DOI: 10.1002/ejic.200900570

16-Electron (Arene)ruthenium Complexes with Superbasic Bis(imidazolin-2-imine) Ligands and Their Use in Catalytic Transfer Hydrogenation

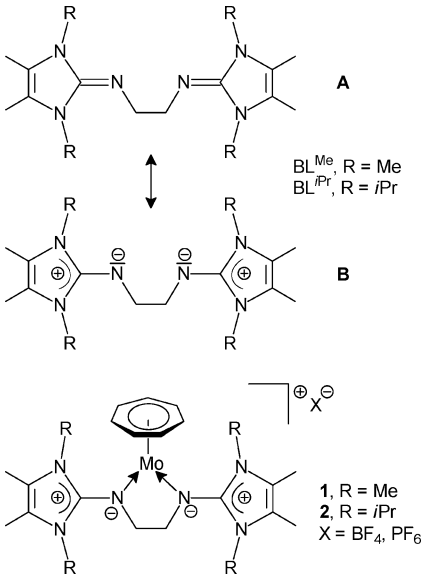
Thomas Glöge,[a] Dejan Petrovic,[a] Cristian Hrib,[a] Peter G. Jones,[a] and Matthias Tamm*[a]

Keywords: Ruthenium / Arene ligands / N ligands / Coordinative unsaturation / Hydrogenation

The ligands *N*,*N*′-bis(1,3,4,5-tetramethylimidazolin-2-ylidene)-1,2-ethanediamine (BL^{Me}) and *N*,*N*′-bis(1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidene)-1,2-ethanediamine (BL^{iPr}) react with $[(\eta^5\text{-}C_5Me_5)RuCl]_4$ to afford cationic 16-electron half-sandwich complexes $[(\eta^5\text{-}C_5Me_5)Ru(BL^R)]^+$ (R = Me, **3**; R = *i*Pr, **4**), which resist coordination of the chloride counterion because of the strong electron-donating ability of the diimine ligands. Upon reaction with $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ or $[(\eta^6\text{-}C_{10}H_{14})RuCl_2]_2$, these ligands stabilize dicationic 16-electron benzene and cymene complexes of the type $[(\eta^6\text{-}C_6H_6)Ru(BL^R)]^{2+}$ (R = Me, **5**; R = *i*Pr, **6**) and $[(\eta^6\text{-}C_{10}H_{14})Ru(BL^R)]^{2+}$ (R = Me, **7**; R = *i*Pr, **8**). The X-ray crystal structure of [**5**]Cl_2 reveals the absence of any direct Ru–Cl interaction, whereas a long Ru–Cl bond, supported by two CH···Cl hydrogen bonds, is observed for [(**6**)Cl]Cl in the solid state. Treatment of the dichlorides of **6** and **8** with $NaBF_4$ affords [**6**]$(BF_4)_2$ and [**8**]$(BF_4)_2$, which are composed of individual dications and tetrafluoroborate ions with no direct Ru–F interaction. All complexes catalyze the transfer hydrogenation of acetophenone in boiling 2-propanol.

Introduction

Poly(guanidine) ligands[1] have found remarkable applications as superbasic proton sponges[2] and as ligands for transition metal complexation,[3] with particular emphasis on copper coordination and dioxygen activation chemistry.[4,5] Moreover, mono- and bis(guanidine) chelate ligands have been used for the preparation of homogeneous catalysts, e.g. for the ring-opening polymerization of lactides and for the atom transfer radical polymerization of styrene.[6,7] In general, guanidine ligands attain their unique properties from the ability to delocalize a positive charge over the guanidine CN_3 moiety, producing compounds with considerably enhanced basicity and nucleophilicity. These characteristics become even more pronounced in poly(imidazolin-2-imine) ligands, since the imidazole ring is particularly effective in stabilizing a positive charge. This induces a strong polarization of the exocyclic C=N bond,[8,9] which can be described by the two resonance structures **A** and **B** for the BL^{iPr} and BL^{Me} ligands (Scheme 1). Upon metal coordination, the contribution of the ylidic form **B** can be expected to increase considerably, and thus these ligands exhibit a particularly strong electron-donating capacity toward transition metal atoms.[10–14]

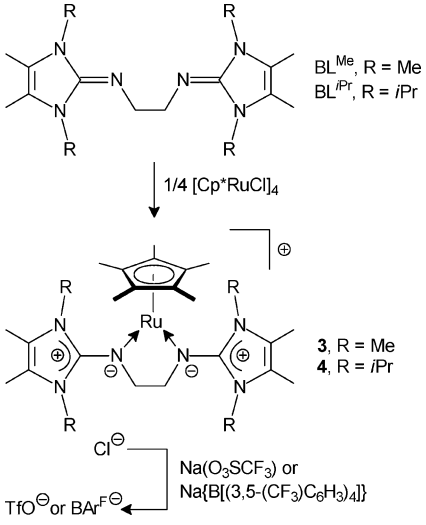


Scheme 1.

The bidentate ligands BL^{iPr} and BL^{Me} can be conveniently synthesized by introducing a CH_2CH_2 bridge between two imidazolin-2-imines, which have proved to be valuable ligands in their own right[11] and can be obtained from the reaction of trimethylsilyl azide (Me_3SiN_3) with N-heterocyclic carbenes of the imidazolin-2-ylidene type.[9] The pronounced electron-donor properties of these bis(imidazolin-2-imines) were documented by the preparation of highly reactive copper(I) complexes, allowing effective

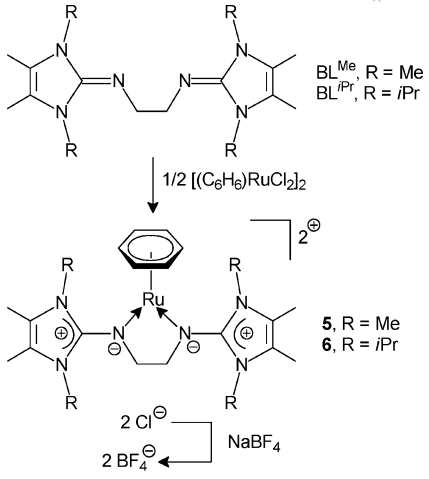
[a] Institut für Anorganische und Analytische Chemie, Technische Universität Carolo-Wilhelmina,
Hagenring 30, 38106 Braunschweig, Germany
Fax: +49-251-391-5309
E-mail: m.tamm@tu-bs.de

O=O and C–Cl bond activation, CO_2 fixation and Cu^I disproportionation.[7,12] Furthermore, it was shown that the unusual stability of coordinatively unsaturated 16-electron molybdenum and ruthenium half-sandwich complexes of the type $[(\eta^7\text{-}C_7H_7)Mo(BL^R)]^+$ (R = Me, **1**; R = *i*Pr, **2**) and $[(\eta^5\text{-}C_5Me_5)Ru(BL^R)]^+$ (R = Me, **3**; R = *i*Pr, **4**) can be ascribed to the strongly π-basic nature of these ligand systems (Schemes 1 and 2).[13,14]

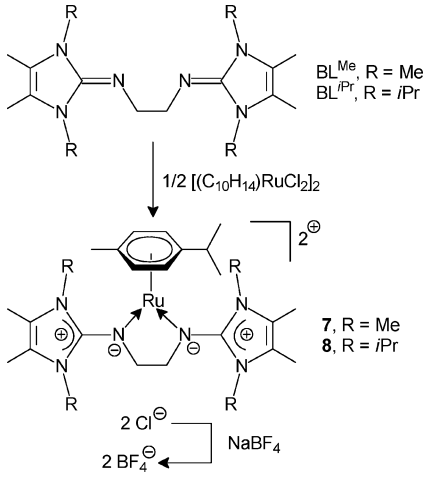


Scheme 2.

Substitution of the Cp* ring in $[(\eta^5\text{-}C_5Me_5)Ru(BL^R)]^+$ by benzene or cymene (1-isopropyl-4-methylbenzene, $C_{10}H_{14}$) affords the half-sandwich complex fragments $[(\eta^6\text{-}C_6H_6)Ru(BL^R)]^{2+}$ (R = Me, **5**; R = *i*Pr, **6**) and $[(\eta^6\text{-}C_{10}H_{14})Ru(BL^R)]^{2+}$ (R = Me, **7**; R = *i*Pr, **8**), respectively, and, because dicationic 16-electron half-sandwich ruthenium complexes are to the best of our knowledge unknown, we aimed at the stabilization of such complexes by the BL^R ligands. The resulting complexes are also potential catalysts for various organic transformations, in view of the fact that 16-electron (arene)ruthenium complexes are frequently encountered as intermediates in ruthenium-catalyzed reactions.[15] In addition, numerous catalytic applications are known for monocationic complexes of the type $[(\eta^6\text{-}C_6H_6)Ru(N^{\cap}N)X]Y$ and $[(\eta^6\text{-}C_{10}H_{14})Ru(N^{\cap}N)X]Y$, where N∩N represents a bidentate nitrogen-donor ligand, X a halogen atom and Y a non-coordinating anion.[16] For instance, these systems have been used as catalysts for the hydrogenation of alkenes,[17] olefin metathesis,[18] Diels–Alder reactions,[19] and, most prominently, for hydrogen-transfer reduction of ketones[20] and imines;[21] the latter reaction has been brought to near perfection with high yields and high enantiopurity by application of ruthenium complexes such as $[(\eta^6\text{-arene})Ru(NH_2CHRCHRNTos)X]$.[22] In a similar fashion, we envisaged that coordinative unsaturation together with the presence of amido-type nitrogen groups (Schemes 1, 2, 3, and 4) renders the Mo and Ru complexes **1**–**8** active in hydrogen transfer catalysis. Accordingly, this contribution provides a comparative study of the catalytic activity of **1**–**8** in transfer hydrogenation of acetophenone with 2-propanol as the hydrogen source.



Scheme 3.



Scheme 4. Synthesis of [**7**] and [**8**].

Results and Discussion

As previously reported in a short communication,[13a] the complexes $[(\eta^5\text{-}C_5Me_5)Ru(BL^{Me})]Cl$ ([**3**]Cl) and $[(\eta^5\text{-}C_5Me_5)Ru(BL^{iPr})]Cl$ ([**4**]Cl) are isolated as violet, crystalline complexes from the reaction of tetrameric $[(\eta^5\text{-}C_5Me_5)RuCl]_4$ (Scheme 2)[23,24] with the ligands BL^{Me} and BL^{iPr}. The chloride counteranions in these complexes can be easily exchanged for the triflate (OTf) or tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (BAr^F) anions by reaction with the corresponding sodium salts. The solid-state structures of [**3**]OTf, [**4**]Cl and [**4**]OTf revealed the presence of cationic 16-electron complexes and the absence of metal–anion contacts.[13a] We have now obtained single crystals of [**3**]Cl from acetone/diethyl ether solution. The shortest Ru–Cl distance is 6.01 Å, indicating a lack of significant contacts between the Ru centers and the chloride anions. As expected, the cationic half-sandwich complex exhibits a two-legged piano-stool geometry with the $\eta^5\text{-}C_5Me_5$ and the η^2-diimine ligands adopting a pseudotrigonal-planar coordination sphere around the ruthenium atom (Figure 1).

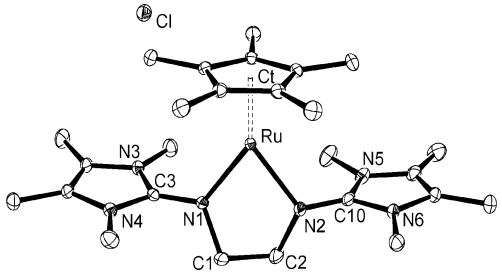


Figure 1. ORTEP diagram of the complex [**3**]Cl with thermal displacement parameters drawn at 50% probability.

The N1–Ru–N2 angle is 77.33(4)°, and the sum of this ligand bite angle and the two Ct–Ru–N angles is 360.0° (Ct = centroid of the Cp* ring). Accordingly, the cation **3** can be regarded as being almost perfectly C_{2v}-symmetric. The Ru–N distances of 2.0626(10) and 2.0741(10) Å are almost identical with those determined for [**3**]OTf [2.0604(17) Å and 2.0729(16) Å];[13a] they are significantly shorter than those in the related complex [(η^5-C_5Me_5)Ru(tmeda)]BAr^F [2.183(7) Å, 2.180(6) Å][25] and fall in the same range as observed for the neutral amidinate complex [(η^5-C_5Me_5)-Ru{*i*PrNC(Me)N*i*Pr}] [2.073(3) Å].[26] The short Ru–N bonds in [**3**]Cl are consistent with the expected strong electron-releasing capability of the BL^{Me} ligand, as indicated by the ylidic resonance structure shown in Scheme 2. Charge separation and delocalization in the coordinated BL^{Me} ligand can also be clearly deduced from the observation of perpendicularly oriented imidazole moieties with respect to the N–Ru–N plane (dihedral angles 81.8 and 86.4°); this orientation rules out the possibility of any substantial π-interaction between the coordinated nitrogen atoms and the imidazole rings. Consequently, the exocyclic C–N bonds [C3–N1 1.3411(14) Å, C10–N2 1.3532(15) Å] are elongated and become almost equal to the intra-ring C3–N3/N4 and C10-N5/N6 bond lengths, respectively. This structural feature can be illustrated by the parameter $\rho = 2a/(b + c)$, with *a*, *b* and *c* representing the exo- (*a*) and endocyclic (*b*, *c*) distances within the CN_3 guanidine moiety.[3b,6b] In agreement with efficient charge delocalization, ρ values of 0.990 and 0.998 are determined for the two different CN_3 sites.

A suitable starting material for providing the [(η^6-C_6H_6)-$Ru]^{2+}$ moiety is dimeric [(η^6-C_6H_6)$RuCl_2]_2$,[27] and its reaction with BL^{Me} afforded [(η^6-C_6H_6)Ru(BL^{Me})]Cl_2 ([**5**]Cl_2) as a deep-blue solid after precipitation from thf solution with *n*-hexane. The resulting complex is soluble in polar solvents such as acetonitrile and dichloromethane. Its ^1H NMR spectrum in CD_3CN exhibits a benzene resonance at δ = 5.15 ppm and three additional singlets at δ = 3.64, 2.88 and 2.21 ppm for the NCH_3, NCH_2 and CCH_3 groups, respectively, indicating fast chlorine exchange or the presence of the C_{2v}-symmetric dication **5** in solution. Single crystals suitable for an X-ray diffraction analysis were grown from dichloromethane solution, and the molecular structure of [**5**]Cl_2, which displays crystallographic C_2 symmetry, is shown in Figure 2. The shortest Ru–Cl distance is 5.15 Å, excluding any metal–chlorine interaction. To the best of our knowledge, **5** is the first example of a stable 16-electron dicationic half-sandwich ruthenium complex, underlining once again the strong electron-donating ability of the BL^{Me} ligand. This affords an exceptionally short Ru–N1 bond of 1.977(2) Å together with an elongated N1–C2 bond of 1.364(3) Å, which even exceeds the values for the intra-ring C2–N2 and C2–N3 distances of 1.340(3) and 1.345(3) Å. Consequently, the ρ value of 1.016 indicates an inversion of the usual bond length distribution in the guanidine system. The dihedral angle between the imidazole and N1–Ru–N1A planes is 88.3°, in agreement with the expected orthogonality.

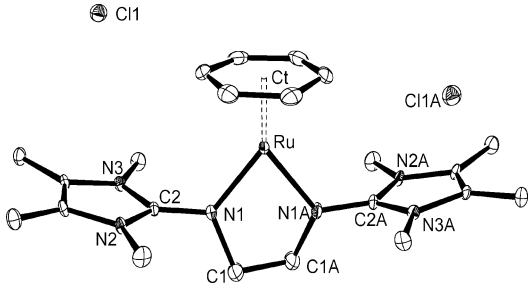


Figure 2. ORTEP diagram of [(η^6-C_6H_6)Ru(BL^{Me})]Cl_2 ([**5**]Cl_2) with thermal displacement parameters drawn at 50% probability. The letter "A" indicates atoms generated via the twofold axis.

In contrast to the blue color of [**5**]Cl_2, treatment of [(η^6-C_6H_6)$RuCl_2]_2$ with BL^{iPr} afforded a dark red solid of the composition [**6**]Cl_2, suggesting the presence of a different coordination sphere. Indeed, X-ray diffraction analysis of [**6**]Cl_2·thf revealed an asymmetric unit that is composed of an [(η^6-C_6H_6)Ru(BL^{iPr})Cl]$^+$ cation together with an uncoordinated chloride counterion and a thf solvate molecule (Figure 3, thf omitted for clarity). The cation exhibits a three-legged piano-stool geometry with ruthenium–nitrogen distances of Ru–N1 2.0732(12) Å and Ru–N2 2.0849(11) Å that are significantly longer than those observed in **5**. Presumably, this elongation is largely a consequence of additional chloride coordination, despite the fact that the Ru–Cl1 distance of 2.4853(4) Å indicates a comparatively weak interaction. In fact, this Ru–Cl bond seems to be the longest ever observed for cationic complexes of the type [(η^6-C_6H_6)-Ru(N∩N)Cl]$^+$,[28] and a longer Ru-Cl distance of 2.521(1) Å has only been observed for a neutral (benzene)ruthenium(II) complex containing the anionic β-diketiminate ligand XyN–C(Me)–CH–C(Me)–NXy (Xy = 2,6-dimethylphenyl).[29]

In view of the larger steric requirements of the BL^{iPr} ligand in comparison with BL^{Me}, the presence of Ru–Cl bonding in [**6**]Cl_2 and its absence in [**5**]Cl_2 seems to be counterintuitive; however, close inspection of the [(η^6-C_6H_6)Ru-(BL^{iPr})Cl]$^+$ structure reveals two additional intracationic CH···Cl1 contacts of 2.64 and 2.82 Å that fall below the sum of the van der Waals radii of 2.95 Å [r_{vdW}(Cl) = 1.75 Å, r_{vdW}(H) = 1.20 Å][30] and might therefore support the weak Ru–Cl interaction in the solid state (Figure 3). In contrast, solution NMR studies indicate C_{2v} symmetry,

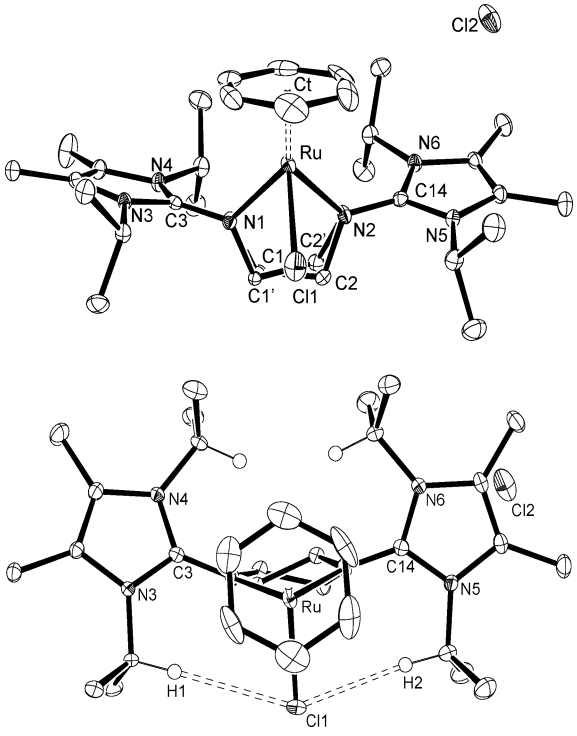


Figure 3. Two ORTEP diagrams of $[(\eta^6\text{-}C_6H_6)Ru(BL^{iPr})Cl]Cl$ in $[\mathbf{6}]Cl_2 \cdot thf$ with thermal displacement parameters drawn at 50% probability; the ethylene bridge is disordered.

which implies rapid dynamic behavior and fast exchange of the chloride anions. Accordingly, the ^1H NMR spectrum in $[D_6]$acetone shows three singlets at δ = 5.20, 2.89 and 2.39 ppm for the C_6H_6, NCH_2 and CCH_3 hydrogen atoms, respectively. The isopropyl groups give rise to a septet, or more specifically a quartet-of-quartets C*H* resonance at δ = 5.62 ppm and to two broad doublets at δ = 1.73 and 1.46 ppm for the diastereotopic methyl groups, indicating a hindered rotation around the N1–C3 and N2–C14 axes at room temperature on the NMR timescale. At lower temperature, only a sharpening of these doublets is observed, whereas the chloride ion is still rapidly exchanged even at –50 °C.

The chloride ions can be easily exchanged by weakly coordinating anions such as tetrafluoroborate. This can be accomplished by addition of 2 equiv. of $NaBF_4$ to a CH_2Cl_2 solution of $[\mathbf{6}]Cl_2$ followed by removal of NaCl (Scheme 3); a deep blue solid is obtained. Single crystals of $[\mathbf{6}](BF_4)_2 \cdot CH_2Cl_2$ were obtained by diffusion of diethyl ether into a saturated dichloromethane solution. In contrast to $[\mathbf{6}]Cl_2$, no metal–anion interaction is observed, affording again a pseudotrigonal-planar coordination sphere at the ruthenium atom (Figure 4). As expected, the Ru–N bonds [1.9818(16) and 1.9883(17) Å] are shorter than those found in $[\mathbf{6}]Cl_2$ and are almost identical to the Ru–N distances in $[\mathbf{5}]Cl_2$. Consequently, similar ρ values of 1.011 and 1.012 are determined. In contrast to the molecular structure of the Cp* complex [**4**]OTf, there is no indication of intramolecular CH···Ru contacts.[13a]

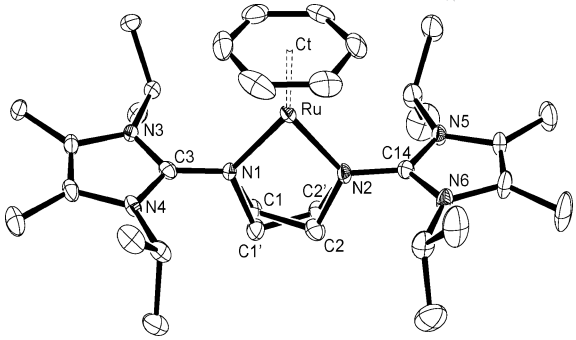


Figure 4. ORTEP diagram of the cation in $[\mathbf{6}](BF_4)_2 \cdot CH_2Cl_2$ with thermal displacement parameters drawn at 50% probability; the ethylene bridge is disordered.

In a similar fashion as described for the preparation of the (benzene)ruthenium complexes (vide supra), the corresponding cymene complexes $[\mathbf{7}]Cl_2$ and $[\mathbf{8}]Cl_2$ were isolated as blue or red solids from the reaction of $[(\eta^6\text{-}C_{10}H_{14})RuCl_2]_2$[27] with BL^{Me} or BL^{iPr}, respectively (Scheme 4). The ^1H and ^{13}C NMR spectra exhibit the typical resonances for the cymene ligand.[17a,18,19b] The signals arising from the coordinated BL^{Me} and BL^{iPr} ligands match those reported for the benzene complexes **5** and **6**, apart from the observation of just one broad singlet for the isopropyl methyl groups in **8**, which indicates a different or more complex dynamic behavior. Addition of 2 equiv. of $NaBF_4$ to a dichloromethane solution of $[\mathbf{8}]Cl_2$ yielded the dark blue complex $[\mathbf{8}](BF_4)_2$. The molecular structure of $[\mathbf{8}](BF_4)_2 \cdot CH_2Cl_2$ was established by X-ray diffraction analysis (Figure 5), revealing the absence of any short Ru–F contacts between the $[(\eta^6\text{-}C_{10}H_{14})Ru(BL^{iPr})]^{2+}$ and the BF_4^- ions. The structural parameters of the dication **8** are very similar to those established for the tetrafluoroborate salt of **6**, and the same pseudotrigonal-planar coordination sphere is observed, with only slightly longer Ru–N bonds of 1.994(2) and 2.003(2) Å. In contrast to the ecliptic orientation of the benzene ring in **6** with respect to the imine C–N and arene C–H bonds, the cymene ligand in **8** is oriented in a stag-

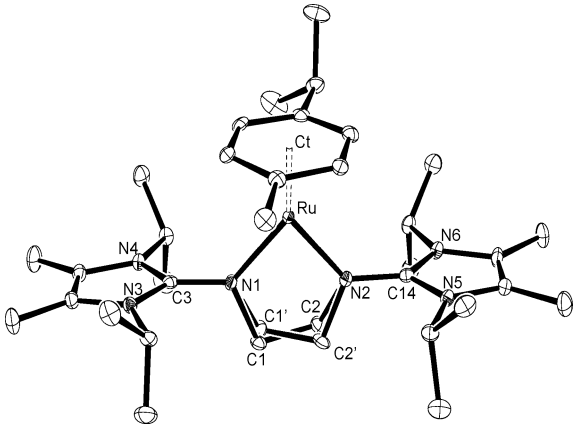
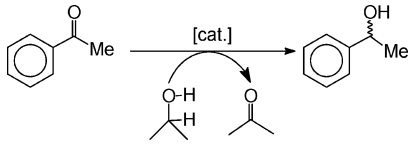


Figure 5. ORTEP diagram of the cation in $[\mathbf{8}](BF_4)_2 \cdot CH_2Cl_2$ with thermal displacement parameters drawn at 50% probability; the ethylene bridge is disordered.

gered fashion, allowing the *i*Pr and Me substituents to adopt the sterically least hindered positions between the two imidazole sites. It should be noted that complex **8** represents the first example of a stable 16-electron dicationic (cymene)ruthenium complex to the best of our knowledge; structurally related complexes have only been obtained with mono- and dianionic κ^2-N∩N ligands.[31] For instance, Ru–N bond lengths of 2.065(6) and 1.897(6) Å have been reported for [(η^6-$C_{10}H_{14}$)Ru(NH–CHPh–CHPh–NTos)][31b] and 1.966(3)/1.946(3) Å for [(η^6-$C_{10}H_{14}$)Ru(sMes-N–N=N–N–Mes)] (sMes = 2,4,6-*t*$Bu_3C_6H_2$, Mes = 2,4,6-$Me_3C_6H_2$), which contains a dianionic tetrazene ligand.[31c]

Transfer Hydrogenation of Acetophenone

Transfer hydrogenation,[32] in particular its asymmetric version,[33] has become a standard method for the reduction of ketones to secondary alcohols, with 2-propanol serving as the most common organic hydrogen source. Because this reaction can be catalyzed efficiently by numerous (benzene)- and (cymene)ruthenium complexes, we have studied the catalytic performance of the molybdenum and ruthenium complexes **1**–**7** in the transfer hydrogenation of acetophenone (Scheme 5). The reactions were performed in boiling 2-propanol (b.p. = 82 °C) with 1 mol-% of catalyst loadings and potassium hydroxide (10 mol-%) as the base. The reaction progress was monitored by gas chromatography (GC), and the results are summarized in Table 1. The Mo complexes [**1**]PF_6 and [**2**]BF_4 proved to be insufficiently active, and only 9% and 18% conversion was determined after 24 h, respectively. In contrast, all Ru complexes are capable of completing this reaction within 1.5–6 h, with the BL^{Me} complexes being generally more active than their BL^{iPr} con-



Scheme 5. Transfer hydrogenation of acetophenone.

Table 1. Catalytic transfer hydrogenation of acetophenone.[a]

Substrate	Catalyst	Time [h]	Conversion [%]
Acetophenone	[**1**]PF_6	24	9
Acetophenone	[**2**]BF_4	24	18
Acetophenone	[**3**]Cl	1.5	96
Acetophenone	[**3**]BAr^F	1.5	98
Acetophenone	[**3**]OTf[b]	6	77
Acetophenone	[**3**]OTf[c]	144	40
Acetophenone	[**3**]OTf[d]	24	7
Acetophenone	[**4**]BAr^F	6	90
Acetophenone	[**4**]BAr^F[e]	24	33
Acetophenone	[**5**]Cl_2	2	96
Acetophenone	[**6**]Cl_2	6	97
Acetophenone	[**7**]Cl_2	2	99

[a] Conditions: 0.02 mmol of cat., 0.2 mmol of KOH, 10 mL of *i*PrOH, 2 mmol of acetophenone, temperature: 82 °C. [b] Without KOH. [c] Room temperature. [d] Room temperature and 5 bar H_2 pressure. [e] 0.1 mol-% catalyst loading.

geners. The impact of the anion on the catalytic activity seems to be negligible, as exemplified for the most active Cp*Ru system by comparison of the conversion/time diagrams for [**3**]Cl and [**3**]BAr^F (Figure 6). In contrast, changes of the reaction conditions strongly influence the progress of the ketone reduction. In the absence of KOH, the reaction slows down significantly; however, [**3**]OTf is still catalytically active, indicating that the diimine ligand BL^{Me} is basic enough to promote activation and deprotonation of 2-propanol. Furthermore, attempts to carry out transfer hydrogenation at room temperature met with only limited success (Table 1).

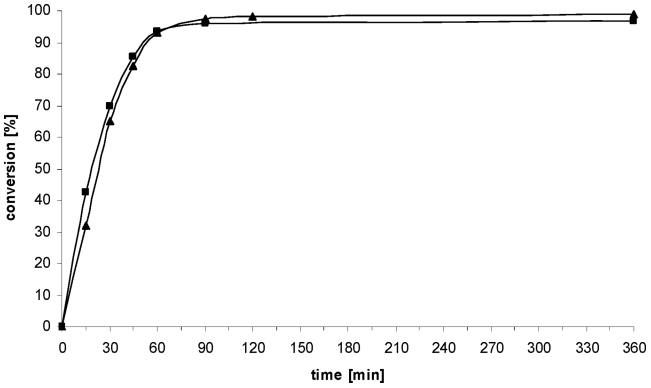


Figure 6. Conversion/time diagrams for [**3**]Cl (squares) and [**3**]BAr^F (triangles).

Conclusions

We have shown that the bis(imidazolin-2-imine) ligands BL^{Me} and BL^{iPr} can stabilize cationic and dicationic 16-electron half-sandwich ruthenium complexes containing pentamethylcyclopentadienyl, benzene or cymene ligands. The unusual stability of these complexes can be ascribed to the strong π-electron-releasing ability of BL^{Me} and BL^{iPr}, leading to a weak propensity of the Ru atom to coordinate other π-basic ligands such as chloride. In accord with the presence of 16-electron species in solution, reasonable activity in transfer hydrogenation of ketones can be observed.

Experimental Section

General: All operations were performed under dry argon by using Schlenk and vacuum techniques. All solvents were purified by standard methods and distilled prior to use. ^1H and ^{13}C NMR spectra were recorded with Bruker DPX 200 and DPX 400 devices. The chemical shifts are given in ppm relative to TMS. The spin coupling patterns are indicated as s (singlet), d (doublet), m (multiplet), sept (septet) and br. (broad, for unresolved signals). Elemental analyses (C, H, N) were performed with an Elementar Vario EL III CHNS elemental analyzer. Mass spectrometry was performed with a Finnigan MAT 90 device. UV/Vis spectra were recorded with a Varian Cary 50 device. Sodium triflate, sodium tetrafluoroborate and sodium BAr^F were obtained from Aldrich and used as received. BL^{Me},[13a] BL^{iPr},[13a] [**1**]PF_6,[14] [**2**]BF_4,[14] the ruthenium heterocubane [Cp*RuCl]$_4$,[23] the ruthenium dimers [(η^6-C_6H_6)$RuCl_2$]$_2$ and

$[(\eta^6\text{-}C_{10}H_{14})RuCl_2]_2$,[27] and phellandrene[34] were prepared according to literature procedures.

$[(\eta^5\text{-}C_5Me_5)Ru(BL^{Me})]Cl$ ([3]Cl): A solution of BL^{Me} (127.9 mg, 0.42 mmol) in thf (5 mL) was added dropwise to an orange suspension of $[(\eta^5\text{-}C_5Me_5)RuCl]_4$ (108.7 mg, 0.10 mmol) in thf (10 mL) at room temperature. During the addition of the ligand the reaction mixture turned purple, and the solution was stirred for 3 h. The volume of thf was reduced to 5 mL, and the product was precipitated with *n*-hexane (20 mL). Filtration, washing with *n*-hexane (2 × 10 mL) and drying in vacuo afforded the product as a purple solid (189 mg, 82%). ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C): δ = 3.69 (s, 12 H, NCH_3), 2.62 (s, 4 H, CH_2), 2.32 (s, 12 H, CCH_3), 1.33 (s, 15 H, $CpCH_3$) ppm. ^{13}C NMR (100.52 MHz, [D$_6$]acetone, 25 °C): δ = 157.2 (NCN), 120.0 ($NCCH_3$), 71.1 (C_5Me_5), 55.1 (CH_2), 31.1 (NCH_3), 11.2 (C_5Me_5), 8.7 (CCH_3) ppm. UV/Vis(CH_2Cl_2): λ_{max} (ε) = 526 (2507) nm. IR (KBr/Nujol): $\tilde{\nu}$ = 1462 (C=N) cm^{-1}. $C_{26}H_{43}ClN_6Ru$ (576.2): calcd. C 54.20, H 7.52, N 14.59; found C 53.59, H 7.23, N 14.32.

$[(\eta^5\text{-}C_5Me_5)Ru(BL^{iPr})]Cl$ ([4]Cl): A solution of BL^{iPr} (175.0 mg, 0.42 mmol) in thf (10 mL) was added dropwise to an orange suspension of $[(\eta^5\text{-}C_5Me_5)RuCl]_4$ (108.7 mg, 0.10 mmol) in thf (5 mL) at room temperature. During the addition of the ligand the reaction mixture turned purple, and the solution was stirred overnight. The volume of thf was reduced to 5 mL, and the product was precipitated with *n*-hexane (20 mL). Filtration, washing with *n*-hexane (2 × 10 mL) and drying in vacuo afforded the product as a purple solid (238 mg, 88%). ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C): δ = 5.27 (sept, 4 H, NCH), 2.60 (s, 4 H, CH_2), 2.40 (s, 12 H, CCH_3), 1.80 (d, 12 H, $CHCH_3$), 1.48 (s, 15 H, $CpCH_3$) 1.42 (d, 12 H, $CHCH_3$) ppm. ^{13}C NMR (100.52 MHz, [D$_6$]acetone, 25 °C): δ = 157.3 (NCN), 118.5 ($NCCH_3$), 70.7 (C_5Me_5), 58.0 (CH_2), 49.1 (NCH), 23.4 ($CHCH_3$), 22.4 ($CHCH_3$), 11.5 (C_5Me_5), 10.5 (CCH_3) ppm. UV/Vis(CH_2Cl_2): λ_{max} (ε) = 494 (1636) nm. IR (KBr/Nujol): $\tilde{\nu}$ = 1462 (C=N) cm^{-1}. $C_{34}H_{59}ClN_6Ru$ (688.40): calcd. C 59.32, H 8.64, N 12.21; found C 58.67, H 8.71, N 11.27.

$[(\eta^5\text{-}C_5Me_5)Ru(BL^{Me})]OTf$ ([3]OTf): A solution of NaOTf (178.9 mg, 1.04 mmol) in thf (15 mL) was added dropwise to a purple solution of **[3]**Cl (600 mg, 1.04 mmol) in thf (25 mL) at room temperature. The solution was stirred for 2 h and then filtered. The volume of thf was reduced to 5 mL and the product precipitated with *n*-hexane (30 mL). Filtration, washing with *n*-hexane (2 × 15 mL) and drying in vacuo afforded the product as a purple solid (681 mg, 95%). ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C): δ = 3.68 (s, 12 H, NCH_3), 2.62 (s, 4 H, CH_2), 2.31 (s, 12 H, CCH_3), 1.33 (s, 15 H, $CpCH_3$) ppm. ^{13}C NMR (100.52 MHz, [D$_6$]acetone, 25 °C): δ = 157.3 (NCN), 122.5 (CF_3), 120.0 ($NCCH_3$), 71.1 (C_5Me_5), 55.1 (CH_2), 31.0 (NCH_3), 11.1 (C_5Me_5), 8.7 (CCH_3) ppm. UV/Vis(CH_2Cl_2): λ_{max} (ε) = 526 (2252) nm. $C_{27}H_{43}F_3N_6O_3RuS$ (689.80): calcd. C 47.01, H 6.28, N 12.18; found C 47.05, H 6.43, N 11.86.

$[(\eta^5\text{-}C_5Me_5)Ru(BL^{iPr})]OTf$ ([4]OTf): A solution of NaOTf (55.1 mg, 0.32 mmol) in thf (10 mL) was added dropwise to a purple solution of **[4]**Cl (222 mg, 0.32 mmol) in thf (15 mL) at room temperature. The solution was stirred for 2 h and then filtered. The volume of thf was reduced to 5 mL, and the product was precipitated with *n*-hexane (20 mL). Filtration, washing with *n*-hexane (2 × 10 mL) and drying in vacuo afforded the product as a purple solid (230 mg, 91%). ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C): δ = 5.27 (sept, 4 H, NCH), 2.60 (s, 4 H, CH_2), 2.40 (s, 12 H, CCH_3), 1.80 (d, 12 H, $CHCH_3$), 1.48 (s, 15 H, $CpCH_3$) 1.42 (d, 12 H, $CHCH_3$) ppm. ^{13}C NMR (100.52 MHz, [D$_6$]acetone, 25 °C): δ = 157.3 (NCN), 122.5 (CF_3), 118.5 ($NCCH_3$), 70.7 (C_5Me_5), 58.0 (CH_2), 49.1 (NCH), 23.4 ($CHCH_3$), 22.4 ($CHCH_3$), 11.5 (C_5Me_5), 10.5 (CCH_3) ppm. UV/Vis(CH_2Cl_2): λ_{max} (ε) = 514 (1801) nm. $C_{35}H_{59}F_3N_6O_3RuS$ (802.01): calcd. C 52.42, H 7.41, N 10.48; found C 50.45, H 6.94, N 9.61.

$[(\eta^5\text{-}C_5Me_5)Ru(BL^{Me})]BAr^F$ ([3]BAr^F): A solution of $NaBAr^F$ (292.4 mg, 0.33 mmol) in thf (15 mL) was added dropwise to a purple solution of $[(\eta^5\text{-}C_5Me_5)Ru(BL^{Me})]Cl$ (188.1 mg, 0.33 mmol) in thf (25 mL) at room temperature. The solution was stirred for 2 h and then filtered. The volume of thf was reduced to 5 mL and the product precipitated with *n*-hexane (30 mL). Filtration, washing with *n*-hexane (2 × 15 mL) and drying in vacuo afforded the product as a purple solid (418.4 mg, 90%). ^{1}H NMR (400 MHz, [D$_6$]-acetone, 25 °C): δ = 7.66 (m, 8 H, *ortho*-BAr^F), 7.54 (m, 4 H, *para*-BAr^F), 3.54 (s, 12 H, NCH_3), 2.49 (s, 4 H, CH_2), 2.16 (s, 12 H, CCH_3), 1.19 (s, 15 H, $CpCH_3$) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]-acetone, 25 °C): δ = 162.5 (B-*ipsoC*), 157.3 (NCN), 135.6 (B-*orthoC*), 129.9 (CF_3), 126.8 (B-*metaC*), 120.3 ($NCCH_3$), 118.5 (B-*paraC*), 71.1 (C_5Me_5), 55.0 (CH_2), 31.0 (NCH_3), 11.1 (CCH_3), 8.6 (C_5Me_5) ppm. $C_{58}H_{55}BClF_{24}N_6Ru$ (1404.0): calcd. C 49.62, H 3.95, N 5.99; found C 49.52, H 4.41, N 5.41.

$[(\eta^5\text{-}C_5Me_5)Ru(BL^{iPr})]BAr^F$ ([4]BAr^F): A solution of $NaBAr^F$ (257.5 mg, 0.29 mmol) in thf (15 mL) was added dropwise to a purple solution of $[(\eta^5\text{-}C_5Me_5)Ru(BL^{iPr})]Cl$ (200.0 mg, 0.29 mmol) in thf (20 mL) at room temperature. The solution was stirred for 2 h and then filtered. The volume of thf was reduced to 5 mL and the product precipitated with *n*-hexane (30 mL). Filtration, washing with *n*-hexane (2 × 15 mL) and drying in vacuo afforded the product as a purple solid (406.3 mg, 92%). ^{1}H NMR (400 MHz, [D$_6$]-acetone, 25 °C): δ = 7.82 (m, 8 H, *ortho*), 7.70 (s, 4 H, *para*), 5.29 (sept, 4 H, NC*H*), 2.63 (s, 4 H, CH_2), 2.42 (s, 12 H, $NCCH_3$), 1.82 (d, 12 H, $CHCH_3$), 1.50 (s, 15 H, Cp*-CH_3), 1.45 (d, 12 H, $CHCH_3$) ppm. ^{13}C NMR (100.52 MHz, [D$_6$]acetone, 25 °C): δ = 163.4 (B-$C_{arom.}$), 162.9 (B-$C_{arom.}$), 162.4 (B-$C_{arom.}$), 161.9 (B-$C_{arom.}$), 157.3 (NCN), 135.6 (CF_3), 130.5 ($C_{arom.}$), 130.2 ($C_{arom.}$), 129.9 ($C_{arom.}$), 129.5 (CF_3), 126.8 ($C_{arom.}$), 124.0 (CF_3), 121.0 (p-*C*H), 118.5 ($NCCH_3$), 118.4 (CF_3), 70.7 (C_5Me_5), 58.0 (NC_2H_4N), 49.1 [$NCH(CH_3)_2$], 23.4 ($NCHCH_3$), 22.4 ($NCHCH_3$), 11.5 (C_5Me_5), 10.5 (CCH_3) ppm. $C_{66}H_{71}BF_{24}N_6Ru$ (1516.2): calcd. C 52.28, H 4.72, N 5.54; found C 52.35, H 4.64, N 4.81.

$[(\eta^6\text{-}C_6H_6)Ru(BL^{Me})]Cl_2$ ([5]Cl_2): A solution of BL^{Me} (63.9 mg, 0.21 mmol) in thf (5 mL) was added dropwise to a brown suspension of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (50.0 mg, 0.10 mmol) in thf (10 mL) at room temperature. During the addition of the ligand the reaction mixture turned blue, and the solution was stirred overnight. The volume of thf was reduced to 5 mL and the product precipitated with *n*-hexane (20 mL). Filtration, washing with *n*-hexane (2 × 10 mL) and drying in vacuo afforded the product as a blue solid (105.8 mg, 95%). ^{1}H NMR (400 MHz, [D$_3$]acetonitrile, 25 °C): δ = 5.15 (s, 6 H, C_6H_6), 3.64 (s, 12 H, NCH_3), 2.88 (s, 4 H, CH_2), 2.21 (s, 12 H, CCH_3) ppm. ^{13}C NMR (100.6 MHz, [D$_3$]-acetonitrile, 25 °C): δ = 157.2 (NCN), 121.1 ($NCCH_3$), 82.0 (C_6H_6), 56.3 (CH_2), 32.6 (NCH_3), 9.1 (CCH_3) ppm. $C_{22}H_{34}Cl_2N_6Ru$ (554.5): calcd. C 47.65, H 6.18, N 15.16; found C 47.30, H 6.27, N 15.30.

$[(\eta^6\text{-}C_6H_6)Ru(BL^{iPr})]Cl_2$ ([6]Cl_2): A solution of BL^{iPr} (250.0 mg, 0.60 mmol) in thf (5 mL) was added dropwise to a brown suspension of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (150.0 mg, 0.3 mmol) in thf (10 mL) at room temperature. During the addition of the ligand the reaction mixture turned red, and the suspension was stirred overnight. The volume of thf was reduced to 5 mL and the product precipitated with *n*-hexane (20 mL). Filtration, washing with *n*-hexane (2 × 10 mL) and drying in vacuo afforded the product as a red solid

(338.5 mg, 85%). ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C): δ = 5.62 (sept, ^3J = 7 Hz, 4 H, NC*H*), 5.20 (s, 6 H, C$_6$*H*$_6$), 2.89 (s, 4 H, C*H*$_2$), 2.39 (s, 12 H, CC*H*$_3$), 1.83 (d, ^3J = 7 Hz, 12 H, CHC*H*$_3$), 1.53 (d, ^3J = 7 Hz, 12 H, CHC*H*$_3$) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone, 25 °C): δ = 156.4 (N*C*N), 122.1 (N*C*CH$_3$), 81.4 (*C*$_6$H$_6$), 56.8 (*C*H$_2$), 49.2 (N*C*H), 22.5 (CH*C*H$_3$), 22.0 (CH*C*H$_3$), 10.5 (C*C*H$_3$) ppm. $C_{30}H_{50}Cl_2N_6Ru$ (666.7): calcd. C 54.04, H 7.56, N 12.60; found C 53.19, H 7.55, N 12.17.

[(η^6-C$_6$H$_6$)Ru(BL^{iPr})](BF$_4$)$_2$ ([6](BF$_4$)$_2$): Solid NaBF$_4$ (32.9 mg, 0.30 mmol) was added to a solution of [(η^6-C$_6$H$_6$)Ru(BL^{iPr})]Cl$_2$ (100.0 mg, 0.15 mmol) in dichloromethane (20 mL) at room temperature and the mixture stirred overnight. During the reaction the mixture turned dark blue. The solution was filtered, and the volume of dichloromethane was reduced to 5 mL, after which the product was precipitated with diethyl ether (40 mL). Filtration, washing with diethyl ether (2 × 10 mL) and drying in vacuo afforded the product as a dark blue solid (92.3 mg, 80%). ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C): δ = 5.74 (s, 6 H, C$_6$*H*$_6$), 5.29 (sept, ^3J = 7 Hz, 4 H, NC*H*), 2.93 (s, 4 H, C*H*$_2$), 2.49 (s, 12 H, CC*H*$_3$), 1.83 (d, ^3J = 7 Hz, 12 H, CHC*H*$_3$), 1.53 (d, ^3J = 7 Hz, 12 H, CHC*H*$_3$) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone, 25 °C): δ = 153.2 (N*C*N), 124.0 (N*C*CH$_3$), 79.1 (*C*$_6$H$_6$), 60.0 (*C*H$_2$), 50.5 (N*C*H), 22.3 (CH*C*H$_3$), 21.8 (CH*C*H$_3$), 10.4 (C*C*H$_3$) ppm. ^{19}F NMR (188.3 MHz, [D$_6$]acetone, 25 °C): δ = –150.9 ppm. $C_{30}H_{50}B_2F_8N_6Ru$ (769.4): calcd. C 46.83, H 6.55, N 10.92; found C 46.88, H 6.61, N 10.55.

[(η^6-C$_{10}$H$_{14}$)Ru(BL^{Me})]Cl$_2$ ([7]Cl$_2$): A solution of BL^{Me} (49.9 mg, 0.164 mmol) in thf (5 mL) was added dropwise to a brown suspension of [(η^6-C$_{10}$H$_{14}$)RuCl$_2$]$_2$ (50.0 mg, 0.082 mmol) in thf (10 mL) at room temperature. During the addition of the ligand the reaction mixture turned blue, and the solution was stirred overnight. The volume of thf was reduced to 5 mL and the product precipitated with *n*-hexane (20 mL). Filtration, washing with *n*-hexane (2 × 10 mL) and drying in vacuo afforded the product as a blue solid (41 mg, 40%). ^{1}H NMR (400 MHz, [D$_3$]acetonitrile, 25 °C): δ = 5.15 (dd, 4 H, C$_6$*H*$_4$), 3.63 (s, 12 H, NC*H*$_3$), 2.83 (s, 4 H, C*H*$_2$), 2.44 (sept, ^3J = 7 Hz, 1 H, C$_6$H$_4$C*H*), 2.25 (s, 12 H, CC*H*$_3$), 2.10 (s, 3 H, C$_6$H$_4$C*H*$_3$), 1.23 [d, ^3J = 7 Hz, 6 H, C$_6$H$_4$CH(C*H*$_3$)$_2$] ppm. ^{1}H NMR (400 MHz, [D$_2$]dichloromethane, 25 °C): δ = 4.92 (m, 4 H, C$_6$*H*$_4$), 3.65 (s, 12 H, NC*H*$_3$), 2.90 (s, 4 H, C*H*$_2$), 2.41 (sept, ^3J = 7 Hz, 1 H, C$_6$H$_4$C*H*), 2.17 (s, 12 H, CC*H*$_3$), 2.09 (s, 3 H, C$_6$H$_4$C*H*$_3$), 1.20 [d, ^3J = 7 Hz, 6 H, C$_6$H$_4$CH(C*H*$_3$)$_2$] ppm. ^{13}C NMR (100.6 MHz, [D$_2$]dichloromethane, 25 °C): δ = 156.8 (N*C*N), 120.0 (N*C*CH$_3$), 101.4 (aryl-*C*CHCH$_3$), 94.4 (aryl-*C*CH$_3$), 81.7 (aryl-*C*H), 79.9 (aryl-*C*H), 55.9 (*C*H$_2$), 32.8 (N*C*H$_3$), 31.1 (aryl-*C*HCH$_3$), 22.7 (CCH*C*H$_3$), 18.7 (aryl-C*C*H$_3$), 9.4 (C*C*H$_3$) ppm. $C_{26}H_{42}Cl_2N_6Ru$ (610.6): calcd. C 51.14, H 6.93, N 13.76; found C 51.09, H 7.02, N 12.83.

[(η^6-C$_{10}$H$_{14}$)Ru(BL^{iPr})]Cl$_2$ ([8]Cl$_2$): A solution of BL^{iPr} (135.8 mg, 0.326 mmol) in thf (5 mL) was added dropwise to a brown suspension of [(η^6-C$_{10}$H$_{14}$)RuCl$_2$]$_2$ (100.0 mg, 0.163 mmol) in thf (10 mL) at room temperature. During the addition of the ligand the reaction mixture turned red, and the suspension was stirred overnight. The volume of thf was reduced to 5 mL and the product precipitated with *n*-hexane (20 mL). Filtration, washing with *n*-hexane (2 × 10 mL) and drying in vacuo afforded the product as a red solid (163.5 mg, 70.6%). ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C): δ = 5.68 (sept, ^3J = 7 Hz, 4 H, NC*H*), 5.25 (dd, 4 H, C$_6$*H*$_4$), 2.93 (s, 4 H, C*H*$_2$), 2.74 (sept, ^3J = 7 Hz, 1 H, C$_6$H$_4$C*H*), 2.35 (s, 12 H, CC*H*$_3$), 2.11 (s, 3 H, C$_6$H$_4$C*H*$_3$), 1.55 (br. s, 24 H, CHC*H*$_3$), 1.23 [d, ^3J = 7 Hz, 6 H, C$_6$H$_4$CH(C*H*$_3$)$_2$] ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone, 25 °C): δ = 157.3 (N*C*N), 121.9 (N*C*CH$_3$), 103.8 (aryl-*C*CHCH$_3$), 92.7 (aryl-*C*CH$_3$), 81.4 (aryl-*C*H), 78.8 (aryl-*C*H), 58.2 (*C*H$_2$), 49.3 (N*C*H), 31.2 (aryl-*C*HCH$_3$), 22.7 (NCH*C*H$_3$), 22.5 (NCH*C*H$_3$), 18.7 (aryl-C*C*H$_3$), 10.8 (C*C*H$_3$), 10.8 (CCH*C*H$_3$) ppm. $C_{34}H_{58}N_6RuCl_2$ (722.9): calcd. C 56.49, H 8.09, N 11.63; found C 55.68, H 7.94, N 10.71.

[(η^6-C$_{10}$H$_{14}$)Ru(BL^{iPr})](BF$_4$)$_2$ ([8](BF$_4$)$_2$): Solid AgBF$_4$ (53.8 mg, 0.28 mmol) was added to a solution of [(η^6-C$_{10}$H$_{14}$)Ru(BL^{iPr})]Cl$_2$ (100.0 mg, 0.14 mmol) in dichloromethane (80 mL) at room tem-

Table 2. Selected bond lengths [Å] and angles [°] for [**3**]Cl, [**5**]Cl$_2$, [**6**]Cl$_2$·thf, [**6**](BF$_4$)$_2$·CH$_2$Cl$_2$ and [**8**](BF$_4$)$_2$·CH$_2$Cl$_2$ with estimated standard deviations in parentheses.

	[**3**]Cl	[**5**]Cl$_2$[a]	[**6**]Cl$_2$·thf	[**6**](BF$_4$)$_2$·CH$_2$Cl$_2$	[**8**](BF$_4$)$_2$·CH$_2$Cl$_2$
Ru–N1	2.0626(10)	1.977(2)	2.0732(12)	1.9883(17)	2.003(2)
Ru–N2	2.0741(10)		2.0849(11)	1.9818(16)	1.994(2)
Ru–C(ring)	2.1163(11)–2.1643(11)	2.150(3)–2.212(3)	2.1571(18)–2.1965(17)	2.149(2)–2.212(2)	2.166(2)–2.192(3)
N1–C3	1.3411(14)		1.3407(17)	1.364(2)	1.364(3)
N1–C2		1.364(3)			
N2–C10	1.3532(15)				
N2–C14			1.3488(18)	1.368(2)	1.367(3)
Ru–Cl1	6.01	5.15	2.4853(4)		
Ru–Cl2			5.45		
Ru–F				5.33–7.93	4.04–7.93
N1–Ru–N2	77.33(4)	78.58(13)	75.88(5)	79.96(7)	80.31(8)
(N–Ru–N)/(C$_3$N$_2$)[b]	81.8, 86.4	88.3	58.1, 76.6	84.8, 89.6	83.4, 86.8
H1···Cl; H2···Cl			2.82; 2.64		
C3–N3	1.3538(15)		1.3528(17)	1.350(3)	1.346(3)
C3–N4	1.3554(15)		1.3629(18)	1.349(2)	1.350(3)
C10–N5	1.3531(16)				
C10–N6	1.3575(14)				
C2–N2		1.340(3)			
C2–N3		1.345(3)			
C14–N5			1.3562(18)	1.352(2)	1.356(3)
C14–N6			1.3542(18)	1.351(3)	1.333(3)
ρ[c]	0.990; 0.998	1.016	0.988; 0.995	1.011; 1.012	1.012; 1.016

[a] The cation has twofold symmetry. [b] Angle between the RuN$_2$ and imidazole ring planes. [c] $\rho = 2a/(b + c)$, with *a*, *b* and *c* representing the exo- (*a*) and endocyclic (*b*, *c*) distances within the CN$_3$ guanidine moiety.

Table 3. Crystallographic data for [**3**]Cl, [**5**]Cl_2, [**6**]Cl_2·thf, [**6**]$(BF_4)_2$·CH_2Cl_2 and [**8**]$(BF_4)_2$·CH_2Cl_2.

	[**3**]Cl	[**5**]Cl_2	[**6**]Cl_2·thf	[**6**]$(BF_4)_2$·CH_2Cl_2	[**8**]$(BF_4)_2$·CH_2Cl_2
Empirical formula	$C_{26}H_{43}ClN_6Ru$	$C_{22}H_{34}Cl_2N_6Ru$	$C_{34}H_{58}Cl_2N_6ORu$	$C_{31}H_{52}B_2Cl_2F_8N_6Ru$	$C_{35}H_{58}B_2Cl_2F_8N_6Ru$
Formula weight	576.18	554.52	738.83	854.38	908.46
Space group	$P2_1/c$	$C2/c$	$P2_1/n$	$P2_1/c$	$P2_1$
a [Å]	12.3542(3)	16.1088(6)	17.6825(2)	19.8375(8)	10.6820(2)
b [Å]	15.5561(3)	10.7763(3)	10.2456(3)	13.4419(6)	15.0442(2)
c [Å]	15.1258(3)	15.4499(5)	21.5597(4)	15.2597(12)	13.9604(2)
α [°]	90	90	90	90	90
β [°]	107.976(3)	116.738(4)	112.491(2)	110.396(10)	112.274(2)
γ [°]	90	90	90	90	90
V [Å^3]	2765.02(10)	2395.21(14)	3608.83(13)	3814.0(4)	2076.06(6)
Z	4	4	4	4	2
T [°C]	–173	–173	–173	–173	–173
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
$D_{calcd.}$ [g cm^{-3}]	1.384	1.538	1.360	1.488	1.453
μ [mm^{-1}]	0.689	0.900	0.618	0.622	0.576
$R(F_o)$	0.0210	0.0314	0.0280	0.0310	0.0310
$R_w(F_o^2)$	0.0564	0.0694	0.0622	0.0724	0.0637

perature and the mixture stirred overnight. During the reaction the mixture turned dark blue. The solution was filtered, washed with 20 mL dichloromethane, and the volume of the solution was reduced to 10 mL, followed by the precipitation of the product with diethyl ether (40 mL). Filtration, washing with diethyl ether (2 × 10 mL) and drying in vacuo afforded the product as a dark blue solid (62.5 mg, 54%). ^{1}H NMR (400 MHz, [D$_3$]acetonitrile, 25 °C): δ = 5.39 (s, 4 H, C_6H_4), 4.94 (sept, ^3J = 7 Hz, 4 H, NC*H*), 2.60 (s, 4 H, CH_2), 2.54 (sept, ^3J = 7 Hz, 1 H, C_6H_4C*H*), 2.43 (s, 12 H, CCH_3), 2.12 (s, 3 H, $C_6H_4CH_3$), 1.81 (d, ^3J = 7 Hz, 12 H, CHCH_3), 1.45 (d, ^3J = 7 Hz, 12 H, CHCH_3), 1.32 [d, ^3J = 7 Hz, 6 H, $C_6H_4CH(CH_3)_2$] ppm. ^{13}C NMR (100.6 MHz, [D$_1$]chloroform, 25 °C): δ = 152.3 (N*C*N), 123.1 (N*C*CH$_3$), 103.8 (aryl-*C*CHCH$_3$), 88.2 (aryl-*C*CH$_3$), 80.4 (aryl-*C*H), 78.0 (aryl-*C*H), 59.4 (*C*H$_2$), 50.0 (N*C*H), 31.5 (aryl-*C*HCH$_3$), 22.9 (NCH*C*H$_3$), 21.4 (NCH*C*H$_3$), 19.0 (aryl-C*C*H$_3$), 10.3 (C*C*H$_3$), 9.9 (CCH*C*H$_3$) ppm. $C_{34}H_{58}B_2F_8N_6Ru$ (825.6): calcd. C 49.47, H 7.08, N 10.18; found C 49.41, H 6.56, N 9.89.

General Procedure for the Transfer Hydrogenation of Acetophenone: Potassium hydroxide (11.2 mg, 0.2 mmol) was added to the catalyst solution (0.02 mmol, 1 mol-%) in 2-propanol (10 mL) at room temperature. The solution was heated to 81 °C, and acetophenone (240 mg, 2 mmol, 0.2 M) was added. Approximately 0.1 mL samples were regularly taken and filtered through the short silica gel column by using diethyl ether as a solvent. The reaction progress was monitored by gas chromatography (GC).

Single-Crystal X-ray Structure Determinations: Data were recorded at low temperature with an Oxford Diffraction Xcalibur S diffractometer by using Mo-K_α radiation. Structures were refined anisotropically on F^2 by using the program system SHELXL-97.[35] Hydrogen atoms were included in the models at geometrically calculated positions and refined by using a riding model or with rigid methyl groups. Special features: The ethylene bridge was disordered over two positions for [**6**]Cl_2·thf, [**6**]$(BF_4)_2$·CH_2Cl_2 and [**8**]$(BF_4)_2$·CH_2Cl_2. Close inspection of diffraction patterns for [**5**]Cl_2 revealed a small extent of twinning by 180° rotation about the x axis; the data reduction was modified appropriately for a twinned crystal, and the structure quality improved significantly. Reflection numbers cannot be counted reliably for twinned crystals. For [**8**]$(BF_4)_2$·CH_2Cl_2 the Flack parameter refined to 0.000(16). CCDC-733779 {[**6**]Cl_2·thf}, CCDC-733780 {[**3**]Cl_2}, CCDC-733781 {[**5**]Cl_2}, CCDC-733782 {[**6**]$(BF_4)_2$·CH_2Cl_2} and CCDC-733783 {[**8**]$(BF_4)_2$·CH_2Cl_2} contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. See Table 2 for selected molecular dimensions and Table 3 for crystallographic data.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) through grant number Ta 189/6-2.

[1] a) S. Herres-Pawlis, *Nachr. Chem.* **2009**, *57*, 20–23; b) S. Herres-Pawlis, A. Neuba, O. Seewald, T. Seshadri, H. Egold, U. Flörke, G. Henkel, *Eur. J. Org. Chem.* **2005**, 4879–4890.

[2] a) A. L. Llamas-Saiz, C. Faces-Focesa, J. Elguero, *J. Mol. Struct.* **1994**, *328*, 297–323; b) V. Raab, J. Kipke, R. M. Gschwind, J. Sundermeyer, *Chem. Eur. J.* **2002**, *8*, 1682–1693; c) U. Wild, O. Hübner, A. Maronna, M. Enders, E. Kaifer, H. Wadepohl, H.-J. Himmel, *Eur. J. Inorg. Chem.* **2008**, 4440–4447.

[3] a) A. Hoffmann, J. Börner, U. Flörke, S. Herres-Pawlis, *Inorg. Chim. Acta* **2009**, *362*, 1185–1193; b) A. Neuba, R. Haase, M. Bernard, U. Flörke, S. Herres-Pawlis, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2511–2517; c) A. Neuba, S. Herres-Pawlis, U. Flörke, G. Henkel, *Z. Anorg. Allg. Chem.* **2008**, *634*, 771–777; d) U. Wild, P. Roquette, E. Kaifer, J. Mautz, O. Hübner, H. Wadepohl, H.-J. Himmel, *Chem. Eur. J.* **2008**, *14*, 7813–7821; e) H. Wittmann, V. Raab, A. Schorm, J. Plackmeyer, J. Sundermeyer, *Eur. J. Inorg. Chem.* **2001**, 1937–1948; f) N. Kuhn, M. Grathwohl, M. Steinmann, G. Henkel, *Z. Naturforsch. Teil B* **1998**, *53*, 997–1003.

[4] a) S. Pohl, M. Harmjanz, J. Schneider, W. Saak, G. Henkel, *J. Chem. Soc., Dalton Trans.* **2000**, 3473–3479; b) S. Herres-Pawlis, U. Flörke, G. Henkel, *Eur. J. Inorg. Chem.* **2005**, 3815–3824.

[5] a) C. Würtele, E. Gaoutchenova, K. Harms, M. C. Holthausen, J. Sundermeyer, S. Schindler, *Angew. Chem.* **2006**, *118*, 3951–3954; *Angew. Chem. Int. Ed.* **2006**, *45*, 3867–3869; b) D. Maiti, D.-H. Lee, K. Gaoutchenova, C. Würtele, M. C. Holthausen, A. A. Narducci Sarjeant, J. Sundermeyer, S. Schindler, K. D. Karlin, *Angew. Chem.* **2008**, *120*, 88–91; *Angew. Chem. Int. Ed.* **2008**, *47*, 82–85; c) S. Herres, A. J. Heuwing, U. Flörke, J. Schneider, G. Henkel, *Inorg. Chim. Acta* **2005**, *358*, 1089–1095; d) D. Maiti, D.-H. Lee, A. A. Narducci Sarjeant, M. Y. M. Pau, E. I. Solomon, K. Gaoutchenova, J. Sundermeyer, K. D. Karlin, *J. Am. Chem. Soc.* **2008**, *130*, 6700–6701; e) S. Herres-Pawlis, P. Verma, R. Haase, P. Kang, C. T. Lyons, E. C. Was-

inger, U. Flörke, G. Henkel, T. D. P. Stack, *J. Am. Chem. Soc.* **2009**, *131*, 1154–1169.

[6] a) J. Börner, S. Herres-Pawlis, U. Flörke, K. Huber, *Eur. J. Inorg. Chem.* **2007**, 5645–5651; b) J. Börner, U. Flörke, K. Huber, A. Döring, D. Kuckling, S. Herres-Pawlis, *Chem. Eur. J.* **2009**, *15*, 2362–2376; c) J. Wu, T.-L. Yu, C.-T. Chen, C.-C. Lin, *Coord. Chem. Rev.* **2006**, *250*, 602–626.

[7] D. Petrovic, L. M. R. Hill, P. G. Jones, W. B. Tolman, M. Tamm, *Dalton Trans.* **2008**, 887–894.

[8] G. Frison, A. Sevin, *J. Chem. Soc. Perkin Trans. 2* **2002**, 1692–1697.

[9] M. Tamm, D. Petrovic, S. Randoll, S. Beer, T. Bannenberg, P. G. Jones, J. Grunenberg, *Org. Biomol. Chem.* **2007**, *5*, 523–530.

[10] N. Kuhn, M. Grathwohl, M. Steimann, G. Henkel, *Z. Naturforsch. Teil B* **1998**, *53*, 997–1003.

[11] a) S. Beer, K. Brandhorst, C. G. Hrib, X. Wu, J. Grunenberg, P. G. Jones, M. Tamm, *Organometallics* **2009**, *28*, 1534–1545; b) S. H. Stelzig, M. Tamm, R. M. Waymouth, *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 6064–6070; c) S. Beer, K. Brandhorst, J. Grunenberg, C. G. Hrib, P. G. Jones, M. Tamm, *Org. Lett.* **2008**, *10*, 981–984; d) S. Beer, C. G. Hrib, P. G. Jones, K. Brandhorst, J. Grunenberg, M. Tamm, *Angew. Chem.* **2007**, *119*, 9047–9051; *Angew. Chem. Int. Ed.* **2007**, *46*, 8890–8894; e) M. Tamm, S. Randoll, E. Herdtweck, N. Kleigrewe, G. Kehr, G. Erker, B. Rieger, *Dalton Trans.* **2006**, 459–467; f) M. Tamm, S. Beer, E. Herdtweck, *Z. Naturforsch.* **2004**, *59*, 1497–1504; g) M. Tamm, S. Randoll, T. Bannenberg, E. Herdtweck, *Chem. Commun.* **2004**, 876–877.

[12] D. Petrovic, T. Bannenberg, S. Randoll, P. G. Jones, M. Tamm, *Dalton Trans.* **2007**, 2812–2822.

[13] a) D. Petrovic, T. Glöge, T. Bannenberg, C. G. Hrib, S. Randoll, P. G. Jones, M. Tamm, *Eur. J. Inorg. Chem.* **2007**, 3472–3475; b) T. Glöge, D. Petrovic, C. G. Hrib, P. G. Jones, M. Tamm, *Z. Naturforsch. Teil B* **2008**, *63*, 1155–1159.

[14] D. Petrovic, C. G. Hrib, S. Randoll, P. G. Jones, M. Tamm, *Organometallics* **2008**, *27*, 778–783.

[15] a) B. M. Trost, M. U. Frederiksen, M. T. Rudd, *Angew. Chem. Int. Ed.* **2005**, *44*, 6630–6666; *Angew. Chem.* **2005**, *117*, 6788–6825; b) B. M. Trost, F. D. Toste, A. B. Pinkerton, *Chem. Rev.* **2001**, *101*, 2067–2096.

[16] a) N. Chatani, *Science of Synthesis* (Eds.: T. Imamoto, R. Noyori), Georg Thieme Verlag, Stuttgart, **2001**, p. 931–972; b) F. Zobi, B. Balali Mood, P. A. Wood, F. P. A. Fabbiani, S. Parsons, P. J. Sadler, *Eur. J. Inorg. Chem.* **2007**, 2783–2796; c) H. Chen, J. A. Parkinson, S. Parsons, R. A. Coxall, R. O. Gould, P. J. Sadler, *J. Am. Chem. Soc.* **2002**, *124*, 3064–3082; d) A. F. A. Peacock, A. Habtemariam, R. Fernndez, V. Walland, F. P. A. Fabbiani, S. Parsons, R. E. Aird, D. I. Jodrell, P. J. Sadler, *J. Am. Chem. Soc.* **2006**, *128*, 1739–1748; e) R. E. Morris, R. E. Aird, P. d. S. Murdoch, H. Chen, J. Cummings, N. D. Hughes, S. Parsons, A. Parkin, G. Boyd, D. I. Jodrell, P. J. Sadler, *J. Med. Chem.* **2001**, *44*, 3616–3621; f) A. Habtemariam, M. Melchart, R. Fernandez, S. Parsons, I. D. H. Oswald, A. Parkin, F. P. A. Fabbiani, J. E. Davidson, A. Dawson, R. E. Aird, D. I. Jodrell, P. J. Sadler, *J. Med. Chem.* **2006**, *49*, 6858–6868; g) H. Chen, J. A. Parkinson, O. Novakova, J. Bella, F. Wang, A. Dawson, R. Gould, S. Parsons, V. Brabec, P. J. Sadler, *Proc. Natl. Acad. Sci. USA* **2003**, *100*, 14623–14628.

[17] a) I. Moldes, E. de la Encarnacion, J. Ros, A. Alvarez-Larena, J. F. Piniella, *J. Organomet. Chem.* **1998**, *566*, 165–174; b) P. Pertici, G. Vitulli, C. Bigelli, R. Lazzaroni, *J. Organomet. Chem.* **1984**, *275*, 113–117.

[18] L. Jafarpour, J. Huang, E. D. Stevens, S. P. Nolan, *Organometallics* **1999**, *18*, 3760–3763.

[19] a) A. J. Davenport, D. L. Davies, J. Fawcett, D. R. Russell, *J. Chem. Soc. Perkin Trans. 1* **2001**, 1500–1503; b) D. L. Davies, J. Fawcett, S. A. Garratt, D. R. Russell, *Organometallics* **2001**, *20*, 3029–3034; c) A. J. Davenport, D. L. Davies, J. Fawcett, S. A. Garratt, D. R. Russell, *J. Chem. Soc., Dalton Trans.* **2000**, 4432–4441.

[20] a) R. Noyori, T. Ohkuma, *Pure Appl. Chem.* **1999**, *71*, 1493–1501; b) S. Hashiguchi, A. Fujii, K.-J. Haack, K. Matsumura, T. Ikariya, R. Noyori, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 288–299; *Angew. Chem.* **1997**, *109*, 300–303; c) T. Ohkuma, K. Tsutsumi, N. Utsumi, N. Arai, R. Noyori, K. Murata, *Org. Lett.* **2007**, *9*, 255–257.

[21] a) R. Noyori, S. Hashiguchi, *Acc. Chem. Res.* **1997**, *30*, 97–102; b) S. Hashiguchi, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1996**, *118*, 4916–4917.

[22] a) R. Noyori, M. Yamakawa, S. Hashiguchi, *J. Org. Chem.* **2001**, *66*, 7931–7944; b) K. C. Nicolaou, J. S. Chen, H. Zhang, A. Montero, *Angew. Chem. Int. Ed.* **2008**, *47*, 185–189; *Angew. Chem.* **2008**, *120*, 191–195; c) Z. M. Heiden, T. B. Rauchfuss, *J. Am. Chem. Soc.* **2009**, *131*, 3593–3600.

[23] P. J. Fagan, M. D. Ward, J. C. Calabrese, *J. Am. Chem. Soc.* **1989**, *111*, 1698–1719.

[24] P. G. Jones, C. G. Hrib, S. Beer, M. Tamm, *Acta Crystallogr., Sect. E* **2007**, *63*, m1785.

[25] C. Gemel, K. Mereiter, R. Schmid, K. Kirchner, *Organometallics* **1997**, *16*, 5601–5603.

[26] Y. Yamaguchi, H. Nagashima, *Organometallics* **2000**, *19*, 725–727.

[27] M. A. Bennett, A. K. Smith, *J. Chem. Soc., Dalton Trans.* **1974**, 233–241.

[28] The Cambridge Structural Database (CSD version 5.30, November **2008**) contains 23 structures of $[(\eta^6\text{-}C_6H_6)Ru(N^{\frown}N)Cl]^+$ complexes; the Ru–Cl distances range from 2.380 to 2.425 Å with a mean value of 2.404.

[29] A. D. Phillips, G. Laurenczy, R. Scopelliti, P. J. Dyson, *Organometallics* **2007**, *26*, 1120–1122.

[30] a) A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441–451; b) R. S. Rowland, R. Taylor, *J. Phys. Chem.* **1996**, *100*, 7384–7391.

[31] a) P. J. Bailey, K. J. Grant, S. Parsons, *Organometallics* **1998**, *17*, 551–555; b) K.-J. Haack, S. Hashiguchi, A. Fujii, T. Ikariya, R. Noyori, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 285–288; *Angew. Chem.* **1997**, *109*, 297–299; c) A. A. Danopoulos, G. Wilkinson, T. K. N. Sweet, M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.* **1996**, 3771–3778.

[32] a) *Handbook of Homogeneous Hydrogenation* (Eds.: J G. de Vries, C. J. Elsevier), Wiley-VCH, Weinheim, **2006**; b) S. Gladiali, E. Alberico, in *Transition Metals for Organic Synthesis* (Eds.: M. Beller, C. Bolm), Wiley-VCH, Weinheim, **2004**, vol. 2, p. 145.

[33] a) C. Wang, X. Wu, J. Xiao, *Chem. Asian J.* **2008**, *3*, 1750–1770; b) T. Ikariya, A. J. Blacker, *Acc. Chem. Res.* **2007**, *40*, 1300–1308; c) K. Everaere, A. Mortreux, J.-F. Carpentier, *Adv. Synth. Catal.* **2003**, *345*, 67–77; d) F. Fache, E. Schulz, M. L. Tommasino, M. Lemaire, *Chem. Rev.* **2000**, *100*, 2159–2231.

[34] a) W. D. Shipe, E. J. Sorensen, *J. Am. Chem. Soc.* **2006**, *128*, 7025–7035; b) L. A. Paquette, R. F. Doehner Jr, *J. Org. Chem.* **1980**, *45*, 5105–5113.

[35] G. M. Sheldrick, *Acta Crystallogr., Sect A* **2008**, *64*, 112–122.

Received: June 22, 2009
Published Online: September 10, 2009

