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Synthesis and Characterization of N-Heterocyclic Carbene Substituted Phosphine and Phosphite Rhodium Complexes and their Catalytic Properties in Hydrogenation Reactions[1]

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Dedicated to Dr. Karl Öfele on the occasion of his 75th birthday and in great admiration of his scientific work as a pioneer in the field of N-heterocyclic carbene chemistry.

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Abstract: Mixed N-heterocyclic carbene-substituted phosphine and phosphite complexes of rhodium were prepared, starting from $[Rh(COE)_2Cl]_2$ (COE = cyclooctene) by addition of free N-heterocyclic carbenes (NHC) and PR_3. All new complexes were characterized by spectroscopy. In addition, the structures of *trans*-chloro(1,3-dicyclohexylimidazol-2-ylidene)-bis(triphenylphosphite)rhodium(I) (**5**), chloro-*trans*-bis(1,3-dicyclohexylimidazol-2-ylidene) (triphenylphosphine)rhodium(I) (**6**), and chloro(η^4-1,5-cyclooctadiene)(1,3-di-[(1*R*,2*S*,5*R*)-2-isopropyl-5-menthylcyclohex-1-yl]imidazol-2-ylidene)rhodium(I) (**8**) were determined by single crystal X-ray analyses. The hydrogenation of cyclohexene using molecular hydrogen has been optimized for some N-heterocyclic carbene-substituted phosphine and phosphite rhodium complexes by variation of the reaction conditions.

Keywords: catalysis; hydrogenation; N-heterocyclic carbenes; phosphines; phosphites; rhodium complexes

Introduction

Wilkinson's catalyst $Rh(PPh_3)_3Cl$ (**3**) has been the historical pioneer in a series of active homogeneous catalysts for olefin hydrogenation[2,3] and hydrosilylation.[4] Other rhodium[5,6] and cationic iridium complexes[5,7] bearing bulky phosphines as ligands have also proven to be active catalysts for directed alkene hydroboration and hydrogenation reactions. Imidazol-2-ylidenes (N-heterocyclic carbenes, NHCs)[8] represent an alternative to the widely utilized phosphine ligands[9] in homogenous catalysis.[10] Studies performed by us and others have demonstrated that replacement of bulky phosphines by an NHC, such as ICy (ICy = 1,3-dicyclohexylimidazol-2-ylidene) (**1**) can result in enhanced catalytic performance over phosphine-bearing analogues in a significant number of catalytic transformations, including C–C coupling reactions,[11] amination reactions,[12] hydroformylation,[13] hydrosilylation,[14] and olefin metathesis.[15] Rhodium carbene complexes have been extensively studied by Lappert et al. in the 1980s.[16–18] Based on these findings and on our continuing work heading towards more efficient and stable catalysts, we examined whether the catalytic activity of $Rh(PPh_3)_3Cl$ (**3**) for olefin hydrogenation can be improved when two phosphine ligands are replaced by the stronger σ-donor NHC ligands.[19–22] We now report a systematic optimization of the catalytic conditions of a newly synthesized $Rh(PPh_3)_2(ICy)Cl$ (**4**) complex in olefin hydrogenation.

The first stable carbene was prepared in 1988 by Bertrand.[23] Two years later, Arduengo achieved the isolation of the first stable N-heterocyclic carbene.[24] Until this point, the synthesis of NHC complexes was only possible by an *in situ* route. A synthetic protocol published by Lappert started from electron-rich olefins, that were cleaved at high temperatures in an inert solvent, and further reacted with metal precur-

sors.[16] This *in situ* method is not applicable for the synthesis of unsaturated N-heterocyclic carbene complexes. For the latter complexes, the direct synthesis of metal complexes *via in situ* deprotonation of the imidazolium salt is comfortable,[25] however some examples for the preparation of carbene substituted rhodium(I) complexes using a free NHC precursor were published in the past.[19,26] The *in situ* procedure has not been essentially changed since the first published NHC metal complexes by Öfele[27] and Wanzlick.[28] A basic metal salt (in most cases an acetate) reacts at high temperatures with an imidazolium or azolium salt. During this reaction, no free carbene is generated and thus no aprotic solvent is necessary. An important additional route for the generation of NHC-substituted rhodium(I) complexes is the carbene transfer reaction starting from NHC-substituted silver(I) complexes, which was first mentioned by Lin.[29,30]

Results and Discussion

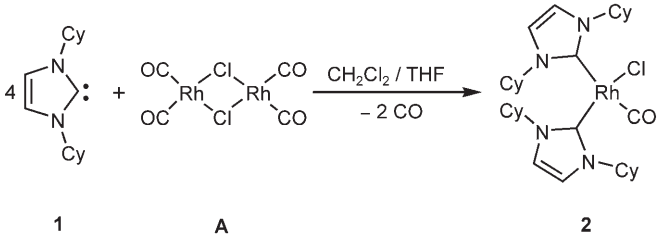
An *in situ* method using basic rhodium precursors, for example, bis[μ-ethoxy-(η^4-1,5-COD)rhodium], was published several years ago. It is very efficient if mono-, di- or tetra-N-heterocyclic carbene-substituted rhodium(I) complexes are desired.[25,31,32] For the synthesis of mixed phosphine- or phosphite-substituted NHC rhodium complexes, the so-called "imidazolium route",[33] is not the most straightforward synthesis route.

We prepared all NHC rhodium complexes by treatment of a rhodium precursor with the corresponding free carbene.[33,34] For example, complex **2** was obtained in good yields from bis[(μ-chloro)dicarbonylrhodium(I)] (**A**) and four equivalents of the free carbene **1** (1,3-dicyclohexylimidazol-2-ylidene) (Scheme 1).

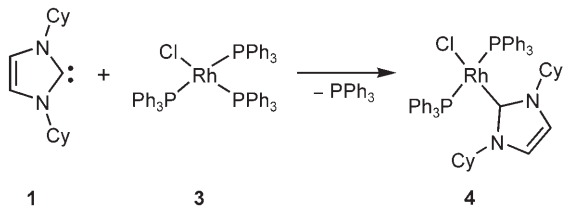
The *cis*-configuration of **2** was unequivocally confirmed by NMR spectroscopy. In the ^{13}C NMR spectrum the carbonyl group shows a chemical shift of 191.0 ppm and a coupling constant of 63.2 Hz, whereas two other signals corresponding to quaternary carbons were observed at 180.9 and 178.3 ppm, with coupling constants of 42.6 and 45.7 Hz, respectively. Also the carbons of the imidazole backbone (119.2, 118.0 ppm) and the α-carbons of the cyclohexyl ring (60.2, 58.3 ppm) vary between the two coordinated carbene ligands, one ligand being *trans* to the chloride and another one *trans* to the carbon monoxide. Similar behavior was observed in the ^{1}H NMR spectra for the imidazole backbone protons (7.29, 7.12 ppm) and the protons coordinated at the α-carbon of the cyclohexyl ring (4.64, 4.32 ppm). The fact that the protons of the imidazole backbone were observed as singlets, shows that both protons in one carbene ligand are equal, and the chemical shift is mainly influenced by the ligands in the *trans* position to the carbene carbon. Given these observations, we could examine the influence of the electronic properties of unsaturated carbene ligands indirectly, using the *trans*-effect that they exert on the CO ligand. The CO stretching frequency of complex **2** is $\nu = 1954$ cm^{-1}, approximately 20–30 cm^{-1} higher than for the *trans* complexes, where a chloride is coordinated *trans* to the carbonyl group.[35]

Mixed N-Heterocyclic Carbene/Phosphine and Phosphite Complexes of Rhodium

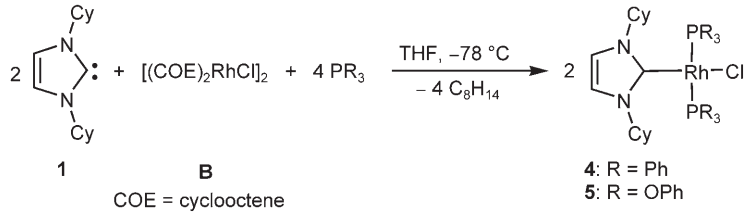
Mixed rhodium complexes where both NHCs and phosphine or phosphite ligands are coordinated, are known from the work of Lappert.[18] However, the conditions (high temperatures) used for the preparation of these complexes are not applicable to the synthesis of unsaturated NHC rhodium complexes. It is not possible to substitute completely the COD ligand by a phosphine when two equivalents of triphenylphosphine are heated with a mono-substituted NHC/COD-rhodium(I) complex in boiling xylene, which is the key step in Lappert's procedure. A much better synthetic route is to substitute weak ligands of a carbonyl or phosphine rhodium(I) complex with free carbenes. Indeed a quantitative substitution under mild conditions is not possible for Wilkinson's catalyst (**3**), because of the fluctional coordinated phosphine ligands and the resulting dissociation equilibrium.[19,22] However, we still obtained complex **4** in an acceptable yield of 67% from the reaction of (**3**) with the free carbene **1** in THF at room temperature (Scheme 2).



Scheme 1. Preparation of complex **2** by cleavage of a dimeric precursor.



Scheme 2. Preparation of complex **4** starting from Wilkinson's catalyst.



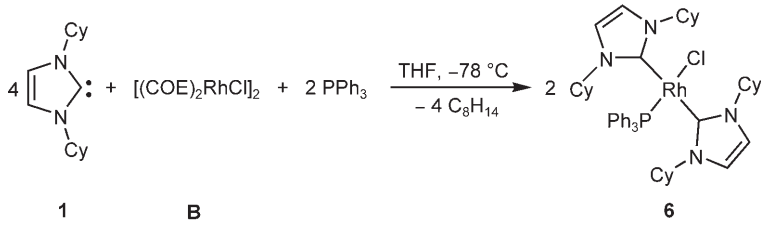
Scheme 3. Preparation of the NHC-rhodium complexes **4** and **5**.

This method is very limited, because neither a variation of the phosphine nor the preparation of dicarbene complexes is possible. We therefore chose a precursor, where more than one ligand can be substituted under mild conditions without forming a stable equilibrium and which is inert towards free carbenes.[19,22] All these requirements are fulfilled by the conveniently prepared bis[(μ-chloro)bis(cyclooctene)rhodium(I)]. The cyclooctene ligands can cleanly be substituted by another donor ligand. Because of the dimeric structure it is possible to introduce a third ligand along this route by cleavage of the bridging structure.

The cleavage of a dimeric COD and carbonylrhodium complex with a free carbene has been reported to be quantitative after several minutes at room temperature.[33] Bis[(μ-chloro)bis(cyclooctene)rhodium(I)] (**B**) was thus reacted at −78 °C in THF with two equivalents of 1,3-dicyclohexylimidazol-2-ylidene (**1**); after five minutes four equivalents of triphenylphosphine were added (Scheme 3). The reaction mixture was kept constantly below −20 °C, even during purification, to prevent the decomposition and ligand scrambling that was observed at room temperature in a parallel experiment. It must be noted that the free carbene was added before the phosphine as, due to the high σ-donor ability of the nucleophilic carbene, a fast and selective cleavage of the precursor is possible, which is not induced by the phosphine. If the phosphine was added before the carbene, a product mixture was obtained, which could not be separated. Complex **5** [*trans*-chloro(1,3-dicyclohexylimidazol-2-ylidene)bis(triphenylphosphite)rhodium(I)] was obtained according to the same procedure as for complex **4**, using triphenyl phosphite instead of triphenylphosphine.

The same procedure was used to obtain the dicarbene complex **6** at low temperatures, starting from the dimeric rhodium precursors with weakly coordinated cyclooctene ligands (Scheme 4). Only one signal set for both carbene ligands was obtained in the ^{13}C NMR spectra. Therefore, a doublet of doublets was obtained at 190.3 ppm for the carbene carbon with coupling constants of 40.7 Hz (C–Rh) and 15.4 Hz (C–P). In the ^{31}P NMR spectra, a doublet at 48.9 ppm with a P–Rh coupling constant of 227.9 Hz was observed.

The single crystal X-ray structure of complex **5** shows two independent enantiomeric molecules with an expected square-planar orientation of the metal center. The two phosphorus atoms are bent away from the chloride ligand towards the carbene-carbon atom, with an P1–Rh1–P2 angle of 174.56(4)° [*174.40(3)*°] (Figure 1). The heterocyclic five-membered ring of the carbene ligand is perpendicular to the plane encompassing the four ligands. The Rh1–C2 carbene bond length is 1.990(3) Å [*1.987(3)* Å] which in comparison to known COD rhodium complexes {[RhCl(ICy)(COD): 2.021 Å],[36] [RhCl(IMe-Bu)-(COD): 2.023 Å],[37] [RhCl(SIPr)(COD): *ca.* 2.054 Å][38]} and phosphine rhodium complexes {[RhCl(IMes)(PPh_3)$_2$; 2.051 Å,[39] [*trans*-(1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene)hydrido-bis(triphenylphosphine)rhodium(I): 2.068 Å][20]} is slightly shorter,[40] a result of the electron-accepting phosphite ligands. A much shorter rhodium-carbene bond length of 1.919 Å was published by Lappert in 1985 using the stronger σ-donor imidazolidin-2-ylidene ligand of chloro-*trans*-(4-isobutyl-1,3-dimethylimidazolidin-2-ylidene)bis(triphenylphosphine)rhodium(I).[41] The difference between both enantiomers of complex **5**, which presumably only exist in the solid state, is



Scheme 4. Preparation of the NHC-rhodium complex **6**.

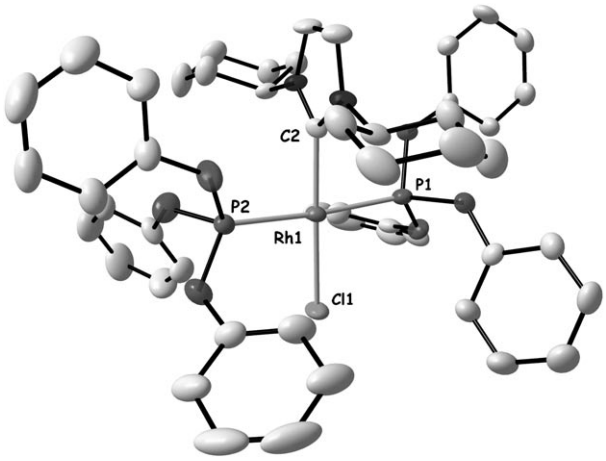


Figure 1. ORTEP style plot[42] of molecule A of compound **5** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Rh1–Cl1 2.3959(8)/*2.3950(8)*, Rh1–P1 2.2474(9)/*2.2392(9)*, Rh1–P2 2.2288(9)/*2.2385(9)*, Rh1–C2 1.990(3)/*1.987(3)*; Cl1–Rh1–P1 91.68(4)/*92.69(3)*, Cl1–Rh1–P2 93.61(3)/*92.81(3)*, Cl1–Rh1–C2 177.94(9)/*178.5(1)*, P1–Rh1–P2 174.56(4)/*174.40(3)*, P1–Rh1–C2 86.7(1)/*88.1(1)*, P2–Rh1–C2 88.1(1)/*86.4(1)*. The corresponding values for the second crystallographic independent molecule β are shown in *italics*.

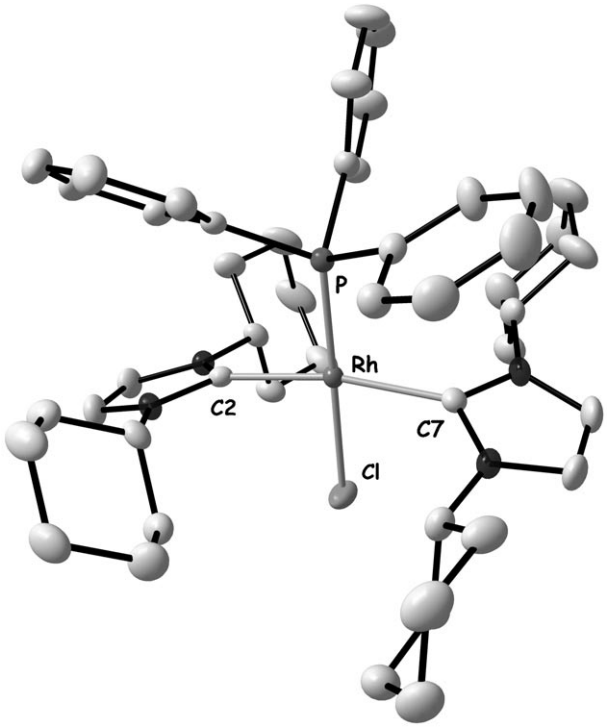


Figure 2. ORTEP style plot[42] of compound **6** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: RhCl 2.4200(5), Rh–P 2.1758(5), Rh–C2 2.033(2), Rh–C7 2.058(2); Cl–Rh–P 178.88(2), Cl–Rh–C2 83.02(5), Cl–Rh–C7 85.09(6), P–Rh–C2 96.09(5), P–Rh–C7 95.81(6), C2–Rh–C7 168.07(8).

the rotation direction of the bonded phenoxy groups. In the direction of the acute angle at the phosphorus all oxygen atoms are pointing in the same direction with the phenyl groups. Two phenoxy groups of each phosphite ligand are pointing towards the metal center, the third phenoxy group points away from the metal center. The angle for the third oxygen [132.4(2)°, 130.1(2)° and *131.7(2)*°, *130.8(2)*°] is larger than for the other two substituents [123.9(2)°, 129.3(2)°, 128.2(2)°, 124.0(3)° and *128.3(2)*°, *125.3(2)*°, *129.8(2)*°, *121.7(2)*°]. Details of the data collection and refinement of complexes **5** (Figure 1), **6**·(CH_2Cl_2) (Figure 2), and **8** (Figure 4) are summarized in the Supporting Information.

The solid-state structure of complex **6** (Figure 2) shows a pseudo-square-planar coordination of the metal center [C2–Rh–C7: 168.07(8)°], with a relatively strong deviation from an ideal square-planar coordination. The rhodium-carbene bond lengths [2.033(2) and 2.058(2) Å] are in the expected range for a rhodium-imidazol-2-ylidene bond length.[35,43,44] In this structure the steric bulk of the phenyl rings of the phosphine ligand have a large influence on the coordination of the NHC ligands.

All newly prepared carbene complexes (**2**, **4**–**6**) are quite reactive towards oxygen in solution, as is the related Wilkinson's catalyst (**3**). This instability is likely to arise from a phosphine dissociation equilibrium, which makes it possible for the oxygen to attack the low-coordinated rhodium center.

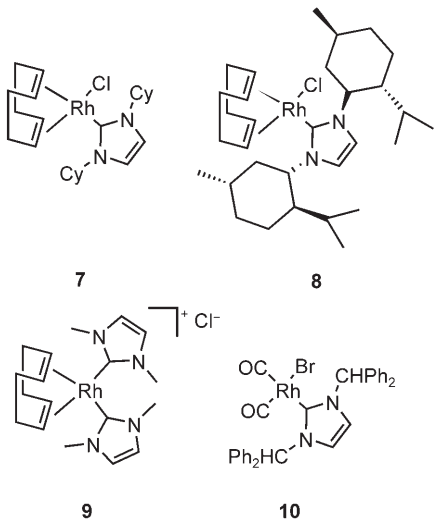


Figure 3. Rhodium carbene complexes **7–10**.

Much more stable are the complexes **7** and **8**, prepared by cleavage of the dimeric bis[(μ-chloro)bis(cyclooctene)rhodium(I)] with the corresponding free carbenes.[36,45] Complex **9** was prepared using the

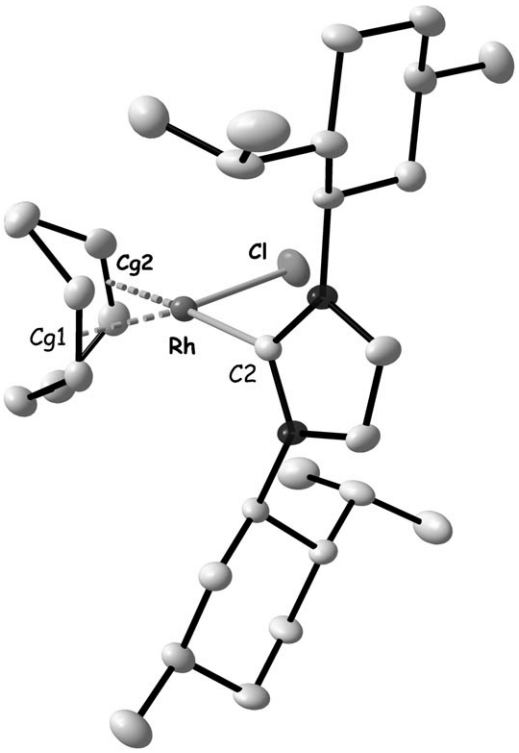


Figure 4. ORTEP style plot[42] of compound **8** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Rh–Cl 2.3832(5), Rh–Cg1 1.991, Rh–Cg2 2.093, Rh–C2 2.052(2); Cl–Rh–Cg1 174.43, Cl–Rh–Cg2 90.13, Cl–Rh–C2 89.89(4), Cg1–Rh–Cg2 86.98, Cg1–Rh–C2 93.34, Cg2–Rh–C2 175.71. Cg1 and Cg2 define the midpoints of the double bonds C31=C32 and C35=C36 in the COD ligand.

bis[μ-ethoxy-(η^4-1,5-COD)rhodium] route with the corresponding chloroimidazolium salt.[33] Complex **10** was prepared in the same way as complex **2**, using bis-[(μ-bromo)dicarbonylrhodium(I)] as precursor.[31]

Hydrogenation

In recent years, many research groups have published NHC-rhodium catalysts for the hydrogenation of 1-octene or cyclohexene.[19,20,45] However, no systematic optimization of the conditions has been reported. We attempted to optimize this reaction under economically viable conditions, for example, a relatively low H_2 pressure and a low quantity of phosphine. The hydrogenation of 1-octene for 3 h in toluene at 80 °C at a hydrogen pressure of 20 bar was chosen for an initial investigation (Scheme 1, Scheme 3, and Scheme 4, as well as Figure 3). The results for this reaction are shown in Table 1.

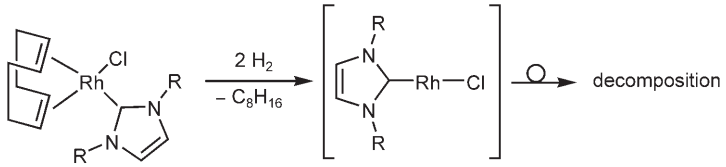
Table 1. Hydrogenation reaction of 1-octene to octane in toluene (80 °C, 20 bar H_2, 3 h).

Catalyst	Conversion [%][a]	Behavior
7	81	dec.
9	33	dec.
9[b]	21	dec.
2	1	stable
10	2	stable
4	61	stable
7[c]	64	stable
9[c]	61	stable

[a] Determined by ^{1}H NMR spectroscopy.
[b] THF was used as solvent instead of toluene.
[c] 4 equivs. of PPh_3 were added to the catalyst.

The tested rhodium complexes are not useful for the hydrogenation, because of decomposition during the reaction or low activity. We found that most of the time only the decomposition products or the formed elemental rhodium show decent to good activities in hydrogenation, after introduction periods of up to one hour. If the carbene-metal bond is presumed to be highly stable, then the olefinic chelating ligand may be reduced under these conditions to an alkane and acts as a leaving group. The resulting coordinated rhodium species cannot be stabilized by a donor substrate, such as THF, and decomposes afterwards to rhodium particles (Scheme 5).[47]

The carbonyl complexes **2** and **9** were found to be inert against hydrogen. This is surprising because in these complexes the second carbonyl ligand is only weakly coordinated and should be easily removed by other ligands such as phosphine.[35] We assume that the combination of a strong σ-donor (carbene) and a strong π-acceptor (CO) ligand largely deactivates the



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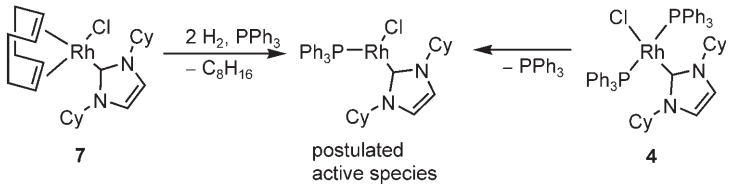
Scheme 5. Possible decomposition pathway of rhodium-COD complexes under hydrogenation reactions.



Scheme 6. Formation of the active catalytic species under hydrogenation conditions.

metal center, that a low-coordinate species can be stabilized, with no oxidative addition of hydrogen occurring. In general, carbon monoxide is an effective catalyst poison for hydrogenation with carbene rhodium complexes.

At the beginning of our work,[48] there were mainly two types of NHC-rhodium complexes known: complexes bearing a carbonyl ligand,[33] that are inactive in catalytic hydrogenation, and complexes where an olefin is coordinated to the metal center.[31,34,36] These olefin complexes have been found to be prone to decomposition during the catalytic cycle.[49] Because adverse electronic effects of an NHC/carbonyl combination can not be overcome easily, we sought another solution to stabilize the catalytically active rhodium intermediate. For the stabilization of the active species, phosphines seem to be the best choice, and these were added to the reaction mixture. We observed no decomposition of the neutral monocarbene complex **7** or the cationic dicarbene complex **6** after addition of 4 equivs. of triphenylphosphine (PPh_3). The phosphine acts as a weakly bound ligand and stabilizes the low-coordinate rhodium species of the active catalyst. The so-called active species should be a tricoordinated species (Scheme 6), with either a chloride, a phosphine and a carbene ligand, or two carbenes and a chloride ligand, as known from the active Wilkinson's catalyst (**3**).[2] Based on the results obtained with complex **4** under the same reaction conditions as with **7**, but without the addition of PPh_3 (Table 1) in each case the catalytically active species should be the tricoordinated species. In fact, the progress of the catalysis is nearly the same for complexes **7**, where 4 equivs. of PPh_3 were added, and **4**; except that for catalyst **4** nearly no induction period was noted.

Isomerization products were observed for all hydrogenation reactions of 1-octene. These isomerization products, 2-octene, 3-octene, 4-octene and 3-methyleneheptane, were only obtained if the reaction was stopped before completion. These isomerization products are also hydrogenated during the catalysis, but at a much slower rate than the 1-octene.[21] At the end of the reaction we found 2–4% of 3-methylheptane as a minor product. To suppress these minor products and to standardize the kinetic measurements to one unique substrate, we used cyclohexene as the substrate in the following optimization reactions.

Optimization of the Reaction Conditions for the Hydrogenation of Cyclohexene

Starting from precatalyst **7**, the active catalyst is formed in all optimization reactions *in situ*. The parameters of temperature, H_2 pressure, solvent, and added phosphine were optimized for the hydrogenation reaction of cyclohexene. All reactions were carried out with 20 mmoles of cyclohexene, 10 μmoles precatalyst **7** (0.05 mol%) in 3 mL of solvent.

Variation of the Solvent

For the hydrogenation the usual solvents ethanol and toluene were used; as strong donor solvents THF and acetonitrile were chosen. The reaction was carried out at 80 °C and 20 bar H_2 pressure. In addition 4 equivs. PPh_3 were used in relation to 0.05 mol% precatalyst (**7**). The results obtained by varying the solvents are depicted in Figure 5.

From the results it seems that ethanol is the best choice as compared to the other three solvents. The induction period is the shortest (0.5 h), and a quantitative conversion was observed after 2.5 h; this is nearly ten times faster than the same reaction carried out in toluene. Ethanol seems to be polar enough to stabilize ionic or polar transition states, but not such a

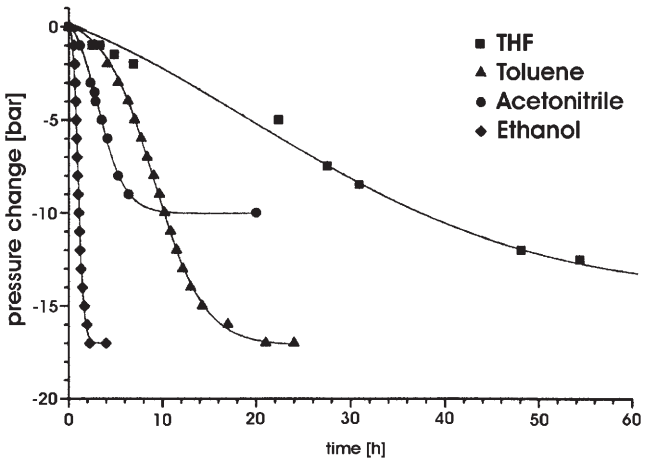


Figure 5. Hydrogenation of cyclohexene in different solvents (80 °C, 20 bar H_2, 4 equivs. PPh_3).

strong donor as to interfere with the catalytic cycle. The strong donor solvents THF and acetonitrile are not suitable for this reaction, because of the long reaction time (THF) and the low conversion (THF and acetonitrile). Without the addition of phosphine, the catalyst cannot be stabilized in these solvents, and quickly loses activity in the presence of phosphine, although at the end of the reaction no metal mirror was detected. The induction period for THF is the longest of all chosen solvents (90 min) and after 90 h only around 60% of the substrate is converted. In acetonitrile the induction period is relatively short (1 hour), but after 10 h the catalyst is no longer active and only a conversion of 50% of the substrate was obtained.

Table 2. Hydrogenation of cyclohexene at various temperatures in ethanol (20 bar H_2, 2 or 4 equivs. PPh_3).

Temp. [°C]	Induction period [min]	Reaction time [h]	Conversion [%]
40	330	32	100[a]
50	135	10	100[a]
60	70	10	100[a]
60	75	10	100[b]
80	30	2.5	100[b]
100	15	1.5	54[b]

[a] 2 equivs. of PPh_3 were added relative to the metal precursor.

[b] 4 equivs. of PPh_3 were added relative to the metal precursor.

Variation of the Temperature

Because toluene has a wider range for varying the temperature, it was used for the initial optimizations instead of ethanol. The reaction conditions (20 bar H_2, 4 equivs. PPh_3) were kept the same as for the solvent optimization. The results for the temperature dependency in toluene are shown in Figure 6. The corresponding tabulated data given in the Supporting Information. The dependence of the temperature on the reaction rate is very marked at low temperatures and becomes less intense at high temperatures. The reaction time is strongly influenced by the temperature; an increase of 20 °C decreases the reaction time by a factor of 2.5. At the same time, the catalyst is quickly deactivated at temperatures above 100 °C, which results in incomplete conversions. It is thus advisable to use temperatures within a small range around 80–100 °C.

The same reaction was carried out in ethanol, with nearly the same results for the temperature dependency (Table 2). The relative induction period decreases on increasing the temperature. A decrease in activity was also obtained in ethanol at temperatures above 80 °C, which results in only ~50% conversion of the starting material. The temperature region between 40 and 60 °C was also tested using two equivalents of PPh_3 instead of four. At low temperatures, the induction period is very sensitive to temperature changes. At 40 °C the conversion is extremely slow with an induction period of 330 min and a reaction time for full conversion of *ca.* 32 h. A reaction temperature between 50 and 80 °C seems to be the best choice for the hydrogenation of cyclohexene under the chosen reaction conditions, due to shorter induction times and better catalyst lifetimes.

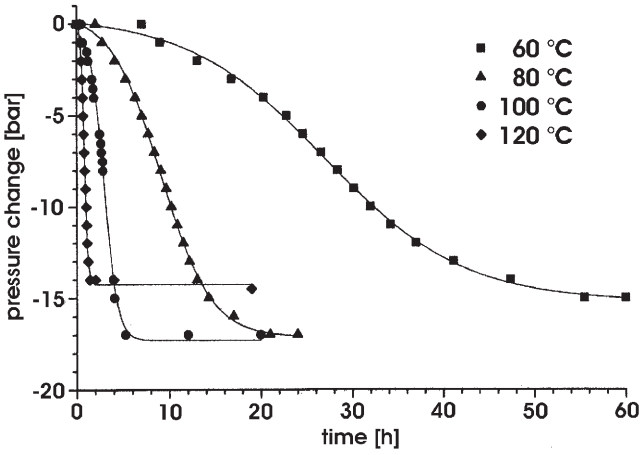


Figure 6. Hydrogenation of cyclohexene in toluene at different temperatures (20 bar H_2, 4 equivs. PPh_3).

Variation of the Pressure

The dependency of the reaction rate by varying the hydrogen pressure was investigated in ethanol at 60 °C with 4 equivs. PPh_3. The results are shown in Figure 7. The dependency of the reaction curve on the varying pressure is not so strong as compared to the variation of the temperature. Increasing the hydrogen pressure from 10 to 20 bar results in both a shorter induction period and shorter reaction times. A further increase to higher pressures results only in small changes. An important goal is to decrease the hydrogen pressure as much as possible, but to avoid a large fluctuation in the pressure over the whole reaction time. With this background a standard pressure of 20 bar appears ideal.

Variation of the Phosphine Concentration

The addition of a phosphine is necessary to prevent decomposition of the catalytically active species. Most likely one phosphine is coordinated to the active species throughout the catalytic cycle. On the other

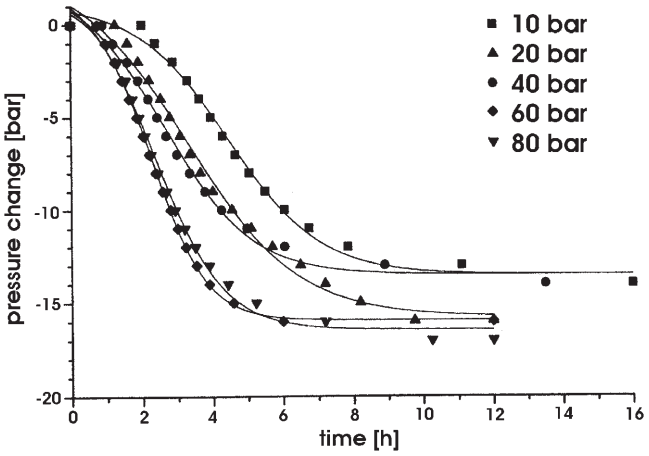


Figure 7. Hydrogenation of cyclohexene in ethanol using different hydrogen pressures (60 °C, 4 equivs. PPh_3).

hand, the phosphine can act as a donor ligand and hinder the catalytic cycle, by blocking the metal center. For this reason it is of great importance to use only a minimal amount of phosphine. The influence of the phosphine concentration is shown in Figure 8. All reactions were carried out at 60 °C in ethanol at 20 bar H_2 pressure.

Using more than 4 equivs. of PPh_3 decreases the activity of the catalyst; the reaction time increases, and full conversion was no longer obtained. No significant influence was noted for the reaction time and the conversion using less than 4 equivs. of PPh_3. One equivalent of phosphine is sufficient for this reaction to prevent decomposition of the catalyst. Accordingly, the active catalyst could indeed be the postulated three-membered species, shown in Scheme 6. Two equivalents of phosphine appear to be optimum for the hydrogenation, because it provides the shortest reaction time and prevents the loss of phosphine as a result of decomposition.

In summary, the best results were obtained for the hydrogenation of cyclohexene using precatalyst **7** in ethanol at a temperature of 60 °C and a hydrogen pressure of 20 bar with 2 equivs. PPh_3. The sigmoid reaction profile results from the initial formation of the precatalyst and active species, and at the end of the reaction the reduced hydrogen pressure and the small amount of remaining substrate minimize the activity of the catalyst.

Optimization of the Catalyst

The activity of **4**, which presumably generates the same active species as complex **7**, shows only moderate activity for a hydrogenation catalyst with turnover frequencies (TOF) of around 700 h^{-1} [mol product mol catalyst^{-1} hour^{-1}] at 60 °C under optimized conditions. The obtained TOF may be compared to that of Wilkinson's catalyst, where at room temperature TOFs of 1300 h^{-1} and at 60 °C 8000 h^{-1} are observed. This suggests that the carbene-metal bond is stable during the hydrogenation process. At room temperature the activity of the Wilkinson's catalyst **3** is around five times higher than for **4**; by increasing the temperature to 60 °C: catalyst **1** is a full order of magnitude more active than **4**. Indeed, complex **4** shows at high temperatures after some hours a considerable deactivation (Figure 9). All hydrogenation experiments were carried out with 20 mmol cyclohexene, 10 μmol catalyst (0.05 mol%) in 3 mL ethanol and a pressure of 20 bar.

It is well established that rhodium catalysts show the highest activity in hydrogenation reactions when the electron density at the metal center is decreased.[21] For example, the activity is drastically re-

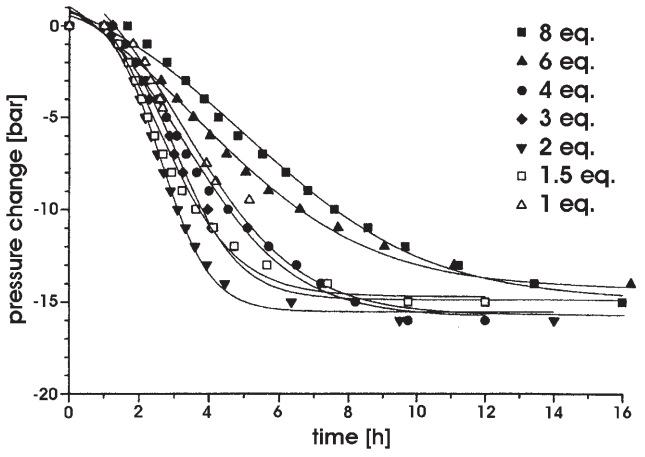


Figure 8. Hydrogenation of cyclohexene in ethanol using different amounts of triphenylphosphine (60 °C, 20 bar H_2).

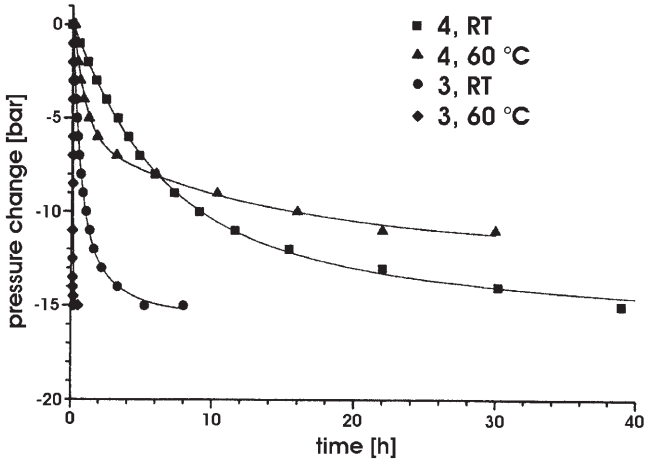


Figure 9. Hydrogenation of cyclohexene in ethanol using catalysts **3** and **4**.

duced if the triphenylphosphine groups of Wilkinson's catalyst (**3**) are substituted by tricyclohexylphosphine ligands.[50] However, low activity, resulting from catalyst decomposition, can occur when the electron density on the metal is reduced too much.[48] Currently, common systems are based on cationic complexes, where a chelating phosphine and an olefin or donor solvent are coordinated to the metal center. These complexes are produced *in situ*, but are not able to match the activity of the original Wilkinson's catalyst (**3**).[2,3,48]

The donor properties of imidazol-2-ylidene ligands and tricyclohexylphosphine are relatively similar; therefore a decrease in activity is obtained by substitution of triphenylphosphine with a carbene ligand. Another reason might be that the increased electron density at the metal center results in a stronger back bonding with the phosphine ligand, which is disadvantageous for the necessary dissociation of the phosphine. To obtain highly active catalysts, this effect of the higher electron density at the metal center, resulting from the carbene ligand, should be neutralized by the other coordinated ligands. The substitution of the coordinated chloride anion by a weakly coordinated anion, such as acetate or a non-coordinating anion results in increased activity. With this in mind complexes **5** and **6** were synthesized. In complex **6** a second triphenylphosphine ligand is substituted by a carbene, which results in a further decrease in activity (TOF = 429 h^{-1}), which is significantly lower in magnitude compared to the first substitution of a phosphine, where a decrease in the turnover frequency from 8000 (**3**) to 667 h^{-1} (**4**) occurs. With these examples we show that a carbene (strong σ-donor) has a negative influence on the rhodium-catalyzed hydrogenation (Figure 10).

To compensate for the negative influence of the carbene ligand the two triphenylphosphine ligands of complex **4** are substituted by triphenylphosphite ligands, forming complex **5**. This complex shows a turnover frequency of 400 h^{-1}, a disappointing result, which can be explained by the poorer dissociation abilities of the phosphite ligand. Although complex **4** has the highest starting activity, it shows considerable decomposition at higher temperatures over time.

The results for variation of the phosphine in the hydrogenation of cyclohexene are presented in Table 3, starting from complex **7** as the metal precursor. The active catalytic species was prepared *in situ* by addition of 2 equivalents of the corresponding phosphine or phosphite to the reaction mixture. The turnover frequencies given in Table 3 and Figure 11 are obtained at the turning point of the sigmoidal curve and correspond to the maximum turnover frequency for each reaction. The phosphite ligand [$P(OPh)_3$] is unsuitable for this reaction. Using 2 equivalents of $P(OPh)_3$, an induction period of 90 min was obtained,

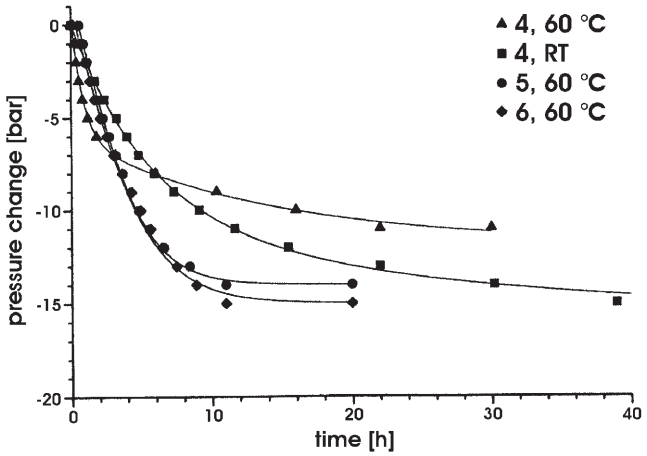


Figure 10. Hydrogenation of cyclohexene in ethanol using catalysts **4–6**.

Table 3. Hydrogenation of cyclohexene in ethanol using catalyst 7 (60 °C, 20 bar H_2, 2 equivs. phosphine).

Phosphine	Induction period [min]	Reaction time [h]	TOF [h^{-1}]	Conversion [%]
PPh_3	70	10	750	100
PCy_3	180	190	20	59
PPy_3	660	95	38	100
$P(OPh)_3$ [4 equivs.]	no reaction	20	no reaction	3
dppe, $NaBPh_4$ [1 equivs.]	35	1.25	3000	100

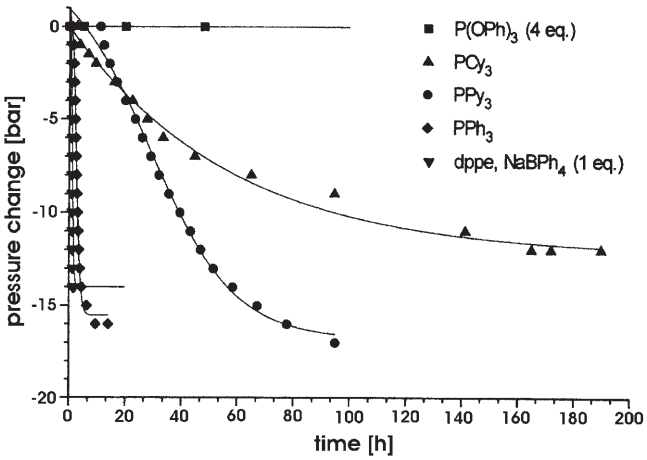


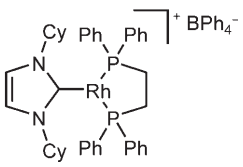
Figure 11. Hydrogenation of cyclohexene in ethanol using different phosphines.

and the reaction was completed after 3 h, however, elemental rhodium was found after the reaction. Thus, it can be assumed the conversion was quantitative because of the colloidal rhodium formed during the re-

action. If 4 equivalents of $P(OPh)_3$ are used for the hydrogenation reaction, no reaction could be obtained after 20 h. The reaction mixture was light yellow in color; an indication that possibly a potentially active catalyst was formed, such as for complex **5**, but because of the large excess of phosphite this species is deactivated by the additional coordination of another phosphite ligand. If tri-*N*-pyrrolylphosphine (PPy_3) used as the phosphine source, which also has good π-acceptor ability,[51] no decomposition was noted at full conversion. The turnover frequency of 40 h^{-1} is more than 10 times lower than in the reaction where triphenylphosphine was used. A much smaller activity was obtained using tricyclohexylphosphine, where a TOF of only 20 h^{-1} and a conversion of 59 % was observed.

Another possibility is to use chelating phosphines, for example, dppe (diphenylphosphinoethane). However, the described procedure seems not to be suitable, because during the reaction of the precursor with the phosphine an exchange/substitution of the olefin has to occur. The stabilization of the complex with the chelating phosphine has to result before decomposition of the precursor occurs. Another point is that the metal center with four coordinating ligands should be inactive in catalysis. Both problems were solved by the abstraction of the chloro ligand and substitution with a non-coordinating anion (BPh_4^-). The coordination of the phosphine is favored if the chloro ligand is substituted before the dissociation of the olefinic ligand appears. The proposed structure of the *in situ* formed complex is depicted in Scheme 7. In this species the electron density at the metal center is reduced, and the catalytic activity for the hydrogenation should be much higher.

Presumably the catalytic activity for this *in situ* complex (Scheme 7) results from decomposition products formed after an induction period of 90 min. If one equivalent of sodium tetraphenylborate ($NaBPh_4$) is added to the reaction mixture, no decomposition of the catalyst was obtained and the activity reaches values near to those of the original Wilkinson catalyst (**3**) with turnover frequencies of 3000 h^{-1}. Such high turnover frequencies of *ca.* 3000–4000 h^{-1} were only observed for much more expensive iridium-BAr^F carbene complexes {BAr^F = tetrakis[3,5-bis(trifluoromethylphenyl)]borate}.[21] This effect was not



Scheme 7. The putative active species formed by the reaction of **7** with dppe and $NaBPh_4$.

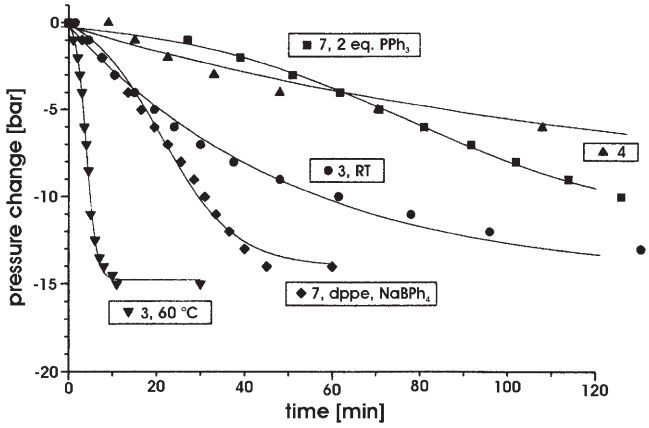


Figure 12. Comparison of different catalytic systems.

obtained by substitution of the chloride by acetate or in the presence of a non-coordinating ligand. Therefore the same results were obtained with the acetate analogue of complex **7** by addition of 2 equivalents of triphenylphosphine at 40 °C. The activity is also decreased compared to the standard conditions (2 equivs. PPh_3, 60 °C) for complex **7**, if 2 equivalents of PPh_3 and additional $NaBPh_4$ are reacted at 60 °C. At the end of the reaction small amounts of a yellow precipitate are found, which could explain the small loss in activity. Figure 12 depicts the most active systems. The induction period for each curve was removed for a better comparison of the activities.

Conclusions

With regard to hydrogenation, the mixed catalytic systems based on heterocyclic carbenes of the imidazolium type are relatively similar to the pure phosphine complexes in their catalytic behavior. However, an optimization of the activity is needed to fine-tune the electronic properties. The experiments carried out in this work clearly show that the metal-carbene bond is stable during the entire catalytic cycle, thus opening the possibility for the use of chiral carbenes as ligands for the use in related reactions. Our results demonstrate that NHC-derived catalysts can provide a relatively wide range of electronic properties of the catalytically active metal, and that they are flexible in their application.

Experimental Section

General Considerations

All reactions were carried out under an atmosphere of dry argon using standard Schlenk techniques or in an MBraun glove box containing less than 1 ppm of oxygen and water.

The 1,3-dicyclohexylimidazolium salt and the corresponding carbene **1**,[36] and bis[μ-ethoxy-(η^{4-}-1,5-COD)rhodium] were prepared according to the literature.[52] ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a JEOL-JMX-GX 270 or 400 MHz spectrometer at room temperature and referenced to the residual ^{1}H and ^{13}C signals of the solvents or 85% H_3PO_4 as an external standard (^{31}P). NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, hept. = heptet, m = multiplet, br. = broad signal. Coupling constants *J* are given in Hz. Elemental analyses were carried out by the Microanalytical Laboratory at the TU München. IR spectra were recorded using KBr discs at a Perkin–Elmer FTIR 1600 spectrometer.

cis-Carbonylchloro-bis(1,3-dicyclohexylimidazol-2-ylidene)rhodium(I) (2)

Bis[(μ-chloro)dicarbonylrhodium(I)] (139 mg, 0.36 mmol) was dissolved in a mixture of 3 mL of CH_2Cl_2 and 2 mL of THF, a solution of 1,3-dicyclohexylimidazol-2-ylidene (**1**) (334 mg, 1.44 mmol) in 15 mL of THF was slowly added. The solution was stirred for 40 min at room temperature and afterwards the solvent was removed under vacuum. The residue was washed with diethyl ether and purified by a silica column [CH_2Cl_2/methanol (10:1), R_f = *ca.* 0.4). The product was crystallized from a CH_2Cl_2/*n*-pentane solution to obtain yellow crystals; yield: 161 mg (0.26 mmol, 36%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (2H, s, NC*HCH*N), 7.12 (2H, s, NC*HCH*N), 4.64 (2H, br., *H*CNR$_2$), 4.32 (2H, m, *H*CNR$_2$), 2.24–1.17 (40H, m, C*H*$_2$); ^{13}C{^{1}H}-NMR (100.5 MHz, $CDCl_3$): δ = 191.0 (d, $^1J_{Rh-C}$ = 63.2 Hz, *C*O), 180.9 (d, $^1J_{Rh-C}$ = 42.8 Hz, N*C*N), 178.3 (d, $^1J_{Rh-C}$ = 45.7 Hz, N*C*N), 119.2, 118.0 (N*CHCH*N), 60.2, 58.3 (*C*NR$_2$), 35.6, 34.0, 25.3, 24.9, 24.4, 24.3 (*C*H$_2$). IR (KBr): ν(CO) = 1954 cm^{-1}; anal. calcd. for $C_{31}H_{48}N_4OClRh$ (631.10 g mol^{-1}): C, 58.99; H, 7.67; N, 8.88. Found: C, 59.69; H, 7.99; N, 8.84.

trans-Chloro(1,3-dicyclohexylimidazol-2-ylidene)-bis(triphenylphosphine)rhodium(I) (4)

Method A: A solution of 180 mg (0.25 mmol) bis[(μ-chloro)-bis(cyclooctene)rhodium(I)] in 20 mL of THF was cooled to −78 °C and a solution of 116 mg (0.50 mmol) 1,3-dicyclohexylimidazol-2-ylidene in 5 mL of THF was added. After 5 min a solution of 262 mg (1.00 mmol) triphenylphosphine in 5 mL of THF was added. A color change from brownish to orange occurred. After 1 h the solvent was removed in vacuo. The precipitate was washed with 10 mL of diethyl ether, and crystallized from toluene/*n*-pentane to obtain orange crystals. Yield: 233 mg (0.26 mmol, 52%).

Method B: To a solution of 186 mg (0.20 mmol) chloro-tris(triphenylphosphine)rhodium(I) in 20 mL of THF was added a solution of 47 mg (0.20 mmol) 1,3-dicyclohexylimidazol-2-ylidene in 2 mL of THF. The color changed from dark red to light orange during addition. After the reaction mixture was stirred additionally for 15 min the solvent was removed under vacuum and the residue was crystallized from a CH_2Cl_2/*n*-pentane mixture. Yield: 121 mg (0.14 mmol, 67%) of orange crystals. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.98–6.95 (30H, m), 6.60 (2H, s, NC*HCH*N), 5.09 (2H, m, *H*CNR$_2$), 1.64–0.86 (20H, m, C*H*$_2$); ^{13}C{^{1}H}-NMR (100.5 MHz, CD_2Cl_2): δ = 137.2 (d, *J* = 33.8 Hz, *C*P), 135.7 (d, *J* = 11.5 Hz, *C*CP), 135.3 (d, *J* = 10.7 Hz, *C*CP), 128.1, 127.4, 127.0, 126.9, 126.8, 126.7 (Ar), 116.5 (N*CHCH*N), 60.1 (*C*NR$_2$), 34.4, 32.8, 32.0, 26.3, 26.1, 25.8, 25.7, 25.4 (*C*H$_2$); ^{31}P{^{1}H}-NMR (161.8 MHz, CD_2Cl_2): δ = 33.4 (d, *J* = 155.2 Hz, PPh_3); anal. calcd. for $C_{51}H_{54}N_2P_2ClRh$ (980.24 g mol^{-1}): C 63.72, H 5.76, N 2.86; found: C 63.47, H 5.76, N 2.81.

trans-Chloro(1,3-dicyclohexylimidazol-2-ylidene)-bis(triphenylphosphite)rhodium(I) (5)

A solution of 240 mg (0.33 mmol) bis[(μ-chloro)bis(cyclooctene)rhodium(I)] in 20 mL of THF was cooled to −78 °C and a solution of 156 mg (0.67 mmol) 1,3-dicyclohexylimidazol-2-ylidene in 7 mL of THF was added. After 5 min a solution of 423 mg (1.36 mmol) triphenyl phosphite in 5 mL of THF was added. The solvent was removed under vacuum after 1 h. The precipitate was washed with 20 mL of diethyl ether and crystallized from a CH_2Cl_2/*n*-pentane solution as light yellow plates; yield: 87 mg (0.09 mmol, 13%). ^{1}H NMR (270 MHz, CD_2Cl_2): δ = 7.39–7.09 (30H, m), 6.97 (2H, s, NC*HCH*N), 5.12 (2H, m, *H*CNR$_2$), 1.86–0.72 (20H, m, C*H*$_2$); ^{13}C{^{1}H}-NMR (100.5 MHz, CD_2Cl_2): δ = 151.6 (arom. *C*O), 129.2, 123.9, 121.3 (Ar), 117.3 (N*CHCH*N), 59.2 (*C*NR$_2$), 33.5, 25.3, 25.2 (*C*H$_2$); ^{31}P{^{1}H}-NMR (109.4 MHz, CD_2Cl_2): δ = 112.6 [d, *J* = 256.6 Hz, P(OPh)$_3$]; anal. calcd. for $C_{51}H_{54}N_2P_2O_6ClRh$ (991.26 g mol^{-1}): C 61.79, H 5.49, N 2.83; found: C 61.68, H 5.70, N, 2.70.

Chloro-*trans*-bis(1,3-dicyclohexylimidazol-2-ylidene)(triphenylphosphine)rhodium(I) (6)

A solution of 257 mg (0.36 mmol) bis[(μ-chloro)bis(cyclooctene)rhodium(I)] in 20 mL of THF was cooled to −78 °C and a solution of 336 mg (1.45 mmol) 1,3-dicyclohexylimidazol-2-ylidene in 8 mL of THF was added. After 2 min a solution of 189 mg (0.72 mmol) triphenylphosphine in 4 mL of THF was added to the reaction mixture. The solvent was removed after 1 h under vacuum. The precipitate was washed with 20 mL of diethyl ether and crystallized from a CH_2Cl_2/diethyl ether mixture as orange crystals; yield: 311 mg (0.36 mmol, 50%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.38–7.31, 7.13–7.06 (15H, m), 6.69 (4H, s, NC*HCH*N), 5.43 (4H, m, *J* = 4.0 Hz, HCNR$_2$), 2.69, 1.85–1.09 (40H, m, CH$_2$); ^{13}C{^{1}H}-NMR (100.5 MHz, CD_2Cl_2): δ = 190.3 (dd, $^1J_{Rh-C}$ = 40.7 Hz, $^1J_{C-P}$ = 15.4 Hz, N*C*N), 141.0 (d, *J* = 35.3 Hz, *C*P), 132.4 (d, *J* = 10.7 Hz, *C*CP), 127.3, 127.2, 127.1 (Ar), 115.8 (N*CHCH*N), 58.7 (*C*NR$_2$), 34.8, 32.3, 26.1, 26.0, 25.7 (*C*H$_2$); ^{31}P{^{1}H}-NMR (109.4 MHz, CD_2Cl_2): δ = 49.8 (d, *J* = 227.9 Hz, PPh_3); anal. calcd. for $C_{48}H_{63}N_4PClRh{\cdot}CH_2Cl_2$ (950.28 g mol^{-1}): C 61.93, H 6.89, N 5.90; found: C 61.91, H 7.21, N 5.79.

1,3-Di-[(1*R*,2*S*,5*R*)-2-isopropyl-5-menthylcyclohex-1-yl]imidazolium Perchlorate (8a)

To a solution of 24.2 g (156 mmol) (1*R*,2*S*,5*R*)-1-amino-2-isopropyl-5-menthylcyclohexane[53] in 100 mL of toluene was added 2.3 g (78 mmol) paraformaldehyde and the mixture heated for 30 min at 40 °C. The reaction mixture was then cooled to 0 °C and 23.7 mL (78 mmol) 3.3 N perchloric acid were added dropwise with warming to room temperature. At room temperature 10.5 mL (92 mmol) of a 40% aqueous

glyoxal solution were added and afterward the reaction mixture was heated for 12 h at 35 °C. To the aqueous phase were added 50 mL of diethyl ether and 25 mL of a concentrated Na_2CO_3 solution. The white slime was washed twice with 20 mL of diethyl ether and was extracted once with 30 mL of CH_2Cl_2. The extract was dried over Na_2SO_4, and afterward the solvent was removed and the residue was recrystallized from a methanol/diethyl ether solution to afford light yellow crystals; yield: 7.8 g (17.6 mmol, 23 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 9.11$ (1 H, s, NC*H*N), 7.40 (2 H, s, NC*HCH*N), 4.28 (2 H, m, $J = 4.0$ Hz, *H*CNR$_2$), 2.08–1.04 (18 H, m, C*H* and CH_2), 0.92 (6 H, d, $J = 6.5$ Hz, CH_3), 0.84 [6 H, d, $J = 7.0$ Hz, CH(CH_3)$_2$], 0.75 [6 H, d, $J = 7.0$ Hz, CH(CH_3)$_2$]; ^{13}C{^{1}H}-NMR (100.5 MHz, $CDCl_3$): $\delta = 134.6$ (N*C*HN), 120.7 (N*CHCH*N), 62.5 (*C*-1), 47.2 (*C*-2), 42.7 (*C*-6), 33.5 (*C*-4), 31.9 (*C*-5), 26.7 (*C*(CH$_3$)$_2$), 23.6 (*C*-3), 21.6 (*C*H$_3$), 20.7, 15.5 [C(*C*H$_3$)$_2$]; anal. calcd. for $C_{23}H_{41}N_2O_4Cl$ (445.04 g mol^{-1}): C 62.07, H 9.29, N 6.29; found: C 62.06, H 9.23, N 6.12.

1,3-Di-[(1*R*,2*S*,5*R*)-2-isopropyl-5-menthylcyclohex-1-yl]imidazol-2-ylidene (8b)

To a mixture of 100 mL of liquid ammonia and 30 mL of THF, 1.34 g (3.00 mmol) 1,3-di-[(1*R*,2*S*,5*R*)-2-isopropyl-5-menthylcyclohex-1-yl]imidazolium perchlorate (**8a**) and 224 mg (9.30 mmol) of NaH were added. The solvent was removed under vacuum and the residue was extracted twice with 20 mL of *n*-hexane. The *n*-hexane was removed under vacuum to afford a pale yellow solid; yield: 1.02 g (2.95 mmol, 98 %); ^{13}C{^{1}H}-NMR (100.5 MHz, THF-d_8): $\delta =$ 212.7 (N*C*N), 117.2 (N*CHCH*N), 62.2 (*C*-1), 48.9 (*C*-2), 45.0 (*C*-6), 35.6 (*C*-4), 33.4 (*C*-5), 27.0 [*C*(CH$_3$)$_2$], 25.0 (*C*-3), 22.7 (*C*H$_3$), 21.4, 16.3 [C(*C*H$_3$)$_2$].

Chloro(η^4-1,5-cyclooctadiene)(1,3-di-[(1*R*,2*S*,5*R*)-2-isopropyl-5-menthylcyclohex-1-yl]imidazol-2-ylidene)rhodium(I) (8)

A solution of 247 mg (0.50 mmol) bis[μ-chloro(η^4-1,5-cyclooctadiene)rhodium(I)] in 20 mL of THF was cooled to −78 °C and a solution of 345 mg (1.00 mmol) 1,3-di-[(1*R*,2*S*,5*R*)-2-isopropyl-5-menthylcyclohex-1-yl]imidazol-2-ylidene (**8b**) in 10 mL of THF was added. The solution was stirred for 45 min and afterward the solvent was removed under vacuum. The precipitate was washed with 15 mL of diethyl ether and crystallized from a CH_2Cl_2/diethyl ether solution to afford yellow crystals; yield: 256 mg (0.46 mmol, 43 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.81$ (2 H, m, NC*HCH*N), 5.22 (1 H, m, *H*CNR$_2$), 5.05 (1 H, m, *H*CNR$_2$), 4.89 (2 H, m, C*H*), 3.43 (1 H, m, C*H*), 3.33 (1 H, m, C*H*), 2.80, 2.39–2.26, 1.93–0.85 (26 H, m, C*H*, CH_2), 1.03 (3 H, d, $J = 7.0$ Hz, CH_3), 0.95 (3 H, d, $J = 7.0$ Hz, CH_3), 0.93 [3 H, d, $J = 7.0$ Hz, CH(CH_3)$_2$], 0.88 [3 H, d, $J = 6.5$ Hz, CH(CH_3)$_2$], 0.83 [3 H, d, $J = 7.0$ Hz, CH(CH_3)$_2$], 0.80 [3 H, d, $J = 7.0$ Hz, CH(CH_3)$_2$]; ^{13}C{^{1}H}-NMR (100.5 MHz, $CDCl_3$): $\delta = 180.2$ (d, $J = 51.5$ Hz, N*C*N), 117.4, 117.2 (N*CHCH*N), 97.4 (d, $J =$ 6.8 Hz, *C*H), 97.1 (d, $J = 6.8$ Hz, *C*H), 67.5 (d, $J = 14.6$ Hz, *C*H), 66.7 (d, $J = 14.6$ Hz, *C*H), 62.0, 61.4 (*C*-1), 48.6, 47.9 (*C*-2), 45.8, 44.2 (*C*-6), 34.7, 34.6 (*C*-4), 33.3, 32.8 (*C*H$_2$), 32.8, 31.9 (*C*-5), 29.2, 28.4 (*C*H$_2$), 25.9, 25.1 [*C*(CH$_3$)$_2$], 24.5, 24.4 (*C*-3), 22.3, 22.2 (*C*H$_3$), 22.3, 21.9, 18.3, 17.6 [C(*C*H$_3$)$_2$]; anal. calcd. for $C_{31}H_{52}N_2ClRh$ (591.11 g mol^{-1}): C 62.99, H 8.87, N 4.74; found: C 62.82, H 9.07, N 4.59.

Catalytic Hydrogenation

The catalyst (0.05 mol %) was dissolved in 3 mL of the used solvent under argon. The substrate (20 mmol) was added in one portion. The resulting mixture was transferred to a Parr autoclave with glass tube inlet *via* syringe under argon. For an internal standard isooctane was chosen. The autoclave was filled and flushed three times with hydrogen before it was finally pressurized (10–80 bar). The autoclave was heated to the desired temperature and the pressure inside the autoclave was monitored digitally *via* a sensor (0–250 bar). The pressure was kept constant during the reaction in a range of ±5 bar.

Single Crystal X-Ray Structure Determination of Compounds 5, 6·(CH_2Cl_2), and 8

Crystallographic data are presented in the Supporting Information.[54] Preliminary examination and data collection were carried out on an area detecting system (Stoe & Cie, IPDS) at the window of a rotating anode (Nonius, FR591) and graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å). Data collections were performed at 193 K (Oxford Cryosystems). Raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure, for latent decay and absorption effects.[55] The structures were solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2\text{-}F_c^2)^2$ with SHELXL-97 weighting scheme. The final residual electron density maps showed no remarkable features. Programs used: SIR92,[56] SHELXL-97[57] and PLATON.[58]

5: As shown by Flack's parameter the crystal is twinned. A correction was applied using the SHELXL-97 procedure [TWIN/BASF = 0.75(2)]. The asymmetric unit cell contains two crystallographically independent molecules **A** and **B**. All hydrogen atom positions were calculated in ideal positions (riding model).

6·(CH_2Cl_2): The hydrogen positions were refined with individual isotropic displacement parameters.

8: The hydrogen positions were refined with individual isotropic displacement parameters. The correct enantiomere is proved by Flack's parameter $\varepsilon = -0.036(13)$.

Supporting Information

Additional graphs and table for the hydrogenation experiments, details of the X-ray crystallographic data and refinement of complexes **5**, **6**·(CH_2Cl_2), and **8** are given.[59]

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References

[1] N-Heterocyclic Carbenes, Part 51. For part 50, see ref.[59].

[2] a) J. A. Osborn, F. H. Jardine, J. F. Young, G. Wilkinson, *J. Chem. Soc. (A)* **1966**, 1711–1732; b) G. Wilkinson, *German Patent* DE 1816063 A1, **1969**.

[3] a) F. H. Jardine, J. A. Osborn, G. Wilkinson, *J. Chem. Soc. (A)* **1967**, 1574–1578; b) S. Montelatici, A. van der Ent, J. A. Osborn, G. Wilkinson. *J. Chem. Soc. (A)* **1968**, 1054–1058; c) P. Kalk, R. Poilblanc, A. Gaset, (Produits Chimiques Ugine Kuhlmann), *Belgium Patent* BE 871814 A1, **1979**; *French Patent* FR 2408388 A1, **1979**; d) J. C. Briggs, G. Dyer, (Johnson, Matthey PLC), *British Patent* GB 2100260 A, **1982**; e) J. Kralik, C. Muermann, S. Lehmann, E. Poetsch, V. Meyer, W. Binder, (Merck Patent GmbH), *German Patent* DE 102004036068 A1, **2005**.

[4] R. N. Haszeldine, R. V. Parish, D. J. Parry, *J. Organomet. Chem.* **1967**, *9*, P13-P14.

[5] D. A. Evans, G. C. Fu, A. H. Hoveyda, *J. Am. Chem. Soc.* **1992**, *114*, 6671–6679.

[6] For direct hydroboration see: a) D. A. Evans, G. C. Fu, *J. Am. Chem. Soc.* **1991**, *113*, 4042–4043; b) J. A. Brinkman, T. T. Nguyen, J. R. Sowa Jr., *Org. Lett.* **2000**, *2*, 981–983; c) C. Bianchini, P. Barbaro, M. Macchi, A. Meli, F. Vizza, *Helv. Chim. Acta* **2001**, *84*, 2895–2923.

[7] For direct hydrogenation see: a) G. Stork, D. E. Kahne, *J. Am. Chem. Soc.* **1983**, *105*, 1072–1073; b) R. H. Crabtree, M. W. Davis, *Organometallics* **1983**, *2*, 681–682.

[8] a) W. A. Herrmann, M. Elison, J. Fischer, C. Köcher, G. R. J. Artus, *Angew. Chem.* **1995**, *107*, 2602–2605; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2371–2374; b) M. Regitz, *Angew. Chem.* **1996**, *108*, 791–794; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 725–728; c) W. A. Hermann, C. Köcher, *Angew. Chem.* **1997**, *109*, 2256–2282; *Angew. Chem,. Int. Ed. Engl.* **1997**, *31*, 2162–2187; d) A. J. Arduengo III, R. Krafczyk, *Chem. Unserer Zeit* **1998**, *32*, 6–14; e) J. E. L. Dullius, P. A. Z. Suarez, S. Einloft, R. F. de Souza, J. Dupont, J. Fischer, A. De Cian, *Organometallics* **1998**, *17*, 815–819; f) A. J. Arduengo III, *Acc. Chem. Res.* **1999**, *32*, 913–921.

[9] Phosphine ligands in homogeneous catalysis: a) G. W. Parshall, S. Ittel, in: *Homogenous Catalysis*, John Wiley and Sons, New York, **1992**; b) L. H. Pignolet (Ed.), in: *Homogenous Catalysis with Metal Phosphine Complexes*, Plenum, New York, **1983**.

[10] a) W. A. Herrmann, T. Weskamp, V. P. W. Böhm, *Adv. Organomet. Chem.* **2001**, *48*, 1–69; b) W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1343–1363; *Angew. Chem. Int. Ed.* **2002**, *41*, 1290–1309; c) S. P. Nolan (Ed.), in: *N-heterocyclic Carbenes in Synthesis* Wiley-VCH, Weinheim, **2006**; d) F. Glorius (Ed.), in: *Topics in Organometallic Chemistry*, Vol. 21, *N-heterocyclic Carbenes in Transition Metal Catalysis*, Springer, Berlin/Heidelberg, **2007**.

[11] a) B. Cetinkaya, I. Özdemir, P. H. Dixneuf, *J. Organomet. Chem.* **1997**, *534*, 153–158, b) J. Huang, S. P. Nolan, *J. Am. Chem. Soc.* **1999**, *121*, 9889–9890; c) C. Zhang, J. Huang, M. L. Trudell, S. P. Nolan, *J. Org. Chem.* **1999**, *64*, 3804–3805; d) H. M. Lee, S. P. Nolan, *Org. Lett.* **2000**, *2*, 1307–1310; e) V. P. W. Böhm, C. W. K. Gstöttmayer, T. Weskamp, W. A. Herrmann, *J. Organomet. Chem.* **2000**, *595*, 186–190; f) D. McGuiness, K. J. Cavell, *Organometallics* **2000**, *19*, 741–748; g) G. A. Grasa, S. P. Nolan, *Org. Lett.* **2001**, *3*, 119–122; h) S. Gründemann, M. Albrecht, J. A. Loch, J. W. Faller, R. H. Crabtree, *Organometallics* **2001**, *20*, 5485–5488; i) S. Caddick, F. G. N. Cloke, J. K. B. Clentsmith, G. P. B. Hitchcock, D. McKerrecher, L. R. Titcomb, M. R. V. Williams, *J. Organomet. Chem.* **2001**, *617*, 635–639; j) L.-C. Campeau, P. Thansandote, K. Fagnou, *Org. Lett.* **2005**, *7*, 1857–1860; k) F. E. Hahn, *Angew. Chem.* **2006**, *118*, 1374–1378; *Angew. Chem. Int. Ed.* **2006**, *45*, 1348–1352, and references cited therein; l) T. Scherg, S. K. Schneider, G. D. Frey, J. Schwarz, E. Herdtweck, W. A. Herrmann, *Synlett* **2006**, 2894–2907; m) E. A. B. Kantchev, C. J. O'Brien, M. G. Organ, *Aldrichimica Acta* **2006**, *39*, 97–111, and references cited therein; n) C. J. O'Brien, E. A. B. Kantchev, C. Valente, N. Hadei, G. A. Chass, A. Lough, A. C. Hopkinson, M. G. Organ, *Chem. Eur. J.* **2006**, *12*, 4743–4748.

[12] a) J. Huang, G. A. Grasa, S. P. Nolan, *Org. Lett.* **1999**, *1*, 1307–1309; b) S. R. Stauffer, S. Lee, J. P. Stambuli, S. I. Hauck, J. F. Hartwig, *Org. Lett.* **2000**, *2*, 1423–1426; c) G. A. Grasa, M. S. Viciu, J. Huang, S. P. Nolan, *J. Org. Chem.* **2001**, *66*, 7729–7737; d) L. D. Field, B. A. Messerle, K. Q. Vuong, P. Turner, *Organometallics* **2005**, *24*, 4241–4250.

[13] a) A. C. Chen, L. Ren, A. Decken, C. M. Crudden, *Organometallics* **2000**, *19*, 3459–3461; b) A. C. Chen, D. P. Allen, C. M. Crudden, R. Wang, A. Decken, *Can. J. Chem.* **2005**, *83*, 943–957.

[14] a) J. E. Hill, T. A. Nile, *J. Organomet. Chem.* **1977**, *137*, 293–300; b) M. Poyatos, E. Mas-Marza, J. A. Mata, M. Sanau, E. Peris, *Eur. J. Inorg. Chem.* **2003**, 1215–1221; c) G. Rivera, R. H. Crabtree, *J. Mol. Catal. A: Chem.* **2004**, *222*, 59–73; d) J. Y. Zeng, M.-H. Hsieh, H. M. Lee, *J. Organomet. Chem.* **2005**, *690*, 5662–5671.

[15] a) J. Huang, E. D. Stevens, S. P. Nolan, J. L. Petersen, *J. Am. Chem. Soc.* **1999**, *121*, 2674–2678; b) M. Scholl, T. M. Trnka, J. P. Morgan, R. H. Grubbs, *Tetrahedron Lett.* **1999**, *40*, 2247–2250; c) L. Ackermann, A. Fürstner, T. Weskamp, F. J. Kohl, W. A. Herrmann, *Tetrahedron Lett.* **1999**, *40*, 4787–4790; d) J. Huang, H.-J. Schanz, E. D. Stevens, S. P. Nolan, *Organometallics* **1999**, *18*, 2370–2375; e) L. Jafarpour, H.-J. Schanz, E. D. Stevens, S. P. Nolan, *Organometallics* **1999**, *18*, 5416–5419; f) M. Scholl, S. Ding, C. W. Lee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 953–956; g) A. K. Chatterjee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 1751–1753; h) D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–92, and references cited therein; i) T. M. Trnka, R. H. Grubbs, *Acc. Chem. Res.* **2001**, *34*, 18–29.

[16] a) D. J. Cardin, M. J. Doyle, M. F. Lappert, *J. Chem. Soc., Chem. Commun.* **1972**, 927–928; b) D. J. Cardin,

M. J. Doyle, M. F. Lappert, *J. Organomet. Chem.* **1974**, *65*, C13-C16; c) M. J. Doyle, M. F. Lappert, *J. Chem. Soc., Chem. Commun.* **1974**, 679–680; d) M. J. Doyle, M. F. Lappert, G. M. McLaughlin, J. McMeeking, *J. Chem. Soc., Dalton Trans.* **1974**, 1494–1501.
[17] M. F. Lappert, R. K. Maskell, *J. Organomet. Chem.* **1984**, *264*, 217–228.
[18] a) M. J. Doyle, M. F. Lappert, P. L. Pye, P. Terreros, *J. Chem. Soc., Dalton Trans.* **1984**, 2355–2364; b) M. F. Lappert, *J. Organomet. Chem.* **1988**, *358*, 185–213.
[19] a) D. P. Allen, C. M. Crudden, L. A. Calhoun, R. Wang, *J. Organomet. Chem.* **2004**, *689*, 3203–3209; b) D. P. Allen, C. M. Crudden, L. A. Calhoun, R. Wang, A. Decken, *J. Organomet. Chem.* **2005**, *690*, 5736–5746.
[20] W. A. Herrmann, D. Baskakov, E. Herdtweck, S. D. Hoffmann, T. Bunlaksananusorn, F. Rampf, L. Rodefeld, *Organometallics* **2006**, *25*, 2449–2456.
[21] L. D. Vazquez-Serrano, B. T. Owens, J. M. Buriak, *Inorg. Chim. Acta* **2006**, *359*, 2786–2797.
[22] S. Douglas, J. P. Lowe, M. F. Mahon, J. E. Warren, M. K. Whittlesey, *J. Organomet. Chem.* **2005**, *690*, 5027–5035.
[23] A. Igau, H. Grützmacher, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc.* **1988**, *110*, 6463–6466.
[24] a) A. J. Arduengo, III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361–363; b) A. J. Arduengo, III, J. R. Goerlich, W. J. Marshall, *J. Am. Chem. Soc.* **1995**, *117*, 11027–11028.
[25] W. A. Herrmann, J. Schütz, G. D. Frey, E. Herdtweck, *Organometallics* **2006**, *25*, 2437–2448, and references cited therein.
[26] a) N. M. Scott, R. Dorta, E. D. Stevens, A. Correa, L. Cavallo, S. P. Nolan, *J. Am. Chem. Soc.* **2005**, *127*, 3516–3526; b) M. Moser, B. Wucher, D. Kunz, F. Rominger, *Organometallics* **2007**, *26*, 1024–1030; c) J. M. Praetorius, M. W. Kotyk, J. D. Webb, R. Wang, C. M. Crudden, *Organometallics* **2007**, *26*, 1057–1061.
[27] K. Öfele, *J. Organomet. Chem.* **1968**, *12*, P42-P43.
[28] H.-W. Wanzlick, H.-J. Schönherr, *Angew. Chem.* **1968**, *80*, 154; *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 141–142.
[29] a) H. M. J. Wang, I. J. B. Lin, *Organometallics* **1998**, *17*, 972–975; b) S. Saravanakumar, A. I. Oprea, M. K. Kindermann, P. G. Jones, J. Heinicke, *Chem. Eur. J.* **2006**, *12*, 3143–3154; c) H. Türkmen, O. Şahin, O. Büyükgüngör, B. Cetinkaya, *Eur. J. Inorg. Chem.* **2006**, 4915–4921; d) D. Baskakov, W. A. Herrmann, E. Herdtweck, S. D. Hoffmann, *Organometallics* **2007**, *26*, 626–632.
[30] X.-Y. Yu, B. O. Patrick, B. J. James, *Organometallics* **2006**, *25*, 2359–2363.
[31] C. Köcher, W. A. Herrmann, *J. Organomet. Chem.* **1997**, *532*, 261–265.
[32] G. D. Frey, C. F. Rentzsch, D. von Preysing, T. Scherg, M. Mühlhofer, E. Herdtweck, W. A. Herrmann, *J. Organomet. Chem.* **2006**, *691*, 5725–5738, and references cited therein.
[33] W. A. Herrmann, M. Elison, J. Fischer, C. Köcher, G. R. J. Artus, *Chem. Eur. J.* **1996**, *2*, 772–780.
[34] a) W. A. Herrmann, L. J. Goossen, C. Köcher, G. R. J. Artus, *Angew. Chem.* **1996**, *108*, 2980–2982; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2805–2807; b) W. A. Herrmann, L. J. Goossen, G. R. J. Artus, C. Köcher, *Organometallics* **1997**, *16*, 2472–2477.
[35] A. Neveling, G. R. Julius, S. Cronje, C. Esterhuysen, H. G. Raubenheimer, *J. Chem. Soc., Dalton Trans.* **2005**, 181–192.
[36] W. A. Herrmann, C. Köcher, L. J. Goossen, G. R. J. Artus, *Chem. Eur. J.* **1996**, *2*, 1627–1636.
[37] K. H. Park, S. Y. Kim, S. U. Son, Y. K. Chung, *Eur. J. Org. Chem.* **2003**, 4341–4345.
[38] S. I. Lee, S. Y. Park, J. H. Park, I. G. Jung, S. Y. Choi, Y. K. Chung, B. Y. Lee, *J. Org. Chem.* **2006**, *71*, 91–96.
[39] G. A. Grasa, Z. Moore, K. L. Martin, E. D. Stevens, S. P. Nolan, V. Paquet, H. Lebel, *J. Organomet. Chem.* **2002**, *658*, 126–131.
[40] E. Cetinkaya, P. B. Hitchcock, M. F. Lappert, D. B. Shaw, K. Spyropoulos, N. J. W. Warhurst, *J. Organomet. Chem.* **1993**, *459*, 311–317.
[41] A. W. Coleman, P. B. Hitchcock, M. F. Lappert, R. K. Maskell, J. H. Müller, *J. Organomet. Chem.* **1985**, *296*, 173–196.
[42] K. Brandenburg, *Diamond, Version 3.1d*, Crystal Impact GbR, Bonn, Germany, **2006**.
[43] W. A. Herrmann, J. Fischer, K. Öfele, G. R. J. Artus, *J. Organomet. Chem.* **1997**, *530*, 259–262.
[44] J. Huang, E. D. Stevens, S. P. Nolan, *Organometallics* **2000**, *19*, 1194–1197.
[45] A detailed structure discussion for complex **8** will be published soon: S. K. Schneider, G. D. Frey, J. Eppinger, M. Steinbeck, E. Herdtweck and W. A. Herrmann, in preparation.
[46] M. F. Lappert, in: *Transition Metal Chemistry*, (Ed.: A. Müller, E. Diemann), Verlag Chemie, Heidelberg, **1981**, pp. 287–298.
[47] Decomposition mechanism similar to that in ref.[2]
[48] M. Steinbeck, *PhD Thesis*, Technische Universität München, Germany, **1998**.
[49] C. Köcher, *PhD Thesis*, Technische Universität München, Germany, **1997**.
[50] a) W. Strohmeier, W. Rehder-Stirnweiss, *J. Organomet. Chem.* **1969**, *18*, P28-P29; b) W. Strohmeier, W. Rehder-Stirnweiss, *Z. Naturforsch., B: Chem. Sci.* **1971**, *26*, 61–62.
[51] K. G. Moloy, J. L. Petersen, *J. Am. Chem. Soc.* **1995**, *117*, 7696–7710.
[52] J. Chatt, L. M. Venanzi, *J. Chem. Soc.,* **1957**, 4735–4741.
[53] a) O. Wallach, *Liebigs Ann. Chem.* **1913**, *397*, 181–219; b) H. Feltkamp, F. Koch, T. N. Thanh, *Liebigs Ann. Chem.* **1967**, *707*, 78–86.
[54] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC-641591 (**5**), CCDC-641592 [**6**·(CH_2Cl_2)], and CCDC-641593 (**8**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44)1223–336–033; e-mail: deposit@ccdc.cam.ac.uk].
[55] *IPDS Operating System, Version 2.8;* Stoe & Cie. GmbH, Darmstadt, Germany, **1997**.

[56] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *SIR92*, *J. Appl. Crystallogr.* **1994**, *27*, 435–436.
[57] G. M. Sheldrick, *SHELXL-97*, Universität Göttingen, Germany, **1998**.
[58] A. L. Spek, *PLATON – A Multipurpose Crystallographic Tool*, Utrecht University, The Netherlands, **2001**.
[59] A. D. Tanase, G. D. Frey, E. Herdtweck, S. D. Hoffmann, W. A. Herrmann, *J. Organomet. Chem.* **2007**, *692*, doc: 10.1016/j.jorganchem.2007.03.020.

