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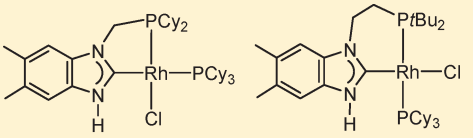
# Synthesis of Rhodium(I) Complexes Bearing Bidentate NH,NR-NHC/Phosphine Ligands

Abbas Raja Naziruddin, Alexander Hepp, Tania Pape, and F. Ekkehardt Hahn*

Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstrasse 30, D-48149 Münster, Germany

Supporting Information

**ABSTRACT:** The *N*-alkyphosphine-substituted benzimidazoles **5** (R = methylenedicyclohexylphosphine), **7** (R = ethylene-di(*t*Bu)phosphine), and **8** (R = ethylenedicyclohexylphosphine) have been prepared. The benzimidazoles react with $[RhCl(COE)_2]_2$ in the presence of tertiary phosphines under formal tautomerization of the benzimidazole and chelating coordination of the resulting bidentate NH,NR-NHC/phosphine ligand (P^C) to give complexes $[RhCl(P^C)PR_3]$ [**6**]−[**9**]. Depending on the steric demand of the $PR_3$, the phosphines of the P^C ligands, and on the spacer linking the benzimidazole ring nitrogen atom to the alkylphosphine, complexes with *cis*-P,P and *trans*-P,P geometry have been obtained and crystallographically characterized.




[6] [9]

## INTRODUCTION

Many enzymatic reactions are based on the combination of molecular recognition and catalysis. Multiple noncovalent interactions between the substrate and the active site of the enzyme can lead to a high degree of substrate selectivity and to a regio- and stereoselective catalytic reaction.[1] The transformation of these principles to homogeneous catalysis with transition-metal complexes has led to the emerging field of supramolecular catalysis where the substrate selection by the catalyst is based on specific supramolecular interactions.[2] Various research groups have tried to combine transition-metal catalysis with noncovalent substrate recognition and binding,[3] but only a few successful approaches combining high substrate selectivity and rate enhancement have been reported. Among those are the asymmetric hydrogenation of trisubstituted acrylic acids in the presence of a chiral (aminoalkyl)ferrocenylphosphine, a reaction that is believed to result from an attractive interaction of the amino group of the ferrocenylphosphine with the carboxyl group of the substrate.[4] Metalloporphyrins with attached cyclodextrin groups have been shown to catalyze the regioselective hydroxylation of steroid derivatives via interaction of the steroid substituents with the cyclodextrin groups, thereby causing the proper orientation of the substrate.[5] Hydrogen bonding between the carboxylic acid groups of a $Mn(\mu\text{-}O_2)Mn$ coordinated ligand and the carboxyl group of a substrate also led to a specific substrate orientation and a modified regioselectivity for the $sp^3$ C−H oxidation.[6] Finally, Breit et al. introduced the concept of a temporary substrate-bound catalyst-directing group for catalytic hydroformylations. Here, the substrate is covalently linked to a phosphine. Simultaneous coordination of the phosphine and the functional group of the substrate to rhodium(I) allowed for highly regio- and stereoselective transformations. The major drawback of this approach is the required covalent linkage of the substrate to the phosphine.[7]

More recent efforts have been directed toward the design of ligands that can bind and orient selected substrates via noncovalent interactions. This is often achieved via hydrogen bonds between a ligand coordinated to the catalytically active metal center and a functional group of the substrate.[8] Such an arrangement enforced a substrate orientation that enabled highly selective rhodium-catalyzed hydrogenation[9] or hydroformylation[10] reactions.

We became interested in supramolecular catalysis using complexes bearing *N*-heterocyclic carbenes (NHCs).[11] NHC ligands have been employed as spectator ligands for the preparation of various catalytically active complexes[12] where the NHC ligand imparts the desired steric and electronic properties to the metal center. In complexes with the commonly used NR,NR-substituted NHC ligands (**A**, Figure 1), all catalytic transformations take place at the NHC coordinated metal center. As an alternative, we have also developed the coordination chemistry of complexes bearing protic NHC ligands, that is, NHC ligands featuring an NH,NR (**B**) or NH,NH (**C**) substitution pattern (Figure 1),[13] which are valuable building blocks for the template synthesis of macrocyclic ligands featuring NHC donors.[14] Furthermore, the N−H group of NH,NR-substituted NHC ligands in complexes of type **B** can act as a hydrogen bond donor and thus function as a recognition unit via the formation of hydrogen bonds. In contrast to many related systems,[6,9,10] the recognition unit is located in close proximity to the catalytically active metal center. As expected, tungsten complex **D** forms a hydrogen bond between the N−H group of the NHC ligand and the hydrogen bond acceptor DMPU in solution (Figure 1), which was confirmed by $^1H$ NMR spectroscopy.[15]

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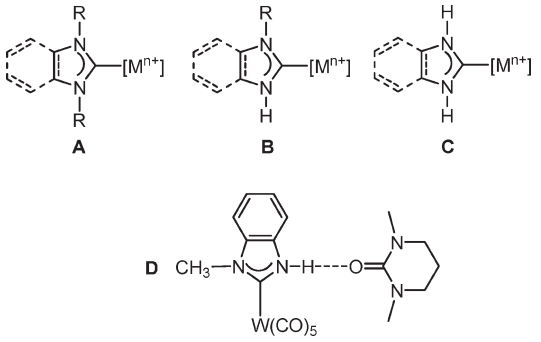
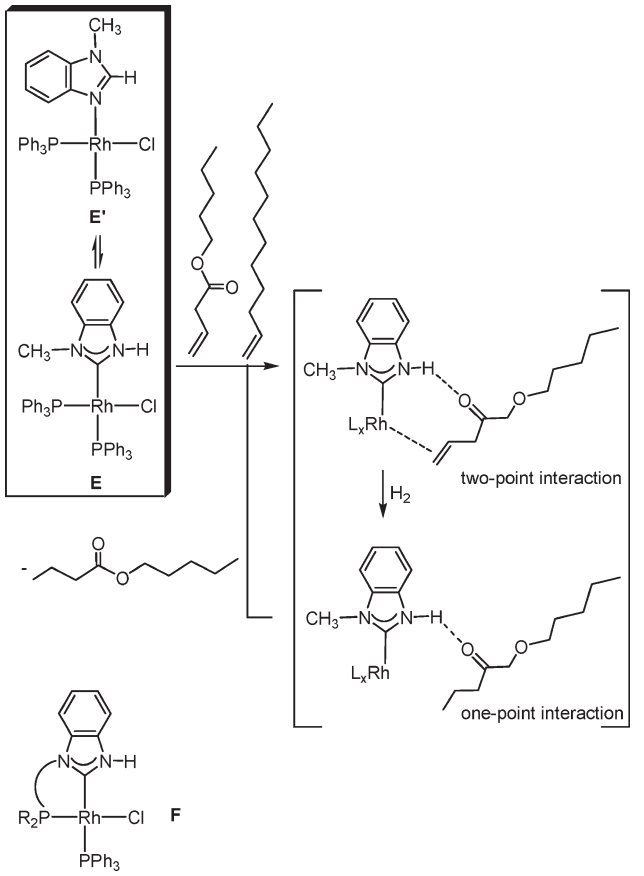


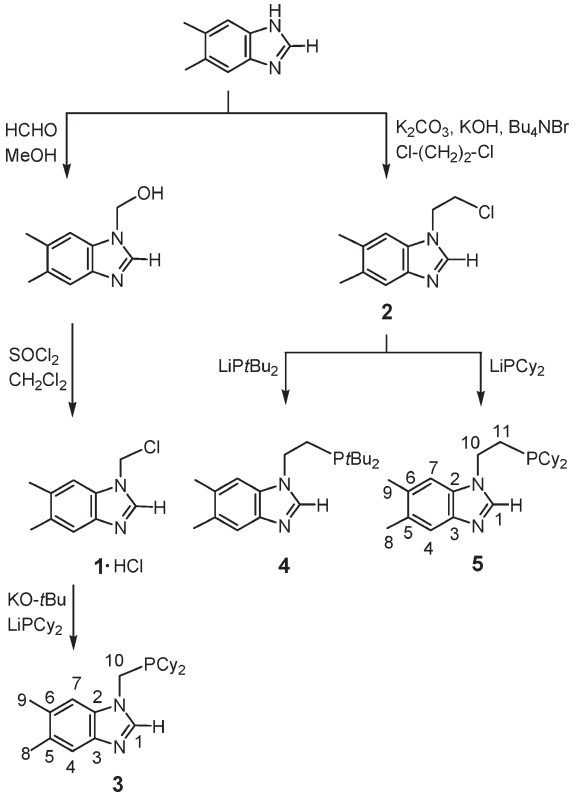

**Figure 1.** Complexes bearing NR,NR-, NH,NR-, and NH,NH-substituted NHCs and hydrogen bonding between complex **D** and DMPU.

**Scheme 1. Concept of Interaction/Recognition of Substrates with Complexes Bearing NH,NR-Substituted NHCs and Complexes of Type F**




The $Rh^{I}$ complex **E** (Scheme 1) provided proof of the concept of supramolecular recognition with protic NHC ligands. In competitive hydrogenation experiments with 1-dodecene and 3-butenoic acid ester using **E** as a catalyst, the substrate with the carbonyl function was clearly preferred, most likely by interaction of the carbonyl group with the N−H group of the NH,NR-NHC ligand under formation of a two-point interaction prior to the catalytic transformation (Scheme 1). Hydrogenation of the C=C double bond leads to a one-point interaction and substitution of the hydrogenated substrate for another molecule

**Scheme 2. Synthesis of Donor-Functionalized Benzimidazoles**[a]




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

of 3-butenoic acid ester, thereby preventing the deactivation of the catalyst. Unfortunately, complex **E** is not stable under the reaction conditions but tautomerizes to give complex **E′** with the *N*-coordinated benzimidazole ligand.[15] The reverse reaction of this tautomerization has been used for the synthesis of complexes bearing NH,NR-substituted NHCs from azole complexes.[13o−q]

In this contribution, we describe the preparation of rhodium(I) complexes bearing donor-functionalized NH,NR-substituted NHCs of type **F** with different linkers between the NHC nitrogen atom and the attached phosphine. Because of the simultaneous coordination of the NHC and the phosphine donor in these P^C-chelate ligands (Scheme 1, bottom), tautomerization is not possible, which leads to stable complexes with NH, NR-NHCs (Scheme 1).

## RESULTS AND DISCUSSION

The *N*-alkylphosphine-substituted benzimidazoles **3**, **4**, and **5**, featuring either a methylene or an ethylene spacer between the heterocycle and the phosphine donor, have been prepared starting from 5,6-dimethylbenzimidazole using a methodology previously described.[16] The preparation of the methylene bridged ligand precursor proceeded via the alcohol and the hydrochloride derivative **1**·HCl,[16] which was finally reacted with KO*t*Bu and $LiPPh_2$ to give **3** (Scheme 2). Ligand precursors **4** and **5** were obtained by alkylation of 5,6-dimethylbenzimidazole[17] to give **2**,[16] followed by reaction with $LiPtBu_2$ or $LiPCy_2$ to give compounds **4** and **5**, respectively. The *N*-alkylphosphine-substituted benzimidazoles were obtained as hygroscopic, off-white solids. Related

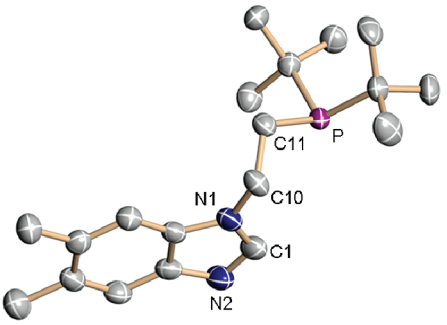



**Figure 2.** Molecular structure of **4** (50% displacement ellipsoids, hydrogen atoms have been omitted for clarity, only one of the two essentially identical molecules in the asymmetric unit is shown). Selected bond lengths (Å) and angles (deg) for molecule 1 [molecule 2]: N1−Cl 1.363(3) [1.356(3)], N2−C1 1.313(3) [1.316(3)]; N1−C1−N2 114.7(2) [114.7(2)].

*N*-alkylpyridyl-functionalized benzimidazoles[18] and diphenylphosphine-substituted imidazoles[19] have also been described.

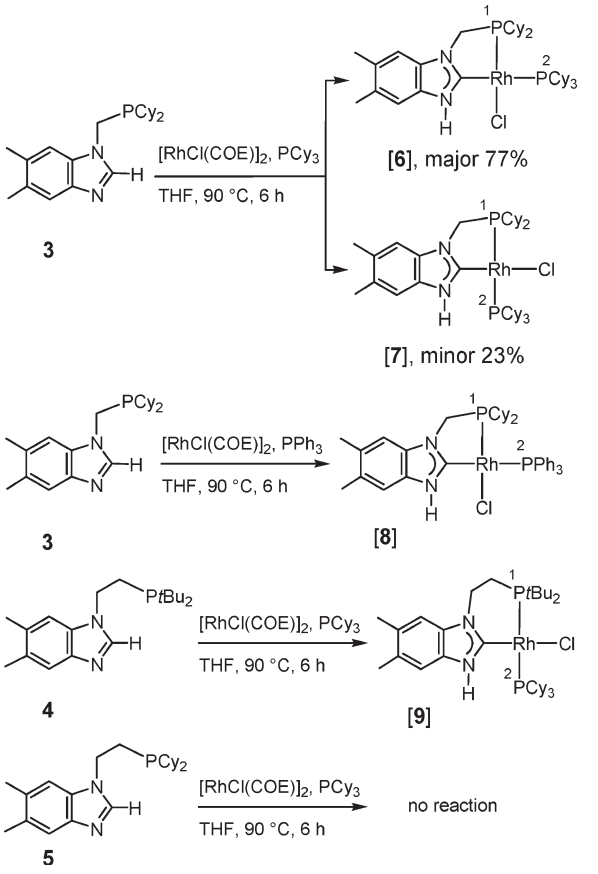
In addition to NMR spectroscopic and microanalytical data for **3**, **4**, and **5**, compound **4** was also characterized by an X-ray diffraction study. This study confirmed the connectivity in the molecule (Figure 2). The N2−C1 bond length (1.313(3) Å) is significantly shorter than the N1−C1 (1.363(3) Å, molecule 1) distance, in accord with a localized N═C double bond. The N1−C1−N2 angle (114.7(2)°) is larger than the equivalent angle in *N*,*N*′-dialkylated benzimidazolium cations where N−C−N angles of about 110° are normally observed.[20]

Next, we have reacted the *N*-alkylphosphine-substituted benzimidazoles **3**, **4**, and **5** with $[RhCl(COE)_2]_2$ in the presence of different tertiary phosphines (Scheme 3). Compounds **3** and **4** react with formation of square-planar $Rh^I$ P^C chelate complexes. In the presence of the sterically demanding tricyclohexyl phosphine, compound **3** yields a mixture of the *cis*-P,P ([**6**], major 77%) and the *trans*-P,P complexes ([**7**], minor 23%). With the sterically less demanding triphenyl phosphine, the same reaction of **3** with $[RhCl(COE)_2]$ yields only the *cis*-P,P-complex [**8**]. The P^C ligand precursor **4** with an ethyl spacer between the ring nitrogen atom and the di(*t*Bu)phosphine donor yields, in the presence of $PCy_3$, exclusively the *trans*-P,P complex [**9**] (Scheme 3). No defined reaction products apart from phosphine complexes could be isolated from the reaction of $[RhCl(COE)_2]_2$ with **5** in the presence of $PCy_3$. In all complex formations, the P^C ligand precursor *formally* reacts under tautomerization to a NH,NR-substituted NHC, which then coordinates in a chelating fashion to the metal center. Most likely, the formation of complexes [**6**]−[**9**] involves an initial oxidative addition of the C2−H bond to $Rh^I$, and selected features of this reaction will be discussed below.

In addition to X-ray diffraction structure analyses for [**6**] and [**9**], all new complexes have been characterized by NMR spectroscopic methods. Complex [**6**] could be isolated in pure form by multiple recrystallization steps from the mixture [**6**]/[**7**]. This was not possible for complex [**7**] due to its low concentration in the mixture. In the mixture of [**6**] and [**7**], complex [**6**] (*cis*-P,P) can be distinguished from the *trans*-P,P derivative [**7**] by the magnitude of the $^2J_{P1P2}$ coupling constant. The $^{31}P$ NMR spectrum for [**6**] showed the resonances for the two chemically different phosphorus atoms at $\delta$ 78.0 (dd, $^1J_{P2Rh}$ = 209.0 Hz, $^2J_{P2P1}$ = 28.0 Hz, P2) ppm and $\delta$ 31.8 (dd, $^1J_{P1Rh}$ = 111.4 Hz, $^2J_{P1P2}$ = 28.0 Hz, P1) ppm. Two additional resonances at slightly different chemical shifts of $\delta$ 68.3 (dd, $^1J_{P2Rh}$ = 156.0 Hz, $^2J_{P2P1}$ = 339 Hz, P2) ppm and $\delta$ 31.7 (dd, $^1J_{P1Rh}$ = 137.0 Hz, $^2J_{P1P2}$ = 339.0 Hz, P1) ppm, but featuring the large $^2J_{PP}$ coupling constant of 339 Hz,[21] indicate the presence of complex [**7**] with the *trans*-P,P geometry. The $^{13}C$ $\{^1H\}$NMR spectrum shows the resonance for the carbene carbon atom of the *cis*-P,P complex [**6**] at $\delta$ 193.0 (ddd, $^1J_{CRh}$ = 46.5 Hz, $^2J_{CP2}$ = 103.4 Hz, $^2J_{CP1}$ = 14.0 Hz) ppm, whereas the resonance for the carbene carbon atom of [**7**] was not observed due to its low concentration in the mixture of complexes. Both the chemical shift and the observed coupling constants of the $^{13}C$ NMR carbene resonance in [**6**] match previously reported values obtained for $Rh^I$ complexes bearing classical NR,NR-functionalized NHCs and two additional phosphine ligands in cis and trans positions to the NHC ligand.[22]

Given the high steric demand of the $PCy_3$ ligand, which, under standard conditions, yields with $Rh^I$ the 14-electron complex $[RhCl(PCy_3)_2]$,[23] the formation of the two isomeric complexes [**6**] and [**7**] due to steric interactions of the phosphine ligands is not surprising. To avoid the formation of geometric isomers, we reacted the ligand precursor **3** with $[RhCl(COE)_2]_2$ in the presence of the sterically less demanding triphenyl phosphine (Scheme 3). As expected, this reaction gives exclusively the *cis*-P,P complex [**8**] in an excellent yield of 92% (Scheme 3). Complex [**8**] (*cis*-P,P) was also identified by NMR spectroscopy. The

**Scheme 3. Reactions of 3, 4, and 5 with $[RhCl(COE)_2]$ in the Presence of Different Phosphines**[a]




[a] The numbering refers to the assignment of the $^{31}P\{^1H\}$ NMR resonances.

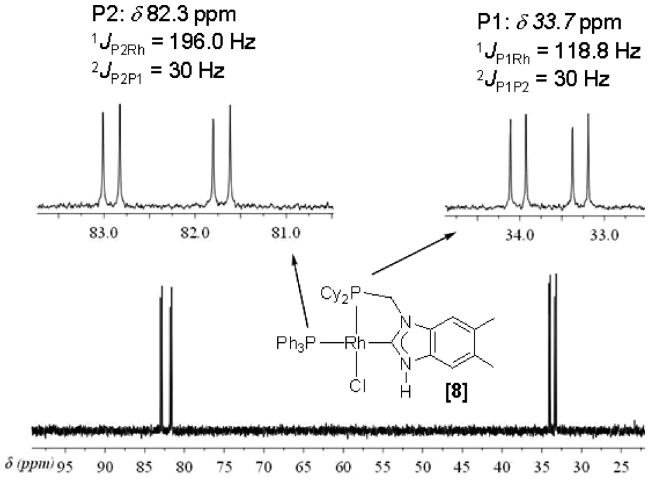



**Figure 3.** $^{31}P\{^1H\}$ NMR spectrum of [**8**] in THF.

$^{13}C\{^1H\}$ NMR spectrum features the resonance for the carbene carbon atom at $\delta$ 194.0 (ddd, $^1J_{CRh}$ = 46.4 Hz, $^2J_{CP2}$ = 111.2 Hz, $^2J_{CP1}$ = 12.3 Hz) ppm with coupling to the rhodium atom and the two phosphorus atoms. The $^{31}P\{^1H\}$ NMR spectrum (Figure 3) features two resonances for the phosphorus atoms at $\delta$ 82.3 ($^1J_{P2Rh}$ = 196.0 Hz, $^2J_{P2P1}$ = 30.0 Hz, P2) ppm and $\delta$ 33.7 ($^1J_{P1Rh}$ = 118.8 Hz, $^2J_{P1P2}$ = 30.0 Hz, P1) ppm. The NMR data and, in particular, the small $^2J_{PP}$ coupling constants for [**6**] and [**8**] are quite similar, indicating the *cis*-P,P configuration for both complexes. This geometrical arrangement was confirmed by X-ray crystallography for [**6**] (vide infra).

Finally, we synthesized the rhodium(I) complex from the ligand precursor **4** in the presence of tricyclohexyl phosphine. In **4**, the phosphine donor is linked by an ethylene spacer to the benzimidazole ring nitrogen atom (Scheme 3). Upon coordination of the P^C chelate ligand, a six-membered chelate ring forms. It is expected that the P1−Rh−$C_{carbene}$ angle in this six-membered chelate ring is larger than the equivalent angle in complexes [**6**]−[**8**], featuring five-membered chelate rings. This angle expansion should have consequences for the complex geometry and, in particular, for the position of the monodentate phosphine. In fact, the reaction of $[RhCl(COE)_2]_2$ with **4** in the presence of $PCy_3$ leads exclusively to the formation of complex [**9**] (70%) with a *trans*-P,P arrangement of the phosphine ligands. The larger P1−Rh−$C_{carbene}$ angle in [**9**] apparently prevents the coordination of a second bulky phosphine ligand in a cis position.

The *trans*-P,P complex [**9**] was identified by $^{13}C\{^1H\}$ NMR spectroscopy, showing the resonance for the carbene carbon atom at $\delta$ 197.0 ($^1J_{CRh}$ = 53.3 Hz, $^2J_{CP}$ = 15.1 Hz, $^2J_{CP}$ = 13.7 Hz.) ppm. More information about the geometry of the complex can be drawn from the $^{31}P\{^1H\}$ NMR spectrum. Here, two resonances at $\delta$ 47.6 ($^1J_{P1Rh}$ = 154.0 Hz, $^2J_{P1P2}$ = 325.2 Hz, P1) ppm and $\delta$ 27.4 ($^1J_{P2Rh}$ = 149.0 Hz, $^2J_{P2P1}$ = 325.2 Hz, P2) ppm have been observed. The very large $^2J_{PP}$ coupling constants of 325.2 Hz clearly indicate the presence of the *trans*-P,P complex,[21] whereas the *cis*-P,P complexes [**6**] and [**8**] show much smaller $^2J_{PP}$ coupling constants of about 30 Hz. The $^2J_{PP}$ coupling constant in [**9**] is of similar magnitude as the $^2J_{PP}$ coupling constant in [**7**] ($^2J_{P1P2}$ = 339 Hz), confirming the assignment of [**7**] as a *trans*-P,P complex. Both, the length of the spacer between the benzimidazole nitrogen atom and the phosphorus atom P1, leading to a larger P1−Rh−$C_{carbene}$ angle, and the bulkiness of the tricylohexyl phosphine,[23] contribute to the formation of the *trans*-P,P complex [**9**] compared to the *cis*-P, P complexes [**6**] and [**8**]. However, even with the P^C chelate ligand featuring a methylene spacer obtained from **3**, formation of *trans*-P,P complexes like [**7**] as a minor reaction was observed in the presence of a bulky monodentate phosphine like $PCy_3$.

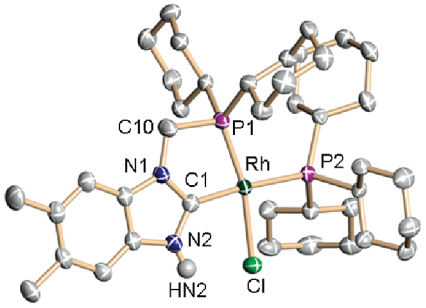



**Figure 4.** Molecular structure of the complex [**6**] in [**6**]·0.5$C_6H_6$ (50% displacement ellipsoids, hydrogen atoms have been omitted with the exception of the hydrogen atom bound to N2). Selected bond lengths (Å) and angles (deg): Rh−Cl1 2.4286(12), Rh−P1 2.1951(12), Rh−P2 2.3693(11), Rh−C1 1.980(4), P1−C10 1.878(5), N1−C10 1.438(6), N1−C1 1.364(5), N2−C1 1.352(5); Cl−Rh−P1 166.84(4), Cl−Rh−P2 89.10(4), Cl−Rh−C1 85.63(13), P1−Rh−P2 103.58(4), P1−Rh−C1 81.63(13), P2−Rh−C1 174.63(13), N1−C1−N2 104.7(4).

The conclusions drawn from NMR spectroscopy were confirmed by X-ray molecular structure analyses. Complex [**6**] crystallized from benzene as [**6**]·0.5$C_6H_6$. The structural analysis (Figure 4) confirmed the cis arrangement of the phosphine donors. The Rh−C1 distance (1.980(4) Å) is remarkably short for the $Rh^I$ complex with an NHC in a trans position to a phosphine where normally Rh−C separations of about 2.05 Å are observed.[22b] This may be a consequence of the incorporation of the NHC into a chelate ligand and the small hydrogen substituent at atom N2. We take the short Rh−$C_{carbene}$ separation as another indication for the high stability of complexes of type [**6**], which cannot undergo tautomerization easily. Contrary to the free benzimidazole **4**, the metric parameters within the diamino heterocycle indicate the presence of a typical NHC with equally long N−$C_{carbene}$ bond distances and an N−$C_{carbene}$−N angle of 104.7(4)°.[11] The Rh−P distances are significantly different with the Rh−P1 separation (2.1951(12) Å, trans to the $\sigma,\pi$-donor Cl) significantly shorter than the Rh−P2 distance (2.3693(11) Å, trans to the $\sigma$-donor/$\pi$-acceptor tricyclohexyl phosphine). The square-planar coordination geometry around the metal center is strongly distorted with P1−Rh−C1 and Cl−Ru−C1 angles of only 81.63(13)° and 85.63(13)°, respectively. The coordination geometry around the metal center is clearly determined by the bulky phosphine donors.

Complex [**9**] has been crystallized as [**9**]·$CH_2Cl_2$·$H_2O$ from a dichloromethane solution. The X-ray diffraction analysis (Figure 5) confirmed the trans arrangement of the phosphine ligands in a slightly distorted square-planar rhodium(I) complex. This arrangement only leads to a small change of the Rh−$C_{carbene}$ separation (1.980(4) Å in [**6**], 1.922(3) Å in [**9**]). The same is true for the Ru−Cl distances, which are identical within experimental error for [**6**] and [**9**]. Because the phosphine ligands are arranged in trans positions to each other in [**9**], the Rh−P separations are not as different as in [**6**] but approach almost

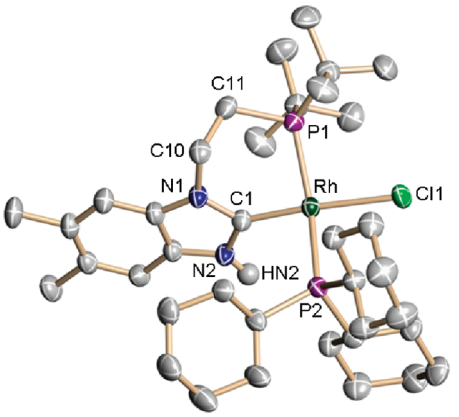
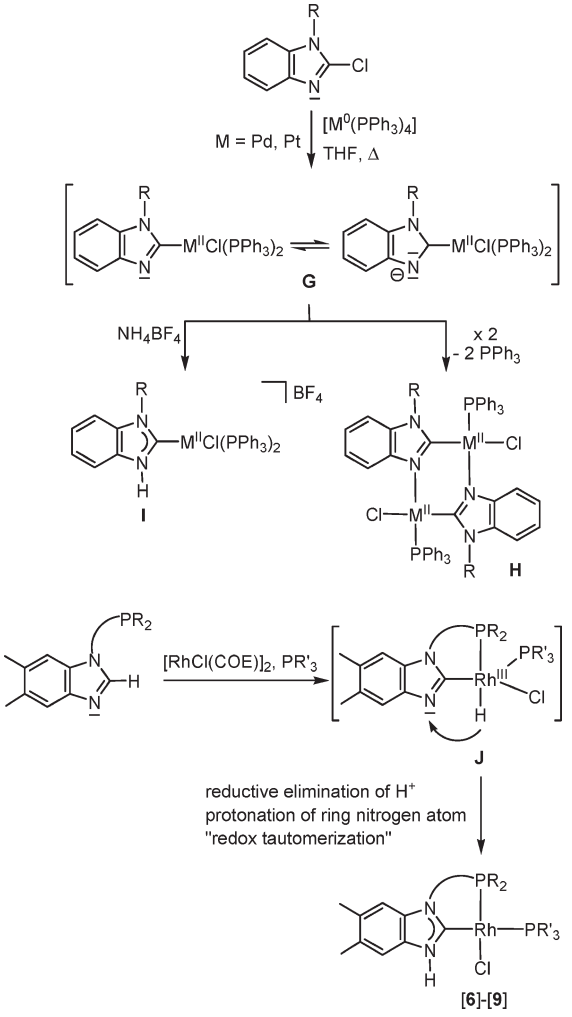



**Figure 5.** Molecular structure of the complex [**9**] in [**9**]·$CH_2Cl·H_2O$ (50% displacement ellipsoids, hydrogen atoms have been omitted with the exception of the hydrogen atom bound to N2). Selected bond lengths (Å) and angles (deg): Rh−Cl 2.4253(8), Rh−P1 2.3402(9), Rh−P2 2.3219(9), Rh−C1 1.922(3), P1−C11 1.861(3), N1−C10 1.458(4), N1−C1 1.368(4), N2−C1 1.379(4); Cl−Rh−P1 95.83(3), Cl−Rh1−P2 88.04(3), Cl−Rh1−C1 171.34(9), P1−Rh−P2 165.53(3), P1−Rh−C1 86.56(9), P2−Rh−C1 91.69(9), N1−C1−N2 104.0(2).

equidistant values (Rh−P1 2.3402(9) Å, Rh−P2 2.3219(9) Å). The angle P1−Ru−C1 within the chelate ring is significantly expanded to 86.56(9)° in comparison to [**6**] (81.63(13)°). Overall, the larger chelate ring formed by the P^C chelate in [**9**] and the trans arrangement of the phosphine donors lead to a much less distorted square-planar coordination geometry in [**9**] than was observed for [**6**]. The trans arrangement of the NHC and the chloride is optimal for a catalytic hydrogenation reaction with previous substrate recognition/orientation. The remaining labile ligand ($PCy_3$) for substrate coordination in a Wilkinson-type hydrogenation is located in a cis position to the NH,NR-NHC ligand containing the NH group for hydrogen bonding to selected substrates.

The mechanism for the formation of complexes [**6**]−[**9**] has not unambiguously been established. Related complexes bearing bidentate imidazolin-2-ylidene/donor[18,19] or benzimidazolin-2-ylidene/donor[16] ligands have been described as formed by tautomerization of the azole to the NH,NR-substituted NHC, which then coordinates to the metal center. This rather simple type of reaction is not very likely to be operative. We have recently shown that neutral 2-chloro-*N*-methylbenzimidazole, similar to the well-known reaction of C2−X substituted azolium cations,[24] can oxidatively add to $Pd^0$ and $Pt^0$, leading to the intermediate **G**, which contains a strongly basic, partly anionic nitrogen atom within the heterocycle (Scheme 4). Because of this basic ring nitrogen atom, complex **G** subsequently either dimerizes to the neutral dinuclear complexes **H** or reacts with a proton source to give the cationic complexes **I** with a neutral NH, NR-substituted NHC ligand.[25] We propose that the ligands **3** and **4** initially also react with rhodium(I) under C2−H oxidative addition to give a five- or six-coordinated intermediate **J**. This type of oxidative addition has been observed multiple times with the C2−H bond of azolium salts.[24] In contrast to intermediate **G**, the hydrido complex **J** is not stable but reacts under reductive elimination of a proton, which subsequently protonates the basic nitrogen atom of the heterocycle under transformation of the anionic carbene ligand into a neutral NH,NR-substituted NHC

**Scheme 4. Oxidative Addition of 2-Chloro-*N*-methylbenzimidazoles to $Pd^0$ and $Pt^0$ (Top) and Proposed Mechanism for the Redox Tautomerization of C2−H Azoles (Bottom)**




ligand. The related reductive elimination of a proton from NHC/hydrido complexes is a well-documented reaction.[26] We propose to name the reaction of C2−H-substituted azoles with transition metals under formation of complexes with NH,NR-substituted NHC ligands a redox tautomerization.

## ■ CONCLUSIONS

We have prepared the phosphine-functionalized benzimidazoles **3**, **4**, and **5**. The precursors for bidentate NH,NR-NHC/phosphine ligands **3** and **4** react with $[RhCl(COE)_2]_2$ under *formal* tautomerization to give the phosphine-substituted NH, NR-NHCs, which coordinate to $Rh^I$ in a chelating fashion. The resulting complexes are stable and cannot tautomerize under formation of the *N*-coordinated azole complexes. The length of the spacer between the benzimidazole nitrogen atom and the attached phosphine phosphorus atom and the steric demand of the additional monodentate phosphine determine the geometry of the resulting rhodium(I) complexes. On the basis of published data, it appears that the *formal* tautomerization observed during complex formation with the ligand precursors **3** and **4** actually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involves an oxidative addition of the C2−H bond of the benzimidazole moiety to $Rh^I$, followed by reductive elimination of the metal bound hydrogen atom as a proton, which subsequently protonates the free nitrogen atom of the heterocycle. This type of "redox tautomerization" may be operative for the various formal tautomerization reactions described in the literature leading to complexes with NH,NR-NHCs. Further studies in this laboratory are directed toward the elucidation of the mechanism for the reaction of C2−H-substituted benzimidazoles with transition metals and toward the use of complexes of type [**9**] in catalytic hydrogenation reactions.

## EXPERIMENTAL SECTION

**General Comments.** All syntheses were carried out under an argon atmosphere using conventional Schlenk techniques. Solvents were dried and degassed by standard methods prior to use. 1-Chloromethyl-5,6-dimethylbenzimidazolium hydrochloride,[16] **1**·HCl; 2-chloroethyl-5,6-dimethylbenzimidazole,[16] **2**; and $[RhCl(coe)_2]_2$[27] have been prepared by published methods. NMR spectra were recorded with a Bruker Avance I 400 NMR spectrometer. MALDI, EI, and ESI-HRMS mass spectra were obtained with Bruker Reflex IV, Finnigan MAT 95, and Bruker Daltronics MicroTof spectrometers, respectively. For NMR signal assignments and numbering, see Scheme 1.

**Compound 3.** A sample of 1-chloromethyl-5,6-dimethylbenzimidazolium hydrochloride, **1**·HCl (400 mg, 1.73 mmol), in THF (10 mL) cooled to 0 °C was transformed into the free amine by addition of 194 mg (1.73 mmol) of KO-*t*Bu. The resulting solution was stirred at 0 °C for 30 min. Removal of the solvent gave a white precipitate. To this precipitate was added at 0 °C a solution of $LiPCy_2$ obtained by treatment of $PHCy_2$ (343 mg, 1.73 mmol) with 1.1 mL of 1.6 M *n*BuLi (1.76 mmol) in THF (10 mL) at −78 °C. The reaction mixture was stirred at ambient temperature for 12 h and was then quenched by addition of 2.0 mL of methanol while vigorously stirring for another 10 min. All solvents were then removed in vacuo. The solid residue was extracted with ethyl acetate (20 mL), and the extract was washed with water. Drying of the organic phase over $Na_2SO_4$ and removal of the solvent under reduced pressure gave compound **3** as a highly hygroscopic white solid. Yield: 230 mg (0.65 mmol, 38%). $^1$H NMR (400 MHz, THF-$d_8$): $\delta$ 7.90 (s, 1H, H1), 7.37 (s, 1H, H7), 7.28 (s, 1H, H4), 4.35 (d, $^2J_{HP}$ = 3.2 Hz, 2H, H10), 2.35 (s, 3H, H9), 2.31 (s, 3H, H8), 1.74 (m, 11H, Cy-H), 1.26 (m, 11H, Cy-H). $^{13}$C{$^1$H} NMR (100 MHz, THF-$d_8$): $\delta$ 144.3 (s, C3), 143.1 (d, $^3J_{CP}$ = 7.0 Hz, C1), 134.2 (s, C2), 131.4 (s, C6), 130.4 (s, C5), 121.1 (s, C4), 111.3 (s, C7), 40.3 (d, $^1J_{CP}$ = 21.7 Hz, C10), 33.9 (d, $^1J_{CP}$ = 15.0 Hz, Cy-C), 30.6 (d, $^2J_{CP}$ = 13.5 Hz, Cy-C), 30.0 (d, $^2J_{CP}$ = 15.0 Hz, Cy-C), 28.6 (d, $^3J_{CP}$ = 8.3 Hz, Cy-C), 28.1 (d, $^3J_{CP}$ = 10.8 Hz, Cy-C), 27.3 (s, Cy-C), 20.7 (s, C9), 20.3 (s, C8). $^{31}$P{$^1$H} NMR (162 MHz, THF-$d_8$): $\delta$ −9.7 (s). MS (EI, 50 eV) *m*/*z* (%): 356 (100) [**3**]$^+$. Anal. Calcd: C, 74.11; H, 9.34; N, 7.86. Found: C, 73.23; H, 9.30; N, 7.78.

**Compound 4.** Compound **4** was obtained by addition of 235 mg (1.56 mmol) of solid $LiPtBu_2$[28] to a THF (10 mL) solution of 2-chloroethyl-5,6-dimethyl benzimidazole **2** (322 mg, 1.54 mmol) at −60 °C. The reaction mixture was stirred at −60 °C for 1 h and was then slowly warmed up to ambient temperature. During this warm up, the color of the initially green solution changed to pale orange. The reaction mixture was stirred at ambient temperature for 1 h and then heated under reflux for another 3 h. After cooling to ambient temperature, the reaction mixture was quenched with methanol (3 mL) and all solvents were removed in vacuo. The solid obtained was dissolved in dichloromethane (20 mL), and the solution was washed with water (20 mL). The organic phase was dried over $MgSO_4$, and the volume of the solution was reduced to 2 mL. Addition of pentane (20 mL) led to precipitation of **4** as a highly hygroscopic off-white solid. Yield: 194 mg (0.61 mmol, 40%). $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 7.90 (s, 1H, H1), 7.16 (s, 1H, H4), 7.11 (s, 1H, H7), 3.84 (m, 2H, H10), 2.26 (s, 3H, H9), 2.20 (s, 3H, H8), 1.56 (m, 2H, H11), 0.93 (s, 9H, *t*Bu-H), 0.90 (s, 9H, *t*Bu-H). $^{13}$C{$^1$H} NMR (100 MHz, $C_6D_6$): $\delta$ 144.0 (s, C3), 142.4 (s, C1), 132.8 (s, C2), 131.4 (s, C6), 130.7 (s, C5), 121.7 (s, C4), 110.0 (s, C7), 45.8 (d, $^2J_{CP}$ = 39.5 Hz, C10), 31.2 (d, $^1J_{CP}$ = 21.7 Hz, C11), 29.5 (d, $^2J_{CP}$ = 14.1 Hz, C−$CH_3$), 22.8 (d, $^1J_{CP}$ = 25.1 Hz, $C$−$CH_3$), 20.7 (s, C9), 20.3 (s, C8). $^{31}$P{$^1$H} NMR (162 MHz, $C_6D_6$): $\delta$ 23.5. MS (EI, 50 eV) *m*/*z* (%): 318 (100) [**4**]$^+$. Anal. Calcd: C, 71.66; H, 9.81; N, 8.80. Found: C, 71.54; H, 9.27; N, 9.59.

**Compound 5.** A sample of $LiPCy_2$ was prepared by the addition of *n*BuLi (0.77 mL of a 1.6 M solution, 1.23 mmol) to a solution of dicyclohexyl phosphine (242 mg, 1.22 mmol) in THF (10 mL) at −78 °C. This solution was added to a solution of 2-chloroethyl-5,6-dimethyl benzimidazole **2** (220 mg, 1.05 mmol) in THF (8 mL), and the reaction mixture was stirred at ambient temperature for 2 days. The reaction mixture was then quenched with methanol (2 mL), and all solvents were subsequently removed in vacuo. The residue was suspended in water (20 mL), and compound **5** was extracted with benzene (3 × 10 mL). The combined organic phases were dried over $Na_2SO_4$, and the volume of the solution was reduced to 2 mL. Addition of pentane (20 mL) led to precipitation of **5** as a colorless solid. Yield: 240 mg (0.65 mmol, 62%). $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 7.92 (s, 1H, H4), 7.58 (s, 1H, H1), 7.10 (s, 1H, H7), 3.83 (d, $^3J_{HP}$ = 7.2 Hz, H10), 2.27 (s, 3H, H9), 2.20 (s, 3H, H8), 1.56 (d, $^2J_{HP}$ = 8.6 Hz, 2H, H11), 1.69−1.04 (m, 22H, Cy-H). $^{13}$C{$^1$H} NMR (100 MHz, $C_6D_6$): $\delta$ 144.3 (s, C3), 142.3 (s, C1), 132.9 (s, C2), 131.5 (s, C6), 130.6 (s, C5), 121.0 (s, C4), 110.0 (s, C7), 44.6 (d, $^2J_{CP}$ = 33.8 Hz, C10), 33.5 (d, $^1J_{CP}$ = 13.9 Hz, Cy-C), 30.5 (d, $^2J_{CP}$ = 15.0 Hz, Cy-C), 29.2 (d, $^2J_{CP}$ = 8.6 Hz, Cy-C), 27.5 (d, $^3J_{CP}$ = 11.3 Hz, Cy-C), 27.4 (d, $^3J_{CP}$ = 7.0 Hz, Cy-C), 26.4 (s, Cy-C), 22.9 (d, $^1J_{CP}$ = 21.6 Hz, C11), 20.7 (s, C9), 20.3 (s, C8). $^{31}$P{$^1$H} NMR (162 MHz, $C_6D_6$): $\delta$ −8.9. MS (EI, 50 eV) *m*/*z* (%): 370 (100) [**5**]$^+$. Anal. Calcd: C, 74.56; H, 9.52; N, 7.56. Found: C, 73.41; H, 9.42; N, 7.42.

**Complex [6].** A thick-walled screw-capped vial was charged with compound **3** (25.0 mg, 0.07 mmol), tricyclohexyl phosphine (20.0 mg, 0.07 mmol), $[RhCl(COE)_2]_2$ (25 mg, 0.035 mmol), and THF (8 mL). The reaction mixture was stirred at ambient temperature for 10 min, followed by heating to 90 °C for 6 h. A brown solution was obtained, which was cooled to ambient temperature, and the solvent was removed under vacuo to give a brown solid. The solid was washed with pentane (3 × 10 mL) and then dried in vacuo to give a mixture of complexes [**6**] (77%) and [**7**] (23%) as a brownish solid. Yield: 30 mg (0.04 mmol, 57% of the complex mixture). Both complexes in the mixture have been identified by $^{31}$P{$^1$H} NMR spectroscopy. Pure [**6**] was obtained by recrystallization from benzene, whereas [**7**] could not be isolated in analytically pure form due to its low concentration in the mixture and contamination with [**6**]. Analytical data for complex [**6**]: $^1$H NMR (400 MHz, THF-$d_8$): $\delta$ 11.40 (s, 1H, NH), 7.18 (s, 1H, H4), 7.05 (s, 1H, H7), 3.74 (d, $^2J_{HP}$ = 4.8 Hz, 2H, H10), 2.29 (s, 3H, H9), 2.28 (s, 3H, H8), 1.81−1.69 (m, 33H, $PCy_3$-H), 1.34−1.23 (m, 22H, $PCy_2$-H). $^{13}$C{$^1$H} NMR (100 MHz, THF-$d_8$): $\delta$ 193.0 (ddd, $^1J_{CRh}$ = 46.5 Hz, $^2J_{CP2}$ = 103.4 Hz, $^2J_{CP1}$ = 14.0 Hz, C1), 132.4 (d, $^3J_{CRh}$ = 2.3 Hz, C3), 131.7 (d, $^3J_{CRh}$ = 9.8 Hz, C2), 130.3 (s, C5), 129.6 (s, C6), 111.3 (s, C7), 110.5 (s, C4), 42.6 (dd, $^1J_{CP1}$ = 28.6 Hz, $^2J_{CRh}$ = 4.5 Hz, C10), 36.7 (d, $^1J_{CP}$ = 20.9 Hz, Cy-C), 33.3 (d, $^1J_{CP}$ = 28.4 Hz, Cy-C), 28.2 (d, $^1J_{CP}$ = 9.6 Hz, Cy-C), 27.6 (d, $^1J_{CP}$ = 9.1 Hz, Cy-C), 27.0 (d, $^1J_{CP}$ = 9.3 Hz, Cy-C), 24.8−24.0 (m, Cy-C), 19.2 (s, C9), 19.3 (s, C8). $^{31}$P{$^1$H} NMR (162 MHz, THF-$d_8$): $\delta$ 78.0 (dd, $^1J_{P2Rh}$ = 209.0 Hz, $^2J_{P2P1}$ = 28.0 Hz, P2), 31.8 (dd, $^1J_{P1Rh}$ = 111.4 Hz, $^2J_{P1P2}$ = 28.0 Hz, P1). MS (ESI HRMS) *m*/*z*: 739.3753 (calcd for [**6** − Cl]$^+$ 739.3756). Anal. Calcd (for [**6**]/[**7**]): C, 61.97; H, 8.58; N, 3.61. Found: C, 61.39; H, 8.72; N, 2.96. NMR data for [**7**] in the complex mixture [**6**]/[**7**]: $^{31}$P{$^1$H} NMR (162 MHz, THF-$d_8$): $\delta$ 68.3 (dd, $^1J_{P2Rh}$ = 156.0 Hz, $^2J_{P2P1}$ = 339 Hz, P2), 31.7 (dd, $^1J_{P1Rh}$ = 137.0 Hz, $^2J_{P1P2}$ = 339.0 Hz, P1).

**Complex [8].** A thick-walled screw-capped vial was charged with compound **3** (21.0 mg, 0.06 mmol), triphenyl phosphine (16.0 mg, 0.06 mmol), $[Rh(COE)_2Cl]_2$ (22.0 mg, 0.03 mmol), and THF (6 mL). The mixture was stirred at ambient temperature for 10 min, followed by heating to 90 °C for 6 h. The solvent was then removed in vacuo, and the solid brown residue was washed with pentane (4 mL). Drying of the resulting solid in vacuo gave [**8**] as a dark orange solid. Yield: 42 mg (0.055 mmol, 92%). $^1$H NMR (THF, 400 MHz): $\delta$ 11.40 (s, 1H, NH), 7.88−7.84 (m, 6H, $PPh_3$-H), 7.28 (s, 9H, $PPh_3$-H), 7.26 (s, 2H, H4 and H7), 3.76 (d, $^2J_{HP}$ = 4.9 Hz, 2H, H10), 2.32 (s, 3H, H8), 2.30 (s, 3H, H9), 1.72−1.31 (m, 11H, Cy-H), 1.06−0.88 (m, 11H, Cy-H). $^{13}C\{^1H\}$ NMR (100 MHz, THF-$d_8$): $\delta$ 194.0 (ddd, $^1J_{CRh}$ = 46.4 Hz, $^2J_{CP2}$ = 111.2 Hz, $^2J_{CP1}$ = 12.3 Hz, C1), 139.3 (d, $^1J_{CP}$ = 31.8 Hz, $PPh_3$-C), 136.7 (d, $^2J_{CP}$ = 12.3 Hz, $PPh_3$-C), 133.4 (d, $^3J_{CRh}$ = 3.0 Hz, C3), 132.1 (d, $^3J_{CRh}$ = 3.0 Hz, C2), 131.8 (s, C5), 131.3 (s, C6), 129.4 (s, $PPh_3$-C), 128.0 (d, $^3J_{CP}$ = 8.9 Hz, $PPh_3$-C), 112.7 (s, C7), 111.6 (s, C4), 42.8 (dd, $^1J_{CP1}$ = 26.6 Hz, $^2J_{CRh}$ = 4.5 Hz, C10), 35.3 (d, $^1J_{CP}$ = 23.2 Hz, Cy-C), 30.1 (d, $^3J_{CP}$ = 5.18 Hz, Cy-C), 27.9 (d, $^2J_{CP}$ = 9.1 Hz, Cy-C), 27.3 (s, Cy-C), 20.3 (s, C9), 20.2 (s, C8). $^{31}P\{^1H\}$ NMR (162 MHz, THF-$d_8$): $\delta$ 82.3 (dd, $^1J_{P2Rh}$ = 196.0 Hz, $^2J_{P2P1}$ = 30.0 Hz, P2), 33.7 (dd, $^1J_{P1Rh}$ = 118.8 Hz, $^2J_{P1P2}$ = 30.0 Hz, P1). MS (ESI HRMS) *m*/*z*: 721.2346 (calcd for $[\mathbf{8} - Cl]^+$ 721.2348). Anal. Calcd (for [**8**]): C, 63.45; H, 6.39; N, 3.70. Found: C, 63.60; H, 6.65; N, 3.21.

**Complex [9].** A thick screw-capped vial was charged with compound **4** (23 mg, 0.072 mmol), $[Rh(COE)_2Cl]_2$ (25 mg, 0.035 mmol), tricyclohexyl phosphine (21 mg, 0.075 mmol), and THF (5 mL). The reaction mixture was stirred at ambient temperature for 10 min, followed by heating to 90 °C for 6 h. During this period, the color of the mixture changed from dark red to light orange. The reaction mixture was cooled to ambient temperature, and the solvent was removed in vacuo, giving a yellow solid. This solid was washed with pentane and dried in vacuo to give [**9**] as a yellow solid. Yield: 36 mg (0.049 mmol, 70%). $^1$H NMR (400 MHz, THF-$d_8$): $\delta$ 9.98 (s, 1H, NH), 7.00 (s, 1H, H4), 6.94 (s, 1H, H7), 5.61 (m, 2H, H10), 4.42 (d, $^2J_{HP}$ = 17.2 Hz, 2H, H11), 2.28 (s, 3H, H8), 2.25 (s, 3H, H9), 1.77−1.58 (m, 30H, Cy-H), 1.29 (s, 9H, *t*Bu-H), 1.26 (s, 9H, *t*Bu-H), 1.11−1.04 (m, 3H, Cy-H). $^{13}C\{^1H\}$ NMR (100 MHz, THF-$d_8$): $\delta$ 197.0 (ddd, $^1J_{CRh}$ = 53.3 Hz, $^2J_{CP}$ = 15.1 Hz, $^2J_{CP}$ = 13.6 Hz, C1), 134.7 (d, $^4J_{CP}$ = 1.9 Hz, C3), 133.1 (s, C2), 130.7 (s, C6), 130.1 (s, C5), 129.7 (s, C4), 109.2 (s, C7), 45.4 (dd, $^2J_{CP1}$ = 7.9 Hz, $^3J_{CRh}$ = 4.2 Hz, C10), 36.9 (dd, $^1J_{CP}$ = 7.5 Hz, $^2J_{CRh}$ = 3.3 Hz, C11), 35.7 (d, $^1J_{CP2}$ = 14.2 Hz, Cy-C), 32.8 (d, $^1J_{CP2}$ = 18.0 Hz, Cy-C), 32.1 (d, $^1J_{CP2}$ = 12.8 Hz, Cy-C), 31.5 (s, Cy-C), 30.9 (d, $^2J_{CP2}$ = 5.9 Hz, Cy-C), 30.1 (s, C−$CH_3$), 29.0 (d, $^2J_{CP2}$ = 10.2 Hz, Cy-C), 28.5 (d, $^2J_{CP2}$ = 9.0 Hz, Cy-C), 27.8 (s, Cy-C), 27.5 (s, Cy-C), 27.0 (s, Cy-C), 26.2 (s, Cy-C), 20.2 (s, C8), 20.1 (s, C9), 19.8 (m, C−$CH_3$). $^{31}P\{^1H\}$ NMR (162 MHz, THF-$d_8$): $\delta$ 47.6 (dd, $^1J_{P1Rh}$ = 154.0 Hz, $^2J_{P1P2}$ = 325.2 Hz, P1), 27.4 (dd, $^1J_{P2Rh}$ = 149.0 Hz, $^2J_{P2P1}$ = 325.2 Hz, P2). MS (ESI HRMS) *m*/*z*: 717.3524 $[\mathbf{9} - Cl + O]^+$ (calcd for $[\mathbf{9} - Cl + O]^+$ 717.3549).

**X-ray Diffraction Studies.** X-ray diffraction data were collected at $T$ = 153(2) K with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode using monochromated Cu−K$\alpha$ radiation ($\lambda$ = 1.54178 Å) for **4** or Mo−K$\alpha$ radiation ($\lambda$ = 0.71073 Å) for [**6**]·0.5$C_6H_6$ and [**9**]·$CH_2Cl_2$·$H_2O$. Diffraction data were collected over the full sphere and were corrected for absorption. Structure solutions were found with the SHELXS-97[29] package using direct methods and were refined with SHELXL-97[29] 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 (for exceptions, see description of the individual molecular structures).

**4.** Crystals suitable for an X-ray diffraction study were obtained by diffusion of pentane into a dichloromethane solution of the compound. $C_{19}H_{31}N_2P$: $M$ = 318.43 g·mol$^{-1}$, pale yellow crystal, 0.34 × 0.12 × 0.05 mm$^3$, triclinic, space group $P\bar{1}$, $Z$ = 4, $a$ = 11.8331(5) Å, $b$ = 11.8394(6) Å, $c$ = 14.7275(6) Å, $\alpha$ = 101.262(3)°, $\beta$ = 110.223(2)°, $\gamma$ = 90.239(3)°, $V$ = 1893.03(15) Å$^3$, $\rho_{calc}$ = 1.117 g·cm$^{-3}$, Mo−K$\alpha$ radiation ($\lambda$ = 0.71073 Å), $\mu$ = 1.258 mm$^{-1}$, $\omega$- and $\varphi$-scans, 11 114 measured intensities (6.5° ≤ 2$\theta$ ≤ 143.0°), semiempirical absorption correction (0.674 ≤ $T$ ≤ 0.940), 6406 independent ($R_{int}$ = 0.0534) and 4974 observed intensities ($I \geq 2\sigma(I)$), refinement of 413 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. $R$ = 0.0528, $wR$ = 0.1439, $R_{all}$ = 0.0659, $wR_{all}$ = 0.1514. The asymmetric unit contains two formula units featuring identical metric parameters within experimental error limits.

**[6]·0.5$C_6H_6$.** Crystals suitable for an X-ray diffraction study were obtained by recrystallization from benzene. $C_{43}H_{69}N_2ClP_2Rh$: $M$ = 814.30 g·mol$^{-1}$, pale yellow crystal, 0.06 × 0.04 × 0.02 mm$^3$, triclinic, space group $P\bar{1}$, $Z$ = 2, $a$ = 9.5232(5) Å, $b$ = 10.4892(6) Å, $c$ = 21.0399(12) Å, $\alpha$ = 86.6200(10)°, $\beta$ = 86.9030(10)°, $\gamma$ = 79.1000(10)°, $V$ = 2058(2) Å$^3$, $\rho_{calc}$ = 1.314 g·cm$^{-3}$, Mo−K$\alpha$ radiation ($\lambda$ = 0.71073 Å), $\mu$ = 0.589 mm$^{-1}$, $\omega$- and $\varphi$-scans, 20 701 measured intensities (1.9° ≤ 2$\theta$ ≤ 45.0°), semiempirical absorption correction (0.966 ≤ $T$ ≤ 0.988), 9453 independent ($R_{int}$ = 0.0568) and 6560 observed intensities ($I \geq 2\sigma(I)$), refinement of 433 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. $R$ = 0.0545, $wR$ = 0.1247, $R_{all}$ = 0.0915, $wR_{all}$ = 0.1419. The asymmetric unit contains one formula unit [**6**]·0.5$C_6H_6$. The benzene molecule resides on an inversion center between two asymmetric units; no hydrogen positions for the benzene molecule were calculated.

**[9]·$CH_2Cl_2$·$H_2O$.** Crystals suitable for an X-ray diffraction study were obtained by recrystallization from dichloromethane. $C_{38}H_{68}N_2Cl_3OP_2Rh$: $M$ = 840.14 g·mol$^{-1}$, orange crystal, 0.21 × 0.16 × 0.07 mm$^3$, monoclinic, space group $C2/c$, $Z$ = 8, $a$ = 30.542(5) Å, $b$ = 14.614(2) Å, $c$ = 23.612(6) Å, $\beta$ = 122.925°, $V$ = 8846(3) Å$^3$, $\rho_{calc}$ = 1.262 g·cm$^{-3}$, Mo−K$\alpha$ radiation ($\lambda$ = 0.71073 Å), $\mu$ = 669 mm$^{-1}$, $\omega$- and $\varphi$-scans, 50 917 measured intensities (3.2° ≤ 2$\theta$ ≤ 60.0°), semiempirical absorption correction (0.872 ≤ $T$ ≤ 0.955), 12 898 independent ($R_{int}$ = 0.0236) and 10 631 observed intensities ($I \geq 2\sigma(I)$), refinement of 450 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. $R$ = 0.0513, $wR$ = 0.1642, $R_{all}$ = 0.0630, $wR_{all}$ = 0.1785. The asymmetric unit contains one molecule of [**9**] and one water molecule in addition to 1/2 $CH_2Cl_2$ with SOF = 0.5. A second $CH_2Cl_2$ molecule (SOF = 1.0) resides on a 2-fold axis between two asymmetric units. No hydrogen positions have been calculated for the $CH_2Cl_2$ molecules and the water molecule.

## ■ ASSOCIATED CONTENT

**Supporting Information.** X-ray crystallographic files for complexes **4**, [**6**]·0.5$C_6H_6$, and [**9**]·$CH_2Cl_2$·$H_2O$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

**Corresponding Author**
*E-mail: fehahn@uni-muenster.de.

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