Rhodium(III) Complexes Containing C4-Bound N-Heterocyclic Carbenes: Synthesis, Coordination Chemistry, and Catalytic Activity in Transfer Hydrogenation

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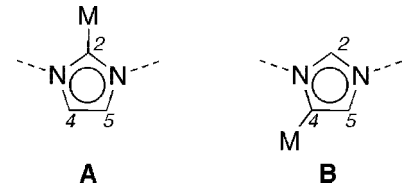
Direct metalation of C2-protected diimidozolium salts with $RhCl_3$ or $[RhCl(cod)]_2$ and KI afforded a series of new rhodium(III) complexes with abnormally C4-bound, *cis*-chelating NHC ligands. The complexes were isolated as dimetallic species containing two $(\mu^2\text{-I})_3$-bridged rhodium(III) centers. In the presence of coordinating ligands such as CH_3CN, PPh_3, or dppe, the dimeric structure is readily cleaved and yields monometallic complexes. Crystallographic analysis of representative structures indicates a higher *trans* influence of abnormally C4-bound carbenes as compared to normal NHCs. The exceptionally strong donor ability of carbenes in such a C4 coordination mode increases the catalytic activity of the rhodium center and allows for efficient transfer hydrogenation of ketones in *i*PrOH/KOH.

Introduction

N-Heterocyclic carbenes (NHCs) have emerged as a very powerful class of ligands in organometallic chemistry and homogeneous catalysis.[1] Most of the reported NHCs are derived from imidazolium salts and bind the metal via the C2 carbon (Chart 1) and hence comprise a classical carbene bonding mode.[2] Recently, it has been reported that, under specific conditions, metalation of imidazolium salts takes place at the C4 or C5 position (Chart 1).[3] These so-called abnormal carbenes are exceptionally basic ligands with a higher donor power than their C2-bound analogues.[4,5] The first evidence has been provided for the beneficial impact of such C4-bound carbenes on the catalytic activity of the coordinated metal center.[5,6]

Chart 1. Normally C2-Bound Imidazolylidene Ligand (A) and Abnormally C4-Bound Carbene Ligand (B)



Theoretical investigations on the reactivity of imidazolium salts have indicated that formation of the free C4-carbene is less favored than the C2-carbene by approximately 80 kJ mol^{-1}.[7] Similarly, the pK_a of the C4-bound hydrogen has been calculated to be about 5−8 pK_a units higher[8] than that of the hydrogen attached to C2.[9] Despite these drawbacks, various methods have been established for installing the metal selectively at the C4

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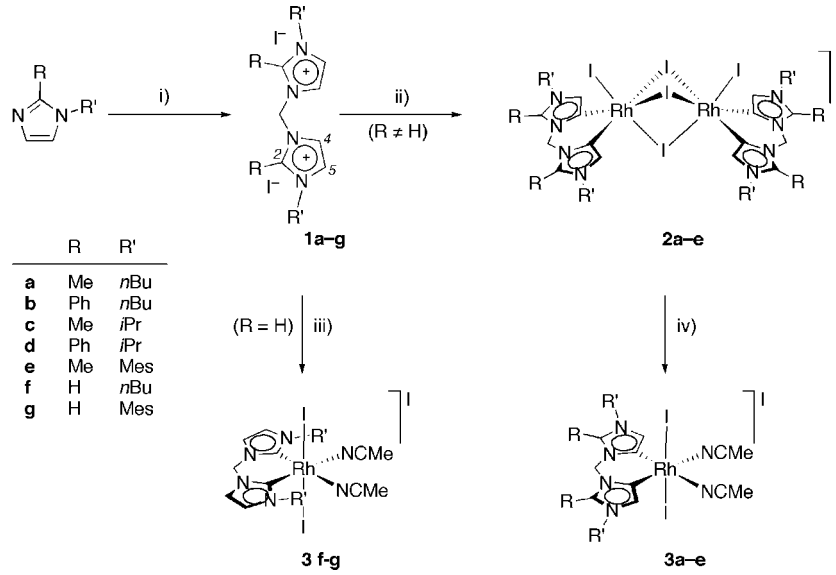
Scheme 1. Synthesis of C2- and C4-Bound Dicarbene Rhodium(III) Complexes 3a−g[a]



	R	R'
a	Me	*n*Bu
b	Ph	*n*Bu
c	Me	*i*Pr
d	Ph	*i*Pr
e	Me	Mes
f	H	*n*Bu
g	H	Mes

[a] Reagents and conditions: (i) CH_2I_2, toluene, reflux; (ii) $[RhCl(cod)]_2$, NaOAc, KI, MeCN, reflux, *or* $RhCl_3$, NaOAc, MeCN, reflux, then NaI, acetone; (iii) $[RhCl(cod)]_2$, NaOAc, KI, MeCN, 60 °C; (iv) MeCN, RT.

position.[10] Some approaches are highly reagent-specific such as oxidative C−H bond activation,[11] rearrangement of C2-imidazolylidenes,[12] and anion-triggered differentiation between the C2−H and C4−H positions.[3,13] A more general access to C4-bound NHC complexes consists of quaternizing an anionic azolyl ligand[14] or using halide-functionalized imidazolium salts for oxidative addition.[15] A particularly useful route was introduced by Crabtree and co-workers and relies on the protection of the imidazolium C2 position,[4] typically by an alkyl or aryl substituent.[16] On the basis of this approach, we have recently prepared chelating C4-bound dicarbene palladium complexes.[5] Owing to the rigid *cis*-chelation of the dicarbene and the strong donor power of the ligand, these complexes are significantly better catalysts for olefin hydrogenation than their C2-bound analogues. These results stimulated our interest in extending the abnormal carbene concept to different catalytic processes where bond activation requires electron-rich metal centers.[17] Here we report on the synthesis and (catalytic) reactivity of the first rhodium(III) complexes bound to C4-coordinating N-heterocyclic dicarbenes. Most strikingly, the catalytic activity of the rhodium center in transfer hydrogenation is markedly increased when bound to C4- rather than C2-coordinating carbenes. These results underline the high potential of this class of carbene ligands in catalysis.

Results and Discussion

Synthesis of the Ligands and Rhodium(III) Complexes. The C2-protected diimidazolium salts **1a**−**e** were prepared from the corresponding 1,2-disubstituted imidazoles[18] by condensation with CH_2I_2 in an apolar solvent (Scheme 1).[19] Complexation of these ligand precursors was accomplished according to a procedure similar to the one established for the metalation of C2-bonding dicarbene precursors.[20] Reaction of the C2-protected diimidazolium salts **1a**−**e** with $[RhCl(cod)]_2$ (cod = 1,5-cyclooctadiene) in the presence of iodide ions and acetate as a mild base induced C−H bond activation and metalation at the C4 position (Scheme 1).[21] Purification by column chromatography and subsequent recrystallization afforded the rhodium(III) complexes **2a**−**e** as dimeric tris-(μ^2-iodo)-bridged species. Notably, no methyl C−H bond activation was detected when using ligand **1a**, **1c**, or **1e**. This contrasts with previous metalation results using Ag(I) and Ir(III) precursors, where

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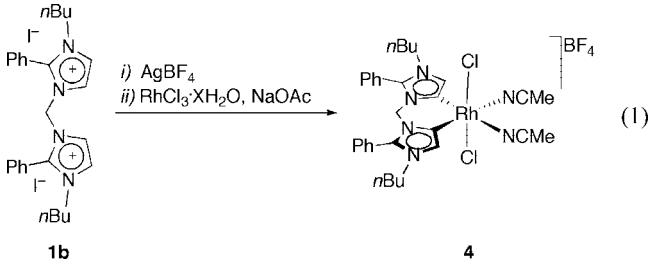
(21) Formally, metalation of the diimidazolium precursors **1** occurs at the C5 position. For reasons of consistency with the literature, the atom numbering as shown in Chart 1 is adopted here.

C_{alkyl}−H activation and carbene formation are competitive processes.[16a,b]

While some of the metalation yields were rather low, they were consistently higher when the complexation was performed in air rather than under rigorous argon atmosphere. This suggests a cascade-type mechanism, in which iodide is oxidized to iodine, perhaps mediated by oxygen, followed by I_2 oxidation of the metal center to the rhodium(III) species. Indeed, performing the metalation with commercially available $RhCl_3$ as rhodium(III) precursor induced straightforward complexation and afforded the dicarbene complex **4**, which was converted into complex **2b** by halide metathesis (eq 1). Starting directly from rhodium(III) precursors provides a simplified metalation procedure, and in addition, the product is formed in higher purity and yield as compared to metalation with $[RhCl(cod)]_2$. These results suggest that the cascade redox process proposed in the formation of **2** from rhodium(I) salts occurs *prior* to metal−carbene bond formation. This hypothesis is further supported by the fact that metalation in the absence of KI proceeded sluggishly, while replacing KI by molecular I_2 had no negative effect on the yield.



(1)

All dimeric complexes **2** are stable toward air and moisture, and they are moderately soluble in chlorinated solvents and THF. The ^{1}H NMR spectrum of **2b** in CD_2Cl_2 is illustrative and shows the presence of three signals for the methylene group in a 10:1:1 ratio as well-separated AB doublets between 5.5 and 6.5 ppm. This points to the presence of different isomers, perhaps due to the different conformations that can be adopted by the dimer **2**, including a *syn* and an eclipsed orientation of the nonbridging iodides. In the $^{13}C\{^1H\}$ NMR spectrum of **2b** only the signals of the major isomer are well resolved. Two sets of signals are observed in a 1:1 ratio, thus suggesting a dissymmetric arrangement of the two heterocycles of the dicarbene ligand. The largest shift difference has been noted for the rhodium-bound carbene nuclei (δ_C 139.4 and 137.2). These signals appear as doublets, each with a characteristic coupling constant, $^1J_{CRh}$ = 42.0 Hz.

While NMR spectroscopic analyses did not allow us to conclusively determine the structure of complexes **2**, elemental analyses were in good agreement with a compound of general formula $[RhI_3(dicarbene)]_n$. A crystal structure analysis of **2b** provided unambiguous evidence for the anticipated dimeric arrangement (Figure 1). The two rhodium centers are both coordinated to a chelating C4-bound dicarbene ligand. The distorted octahedral geometry around rhodium is completed by one μ^1-coordinating and three μ^2-bridging iodides. The μ^1-bound iodides are in mutual *cis* position, thus implying an apparent C_s symmetry in the solid state. As observed in related palladium chemistry,[5] the metal−carbon bond lengths are not significantly different from those of C2-bound imidazolylidene complexes. The Rh−I bonds that are *trans* to carbenes (Rh−I1 and Rh−I2) are significantly longer than the Rh−I3 bond *trans* to the nonbridging iodide, thus reflecting the high *trans* influence of C4-bound carbene ligands.

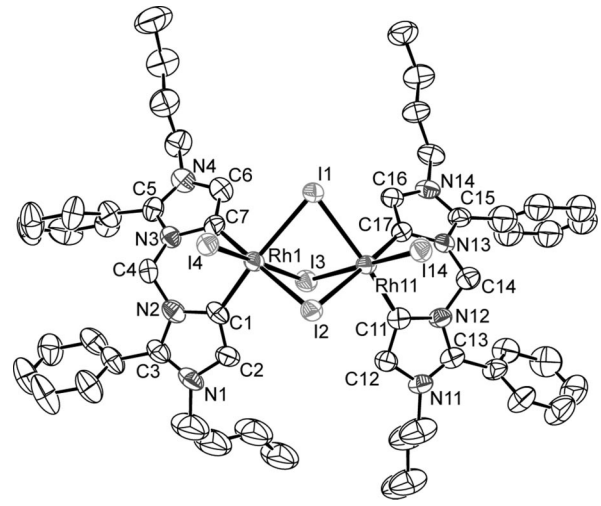


Figure 1. ORTEP representation of the cationic portion of complex **2b** (50% probability level, cocrystallized solvent molecules and the disordered iodide anion omitted for clarity).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex 2b

Bond Lengths			
Rh1−C1	1.979(11)	Rh2−C28	2.003(11)
Rh1−C7	1.998(12)	Rh2−C34	1.991(11)
Rh1−I1	2.8130(11)	Rh2−I1	2.8140(10)
Rh1−I2	2.7578(11)	Rh2−I2	2.7664(11)
Rh1−I3	2.6524(11)	Rh2−I3	2.6463(11)
Rh1−I5	2.6585(11)	Rh2−I4	2.6792(12)
C1−C2	1.369(17)	C28−C29	1.373(16)
C6−C7	1.371(17)	C33−C34	1.368(15)
Bond Angles			
C1−Rh1−C7	88.8(5)	C28−Rh2−C34	88.0(4)
C1−Rh1−I1	173.4(4)	C28−Rh2−I1	173.9(3)
C1−Rh1−I2	92.0(4)	C28−Rh2−I2	92.9(3)
C1−Rh1−I3	90.3(4)	C28−Rh2−I3	90.6(3)
C1−Rh1−I5	91.1(4)	C28−Rh2−I4	91.5(3)
I1−Rh1−I2	85.60(3)	I1−Rh2−I2	85.41(3)
I1−Rh1−I3	83.40(3)	I1−Rh2−I3	83.49(3)
I2−Rh1−I3	84.48(3)	I2−Rh2−I3	84.42(3)

Complexes **2a**−**e** are unstable in coordinating solvents. In the presence of even weak ligands such as MeCN, instantaneous cleavage of the dimeric structure gave the monometallic complexes **3a**−**e**. The ^{1}H and ^{13}C NMR spectra of complexes **3a**−**e** in CD_3CN are significantly simpler than those of the corresponding dimers **2** and reveal a single set of signals. The ^{1}H NMR spectrum of **3a**, for example, shows a sharp singlet for the protons of the heterocycle (δ_H 6.90) and also for the methylene group (δ_H 6.19). This is in good agreement with a C_{2v}-symmetric structure comprising a flexible metallacycle that undergoes rapid inversion of its boat-type conformation. In the $^{13}C\{^1H\}$ NMR spectrum, a doublet for the metal-bound carbon is observed at δ_C 130.0 ($^1J_{CRh}$ = 38.0 Hz). The related rhodium(III) complexes **3f** and **3g** comprising C2-bound dicarbene ligands have been prepared for comparative purposes and according to an established procedure (Scheme 1).[22]

Solid State Structures. Unambiguous structural information on complexes **3a**−**f** was obtained from X-ray analyses (Figure 2). Selected bond lengths and angles are listed in Table 2. In all structures, the rhodium atom is in a slightly distorted octahedral geometry that is defined by the *cis*-chelating dicarbene, two MeCN molecules, and two iodides in mutual *trans* position. Such an arrangement may be surmised from the

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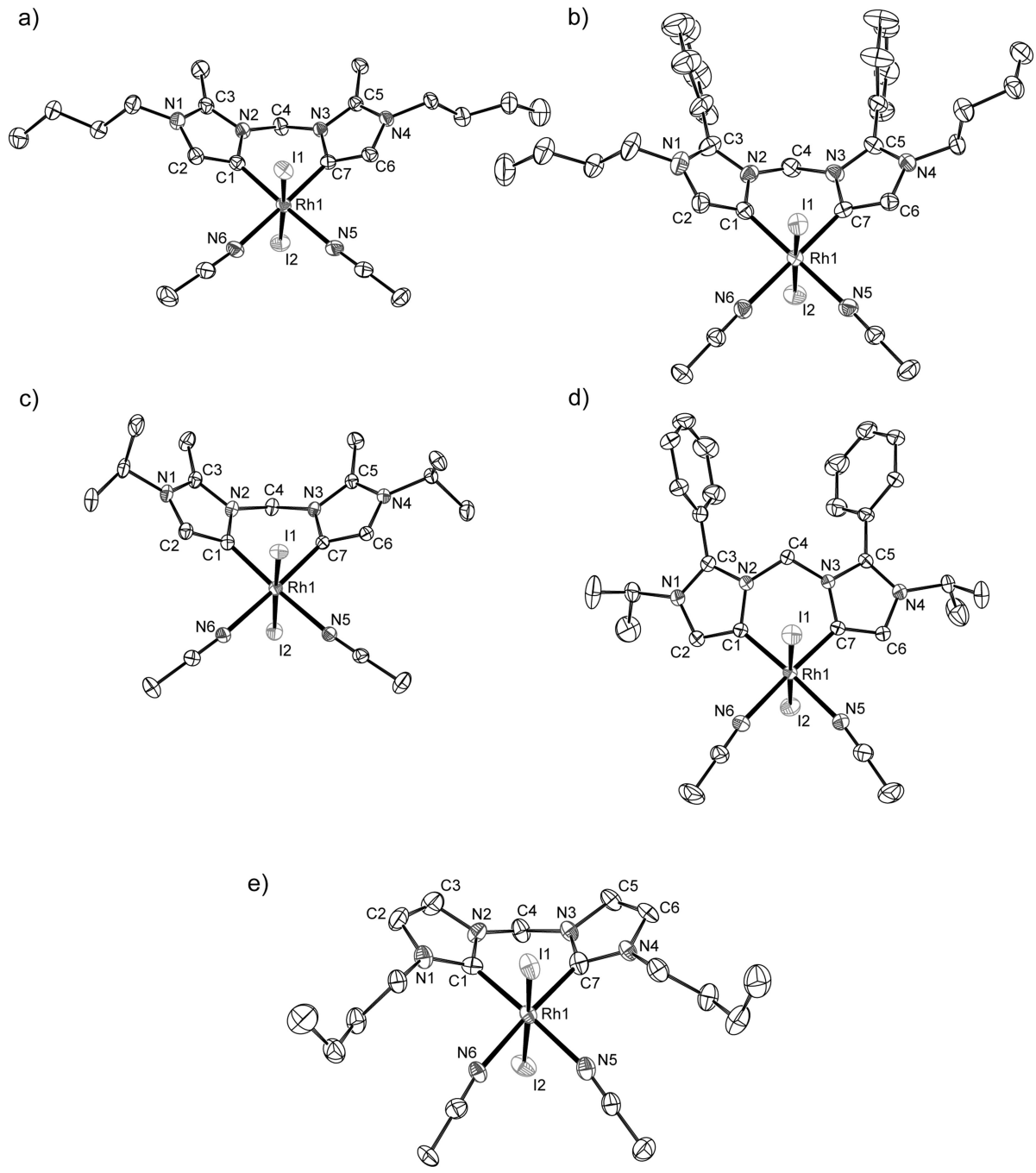


Figure 2. ORTEP representation of the cations of the C4-bound carbene complexes **3a** (a), **3b** (b), **3c** (c), and **3d** (d) and of the C2-bound dicarbene complex **3f** (e). Ellipsoids are drawn at the 50% probability level (**3c** at 30%); hydrogen atoms and cocrystallized solvent molecules and I_2 (for **3c**) have been omitted for clarity.

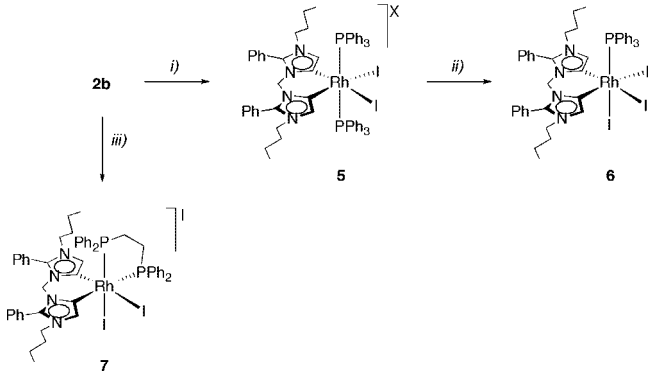
different *trans* influence of the ligands (carbene > I^- > MeCN) and indicates the formation of the thermodynamically most stable products. The average Rh−C bond distance in the C4-bound dicarbene complexes is 1.985(4) Å and does not differ significantly from the Rh−C bond length in similar C2-bound rhodium(III) dicarbenes such as complex **3f**. The $Rh-N_{MeCN}$ distances of complexes **3a**−**d** are in the range 2.10−2.12 Å and hence only slightly longer than those in the C2-bound systems (Rh−N 2.07−2.11 Å; cf. **3f** and ref 22). This similarity may be a superimposition of the higher *trans* influence of the C4-bound carbene and the smaller steric shielding due to the more remote location of the wingtip substituents (cf. the different bond angles around Rh). Notably, the heterocyclic C−C bond in **3a**−**d** is predominantly conjugated (average C−C 1.360(5) Å), while in the C2-bound analogues, this bond resembles rather a localized olefinic C=C bond (1.33 Å). Similarly long C−C bonds were also observed in related C4-bound carbene palladium complexes.[5] This may be due to a C−C−Rh three-center four-electron interaction as the principal contribution for metal bonding, thus pointing to a weak π-electron delocalization within the heterocycle.[7b] Interestingly, complex **3c** cocrystallized with one molecule of I_2, which provides additional support for the proposed cascade mechanism proposed for the formation of these rhodium(III) complexes from $[RhCl(cod)]_2$ (vide supra).

Ligand Substitution Reactions. The dimer **2** is a useful starting material for investigating the coordination properties of the rhodium center in a C4-bound dicarbene ligand environment. For example, treatment of complex **2b** with PPh_3 afforded

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes 3a−d and 3f

	3a	3b	3c	3d	3f
Rh1−C1	1.988(2)	1.983(3)	1.976(3)	1.989(2)	1.994(4)
Rh1−C7	1.987(2)	1.981(3)	1.988(3)	1.985(2)	1.988(4)
Rh1−N5	2.115(2)	2.109(3)	2.102(3)	2.118(2)	2.109(4)
Rh1−N6	2.103(2)	2.117(3)	2.113(3)	2.124(2)	2.092(4)
Rh1−I1	2.6809(3)	2.6510(3)	2.6671(3)	2.6874(3)	2.6665(5)
Rh1−I2	2.6647(3)	2.6714(3)	2.6822(3)	2.6523(3)	2.6746(5)
C1−C2	1.359(3)	1.358(5)	1.367(4)	1.361(3)	
C6−C7	1.357(3)	1.364(4)	1.350(4)	1.361(4)	
C1−Rh1−C7	88.60(9)	88.19(12)	87.41(12)	90.03(10)	87.15(17)
C1−Rh1−N6	89.93(9)	91.38(11)	89.86(12)	92.09(10)	95.55(16)
N6−Rh1−N5	91.84(8)	88.14(10)	92.82(10)	85.43(9)	82.96(14)
N5−Rh1−C7	89.62(8)	92.27(11)	89.92(11)	92.35(10)	94.24(16)
I1−Rh1−I2	176.828(9)	177.613(12)	175.593(12)	177.390(9)	177.20(2)

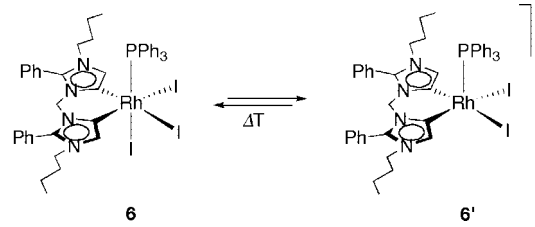
Scheme 2. Reactivity of Dinuclear Rhodium(III) Complexes toward Phosphines[a]



[a] Reagents and conditions: (i) excess PPh_3, CH_2Cl_2; (ii) SiO_2, CH_2Cl_2; (iii) dppe, CH_2Cl_2.

initially the bis(phosphine) complex **5** (Scheme 2). Complex **5** is stable as solid in air, while in solution slow decomposition was observed. The ^1H and ^{31}P NMR spectra of **5** in CD_2Cl_2 showed one major and two minor sets of signals, implying the existence of three isomers in CD_2Cl_2 solution. Again the CH_2 group between the two heterocycles is diagnostic for determining the ratio of these isomers (12:1:1). A similar product distribution is also indicated by ^{31}P NMR, showing a resonance for the major isomer at δ_P 12.5 ($^1J_{PRh} = 89.7$ Hz) and overlapping resonances for the minor species at δ_P 15.3 ($^1J_{PRh} = 93.5$ Hz). Integration and chemical shift values are in agreement with two phosphines coordinated to the metal center in a symmetric arrangement. While electronic arguments would favor a *trans* conformation of the phosphines (*trans* effect carbene > phosphine > iodide), steric repulsion with the twisted carbene heterocycles may force the phosphines into an arrangement in which the phosphines are coplanar with the carbenes and, therefore, the iodides in mutual *trans* position.

In contrast to the measurements in CD_2Cl_2, the NMR spectra in CD_3CN solution showed several sets of signals and in addition also the presence of free PPh_3. This indicates relatively easy solvolysis of complex **5** and concomitant release of PPh_3. Purification of the diphosphine complex **5** by silica gel chromatography indeed induced the clean dissociation of one PPh_3 ligand and gave the monophosphine complex **6**. The ^1H NMR spectrum indicates the presence of two isomers due to the appearance of two AX sets centered at δ_H 6.22 and 5.39 and at δ_H 5.94 and 5.07, respectively ($^2J_{HH} = 13.2$ Hz). Temperature-dependent measurements revealed an equilibrium between the two isomers with the low-field pattern belonging to the exothermic product. Analyses according to the van't Hoff equation gave a reaction enthalpy of $\Delta H° = +24.5$ (±0.1) kJ mol^{-1} and an entropy change of $\Delta S° = -84.2$ (±0.3) J K^{-1} mol^{-1} within the 263−333 K temperature range. The large entropy term makes an intramolecular process unlikely and puts forward a dissociation of iodide from neutral **6** and formation of the ionic complex **6′** at low temperature (eq 2).



(2)

In such a model, the negative entropy term reflects the increased ionic strength in **6′**, which is accompanied by a more pronounced solvatization of the two ions in **6′** as compared to the neutral species **6**.[23] The assignment of ionic **6′** as the exothermic product is further supported by the results obtained from adding KPF_6 to a solution of **6**. Only the signals of **6′** (albeit with a different counterion) were observed, while the resonances attributed to **6** disappeared completely. The equilibrium between **6** and **6′** probably arises as a consequence of the steric congestion imposed by the boat-type metallacycle and the bulky PPh_3 ligand. This is in agreement with the large P−Rh coupling constant ($^1J_{PRh} = 112.8$ Hz) and hence a weak bonding of the *trans*-located ligand.[24] In addition, the strong donor properties of the C4-bound dicarbene ligand facilitate anion dissociation in **6**.

Coordination of two phosphines to the Rh(dicarbene) fragment is more stable when a chelating diphosphine is used rather than an excess of PPh_3. For example, the monomeric complex **7** was obtained in good yields upon treating complex **2b** with diphenylphosphinoethane (dppe) in CH_2Cl_2. The ^1H NMR indicates symmetry-related heterocycles. Similarly, a single resonance is seen in the ^{31}P NMR (δ_P 21.4, $^1J_{RhP} = 75.1$ Hz), thus implying a C_{2v}-symmetric structure in solution. In the solid state, however, C_1 symmetry was established with an all-*trans* ligand coordination (Figure 3). In the crystallized Λ-form, the Rh−I bond *trans* to phosphine is unexpectedly longer (Rh−I2 2.721(1) Å) than the one *trans* to the C4-bound carbene (Rh−I1 2.636(1) Å).

(23) (a) Marcus Y. *Ion Solvation*; Wiley: Chichester; 1985. This concept is also known in biological systems, see for example:(b) Dill, K. A.; Truskett, T. M.; Vlachy, V.; Hribar-Lee, B. *Annu. Rev. Biophys. Biomol. Struct.* **2005**, *34*, 173.

(24) Meek, D. W.; Mazanec, T. J. *Acc. Chem. Res.* **1981**, *14*, 266.

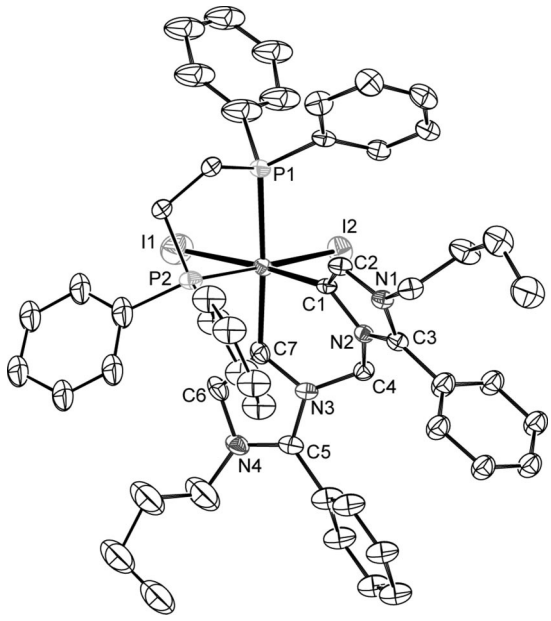
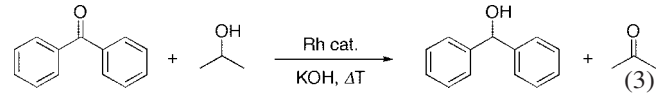


Figure 3. ORTEP representation of complex **7** (30% probability level, hydrogen atoms, the cocrystallized ether molecules, and the I^- anion omitted for clarity; only one of the two disordered positions of the $CH_2CH_2PPh_2$ moiety of the dppe ligand is shown). Selected bond lengths (Å): Rh1−C1 2.031(9), Rh1−C7 2.050(10), Rh1−I1 2.6359(12), Rh1−I2 2.7209(10), Rh1−P1 2.357(2), Rh1−P2 2.237(13), C1−C2 1.370(12), C6−C7 1.352(13). Selected bond angles (deg): C1−Rh1−C7 88.3(4), C1−Rh1−I1 175.9(2), C1−Rh1−I2 92.4(2), C1−Rh1−P1 92.6(2), C1−Rh1−P2 94.9(3), C7−Rh1−P1 176.4(2), C7−Rh1−P2 90.1(4), P1−Rh1−P2 86.7(3), I1−Rh1−I2 89.85(4).

Catalytic Transfer Hydrogenation. The versatility of complexes **2** in coordinating various ligands was further exploited in hydrogen transfer catalysis.[25] The reduction of benzophenone to diphenyl methanol in *i*PrOH was used as a model reaction for probing the catalytic activity of the rhodium(III) complexes (eq 3 and Table 3). A first screening aimed at optimizing reaction conditions was carried out with the dimeric complex **2b** as catalyst. In a typical reaction, the active catalyst was formed by heating a mixture of **2b** in basic *i*PrOH for 10 min prior to substrate addition. When the substrate was added first, the catalytic activity was low. Catalyst manipulation does not need particular precautions, and transfer hydrogenations were generally performed in air and without solvent pretreatment. The base was added as a concentrated aqueous solution, which underlines the stability of the rhodium catalyst system toward moisture. Identical conversions were obtained in a comparative experiment using KO*t*Bu dissolved in *i*PrOH as base, thus avoiding the addition of traces of water (entries 2, 3). A Karl-Fischer titration of the *i*PrOH solvent indicated a water content of 0.5%, which corresponds to 25 μL in the 5 mL volume used for standard reactions. Notably, addition of deliberate amounts of water (0.2 mL) did slow down the reaction slightly (entry 4). Hence, water at low concentration (0.5−1%) does not affect the catalyst, while higher concentrations (>5%) reduce its activity. Much more detrimental is, however, the presence of MeCN (entry 5). Apparently, formation of complexes **3** is faster and competitive to alkoxide/ketone coordination to **2**. An excess of MeCN effectively poisons the catalyst, while equimolar concentrations as in complex **3a** do not reduce the catalytic activity (entry 10).

Table 3. Catalytic Transfer Hydrogenation of Benzophenone with Rhodium(III) Dicarbene Complexes[a]

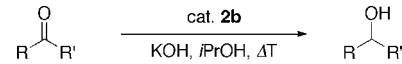


(3)

entry	catalyst	mol %	time (h)	conversion (%)[b]	TON
1			0.5/16	0.6/11	
2	**2b**	0.5	0.5/2	54/97	97
3 [c]	**2b**	0.5	0.5/2	47/94	94
4 [d]	**2b**	0.5	0.5/2	36/73	73
5 [e]	**2b**	0.5	0.5/2	5/14	14
6	**2a**	0.5	0.5/2	45/82	82
7	**2c**	0.5	0.5/2	44/84	84
8	**2d**	0.5	0.5/2	48/87	87
9	**2e**	0.5	0.5/2	60/91	91
10	**3a**	0.5	0.5/2	53/91	91
11	**3f**	1	0.5/2	5/17	17
12	**3g**	1	0.5/2	3/6	6
13	**4**	1	0.5/2	73/97	97
14	**4**	0.1	0.5/40	10/33	330

[a] General conditions: 1 mmol of benzophenone, 5 mL of *i*PrOH, 100 μmol of base (substrate/base 10:1), reflux temperature. [b] Average of at least two runs. [c] KO*t*Bu used as base. [d] Addition of H_2O (0.2 mL). [e] Addition of MeCN (0.2 mL).

Table 4. Catalytic Transfer Hydrogenation of Ketones and Imines with the Dicarbene Complex 2b[a]



(4)

entry	ketone	cat **2b** (mol %)	time (h)	conversion (%)
1	benzophenone	0.5	0.5/2	54/97
2	acetophenone	0.5	0.5/2	66/93
3	propiophenone	0.5	0.5/2	32/74
4	3,3,5,5-Me_4-cy=O	0.5	0.5/2	18/40
5	2-octanone	0.5	0.5/2	17/57
6	3-octanone	0.5	0.5/2	12/40
7	Ph-CH=NMe	0.5	2	<2

[a] General conditions: 1 mmol of ketone, 5 mL of *i*PrOH, 100 μmol of base (substrate/base 10:1), reflux temperature.

The substitution pattern on the dicarbene ligand has a relatively small influence on the catalytic activity. From our limited variation in catalyst design, no clear trend can be deduced and the differences in activity are small (entries 2, 6−9). The turnover frequency at 50% conversion (TOF_{50}) is $100 \pm 20\ h^{-1}$ for all catalyst precursors **2a**−**e**. Dimer cleavage in **2** seems to be fast also during catalysis, and conversions are identical when starting from the dimer **2** or the corresponding monometallic complexes (e.g., **3a**, entry 10). However, rhodium coordination via the C4 position is critical for inducing catalytic activity. The rhodium complexes **3f** and **3g** comprising a C2-bound dicarbene ligand are significantly less active catalysts than the C4-bound complexes and give only poor conversions (entries 11, 12). Apparently, the stronger donor properties of the C4-bound carbene ligands produce a more electron-rich rhodium center, which is supposed to accelerate in particular the product release step in the catalytic cycle.[25]

The relevance of high electron density at the metal center is further strengthened by the catalytic activity of the chloro complex **4**. This complex is the most active catalyst of the series.

(25) (a) Klomp, D.; Hanefeld, U.; Peters, J. A. In *The Handbook of Homogeneous Hydrogenation*; de Vries, J. G., Elsevier, C. J., Eds.; Wiley-VCH: Weinheim, 2007, p 585. (b) Samec, J. S. M.; Bäckvall, J-E.; Andersson, P. G.; Brandt, P. *Chem. Soc. Rev.* **2006**, *35*, 237. (c) Gladiali, S.; Alberico, E. *Chem. Soc. Rev.* **2006**, *35*, 226. (d) Clapham, S. E.; Hadzovic, A.; Morris, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2201.

Transfer hydrogenation is essentially complete in 1 h, and the TOF_{50} is raised to 300 h^{-1} at 1 mol % catalyst loading (entry 13).[26] Lowering the catalyst loading gave only incomplete conversions, and the noncatalyzed background reduction becomes a competitive process (entry 14). Perhaps, catalyst deactivation due to the higher relative water concentration may become relevant at such low rhodium levels.

Different ketones are efficiently hydrogenated with these new dicarbene rhodium catalysts. Acetophenone reduction takes place at slightly faster rates than benzophenone hydrogenation (Table 4, entries 1, 2). Larger alkyl groups are also tolerated. Propiophenone, for example, is converted only a little slower than acetophenone and transfer hydrogenation is complete within 4 h (entry 3). Aliphatic methylketones require longer reaction times than their aryl analogues. This effect is even more pronounced for sterically demanding substrates such as 3-octanone and 3,3,5,5-tetramethylcyclohexanone, for which hydrogenation does not reach completion even after 16 h (entries 4−6). Imines appear to poison the catalytically active species. When using *N*-methylbenzylimine, no amine formation was observed (entry 7). Instead, traces of benzyl alcohol were initially detected, probably originating from hydrolysis of the imine and subsequent transfer hydrogenation of the corresponding aldehyde.[27] However, this reaction does not progress, and even after prolonged reaction time, more than 95% of imine was present in the reaction mixture.

Conclusions

Direct metalation of C2-substituted diimidazolium salts provides access to chelating rhodium dicarbene complexes in which the heterocyclic carbenes are bound unusually via the C4 carbon. This bonding mode increases the electron density at the metal center, thus invoking new reactivity patterns. The exceptionally strong donor properties of such C4-bound carbenes have been utilized for the development of new rhodium catalysts for the transfer hydrogenation of ketones. The catalytic activity of the rhodium center critically depends on the carbene bonding mode and requires C4-bound carbenes, whereas C2-bound analogues are essentially inactive. These results are another indication for the high impact of C4-bound carbene ligands in inducing new (catalytic) properties of the coordinated metal center. Further investigations along these lines are currently in progress in our laboratories, in particular with the aim of catalytically activating otherwise unreactive bonds.

Experimental Section

General Comments. The N-alkylated imidazoles,[18] the ligand precursors **1c** and **1e**,[5] and $[RhCl(cod)]_2$[28] were prepared according to literature procedures. All other reagents are commercially available and were used as received. Unless specified otherwise, NMR spectra were recorded at 25 °C on Bruker spectrometers operating at 400 or 500 MHz (^{1}H NMR), 100 or 125 MHz (^{13}C NMR), and 162 MHz (^{31}P NMR), respectively. Chemical shifts (δ in ppm, coupling constants J in Hz) were referenced to external $SiMe_4$ (^{1}H, ^{13}C) or H_3PO_4 (^{31}P). Assignments are based on homo- and heteronuclear shift correlation spectroscopy. Elemental analyses were performed by the Microanalytical Laboratory of Ilse Beetz (Kronach, Germany).

General Procedure for the Synthesis of Diimidazolium Ligand Precursors 1a−e. A solution of the appropriate 1,2-disubstituted imidazole (20 mmol) and CH_2I_2 (2.67 g, 10 mmol) was stirred in toluene (20 mL) at reflux for 24 h. The formed precipitate was collected by filtration and recrystallized from MeOH/Et_2O at −20 °C.

***N*,*N*-Methylenedi(*N*′-*n*-butyl-2-methyl)imidazolium diiodide (1a):.** white solid (3.8 g, 70%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 7.92 (d, 2H, $^3J_{HH}$ = 2.2 Hz, H_{imi}), 7.83 (d, 2H, $^3J_{HH}$ = 2.2 Hz, H_{imi}), 6.57 (s, 2H, NCH_2N), 4.13 (t, 4H, $^3J_{HH}$ = 7.4 Hz, $NCH_2CH_2CH_2CH_3$), 2.77 (s, 6H, CH_3), 1.71 (quintett, 4H, $^3J_{HH}$ = 7.4 Hz, $NCH_2CH_2CH_2CH_3$), 1.30 (sextet, 4H, $^3J_{HH}$ = 7.4 Hz, $NCH_2CH_2CH_2CH_3$), 0.90 (t, 6H, $^3J_{HH}$ = 7.4 Hz, $NCH_2CH_2CH_2CH_3$). ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz): δ 145.9 (C_{imi}), 122.0 (C_{imi}), 121.3 (C_{imi}), 56.8 (NCH_2N), 47.7 ($NCH_2CH_2CH_2CH_3$), 30.8 ($NCH_2CH_2CH_2CH_3$), 18.9 ($NCH_2CH_2CH_2CH_3$), 13.4 ($NCH_2CH_2CH_2CH_3$), 10.3 (CH_3). Anal. Calcd for $C_{17}H_{30}I_2N_4$ (544.26): C, 37.52; H, 5.56; N, 10.29. Found: C, 37.41; H, 5.44; N, 10.17.

***N*,*N*-Methylenedi(*N*′-*n*-butyl-2-phenyl)imidazolium diiodide (1b):.** light yellow solid (5.0 g, 75%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.06 (d, 2H, $^3J_{HH}$ = 2.2 Hz, H_{imi}), 7.92 (d, 2H, $^3J_{HH}$ = 2.2 Hz, H_{imi}), 7.72 (m, 2H, H_{aryl}), 7.58 (m, 8H, H_{aryl}), 6.29 (s, 2H, NCH_2N), 3.92 (t, 4H, $^3J_{HH}$ = 7.4 Hz, $NCH_2CH_2CH_2CH_3$), 1.57 (quintet, 4H, $^3J_{HH}$ = 7.4 Hz, $NCH_2CH_2CH_2CH_3$), 1.07 (sextett, 4H, $^3J_{HH}$ = 7.4 Hz, $NCH_2CH_2CH_2CH_3$), 0.71 (t, 6H, $^3J_{HH}$ = 7.4 Hz, $NCH_2CH_2CH_2CH_3$). ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz): δ 144.7 (C_{imi}), 132.9 (C_{aryl}), 130.4 (C_{aryl}), 129.7 (C_{aryl}), 122.8 (C_{imi}), 122.2 (C_{imi}), 119.6 (C_{aryl}), 57.9 (NCH_2N), 48.1 ($NCH_2CH_2CH_2CH_3$), 30.7 ($NCH_2CH_2CH_2CH_3$), 18.5 ($NCH_2CH_2CH_2CH_3$), 13.0 ($NCH_2CH_2CH_2CH_3$). Anal. Calcd for $C_{27}H_{34}I_2N_4$ (668.39): C, 48.52; H, 5.13; N, 8.38. Found: C, 48.33; H, 5.16; N, 8.38.

***N*,*N*-Methylenedi(*N*′-isopropyl-2-phenyl)imidazolium diiodide (1d):.** light yellow solid (1.5 g, 23%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.17 (d, 2H, $^3J_{HH}$ = 2.2 Hz, H_{imi}), 7.91 (d, 2H, $^3J_{HH}$ = 2.2 Hz, H_{imi}), 7.72 (m, 2H, H_{aryl}), 7.60 (m, 8H, H_{aryl}), 6.29 (s, 2H, NCH_2N), 4.15 (septet, 2H, $^3J_{HH}$ = 6.6 Hz, $NCH(CH_3)_2$), 1.38 (d, 12H, $^3J_{HH}$ = 6.6 Hz, $NCH(CH_3)_2$). ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz): δ 143.7 (C_{imi}), 132.9 (C_{aryl}), 130.3 (C_{aryl}), 129.8 (C_{aryl}), 122.9 (C_{imi}), 119.7(C_{imi}), 119.4 (C_{aryl}), 57.9 (NCH_2N), 51.6 ($NCH(CH_3)_2$), 22.0 ($NCH(CH_3)_2$). Anal. Calcd for $C_{25}H_{30}I_2N_4$ (640.06) × H_2O: C, 45.61; H, 4.90; N, 8.51. Found: C, 45.73; H, 5.06; N, 8.52.

General Procedure for the Synthesis of $[(\mu\text{-I})_3\{RhI(dicarbene)\}_2]I$ (2a−e). *Method A*: A mixture of the corresponding diimidazolium salt **1** (1 molar equiv), $[RhCl(cod)]_2$ (0.5 molar equiv), KI (4 mol equiv), and NaOAc (8 molar equiv) was stirred in MeCN at reflux temperature for 24 h. After cooling, all volatiles were removed under reduced pressure and the residue was purified by gradient column chromatography. *Method B*: A mixture of the diimidazolium salt (1 molar equiv), $[RhCl_3(H_2O)_x]$ (1 molar equiv), and NaOAc (8 molar equiv) was refluxed in MeCN for 24 h. After cooling, all volatiles were removed under reduced pressure and the residue was purified by gradient column chromatography (SiO_2; CH_2Cl_2/acetone, 5:1). The orange fraction was dissolved in a solution of NaI (10 molar equiv) in acetone and stirred for 24 h. After filtration of the mixture, the volatiles of the filtrate were removed under reduced pressure and subsequently extracted into CH_2Cl_2. Evaporation of this solution to dryness gave complex **2**.

Synthesis of 2a. According to method A, starting from **1a** (272 mg, 0.5 mmol), $[RhCl(cod)]_2$ (123 mg, 0.25 mmol), KI (332 mg,

(26) Notably, this catalyst activity is still 1 to 2 orders of magnitude lower than that of the most active systems known today. See for examples ref 18b and:(a) Mestroni, G.; Zassinovich, G.; Camus, A.; Martinelli, F. *J. Organomet. Chem.* **1980**, *198*, 87. (b) Thoumazet, C.; Melaimi, M.; Ricard, L.; Mathey, F.; Le Floch, P. *Organometallics* **2003**, *22*, 1580. (c) Dani, P.; Karlen, T.; Gossage, R. A.; Gladiali, S.; van Koten, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 743. (d) Yang, H.; Alvarez, M.; Lugan, N.; Mathieu, R. *J. Chem. Soc., Chem. Commun.* **1995**, 1721. (e) For a reverse reaction, see:

(27) Fujita, K.; Li, Z.; Ozeki, N.; Yamaguchi, R. *Tetrahedron Lett.* **2003**, *44*, 2687.

(28) Crabtree, R. H.; Morehouse, S. M.; Quirk, J. M. *Inorg. Synth.* **1986**, *24*, 173.

2.0 mmol), and NaOAc (328 mg, 4.0 mmol). Gradient column chromatography (SiO_2; first CH_2Cl_2 then CH_2Cl_2/acetone, 3:1) gave **2a** as an orange solid (104 mg, 27%). Addition of Et_2O to a suspension of **2a** in CH_2Cl_2 afforded analytically pure material. Anal. Calcd for $C_{34}H_{56}I_6N_8Rh_2$ (1544.10): C, 26.45; H, 3.66; N, 7.26. Found: C, 26.36; H, 3.66; N, 7.34.

Synthesis of 2b. According to method A, starting from **1b** (334 mg, 0.5 mmol), $[RhCl(cod)]_2$ (123 mg, 0.25 mmol), KI (332 mg, 2.0 mmol), and NaOAc (328 mg, 4.0 mmol). Gradient column chromatography (SiO_2; first CH_2Cl_2 then CH_2Cl_2/acetone, 5:1) gave **2b** as an orange solid (140 mg, 31%), which was then crystallized from CH_2Cl_2/hexane. ^1H NMR (CD_2Cl_2, 400 MHz): δ 7.63−7.23 (m, 24H, H_{aryl}, H_{imi}), 6.47 (d, 2H, $^2J_{HH}$ = 12.6 Hz, lowfield AX part of NCH_2N), 5.86 (d, 2H, $^2J_{HH}$ = 12.6 Hz, high-field AX part of NCH_2N), 3.98−3.91 (m, 8H, $CH_2CH_2CH_2CH_3$), 1.84−1.75 (m, 8H, $CH_2CH_2CH_2CH_3$), 1.32−1.27 (m, 8H, $CH_2CH_2CH_2CH_3$), 0.89−0.84 (m, 12H, $CH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz): δ 142.1, 141.8 ($C_{imi\text{-}2}$), 139.4 (d, $^1J_{CRh}$ = 42.0 Hz, $C_{imi\text{-}5}$), 137.2 (d, $^1J_{CRh}$ = 42.0 Hz, $C_{imi\text{-}5}$), 132.1, 131.9 (C_{aryl}), 130.0−129.5 (m, $C_{imi\text{-}4}$, C_{aryl}), 61.1 (NCH_2N), 48.0 ($CH_2CH_2CH_2CH_3$), 32.0, 31.9 ($CH_2CH_2CH_2CH_3$), 19.4, 19.3 ($CH_2CH_2CH_2CH_3$), 12.9 ($CH_2CH_2CH_2CH_3$). The signals of the two minor species are overlapping with the major product in the ^1H NMR spectrum except for the AX-type signal of the NCH_2N group; minor species A: δ 6.31 (d, $^2J_{HH}$ = 12.6 Hz), 5.90 (d, $^2J_{HH}$ = 12.6 Hz); minor species B: δ 6.59 (d, $^2J_{HH}$ = 12.6 Hz), 5.69 (d, $^2J_{HH}$ = 12.6 Hz). Anal. Calcd for $C_{54}H_{64}I_6N_8Rh_2$ (1792.38): C, 36.19; H, 3.60; N, 6.25. Found: C, 36.09; H, 3.62; N, 5.91.

Synthesis of 2c. According to method A, starting from **1c** (260 mg, 0.5 mmol), $[RhCl(cod)]_2$ (123 mg, 0.25 mmol), KI (332 mg, 2.0 mmol), and NaOAc (328 mg, 4.0 mmol). Gradient column chromatography (SiO_2; first CH_2Cl_2 then CH_2Cl_2/acetone, 5:1) gave **2c** as an orange solid (50 mg, 13%). Analytically pure material was obtained by slow diffusion of Et_2O into a solution of **2c** in CH_2Cl_2/CH_3CN (8:1). Anal. Calcd for $C_{30}H_{48}I_6N_8O_{0.5}Rh_2$ (1487.99) × 0.5 Et_2O: C, 25.20; H, 3.50; N, 7.35. Found: C, 25.20; H, 3.78; N, 7.58.

Synthesis of 2d. According to method A, starting from **1d** (320 mg, 0.5 mmol), $[RhCl(cod)]_2$ (123 mg, 0.25 mmol), KI (332 mg, 2.0 mmol), and NaOAc (328 mg, 4.0 mmol). Gradient column chromatography (SiO_2; first CH_2Cl_2 then CH_2Cl_2/acetone, 5:1) gave **2d** as an orange solid (100 mg, 23%), which was crystallized from CH_2Cl_2/hexane. Anal. Calcd for $C_{50}H_{56}I_6N_8Rh_2$ (1736.27): C, 34.59; H, 3.25; N, 6.45. Found: C, 34.21; H, 3.31; N, 6.77.

Synthesis of 2e. According to method B, starting from **1e** (201 mg, 0.3 mmol), $[RhCl_3(H_2O)_x]$ (79 mg, 0.3 mmol), and NaOAc (197 mg, 2.4 mmol) afforded **2e** as an orange solid (110 mg, 41%). Analytically pure material was obtained by slow diffusion of Et_2O into a solution of **2e** in CH_2Cl_2/acetone (1:1). Anal. Calcd for $C_{54}H_{64}I_6N_8Rh_2$ (1792.38): C, 36.19; H, 3.60; N, 6.25. Found: C, 36.23; H, 3.71; N, 6.16.

Synthesis of 3a. Crystallization of **2a** from CH_3CN/Et_2O afforded the monomeric bis-acetonitrile complex **3a**. ^1H NMR (CD_3CN, 400 MHz): δ 6.90 (s, 2H, H_{imi}), 6.19 (s, 2H, NCH_2N), 4.01 (t, 4H, $^3J_{HH}$ = 7.2 Hz, $CH_2CH_2CH_2CH_3$), 2.67 (s, 6H, CH_3), 1.74 (quintet, 4H, $^3J_{HH}$ = 7.2 Hz, $CH_2CH_2CH_2CH_3$), 1.34 (sextet, 4H, $^3J_{HH}$ = 7.2 Hz, $CH_2CH_2CH_2CH_3$), 0.94 (t, 6H, $^3J_{HH}$ = 7.2 Hz, $CH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (CD_3CN, 100 MHz): δ 143.0 (C_{imi}), 130.0 (C−Rh, $^1J_{CRh}$ = 38.0 Hz), 127.2 (C_{imi}), 62.4 (NCH_2N), 48.9 ($CH_2CH_2CH_2CH_3$), 33.3 ($CH_2CH_2CH_2CH_3$), 20.8 ($CH_2CH_2CH_2CH_3$), 14.4 ($CH_2CH_2CH_2CH_3$), 11.2 (CH_3). Anal. Calcd for $C_{21}H_{34}I_3N_6Rh$ (845.15) × CH_3CN: C, 30.86; H, 4.17; N, 10.95. Found: C, 30.96; H, 4.13; N, 10.89.

Synthesis of 3b. Slow diffusion of Et_2O into a solution of **2b** in CH_2Cl_2/CH_3CN (1:1) induced crystallization of complex **3b**. ^1H NMR (CD_3CN, 400 MHz): δ 7.59 (t, 2H, $^3J_{HH}$ = 7.6 Hz, H_{aryl}), 7.48 (t, 4H, $^3J_{HH}$ = 7.6 Hz, H_{aryl}), 7.36 (d, 4H, $^3J_{HH}$ = 7.6 Hz, H_{aryl}), 7.20 (s, 2H, H_{imi}), 6.00 (s, 2H, NCH_2N), 3.91 (t, 4H, $^3J_{HH}$ = 7.2 Hz, $CH_2CH_2CH_2CH_3$), 1.68 (quintet, 4H, $^3J_{HH}$ = 7.2 Hz, $CH_2CH_2CH_2CH_3$), 1.20 (sextet, 4H, $^3J_{HH}$ = 7.2 Hz, $CH_2CH_2CH_2CH_3$), 0.78 (t, 6H, $^3J_{HH}$ = 7.2 Hz, $CH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (CD_3CN, 100 MHz): δ 143.8 (C_{imi}), 133.0 (C_{aryl}), 132.2 (C−Rh, $^1J_{CRh}$ = 38.0 Hz), 131.7 (C_{aryl}), 130.5 (C_{aryl}), 128.0 (C_{imi}), 122.9 (C_{aryl}), 62.8 (NCH_2N), 48.8 ($CH_2CH_2CH_2CH_3$), 32.7 ($CH_2CH_2CH_2CH_3$), 20.0 ($CH_2CH_2CH_2CH_3$), 13.7 ($CH_2CH_2CH_2CH_3$).

Synthesis of 3c. Slow diffusion of Et_2O into a solution of **2c** in CH_3CN yielded crystals of complex **3c**. ^1H NMR (CD_3CN, 400 MHz): δ 6.97 (s, 2H, H_{imi}), 6.25 (s, 2H, NCH_2N), 4.52 (septet, 2H, $^3J_{HH}$ = 6.6 Hz, $CHMe_2$), 2.70 (s, 6H, CH_3), 1.46 (d, 12H, $^3J_{HH}$ = 6.6 Hz, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (CD_3CN, 100 MHz): δ 141.7 (C_{imi}), 129.8 (C−Rh, $^1J_{CRh}$ = 38.0 Hz), 122.4 (C_{imi}), 61.5 (NCH_2N), 50.8 ($CHMe_2$), 22.6 ($CH(CH_3)_2$), 10.8 (CH_3).

Synthesis of 3d. Saturation of a solution of **2d** in CH_2Cl_2/CH_3CN (1:1) with Et_2O gave complex **3d**. ^1H NMR (CD_3CN, 400 MHz): δ 7.59 (t, 2H, $^3J_{HH}$ = 7.6 Hz, H_{aryl}), 7.48 (t, 4H, $^3J_{HH}$ = 7.6 Hz, H_{aryl}), 7.36 (d, 4H, $^3J_{HH}$ = 7.6 Hz, H_{aryl}), 7.28 (s, 2H, H_{imi}), 5.99 (s, 2H, NCH_2N), 4.25 (septet, 2H, $^3J_{HH}$ = 6.6 Hz, $CHMe_2$), 1.44 (d, 12H, $^3J_{HH}$ = 6.6 Hz, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (CD_3CN, 100 MHz): δ 142.9 (C_{imi}), 133.0 (C_{aryl}), 132.6 (C−Rh, $^1J_{CRh}$ = 38.0 Hz), 131.6 (C_{aryl}), 130.5 (C_{aryl}), 124.2 (C_{imi}), 123.0 (C_{aryl}), 62.4 (NCH_2N), 51.8 ($CHMe_2$), 23.0 ($CH(CH_3)_2$).

Synthesis of 3e. Dissolution of **2e** in CH_3CN and subsequent precipitation with Et_2O gave the monometallic complex **3e**. ^1H NMR (CD_3CN, 500 MHz): δ 7.13 (s, 4H, H_{Mes}), 6.88 (s, 2H, H_{imi}), 6.35 (s, 2H, NCH_2N), 2.46 (s, 6H, CH_3), 2.36 (s, 6H, CH_3), 2.03 (s, 12H, CH_3). $^{13}C\{^1H\}$ NMR (CD_3CN, 125 MHz): δ 143.4 (C_{imi}), 141.5 (C_{Mes}), 136.0 (C_{Mes}), 132.2 (C_{Mes}), 130.6 (C−Rh, $^1J_{CRh}$ = 37.9 Hz), 130.3 (C_{Mes}), 126.6 (C_{imi}), 62.3 (NCH_2N), 21.1 (Mes-CH_3), 17.6 (Mes-CH_3), 10.5 (Imi-CH_3).

Synthesis of 3f. A mixture of $[RhCl(cod)]_2$ (100 mg, 0.20 mmol), methylene-1,1′-di(3,3′-*n*-butyl)imidazolium diiodide (212 mg, 0.41 mmol), KI (220 mg, 1.3 mmol), and NEt_3 (0.25 g, 2.5 mmol) was stirred in CH_3CN (12 mL) at 50 °C. The color of the mixture gradually changed from yellow to dark red. After 1 h, the solids were filtered off and the filtrate was evaporated under reduced pressure. The residue was purified by gradient column chromatography (SiO_2, CH_2Cl_2 to CH_2Cl_2/acetone (3:1) as eluents). The red fraction was collected and afforded after evaporation crude **3f** (208 mg, 61%). Recrystallization from CH_3CN/Et_2O/hexanes gave an analytically pure sample of **3f**. ^1H NMR (CD_3CN, 400 MHz): δ 7.43 (d, 2H, $^3J_{HH}$ = 1.9 Hz, H_{imi}), 7.37 (d, 2H, $^3J_{HH}$ = 1.9 Hz, H_{imi}), 6.38 (s, 2H, NCH_2N), 4.40 (m, 4H, $CH_2CH_2CH_2CH_3$), 1.98 (s, 6H, $NCCH_3$), 1.83 (m, 4H, $CH_2CH_2CH_2CH_3$), 1.45 (sextet, 4H, $^3J_{HH}$ = 7.4 Hz, $CH_2CH_2CH_2CH_3$), 1.00 (t, 6H, $^3J_{HH}$ = 7.4 Hz, $CH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (CD_3CN, 100 MHz): δ 149.0 (C−Rh, $^1J_{CRh}$ = 42.7 Hz), 124.2 (C_{imi}), 123.8 (C_{imi}), 65.7 (NCH_2N), 53.3 ($CH_2CH_2CH_2CH_3$), 33.8 ($CH_2CH_2CH_2CH_3$), 20.6 ($CH_2CH_2CH_2CH_3$), 14.1 ($CH_2CH_2CH_2CH_3$). Anal. Calcd for $C_{19}H_{30}I_3N_6Rh$ (825.87): C, 27.62; H, 3.66; N, 10.17. Found: C, 27.69; H, 3.76; N, 9.64.

Synthesis of 3g. Following a procedure as described for **3f**, the title product was obtained from a mixture of $[RhCl(cod)]_2$ (243 mg, 0.50 mmol), *N,N*-methylenedi(*N*′-mesityl)imidazolium diiodide (640 mg, 1.0 mmol), NaI (500 mg, 3.3 mmol), and NEt_3 (0.45 g, 4.5 mmol) in CH_3CN (20 mL) as a red powder (yield 647 mg, 70%). Recrystallization from CH_3CN/Et_2O gave

an analytically pure sample of **3g**. ^{1}H NMR (CD_3CN, 500 MHz): δ 7.58 (d, 2H, $^3J_{HH}$ = 2.2 Hz, H_{imi}), 7.13 (d, 2H, $^3J_{HH}$ = 2.2 Hz, H_{imi}), 6.99 (s, 4H, H_{Mes}), 6.45 (s, 2H, NCH_2N), 2.30 (s, 6H, CH_3), 2.21 (s, 12H, CH_3). ^{13}C{^{1}H} NMR (CD_3CN, 125 MHz): δ 150.87 (C−Rh, $^1J_{CRh}$ = 43.2 Hz), 140.69 (C_{Mes}), 138.23 (C_{Mes}), 136.51 (C_{Mes}), 129.64 (C_{Mes}), 127.83 (C_{imi}), 123.78 (C_{imi}), 65.61 (NCH_2N), 21.03 ($CH_{3\ ortho}$), 20.91 ($CH_{3\ para}$). Anal. Calcd for $C_{29}H_{34}I_3N_6Rh$ (950.24): C, 36.66; H, 3.61; N, 8.84. Found: C, 36.86; H, 3.67; N, 8.82.

Synthesis of [$RhCl_2$(dicarbene)$(MeCN)_2$]BF_4 (4). A suspension of **1b** (460 mg, 0.69 mmol) and $AgBF_4$ (296 mg, 1.5 mmol) in CH_2Cl_2 (100 mL) was stirred at room temperature and in the dark for 24 h. The reaction mixture was filtered and the filtrate concentrated under reduced pressure to ca. 5 mL. Upon addition of Et_2O, an off-white precipitate formed, which analyzed as *N,N*-methylenedi(*N′*-*n*-butyl-2-phenyl)imidazolium $(BF_4)_2$ (**1b′**). Yield: 293 mg (72%). ^{1}H NMR (DMSO-d_6, 360 MHz): δ 8.03 (s, 2H, H_{imi}), 7.89 (s, 2H, H_{imi}), 7.70 (m, 2H, H_{aryl}), 7.60 (m, 4H, H_{aryl}), 7.55 (m, 4H, H_{aryl}), 6.27 (s, 2H, NCH_2N), 3.90 (m, 4H, $^3J_{HH}$ = 7.1 Hz, $NCH_2CH_2CH_2CH_3$), 1.56 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.07 (m, 4H, $NCH_2CH_2CH_2CH_3$), 0.71 (t, 6H, $^3J_{HH}$ = 7.2 Hz, $NCH_2CH_2CH_2CH_3$).

This product **1b′** (293 mg, 0.50 mmol), [$RhCl_3(H_2O)_x$] (131 mg, 0.50 mmol), and NaOAc (327 mg, 4.0 mmol) were suspended in MeCN (40 mL) and stirred at reflux temperature for 24 h. After cooling, all volatiles were removed under reduced pressure, and the residue was purified by gradient column chromatography (SiO_2; first CH_2Cl_2 then CH_2Cl_2/acetone, 10:1). The yellow fraction was collected and evaporated to dryness to give **4** as a yellow, crystalline solid (yield: 177 mg, 55%). Analytically pure crystals of the title product were obtained by slow diffusion of hexane into a solution of **4** in CH_2Cl_2. ^{1}H NMR (CD_3CN, 500 MHz): δ 7.58 (d, 2H, $^3J_{HH}$ = 7.9 Hz, H_{aryl}), 7.46 (t, 4H, $^3J_{HH}$ = 7.9 Hz, H_{aryl}), 7.37 (d, 4H, $^3J_{HH}$ = 7.9 Hz, H_{aryl}), 7.19 (s, 2H, H_{imi}), 6.03 (s, 2H, NCH_2N), 3.93 (t, 4H, $^3J_{HH}$ = 7.5 Hz, $CH_2CH_2CH_2CH_3$), 1.69 (quintet, 4H, $^3J_{HH}$ = 7.5 Hz, $CH_2CH_2CH_2CH_3$), 1.20 (sextet, 4H, $^3J_{HH}$ = 7.5 Hz, $CH_2CH_2CH_2CH_3$), 0.79 (t, 6H, $^3J_{HH}$ = 7.5 Hz, $CH_2CH_2CH_2CH_3$). ^{13}C{^{1}H} NMR (CD_3CN, 125 MHz): δ 143.6 (C_{imi}), 134.3 (C−Rh, $^1J_{CRh}$ = 39.5 Hz), 132.9 (C_{aryl}), 131.5 (C_{aryl}), 130.3 (C_{aryl}), 124.6 (C_{imi}), 122.9 (C_{aryl}), 59.9 (NCH_2N), 48.7 ($CH_2CH_2CH_2CH_3$), 32.7 ($CH_2CH_2CH_2CH_3$), 20.1 ($CH_2CH_2CH_2CH_3$), 13.5 ($CH_2CH_2CH_2CH_3$). Anal. Calcd for $C_{27}H_{32}BCl_2F_4N_4Rh$ (673.19): C, 48.17; H 4.79; N 8.32. Found: C, 48.50; H, 5.20; N, 8.57.

[RhI_2(dicarbene)$(PPh_3)_2$]I (5). To a solution of **2b** (40 mg, 0.02 mmol) in CH_2Cl_2 (5 mL) was added PPh_3 (26 mg, 0.1 mmol). The mixture was stirred at rt for 2 h and subsequently added dropwise to Et_2O (100 mL). The formed precipitate was separated by centrifugation and dried under vacuum (40 mg, 70%). Analytically pure material was obtained by crystallization from ClC_2H_4Cl/Et_2O. The three species show similar ^{1}H NMR spectra except the H_{imi} and bridged CH_2. Major species: ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.67−7.26 (m, 40H, H_{aryl}), 6.65 (s, 2H, H_{imi}), 5.02 (s, 2H, NCH_2N), 3.20 (m, 4H, $CH_2CH_2CH_2CH_3$), 1.41 (m, 4H, $CH_2CH_2CH_2CH_3$), 1.15 (m, 4H, $CH_2CH_2CH_2CH_3$), 0.83 (m, 6H, $CH_2CH_2CH_2CH_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 162 MHz): δ 12.3 (d, $^1J_{PRh}$ = 89.7 Hz). Minor species A: ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 6.57 (s, 2H, H_{imi}), 5.06 (s, 2H, NCH_2N). ^{31}P{^{1}H} NMR (CD_2Cl_2, 162 MHz): δ 15.2 (d, $^1J_{PRh}$ = 93.5 Hz). Minor species B: ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 6.39 (s, 2H, H_{imi}), 5.06 (s, 2H, NCH_2N). ^{31}P{^{1}H} NMR (CD_2Cl_2, 162 MHz): δ 15.2 (d, $^1J_{PRh}$ = 93.5 Hz). Anal. Calcd for $C_{63}H_{62}I_3N_4P_2Rh$ (1420.76): C, 53.26; H, 4.40; N, 3.94. Found: C, 53.33; H, 4.53; N, 3.76.

[RhI_3(dicarbene)PPh_3] (6). A mixture of **2b** (40 mg, 0.02 mmol) and PPh_3 (26 mg, 0.1 mmol) in CH_2Cl_2 (5 mL) was stirred at rt for 2 h. After solvent evaporation, the residue was purified by gradient column chromatography (SiO_2; first CH_2Cl_2 then CH_2Cl_2/acetone, 1:1), thus affording complex **6a** (37 mg, 95%). ^{1}H NMR (CD_3CN, 400 MHz, 333 K): δ 7.7−7.15 (m, 27H, H_{aryl}, H_{imi}), 5.91 (d, 1H, $^2J_{HH}$ = 13.2 Hz, low-field AX part of NCH_2N), 5.03 (d, 1H, $^2J_{HH}$ = 13.2 Hz, high-field AX part of NCH_2N), 3.88−3.73 (m, 4H, $CH_2CH_2CH_2CH_3$), 1.68−1.27 (m, 4H, $CH_2CH_2CH_2CH_3$), 1.14−0.96 (m, 4H, $CH_2CH_2CH_2CH_3$), 0.77 (t, 6H, $^3J_{HH}$ = 7.3 Hz, $CH_2CH_2CH_2CH_3$). ^{13}C{^{1}H} NMR (CD_3CN, 100 MHz, 333 K): δ 143.9 (C_{imi}), 135.8 ($C_{aryl\text{-}P}$, $^3J_{CP}$ = 8.2 Hz), 133.5 (C_{imi}), 132.1 ($C_{aryl\text{-}imi}$), 131.6 ($C_{aryl\text{-}imi}$), 131.1 ($C_{aryl\text{-}P}$, $^2J_{CP}$ = 17 Hz), 131.0 ($C_{aryl\text{-}P}$), 129.2 ($C_{aryl\text{-}P}$, $^1J_{CP}$ = 10.0 Hz), 122.7 ($C_{aryl\text{-}imi}$), 61.9 (NCH_2N), 49.2 ($CH_2CH_2CH_2CH_3$), 33.0 ($CH_2CH_2CH_2CH_3$), 20.3 ($CH_2CH_2CH_2CH_3$), 13.7 ($CH_2CH_2CH_2CH_3$), C−Rh not resolved. ^{31}P{^{1}H} NMR (CD_2Cl_2, 162 MHz): δ 19.4 (d, $^1J_{PRh}$ = 112.8 Hz). Anal. Calcd for $C_{45}H_{47}I_3N_4PRh$ (1158.47): C, 46.65; H, 4.09; N, 4.84. Found: C, 46.55; H, 3.98; N, 4.75.

[RhI_2(dicarbene)(dppe)]I (7). Following a similar procedure as for **6**, reaction of **2b** (40 mg, 0.02 mmol) with dppe (21 mg, 0.05 mmol) yielded complex **7** as a yellow powder (50 mg, 95%). ^{1}H NMR (CD_2Cl_2, 500 MHz, 273 K): δ 7.70−7.38 (m, 28H, H_{aryl}), 7.23 (m, 2H, H_{aryl}), 7.2 (br, 2H, NCH_2N), 6.74 (s, 2H, H_{imi}), 3.80 (m, 4H, $CH_2CH_2CH_2CH_3$), 3.21 (m, 4H, PCH_2), 1.58 (m, 4H, $CH_2CH_2CH_2CH_3$), 1.18 (m, 4H, $CH_2CH_2CH_2CH_3$), 0.81 (m, 6H, $CH_2CH_2CH_2CH_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz, 273 K): δ 142.5 (C_{imi}), 136.8 (C−Rh, $^1J_{CRh}$ = 32.7 Hz, $^2J_{CP\,cis}$ = 10 Hz, $^2J_{CP\,trans}$ = 147 Hz), 133.2 (br, $C_{aryl\text{-}P}$), 131.9 ($C_{aryl\text{-}imi}$), 129.8 ($C_{aryl\text{-}imi}$), 129.7 ($C_{aryl\text{-}P}$, $^1J_{CP}$ = 17 Hz), 129.7 (C_{imi}), 129.5 ($C_{aryl\text{-}P}$), 127.3 ($C_{aryl\text{-}imi}$), 127.2 ($C_{aryl\text{-}P}$, $^2J_{CP}$ = 4.4 Hz), 120.8 ($C_{aryl\text{-}imi}$), 60.3 (NCH_2N), 47.3 ($CH_2CH_2CH_2CH_3$), 31.6 ($CH_2CH_2CH_2CH_3$), 26.9 (m, PC_2H_4P), 18.9 ($CH_2CH_2CH_2CH_3$), 12.8 ($CH_2CH_2CH_2CH_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 162 MHz, 273 K): δ 38.9 (d, $^1J_{RhP}$ = 60.5). Anal. Calcd for $C_{53}H_{56}I_3N_4P_2Rh$ (1294.60): C, 49.17; H, 4.36; N, 4.33. Found: C, 49.00; H, 4.20; N, 4.31.

Typical Procedure for Catalytic Transfer Hydrogenation. The catalyst was either used as a solution (0.6 mL, 4 mM in *i*PrOH, 5 μmol Rh) or weighed off directly into the reaction flask. It was stirred, together with KOH (0.05 mL of 2 M solution in H_2O, 0.1 mmol) and *i*PrOH (5.0 mL) at reflux for 10 min. Then the ketone (1.0 mmol) was added at once. Aliquots (0.2 mL) were taken at fixed times, quenched in hexane (2 mL), and filtered through a short path of silica, and the silica was washed with diethyl ether or *tert*-butyl methyl ether. The combined organic filtrates were evaporated and analyzed by ^{1}H NMR spectroscopy.

Structure Determination and Refinement of the Complexes. A suitable single crystal was mounted on a Stoe Mark II-imaging plate diffractometer system (Stoe & Cie, 2002) equipped with a graphite monochromator. Data collection was performed at −100 °C (−80 °C for **3f**) using Mo Kα radiation (λ = 0.71073 Å) with a nominal crystal to detector distance of 70 mm (for **3f**), 100 mm (for **3a**, **3c**, and **3d**), and 135 mm (for **2b**, **3b**, and **7**), respectively. All structures were solved by direct methods using the program SHELXS-97 and refined by full matrix least-squares on F^2 with SHELXL-97.[29] The hydrogen atoms were included in calculated positions and treated as riding

(29) Sheldrick, G. M. *Acta Crystallogr. A* **2008**, *64*, 112.

Table 5. Crystallographic Data for Complexes 2b, 3a−d, 3f, 6b, and 7

	2b	3a	3b	3c	3d	3f	7
color, shape	yellow plate	orange rod	orange rod	orange rod	orange rod	orange rod	yellow block
cryst size/mm	0.40 × 0.35 × 0.15	0.35 × 0.30 × 0.20	0.45 × 0.30 × 0.25	0.45 × 0.35 × 0.30	0.40 × 0.35 × 0.35	0.50 × 0.30 × 0.20	0.45 × 0.40 × 0.30
empirical formula	$C_{54}H_{64}I_6N_8Rh_2 \times 5\ CHCl_3$	$C_{21}H_{34}I_3N_6Rh \times CH_3CN$	$C_{31}H_{38}I_3N_6Rh \times 3\ CH_3CN$	$C_{19}H_{30}I_3N_6Rh \times 2\ CH_3CN \times 0.5\ I_2$	$C_{29}H_{34}I_3N_6Rh \times 2.5\ CH_3CN$	$C_{19}H_{30}I_3N_6Rh \times 0.25\ C_6H_{14}$	$C_{53}H_{58}I_3N_4P_2Rh \times 1.5\ C_4H_{10}O$
fw	2389.19	895.21	1101.45	908.21	1052.87	874.64	1405.75
T/K	173(2)	173(2)	173(2)	173(2)	173(2)	193(2)	173(2)
cryst syst	monoclinic	triclinic	triclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$C_{2/c}$ (No. 15)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
unit cell							
a/Å	21.4732(10)	9.8916(7)	12.2798(8)	22.7660(9)	11.2799(6)	9.1548(9)	20.4631(8)
b/Å	18.5585(6)	11.2101(7)	14.1168(9)	17.1487(10)	12.3517(6)	11.9397(12)	17.5908(5)
c/Å	21.8116(10)	15.4797(10)	15.6034(11)	18.2406(7)	15.2258(8)	14.1549(13)	17.3128(6)
α/deg	90	105.961(5)	62.889(5)	90	102.957(4)	95.230(12)	90
β/deg	94.105(4)	95.541(5)	66.075(5)	114.912(3)	101.685(4)	107.292(11)	113.300(3)
γ/deg	90	103.501(5)	79.759(5)	90	94.400(4)	93.650(12)	90
V/Å^3	8669.9(6)	1580.8(2)	2200.7(3)	6458.7(5)	2007.9(2)	1464.4(2)	5723.7(3)
Z	4	2	2	8	2	2	4
D_{calc}/g cm^{-3}	1.830	1.881	1.662	1.868	1.741	1.922	1.631
μ/mm^{-1} (Mo Kα)	3.018	3.493	2.527	3.422	2.766	3.763	2.016
no. of total, unique reflns	101 061, 15 441	21 695, 8490	15 495, 7361	35 931, 8578	39 262, 10824	11 716, 5366	73745, 10209
R_{int}	0.0856	0.0290	0.0222	0.0357	0.0282	0.0334	0.0390
transmn range	0.320−0.527	0.226−0.502	0.412−0.570	0.350−0.416	0.396−0.524	0.299−0.389	0.514−0.622
no. params, restrnts	718, 12	314, 0	455, 0	332, 8	406, 6	263, 0	457, 58
R,[a] R_w,[b]	0.0690, 0.1929	0.0248, 0.0584	0.0246, 0.0639	0.0303, 0.0700	0.0314, 0.1030	0.0300, 0.0721	0.0860, 0.2603
GOF	0.981	1.044	1.031	0.945	0.859	0.912	1.050
min./max. resid density/e Å^{-3}	−3.003, 2.744	−1.310, 0.619	−0.647, 1.005	−1.219, 0.635	−1.742, 1.157	−1.313, 1.155	−4.920, 2.783

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ for all $I > 2\sigma(I)$ [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum(w(F_o^4)]^{1/2}$.

atoms using SHELXL-97 default parameters. All non-hydrogen atoms were refined anisotropically. A semiempirical absorption correction was applied using MULscanABS as implemented in PLATON03.[30]

The binuclear complex **2b** crystallizes with five $CHCl_3$ molecules per asymmetric unit (six positions, of which two are half-occupied and two are disordered). In compound **3c**, one of the two cocrystallized acetonitrile molecules and the I_2 molecule are disordered. Complex **3d** crystallizes with three acetonitrile molecules per asymmetric unit; one of them is half-occupied. The cocrystallized hexane molecule in **3f** is on a special position and half-occupied. It is strongly disordered, and therefore, the SQUEEZE option in PLATON has been used to remove the electron density corresponding to the hexane molecule. Nevertheless it has been included in all further calculations. In the structure of **7**, two strongly disordered ether molecules are cocrystallized. It was not possible to find a reasonable model defining the disorder. The SQUEEZE instruction in PLATON03[30] was used to calculate the potential solvent-accessible area in the unit cell; 926 $Å^3$ was calculated containing about 260 electrons. Therefore, 6 ether molecules (6×42 electrons) per unit cell were included in all further calculations. Further details on data collection and refinement parameters are collected in Table 5. Crystallographic data (excluding structure factors) for the structures **2b**, **3a**−**d**, **3f**, and **7** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 688121−688127. Copies of the data can be obtained free of charge on application to CCDS, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (int.) +44-1223-336-033; e-mail: deposit@ccds.cam.ac.uk].

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Supporting Information Available: Crystallographic data for all complexes in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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