimidazole was purchased from Acros Organics, and [RuCp*(μ^3-Cl)]$_4$ has been prepared using a slightly modified version of the published procedure.[13] NMR spectra were recorded with a Bruker Avance I 400 NMR spectrometer, and assignments of the ^{1}H and ^{13}C resonances were made on the basis of 2D NMR experiments. MALDI, EI, and ESI-HRMS mass spectra were obtained with Bruker Reflex IV, Finnigan MAT 95, and Bruker Daltronics MicroTof spectrometers, respectively. For assignment of the NMR resonances see Scheme 2. Satisfactory microanalytical data were difficult to obtain for some derivatives (**4**, [**6**], and [**7**]) due to the hygroscopic nature of these compounds.

Compound 1. A sample of 2.0 g (13.7 mmol) of 5,6-dimethylbenzimidazole was mixed with 5.2 g (92.7 mmol) of potassium hydroxide, 4.1 g (29.7 mmol) of K_2CO_3, and 300 mg (0.93 mmol) of tetrabutylammonium bromide. The mixture was added to 26 mL of 1,2-dichloroethane. The reaction mixture was stirred at 50 °C for 1.5 h. Toward the end of this time, a deep brown suspension was obtained. The organic phase was decanted off, while the residual solids were extracted with dichloromethane (2 × 20 mL), and these extracts were combined with the organic phase. The volume of the organic phase was reduced *in vacuo* to 50%. It was then washed with water (3 × 50 mL) and dried over $MgSO_4$. Half of the solvent was removed under reduced pressure, and to the remaining solution was added *n*-pentane (10 mL). This solution was cooled to −30 °C for 4 h, upon which compound **1** precipitated as colorless crystals. Yield: 2.4 g (11.5 mmol, 84.2%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.93 (s, 1H, H1), 7.58 (s, 1H, H4), 7.14 (s, 1H, H7), 4.46 (t, 2H, H10), 3.83 (t, 2H, H11), 2.39 (s, 3H, H9), 2.37 (s, 3H, H8). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 142.4 (s, C1), 141.9 (s, C3), 132.6 (s, C6), 131.7 (s, C5), 131.6 (s, C2), 120.4 (s, C4), 109.4 (s, C7), 46.6 (s, C10), 42.0 (s, C11), 20.6 (s, C9), 20.2 (s, C8). MS (ESI HRMS) *m*/*z* (%): 209.0831 (100) [**1** + H]$^+$ (calcd for [**1** + H]$^+$ 209.0840). Anal. Calcd: C, 63.31; H, 6.28; N, 13.43. Found: C, 63.23; H, 6.48; N, 12.78.

Compound 2. To a solution of 600 mg (2.9 mmol) of **1** in 20 mL of a mixture of THF and DMSO (9:1, v:v) was added a solution of diphenyl phosphine (520 mg, 2.8 mmol) and KO-*t*Bu (0.34 g, 3.0 mmol) in THF (20 mL). The reaction mixture was stirred at ambient temperature for 3 h. The color of the initially red-orange solution faded to pale yellow over the reaction time. The reaction mixture was then quenched by addition of methanol (2 mL). The solvents were removed, and the solid was suspended in dichloromethane. Insoluble materials were separated by filtration. The organic phase was washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the obtained white solid was once more washed with diethyl ether to give compound **2** as a colorless solid after drying *in vacuo*. Yield: 260 mg (0.73 mmol, 25%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (s, 1H, H1), 7.55 (s, 1H, H4), 7.45 (m, 4H, Ar−H_{ortho}), 7.37 (m, 6H, Ar−H_{meta} and Ar−H_{para}), 6.93 (s, 1H, H7), 4.23 (m, 2H, H10), 2.61 (m, 2H, H11), 2.36 (s, 3H, H8), 2.35 (s, 3H, H9). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 141.4 (s, C1), 141.1 (s, C3), 136.9 (d, $^1J_{CP}$ = 12.0 Hz, Ar−C_{ipso}), 132.7 (d, $^2J_{CP}$ = 7.45, Ar−C_{ortho}), 132.5 (s, C6), 131.7 (s, C5), 131.6 (s, C2), 129.2 (s, Ar−C_{para}), 128.8 (d, $^3J_{CP}$ = 7.1 Hz, Ar−C_{meta}), 119.9 (s, C4), 109.8 (s, C7), 42.3 (d, $^2J_{CP}$ = 25.8 Hz, C10), 29.3(d, $^1J_{CP}$ = 15.3 Hz, C11), 20.6 (C8 and C9). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −21.9. MS (MALDI, positive ions): *m*/*z* (%): 359 (100) [**2** + H]$^+$. Anal. Calcd: C, 77.07; H, 6.47; N, 7.82. Found: C, 73.44; H, 6.02; N, 7.66.

Compound 3. A sample of 2.94 g (20.1 mmol) of 5,6-dimethylbenzimidazole was dissolved in methanol (30 mL). To this was added 2.4 mL of a 37% aqueous solution of formaldehyde (31.9 mmol).

The reaction mixture was heated under reflux for 3 h. Compound **3** precipitated as a tan solid and was isolated by filtration. It could be used without further purification for subsequent reactions. Yield: 3.2 g (18.2 mmol, 90.5%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.10 (s, 1H, H1), 7.42 (s, 2H, H4 and H7), 6.62 (s, 1H, OH), 5.52 (d, 2H, H10), 2.31 (s, 3H, H8), 2.30 (s, 3H, H9). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 142.8 (s, C1), 142.4 (s, C3), 131.9 (s, C2), 130.8 (s, C5), 129.9 (s, C6), 119.3 (s, C4), 110.8 (s, C7), 67.1 (C10), 20.0 (C8) 19.8 (C9). MS (ESI HRMS) m/z (%): 147.0914 (100) [**3** − CH_2OH + H]$^+$ (calcd for [M − CH_2OH + H]$^+$ 147.0917). Anal. Calcd: C, 68.15; H, 6.86; N, 15.90. Found: C, 67.93; H, 6.77; N, 15.73.

Compound 4·HCl. A sample of 0.91 g (5.2 mmol, 6.2 mmol) of **3** was dissolved in dichloromethane (20 mL). To this was added 3.25 mL of $SOCl_2$ (44.8 mmol). The reaction mixture was stirred at ambient temperature for 1 day. The initially soluble reactants started to precipitate during the first 30 min of stirring. However the stirring was continued for one day to complete the reaction. The solvent was removed with a cannula, and the residue remaining was washed twice with dichloromethane (20 mL each). The white solid obtained was dried *in vacuo* to give compound **4**·HCl as a hygroscopic white solid. Yield: 0.93 g (4.04 mmol, 79.2%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.64 (s, 1H, H1), 7.71 (s, 1H, H7), 7.67 (s, 1H, H4), 6.37 (s, 2H, H10), 2.52 (s, 3H, H8), 2.47 (s, 3H, H9). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 143.4 (s, C1), 132.4 (s, C6), 131.5 (s, C5), 129.0 (s, C3), 128.7 (s, C2), 116.3 (s, C4), 114.5 (s, C7), 53.9 (s, C10), 20.7 (s, C8), 20.5 (s, C9). MS (ESI HRMS) m/z (%): 195.0698 (100) [**4** + H]$^+$ (calcd for [**4** + H]$^+$ 195.0689). The downfield shift of the resonance for H1 indicates the formation of the benzimidazolium salt **4**·HCl. The resonance for the N−H proton, however, could not be observed in DMSO over an extended period of time and is therefore not listed here.

Compound 5. A sample of compound **4**·HCl (0.40 g, 1.73 mmol) was dissolved in THF (20 mL). To this was added a solution of diphenylphosphine (318 mg, 1.73 mmol) and KO-*t*Bu (485 mg, 4.33 mmol) in the THF (20 mL). The reaction mixture was stirred at ambient temperature for 3 h. The initially deep red color of the mixture turned pale over the reaction time. Subsequently, all solvents were removed under high vacuum. The oily solid obtained was then dissolved in ethyl acetate (20 mL). Reduction of the volume of the ethyl acetate solution to 2 mL and addition of *n*-pentane (20 mL) led to precipitation of a white solid, which was isolated by filtration. The solid was then washed with pentane and dried *in vacuo* to give analytically pure **5** as a colorless hygroscopic solid. Yield: 175 mg (0.523 mmol, 30.2%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.83 (m, 1H, H4), 7.27 (s, 1H, H1), 7.14 (d, 4H, Ar−H_{ortho}), 7.08 (s, 1H, H7), 7.02 (s, 2H, Ar−H_{para}), 6.98 (m, 4H, Ar−H_{meta}), 4.22 (d, $^2J_{HP}$ = 6.1 Hz, 2H, H10) 2.22 (s, 3H, H9), 2.17 (s, 3H, H8). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 143.9 (s, C3), 142.4 (d, $^3J_{CP}$ = 2.3 Hz, C1), 136.2 (d, $^1J_{CP}$ = 14.5 Hz, Ar−C_{ipso}), 133.3 (s, C2), 133.2 (d, $^2J_{CP}$ = 18.8 Hz, Ar−C_{ortho}), 131.6 (s, C6), 130.9 (s, C5), 129.5 (s, Ar−C_{para}), 129.0 (d, $^3J_{CP}$ = 6.8 Hz, Ar−C_{meta}), 121.4 (s, C4), 110.9 (d, $^4J_{CP}$ = 3.9 Hz, C7), 45.6 (d, $^1J_{CP}$ = 16.9 Hz, C10), 20.6 (s, C9), 20.2 (s, C8). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ −20.5. MS (EI, 50 eV) m/z (%): 344 (100) **5**$^+$.

Complex [6]. A mixture of compound **2** (86.0 mg, 0.24 mmol) and the ruthenium tetramer [RuCp*(μ^3-Cl)]$_4$ (60.1 mg, 0.06 mmol) in THF (10 mL) was heated under reflux for 10 h. The initially brown, soluble starting materials turned into an orange suspension within the first 5 min. Within the next 3 h again a clear orange solution was obtained. At the end of the reaction the solvent was removed under reduced pressure. The residual solid was washed with *n*-pentane, leaving complex [**6**] as a reddish powder, which was dried *in vacuo*. Yield: 102 mg (0.14 mmol, 56%). ^{1}H NMR (400 MHz, THF-d_8): δ 10.60 (s, 1H, NH), 7.59 (d, 2H, Ar−H_{ortho}), 7.40 (m, 2H, Ar−H_{ortho}), 7.31 (m, 2H, Ar−H_{meta}), 7.27 (m, 1H, Ar−H_{para}), 7.23 (m, 1H, H4), 7.10 (m, 1H, Ar−H_{para}), 7.09 (m, 2H, Ar−H_{meta}), 7.07 (s, 1H, H7), 4.74 (m, 1H, H10), 4.07 (m, 1H, H10), 2.75 (m, 1H, H11), 2.28 (m, 1H, H11), 2.29 (s, 3H, H9), 2.28 (s, 3H, H8), 1.39 (s, 15H, Cp-CH_3). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 203.4 (d, $^2J_{CP}$ = 26.0 Hz, C1), 142.1 (m, $^1J_{CP}$ = 34.4 Hz, Ar−C_{ipso}), 139.2 (m, $^1J_{CP}$ = 30.5 Hz, Ar−C_{ipso}), 135.2 (m, $^2J_{CP}$ = 10.0 Hz, Ar−C_{ortho}), 135.0 (s, C2), 134.8 (s, C3), 132.8 (m, $^2J_{CP}$ = 9.5 Hz, Ar−C_{ortho}), 130.3 (s, C6), 129.8 (s, C5), 129.0 (s, Ar−C_{para}), 128.9 (s, Ar−C_{para}), 128.5 (m, $^3J_{CP}$ = 10.0 Hz, Ar−C_{meta}), 127.7 (m, $^3J_{CP}$ = 8.7 Hz, Ar−C_{meta}), 111.2 (s, C4), 109.1 (s, C7), 89.0 (d, $^2J_{Cp}$ = 2.2 Hz, Cp−C), 43.3 (s, C10), 29.7 (m, $^1J_{CP}$ = 29.7 Hz, C11), 20.2(s, C9), 20.1 (s, C8), 10.1 (s, Cp−CH_3). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 40.9. MS (ESI HRMS) m/z: 595.1812 [**6** − Cl]$^+$ (calcd for [**6** − Cl]$^+$ 595.1816). Anal. Calcd: C, 62.80; H, 6.23; N, 4.44. Found: C, 58.30; H, 5.97; N, 4.13. Complex [**6**] was crystallized as red crystals with the composition [**6**]·THF·0.5CH_2Cl_2 by cooling of a THF/CH_2Cl_2 (1:1, v/v) solution of the complex to −30 °C for 1 day.

Table 1. Crystallographic Data for the Complexes [6]·THF·0.5CH_2Cl_2 and [7]

parameter	[**6**]·THF·0.5CH_2Cl_2	[**7**]
formula	$C_{37.5}H_{47}N_2Cl_2OPRu$	$C_{32}H_{36}N_2ClPRu$
cryst size [mm]	0.07 × 0.07 × 0.03	0.06 × 0.05 × 0.03
M_r	744.71	606.12
a [Å]	28.9982(11)	14.4177(11)
b [Å]	28.9982(11)	11.8422(9)
c [Å]	16.8529(8)	16.6450(10)
α [deg]	90.0	90.0
β [deg]	90.0	90.0
γ [deg]	90.0	90.0
V [Å^3]	14171.5(10)	2841.9(4)
Z	16	4
space group	$I4_1/a$	$Pna2_1$
ρ_{calcd} [g cm^{-3}]	1.396	1.440
μ [mm^{-1}]	0.670	6.033
2θ range [deg]	3.8−55.0	9.2−139.8
data collected	41 892	15 744
no. unique data, R_{int}	8134, 0.060	5277, 0.162
no. obsd data [$I \geq 2\sigma(I)$]	5921	2920
R (obsd data)	0.0467	0.0635
wR (all data)	0.1246	0.1435
no. of variables	403	341

Complex [7]. A mixture of the ligand precursor **5** (76.0 mg, 0.22 mmol) and [RuCp*(μ^3-Cl)]$_4$ (60.1 mg, 0.06 mmol) was heated in THF (10 mL) under reflux for 6 h under an argon atmosphere. Subsequently, the solvent was removed *in vacuo* and the solid residue was washed with *n*-pentane several times to obtain the raw complex [**7**] as a red to orange powder, which was very sensitive to air and moisture. The red-orange solid was dissolved in THF, and this solution was cooled to −30 °C to obtain single crystals of [**7**] suitable for X-ray analysis. Yield: 96 mg (0.16 mmol, 71%). ^{1}H NMR (400 MHz, THF-d_8): δ 10.91 (s, 1H, NH), 7.93 (m, 2H, Ar−H_{ortho}), 7.44 (m, 2H, Ar−H_{meta}), 7.43 (m, 1H, Ar−H_{para}), 7.15 (m, 3H, H4 and Ar−H_{meta}), 7.14 (m, 1H, Ar−H_{para}), 6.90 (s, 1H, H7), 6.88 (m, 2H, Ar−H_{ortho}), 4.72 (m, 1H, H10), 4.06 (m, 1H, H10), 2.24 (s, 3H, H9), 2.18 (s, 3H, H8), 1.56 (s, 15H, Cp−CH_3). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8): δ 207.5 (d, $^2J_{CP}$ = 14.3 Hz, C1), 143.4 (d, $^1J_{CP}$ = 36.7 Hz, Ar−C_{ipso}), 136.8 (d, $^2J_{CP}$ = 12.2 Hz, Ar−C_{ortho}), 135.8 (s, C3), 132.9 (d, $^3J_{CP}$ = 9.2 Hz, C2), 132.5 (m, $^1J_{CP}$ = 38.6, Ar−C_{ipso}), 131.1 (d, $^2J_{CP}$ = 9.7, Ar−C_{ortho}), 130.7 (s, Ar−C_{para}), 130.3 (s, C6), 129.8 (s, C5), 129.1 (s, Ar−C_{para}), 128.6 (d, $^3J_{CP}$ = 9.0 Hz, 2 × Ar−C_{meta}), 111.5 (s, C4), 110.4 (s, C7), 89.9 (d, $^2J_{CP}$ = 2.9 Hz, Cp−C), 50.4 (d, $^1J_{CP}$ = 29.8 Hz, C10), 20.2 (s, C9), 20.0 (s, C8), 10.5 (s, Cp−CH_3). ^{31}P{^{1}H} NMR (162 MHz, THF-d_8): δ 79.3. HRMS (ESI) m/z: 597.1609 (calcd for [**7**− Cl + O] 597.1612). Satisfactory microanalytical data could not be obtained in multiple runs.

Titration of [6] with DMPU. Complex [**6**] (10 mg, 0.016 mmol) was placed in an NMR tube. To this was added the appropriate amount of DMPU (DMPU = 1,3-dimethyltetrahydropyrimidin-2(1*H*)-one) dissolved in 0.3 mL of C_6D_6.

X-ray Diffraction Studies. X-ray diffraction data for [**6**]·THF·$0.5CH_2Cl_2$ and [**7**] were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 153(2) K using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) for [**6**]·THF·$0.5CH_2Cl_2$ or Cu Kα radiation (λ = 1.54178 Å) for [**7**]. Diffraction data were collected over the full sphere and were corrected for absorption. The data reduction was performed with the Bruker SMART[18] program package. For further crystal and data collection details see Table 1. Structure solutions were found with the SHELXS-97[19] package using the heavy-atom method and were refined with SHELXL-97[20] 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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Supporting Information Available: X-ray crystallographic files for complexes [**6**]·THF·$0.5CH_2Cl_2$ and [**7**] in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

Note Added after ASAP Publication. This article posted ASAP on July 20, 2010. A correction was to the paragraph beneath Figure 3 to indicate "the ruthenium atom is surrounded in a strongly distorted tetrahedral fashion...". The correct version posted on August 3, 2010.

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