

(Arene)ruthenium(II) Complexes Containing Substituted Bis(pyrazolyl)methane Ligands – Catalytic Behaviour in Transfer Hydrogenation of Ketones

M. Carmen Carrión,^[a] Félix A. Jalón,^[a] Blanca R. Manzano,^{*,[a]} Ana M. Rodríguez,^[b] Francisco Sepúlveda,^[a] and Miguel Maestro^[c]

Dedicated to the memory of Prof. S. Trofimenko

Keywords: Ruthenium / Arene ligands / Homogeneous catalysis / Bis(pyrazolyl)methane / Transfer hydrogenation / X-ray structure determination

A new and safer methodology has been developed for the synthesis of bis(pyrazol-1-yl)methane ligands (NN). Several ligands containing different phenyl groups on the central carbon atom have been obtained. Ruthenium derivatives of the type [Ru(arene)Cl(NN)]BPh₄ (arene = benzene, *p*-cymene) have been synthesised using these ligands. One or two isomers that differ regarding the axial or equatorial disposition of the phenyl group on the metallacycle have been obtained. Their formation is rationalised by considering steric effects. The structures of five derivatives were determined by X-ray diffraction. In four complexes the phenyl substituent is in the axial disposition of the metallacycle and in one case in the equatorial orientation. The dihedral angle formed by the planes of the two pyrazole rings is always bigger for

the complexes containing unsubstituted pyrazolyl heterocycles. The behaviour of the new derivatives in the transfer hydrogenation of benzophenone in the presence of KOH was studied. The benzene derivatives showed higher activity than the *p*-cymene complexes. A marked and positive effect of the methyl groups on the pyrazolyl rings was observed. The effect of the substituents on the benzyl carbon atom was also important. It has been observed that the benzophenone hydrogenation was possible without the addition of complexes. The effect of the KOH concentration was evaluated and a concentration that leads to negligible conversion in a base-only process was chosen.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2007)

Introduction

(Arene)ruthenium(II) complexes constitute an important group of derivatives that have applications in numerous catalytic processes. Although some ruthenium derivatives containing poly(pyrazolyl)borate^[1] or poly(pyrazolyl)methane^[2] ligands have been reported, arene complexes with these groups^[3] are extremely scarce. One of the catalytic applications of arene–ruthenium derivatives is in the transfer hydrogenation of ketones. This process gives high yields and enantiomeric excesses with some ketones and has the advantage over the traditional use of H₂ pressure of greater operational simplicity.^[4] Different Ru–arene systems have

been described for this process including PP, NN, NO and NPN ligands.^[5] In this context, one of the most important breakthroughs was discovered by Noyori and involves the use of “Ru^{II}(arene)” precursors with chiral amino alcohols or diamines^[6] in processes that lead to excellent activities and enantioselectivities. Because of the participation of the ligand in the catalytic reaction, Noyori has proposed the term bifunctional metal–ligand catalysis for this kind of process. He performed theoretical calculations concerning the mechanism and the origin of enantioselectivity.^[7] Other groups have also developed systems based on Ru–arene fragments with amino alcohols,^[8] amino amide^[9] or amino carboxylate^[10] ligands. Interesting papers concerning mechanisms have also appeared.^[11] Besides the metal ligand bifunctional mechanism, other mechanisms involving monohydride or dihydride species have been proposed. Although not involving arene derivatives, it is worth noting that recently Baratta et al.^[12] designed a new type of Ru^{II} catalyst, containing the ligand 2-(aminomethyl)pyridine or its derivatives, that was active in the transfer hydrogenation of acetophenone, using NaOH as cocatalyst with TOF up to $4.0 \times 10^5 \text{ h}^{-1}$.

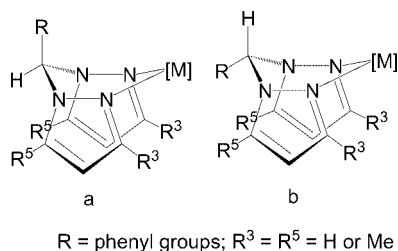
[a] Departamento de Química Inorgánica, Orgánica y Bioquímica, Universidad de Castilla-La Mancha, Facultad de Químicas, Avda. C.J. Cela 10, 13071 Ciudad Real, Spain

[b] Departamento de Química Inorgánica, Orgánica y Bioquímica, Universidad de Castilla-La Mancha, Escuela Técnica Superior de Ingenieros Industriales, Avda. C.J. Cela 3, 13071 Ciudad Real, Spain

[c] Departamento de Química Fundamental, Universidade da Coruña, 15071 A Coruña, Spain

Supporting information for this article is available on the WWW under <http://www.eurjic.org> or from the author.

In recent years we have worked with a series of bis(pyrazolyl)methane derivatives.^[2a,13] These compounds offer the possibility of modulating the steric and electronic properties by introducing substituents in the pyrazole rings and at the central carbon atom. We used ligands that contained differently substituted phenyl rings and pyrazole (pz) or 3,5-dimethylpyrazole (pz*) heterocycles attached to the central carbon atom. We have also explored the coordination chemistry of these ligands, mainly with palladium fragments.^[13] An endobidentate coordination with the formation of metallacycles with a boat conformation has always been found. Interestingly, in all cases the phenyl substituent occupies the axial position in this metallacycle (see Scheme 1a). This is probably due to the steric hindrance that these groups would cause if they were in an equatorial position with respect to the pyrazole rings (Scheme 1b) and also the absence of other interactions in the axial position because of the square-planar environment of the metal centre. We found that with substituted pyrazolyl rings, the bite angle and the dihedral angle formed by the planes NPdN/N₄ were smaller and this influenced the dynamic behaviour of some derivatives.^[13c] These data were rationalised by means of theoretical calculations.^[14] Bis(pyrazolyl)methane complexes in which the substituent (pyrazole or thienyl) on the central CH group is situated in an equatorial position correspond to octahedral derivatives of ruthenium(II)^[15] or platinum(IV).^[16] In both cases, the pyrazolyl rings were unsubstituted.



Scheme 1.

In the work described here we decided to synthesise a series of bis(pyrazolyl)methane ligands in which the central carbon atom bears phenyl rings that have different functional substituents such as OCH₃, NO₂ or NH₂. One objective was to find a method of synthesis that avoided the use of toxic phosgene. The purpose was also the synthesis of new arene (benzene, *p*-cymene) ruthenium derivatives that contain these ligands. Ultimately, we were interested in evaluating the stereochemistry of these complexes and, in particular, the preference for an equatorial or axial disposition of the phenyl ring and the relationship of this fact with the substitution on the pyrazolyl groups and the steric requirements of the arene. An open question concerned whether the change in the type of pyrazole present would also force the same type of distortions found in the related palladium chemistry.

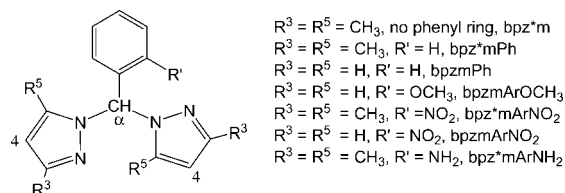
Taking into account that Ru–arene complexes with poly(pyrazolyl)methane ligands have never been studied in hy-

drogenation transfer of ketones, another goal was the use of the new complexes as precatalysts in these processes using 2-propanol as the solvent and reducing agent. Preliminary tests will be presented. The NN ligands are clearly different to those used by Noyori because of the absence of NH groups as donor centres. In any case, it was of interest to evaluate the effect of the functional groups on the benzyl carbon atom outside the coordination centre including the NH₂ fragment.

Results and Discussion

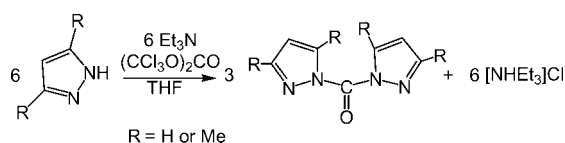
Synthesis of the Ligands and Complexes

The ligands used in this work and their abbreviations are summarised in Scheme 2.



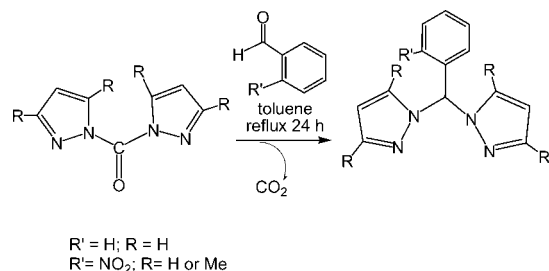
Scheme 2.

The ligands bpz*mPh,^[17] bpzmPhOCH₃^[13c] and bpz*m^[18] have been described previously. The ligands bpz*mArNO₂, bpzmArNO₂ and bpz*mArNH₂ are described in this work for the first time. Until now, the intermediate bis(pyrazol-1-yl)ketone that is necessary for the preparation of these types of ligand, was synthesised by the reaction of pyrazole (substituted or not) and phosgene. In this work we tried to develop a greener method that could avoid the use of this highly toxic gas. The alternative that we have found is the use of the solid triphosgene. Thus, the synthesis of the ligands bpzmPh, bpz*mArNO₂ and bpzmArNO₂ was carried out in the following way. Firstly, the bis(pyrazol-1-yl)ketone species were obtained through the reaction of the corresponding pyrazole with triphosgene in the presence of triethylamine (Scheme 3).



Scheme 3.

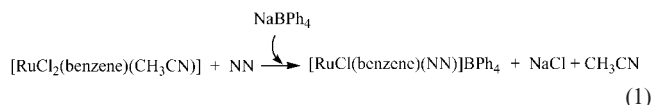
The resulting ketone subsequently reacted with the corresponding aldehyde in toluene under reflux for 24 h (Scheme 4).



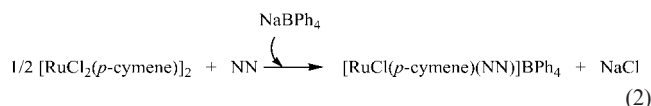
Scheme 4.

The ligand $\text{bpz}^*\text{mArNH}_2$ was obtained by hydrogenation of $\text{bpz}^*\text{mArNO}_2$ using a Pd/C catalyst.

The Ru^{II} -arene (arene = benzene, *p*-cymene) complexes used in this work were obtained by treating the corresponding Ru^{II} starting material, the nature of which depends on the arene, with the desired ligand in MeOH with the addition of $\text{Na[BPh}_4\text{]}$ at the end of the reaction [see Equations (1) and (2)].



NN = bpz^*m , **1**; bpz^*mPh , **3**; bpzmPh , **5**; bpzmArOCH_3 , **7**; $\text{bpz}^*\text{mArNO}_2$, **9**; bpzmArNO_2 , **11**; $\text{bpz}^*\text{mArNH}_2$, **13**.



NN = bpz^*m , **2**; bpz^*mPh , **4**; bpzmPh , **6**; bpzmArOCH_3 , **8**; $\text{bpz}^*\text{mArNO}_2$, **10**; bpzmArNO_2 , **12**; $\text{bpz}^*\text{mArNH}_2$, **14**.

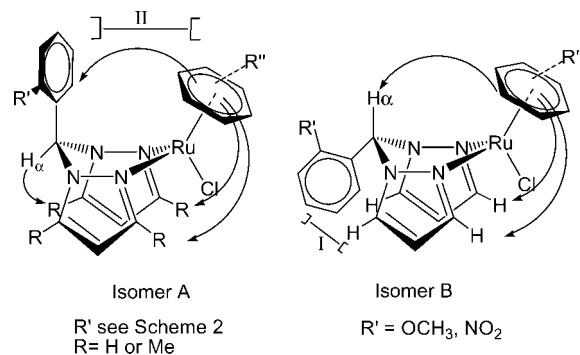
In cases where the nitrogenated ligands contained methylated pyrazolyl groups, only one isomer was obtained for the corresponding ruthenium complexes. A different situation was found when the ligand contained unsubstituted pyrazoles. Apart from the complexes containing bpzmPh , where only one isomer was found, the other derivatives exist as a mixture of two isomers (A and B). The relative ratios of these isomers, determined by NMR before recrystallisation, are shown, where applicable, in the Experimental Section.

The new complexes were characterised by elemental analysis as well as IR, ^1H and ^{13}C NMR spectroscopy and, in some cases, by X-ray diffraction. The bands corresponding to the stretching vibrations of the NO_2 and NH_2 groups were observed in the IR spectra (see Exp. Sect.).

NMR Study

A careful NMR analysis of the new ligands and complexes was carried out. The assignment of the resonances was possible with the help of ^1H , ^1H -COSY, NOESY and *g*-HMQC spectra (in some cases also with *g*-HMBC) and by considering the values of coupling constants. The ^1H NMR

spectroscopic data are gathered in Table S1 of the Supporting Information. Coordination of the nitrogenated ligand to the $[\text{RuCl}(\text{arene})]^+$ fragment results in shifts that, in some cases, were greater than 1 ppm towards higher frequencies for the pyrazolyl ring proton resonances. The same trend was observed for the ^{13}C NMR resonances in cases where the appropriate data for direct comparison are available. This effect was attributed in general to the electron donation of the ligand to the metal cation (the effect of other groups in the molecule on specific protons will be detailed below). The increased electron deficiency of the heterocyclic rings also leads to an increase in the ^1H , ^1H coupling constants.^[19] The assignment of structures to the complexes was done mainly by means of the NOESY spectra. The two possible structures are shown in Scheme 5. These compounds differ in the axial or equatorial orientation of the phenyl ring in the metallacycle. The arrows represent the most important NOEs observed. The disposition of the arene ring bonded to Ru and the chloride proposed in the scheme is thought to be the only possible situation for steric reasons. In the complexes obtained with methylated ligands and the isomers labelled A for the nonmethylated ones, an NOE is always observed between H_α and H^5 (or Me^5) of the pyrazolyl groups. In some cases, an NOE is also observed between resonances of the arene groups and the H atom of the phenyl group *ortho* to the benzyl carbon atom. These data indicate that in these complexes the phenyl ring is situated in an axial position. The structures in which the phenyl ring is in an equatorial disposition are assigned to isomers B. In fact, in complex **12B** an NOE was observed between H_α and the proton H^3 of the *p*-cymene ring. Although it does not provide structural information, a noticeable NOE is frequently observed in both types of isomer between the H^3 or Me^3 pyrazole resonances and signals from the arenes. This must be a consequence of the large dihedral angle NRuN/N_4 in the metallacycle having the boat conformation (see X-ray structures described below).



Scheme 5. Isomers A and B for the arene- Ru^{II} derivatives. The most important NOEs are indicated with arrows. The steric interactions used to rationalise the isomer ratio are indicated by the roman numerals I and II. R'' means that the arene ring is benzene or *p*-cymene.

Concerning the ^1H NMR chemical shifts of the resonances of the two isomers, it is expected that the resonances of the H^5 pyrazole protons or even those of the arene rings would be affected by the position of the phenyl groups. In

fact, the H^5 (pz) protons for isomers A appear in the range 8.23–8.50 ppm and those of isomers B in the range 7.69–7.80 ppm. When the phenyl groups are in an equatorial position, it is clear that these H^5 protons are more shielded. This must be due to the effect of the current anisotropy of the aromatic rings. A similar effect is observed for the aromatic resonances of the arenes. For example, the benzene signals of isomers A are in the region 4.90–5.75 ppm whereas isomers B give rise to signals in the range 6.24–6.27 ppm. This observation implies that, although the phenyl rings will rotate around the $C(ipso)$ – C_α bond, the preferred orientation for the A isomers is that in which the ring forms an angle of approximately 90° with the H_α – C_α – $C(ipso)$ plane. This orientation also leads to an upfield shift of the phenyl resonances of the protons situated *ortho* to C_α , a situation due to the anisotropy effect of the pyrazole rings. These resonances could serve as a way of identifying the structure of a specific isomer. In the case of the $^{13}C\{^1H\}$ NMR resonances, a clear difference is also observed in the C^5 pyrazole signals, similar to that observed in the 1H NMR spectra. For example, a higher chemical shift (difference of about 3–4 ppm) is observed for isomer A than isomer B.

The formation of a single isomer or a mixture of isomers, and even the ratio of isomers, can be rationalised on the basis of steric effects alone. Steric hindrance between the arene rings and the pyrazolyl groups exists in both isomers and probably will not influence their ratio (see Scheme 5). Steric hindrance I will be important in isomers B while steric hindrance II will be operating in isomers A. When the pyrazolyl groups are methylated, interaction I must predominate to induce the unique formation of complexes of type A. For the case of nonmethylated pyrazolyl groups, interaction I will be less important and both interactions may be competitive. In fact, both isomers are formed (see isomer ratio of complexes **7**, **8**, **11** and **12**; complexes **5** and **6** with bpzmPh constitute an exception, see Exp. Sect.), albeit in a ratio that depends on the nature of the arene. For the benzene complexes, isomers of type A are dominant, while for the bulkier *p*-cymene the ratio is nearly 1. In conclusion, in benzene derivatives interaction I is dominant while for the *p*-cymene complexes both interactions must be comparable. In the case of complexes with the ligand bpzmPh where the phenyl group does not have a functional group, it seems that interaction of type II is not very significant and only isomers of type A are formed.

It is interesting to compare these data with those found in square-planar palladium complexes,^[13] in which the phenyl ring is always situated in an axial position, even for methylallyl derivatives.^[13a,13b] The reason must be that in these types of derivatives the geometry of the metal centre means that interactions of type II do not exist or are not important.

In the case of complex **8** we obtained a crystallised sample that was enriched in isomer B and we monitored the evolution of this sample at $50^\circ C$ in a $[D_6]$ acetone solution. Figure 1 reflects the changes that were observed with time. The initial ratio **8B**/**8A** of 77:23 changed to 55:45 after

90 min, which constitutes a clear indication that interconversion between isomers is possible. There is no signal coalescence or broadening of the resonances. Consequently, the energy of the process is high enough not to be observable by coalescence methods. This process cannot take place through a boat-to-boat interconversion of the metallacycle, because, although the axial or equatorial position of the phenyl rings will change with this process, it would not lead to the other isomer but to a species that we consider unstable for steric reasons (see Scheme 6). A possible way of isomer interconversion is through a partial decooordination of the nitrogenated ligand.

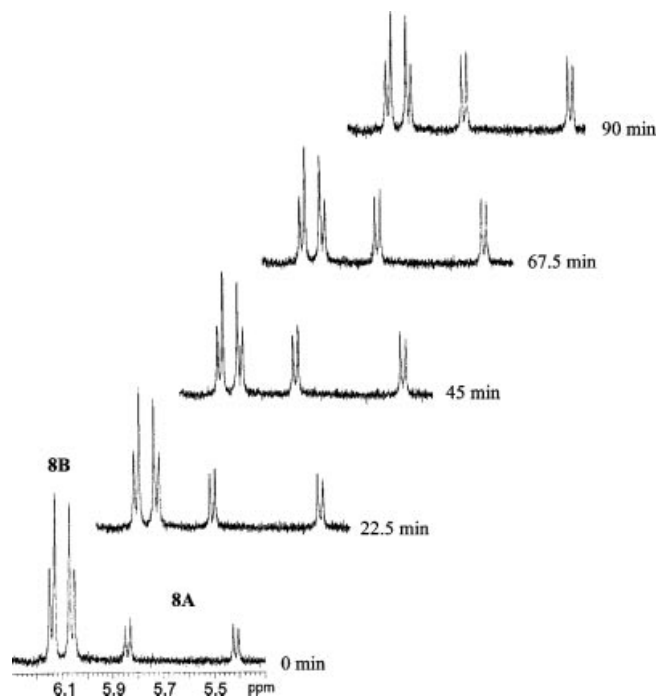
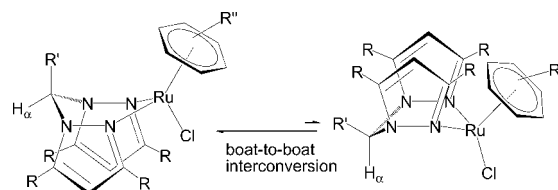


Figure 1. 1H NMR monitoring of the evolution of a **8A**/**8B** mixture with time.



Scheme 6.

X-ray Structure Determinations

The molecular structures of complexes **7A**· $0.5C_2H_4Cl_2$, **8B**, **9**, **10**· $0.5C_2H_4Cl_2$ and **12A** were determined by X-ray diffraction analysis. The crystallographic data are gathered in Table 1 and the most important bond lengths and angles, including some dihedral angles, are given in Table 2. The corresponding ORTEP drawings are shown in Figures 2, 3, 4, 5 and 6. In the case of **10**, two independent molecules exist in the asymmetric unit. The data for both are very

similar and only those of one molecule are given, in Table 2. All complexes have a half-sandwich structure consisting of the coordinated arene, a chloride and the bidentate nitro-genated ligand. In complexes **7**, **9**, **10** and **12** the phenyl group has an axial disposition on the metallacycle having the boat conformation. However, in the case of **8** we were fortunate to crystallise isomer B, in which this group is in an equatorial disposition. The distances between the Ru centre and the coordinated atoms are in the expected range. The average Ru–C distances are slightly longer for the *p*-cymene derivatives than for those containing benzene. The

Ru–N distances are shorter for the nonmethylated pyrazolyl rings. The bite angle is in the range 83.4–85.5°. The values of the dihedral angles NRuN/N₄, which are listed in Table 2, are in the range 151–169°. In contrast to the palladium derivatives, there is no relationship in these ruthenium complexes between the bite angle or the stated dihedral angle and the nature of the substituent on the pyrazolyl rings. However, it is clear that the dihedral angle formed by the planes of the two pyrazole rings is always bigger for the complexes containing unsubstituted pyrazolyl heterocycles. We propose that this effect is due to steric hindrance be-

Table 1. Crystallographic data for complexes **7A**·0.5C₂H₄Cl₂, **8B**, **9**, **10**·0.5C₂H₄Cl₂ and **12A**.

	7A ·0.5C ₂ H ₄ Cl ₂	8B	9	10 ·0.5C ₂ H ₄ Cl ₂	12A
Empirical formula	C ₄₅ H ₄₂ BCl ₂ N ₄ ORu	C ₄₈ H ₄₈ BClN ₄ ORu	C ₄₇ H ₄₅ BClN ₅ O ₂ Ru	C ₅₂ H ₅₅ BCl ₂ N ₅ O ₂ Ru	C ₄₇ H ₄₅ BClN ₅ O ₂ Ru
Formula mass	837.61	844.23	859.21	964.79	859.21
Temperature [K]	130(2)	130(2) K	298(2)	293(2)	298(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	9.8348(2)	9.5852(4)	16.6942(6)	10.0732(5)	18.022(1)
<i>b</i> [Å]	35.361(1)	34.987(2)	12.3963(5)	15.1007(8)	9.6950(8)
<i>c</i> [Å]	11.8454(3)	12.3711(6)	20.9589(8)	32.086(2)	23.868(2)
α [°]				79.224(1)	90
β [°]	106.500(1)	95.854(4)	107.375(1)	82.557(1)	99.785(2)
γ [°]				82.630(1)	90
<i>V</i> [Å ³]	3949.8(2)	4127.1(3)	4139.5(3)	4727.1(4)	4109.8(6)
<i>Z</i>	4	4	4	4	4
<i>D</i> _{calcd} [Mg·m ⁻³]	1.409	1.359	1.379	1.356	1.389
<i>F</i> (000)	1724	1752	1776	2004	1776
Crystal size [mm]	0.26 × 0.22 × 0.18	0.57 × 0.20 × 0.13	0.50 × 0.21 × 0.16	0.18 × 0.17 × 0.12	0.32 × 0.24 × 0.13
Limiting indices	−9 ≤ <i>h</i> ≤ 12 −44 ≤ <i>k</i> ≤ 44 −14 ≤ <i>l</i> ≤ 14	−13 ≤ <i>h</i> ≤ 13 −49 ≤ <i>k</i> ≤ 49 −17 ≤ <i>l</i> ≤ 14	−20 ≤ <i>h</i> ≤ 16 −13 ≤ <i>k</i> ≤ 15 −25 ≤ <i>l</i> ≤ 26	−13 ≤ <i>h</i> ≤ 13 −18 ≤ <i>k</i> ≤ 20 −25 ≤ <i>l</i> ≤ 42	−19 ≤ <i>h</i> ≤ 24 −12 ≤ <i>k</i> ≤ 11 −31 ≤ <i>l</i> ≤ 30
Data/restraints/parameters	8053/0/488	12548/0/509	8458/0/514	21595/0/1115	9754/0/514
θ range for data collection (°)	2.13–26.39	2.83–30.53	1.93–26.37	1.30–28.31	1.73–28.35
Goodness-of-fit on <i>F</i> ²	1.058	1.043	1.014	0.997	1.014
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0444 <i>wR</i> ₂ = 0.0971	<i>R</i> ₁ = 0.0465 <i>wR</i> ₂ = 0.1019	<i>R</i> ₁ = 0.0345 <i>wR</i> ₂ = 0.0789	<i>R</i> ₁ = 0.0750 <i>wR</i> ₂ = 0.1577	<i>R</i> ₁ = 0.0461 <i>wR</i> ₂ = 0.0920
Largest diff. peak/hole [e·Å ⁻³]	1.064, −0.622	1.494, −0.909	0.363, −0.403	1.439, −1.255	0.665, −0.636

Table 2. Selected bond lengths [Å], bond angles [°] and dihedral angles [°] for complexes **7A**·0.5C₂H₄Cl₂, **8B**, **9**, **10**·0.5C₂H₄Cl₂ and **12A**.

7A·0.5C ₂ H ₄ Cl ₂		8B		9		10·0.5C ₂ H ₄ Cl ₂		12A	
Ru1–N3	2.090(3)	Ru1–N1	2.089(2)	Ru1–N1	2.116(2)	Ru1–N1	2.140(5)	Ru1–N3	2.101(3)
Ru1–N2	2.101(3)	Ru1–N3	2.069(2)	Ru1–N3	2.128(2)	Ru1–N3	2.141(5)	Ru1–N1	2.105(3)
Ru1–Cl2	2.3940(8)	Ru1–Cl2	2.4019(6)	Ru1–Cl1	2.3896(8)	Ru1–Cl1	2.381(2)	Ru1–Cl1	2.4134(9)
Ru1–C _{average}	2.183	Ru1–C _{average}	2.197	Ru1–C _{average}	2.185	Ru1–C _{average}	2.211	Ru1–C _{average}	2.198
N3–Ru1–N2	85.54(10)	N3–Ru1–N1	83.41(8)	N1–Ru1–N3	85.40(8)	N1–Ru1–N3	83.6(2)	N3–Ru1–N1	83.8(1)
							84.66		
N3–Ru1–Cl2	82.67(7)	N3–Ru1–Cl2	84.78(6)	N1–Ru1–Cl1	84.49(6)	N1–Ru1–Cl1	84.7(1)	N1–Ru1–Cl1	84.05(7)
N2–Ru1–Cl2	84.90(7)	N1–Ru1–Cl2	84.49(6)	N3–Ru1–Cl1	85.23(6)	N3–Ru1–Cl1	84.6(1)	N3–Ru1–Cl1	85.56(7)
ε ^[a]	143.9	ε ^[a]	131.7	ε ^[a]	119.4	ε ^[a]	110.9	ε ^[a]	126.4
							117.5		
NRuN/N ₄ ^[b]	168.8	NRuN/N ₄ ^[b]	151.2	NRuN/N ₄ ^[b]	160.3	NRuN/N ₄ ^[b]	152.0	NRuN/N ₄ ^[b]	161.8
NCN/N ₄ ^[c]	133.5	NCN/N ₄ ^[c]	131.7	NCN/N ₄ ^[c]	129.1	NCN/N ₄ ^[c]	134.0	NCN/N ₄ ^[c]	133.1
ζ ^[d]	56.1	ζ ^[d]	10.8	ζ ^[d]	85.9	ζ ^[d]	87.6	ζ ^[d]	78.3
				η ^[e]	65.9	η ^[e]	68.8	η ^[e]	54.4

[a] Dihedral angle between both pyrazole rings. [b] Dihedral angle between the plane formed by the four nitrogen atoms and the angle formed by Ru and the two coordinated nitrogen atoms. [c] Dihedral angle between the plane formed by the four nitrogen atoms and the angle formed by the benzyl carbon atom and the two noncoordinated nitrogen atoms. [d] Dihedral angle formed by the plane of the phenyl ring and the plane formed by the atoms H–C–C(*ipso*) (phenyl ring). [e] Dihedral angle formed by the phenyl ring and the plane of the NO₂ group.

tween the methyl groups of the pyrazoles and the arene groups. When the angle between the pyrazoles decreases, this interaction may be reduced. This is clearly reflected in the structure drawing and the space-filling representations in Figure 7.

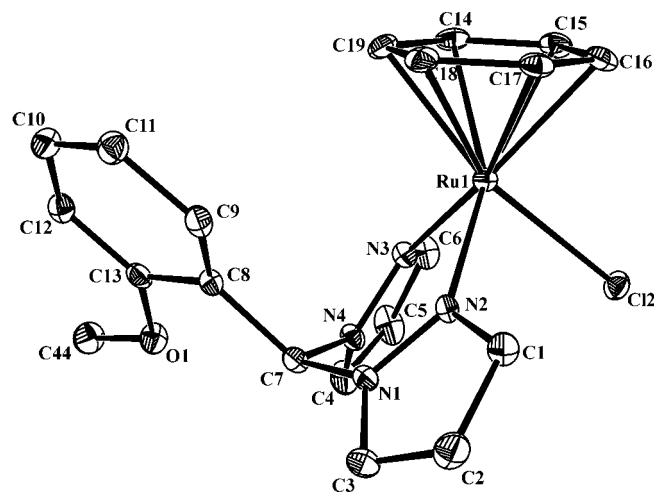


Figure 2. ORTEP view of the cation of complex **7A**·0.5C₂H₄Cl₂. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

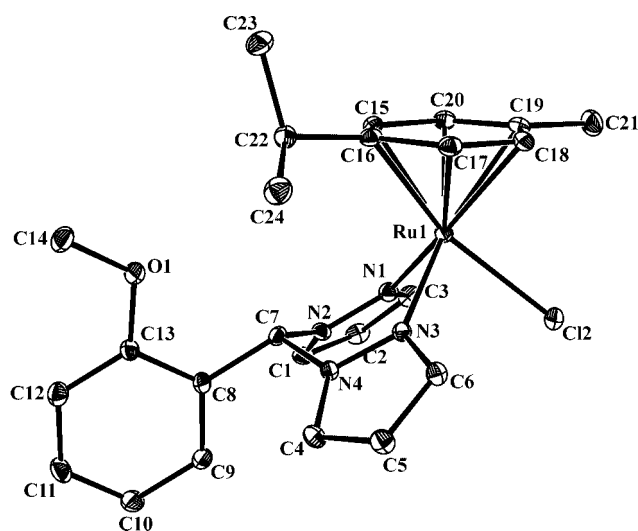


Figure 3. ORTEP view of the cation of complex **8B**. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

The orientation of the phenyl ring with respect to the plane formed by the atoms H_α–C_α–C(*ipso*) is mainly dependent on the axial or equatorial disposition of this ring. When it is axial, the dihedral angle is very close to 90° (in the case of **7A** it is smaller: 56.12°), while for **8B** (where the group is equatorial) the value is only 10.79°.

The methoxy group is approximately in the plane of the phenyl ring. However, it is worth noting the orientation of the NO₂ plane with respect to the corresponding phenyl ring. Unexpectedly, these planes are not parallel, and the values for the dihedral angle are in the range 65–68° for the methylated complexes and 54.4° for the nonmethylated

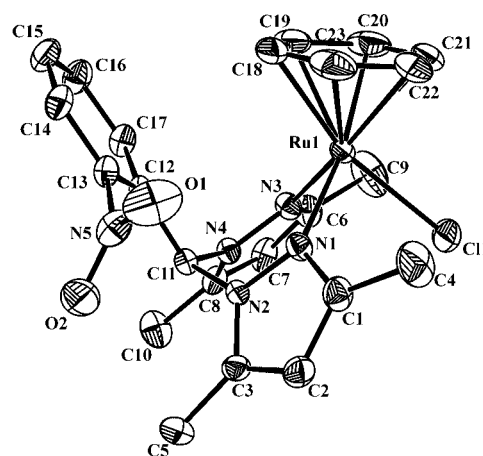


Figure 4. ORTEP view of the cation of complex **9**. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

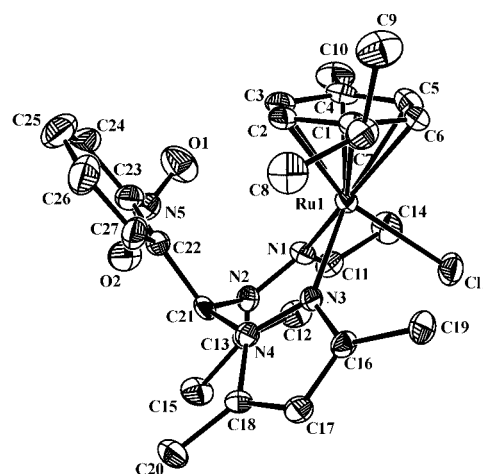


Figure 5. ORTEP view of the cation of complex **10**·0.5C₂H₄Cl₂. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

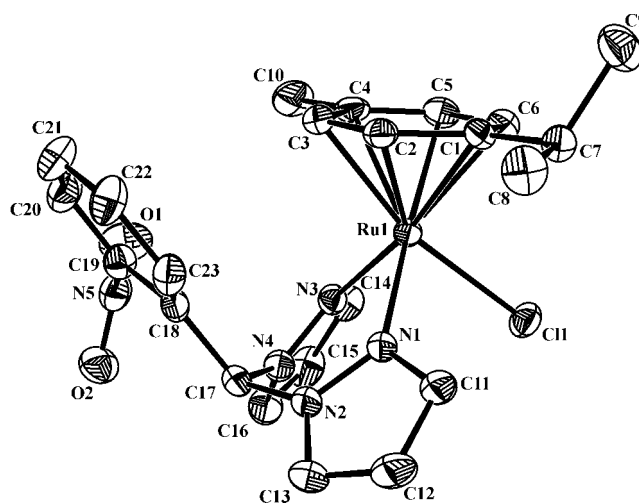


Figure 6. ORTEP view of the cation of complex **12A**. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

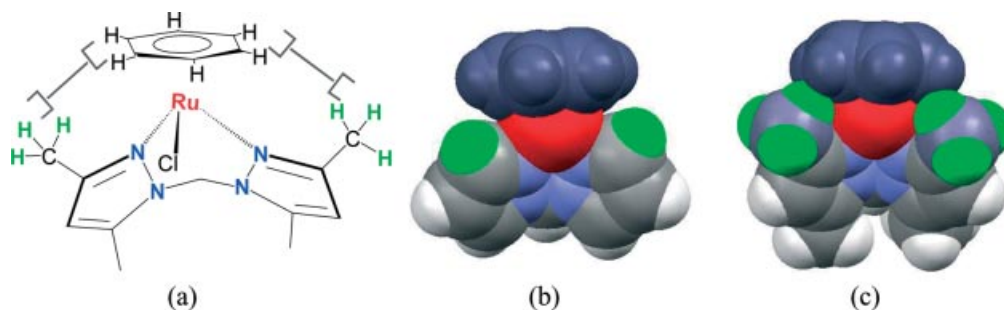
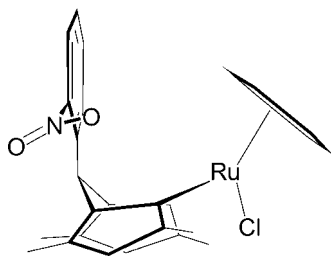


Figure 7. (a) Drawing scheme showing the steric interaction between the pyrazole Me³ groups and the CH bonds of the coordinated benzene that influences the pz–pz interplanar angle (the same is applicable to the *p*-cymene derivatives). (b and c) Comparison of such interactions in a space-fill drawing of the X-ray structures of complexes **7** and **9** respectively (Cl ligands and benzyl groups on the C_α atom have been omitted for clarity).

system. A closer inspection of the structure provides a plausible explanation for this observation. If the NO₂ plane was parallel to the phenyl ring, one of the oxygen atoms (with a negative charge density) would be situated very close to the π electron density of one pyrazole ring, and the aim of the torsion is probably to prevent this repulsive interaction. On the other hand, another orientation of the phenyl ring to minimise this problem would involve greater steric hindrance, because the phenyl ring would be too close to the arene that is bonded to the ruthenium centre (see Scheme 7).



Scheme 7.

As far as the orientation of the *p*-cymene ring in complexes **8B**, **10** and **12A** is concerned, there are two situations that are clearly different. In the case of complexes **10** and **12A**, where the phenyl ring has an axial orientation, the disposition of the *p*-cymene is such that the steric hindrance with this ring is reduced. The orientation in the case of **8B**, where the anisole ring is in an equatorial position, is clearly different and the isopropyl group is oriented towards the methoxy group. Closer inspection of the structure of **8B** reveals the existence of a hydrogen bond between the C–H fragment of the isopropyl group and the oxygen atom of the methoxy group. The C...O distance is 3.427 Å and the angle C–H–O is 142°. These data allow us to conclude that this hydrogen bond is weak.^[20]

Hydrogen Transfer Catalytic Tests

Preliminary tests were done concerning the behaviour of some of the new derivatives in catalytic transfer hydrogenation reactions of benzophenone using 2-propanol as the

reducing agent and solvent in the presence of KOH as the base [Equation (3)]:



Conversion was not observed at room temperature. For example, on using complex **7** there was no conversion after 36 h (see Exp. Sect. for conditions). Consequently, the boiling point of the solvent (85 °C) was used as the temperature in all the experiments. Initially we performed catalytic tests with complexes **1** and **3** with a substrate/KOH/complex ratio of 1000:100:1. Only moderate yields of the alcohol were obtained after 24 h of reaction (28% for **1** and 15% for **3**). We decided to evaluate the influence of the base concentration and we increased the number of equivalents of KOH without changing other factors. We performed tests with 250, 500 and 1000 of KOH per mole of complex and a steady increase in the TOF number and yield was observed. At this point it is necessary to consider the possibility of a high effect of the base that could obscure the catalytic effect of the complex. Processes of hydrogenation have been described with molecular hydrogen of benzophenone with a base (mainly *tert*-butoxide) in the absence of a catalyst, but using very drastic conditions (about 200 °C, >100 bar H₂).^[21] Regarding transfer hydrogenation, a conversion of 60% of acetophenone to the corresponding alcohol in boiling 2-propanol with NaOH 0.5 M^[22] in 4 h and very low activity in 0.02 M KOH solutions has been reported.^[23] Our highest concentration was 0.2 M. In any case, we decided to perform an analysis of the base-only reaction at different KOH concentrations. We found that KOH is able to catalyse the benzophenone hydrogenation with 2-propanol at 85 °C. When the alcohol yield is represented against different KOH concentrations, a straight line with positive slope (% yield = 0.91894 + 306.60015[KOH]; *R* = 0.99421) is obtained. The results are reflected in Table 3. In Figure 8 a representation of conversion against time is reflected for two experiments without a catalyst (KOH 0.008 M and 0.2 M) and another two experiments with KOH 0.2 M in the presence of complexes **3** or **13** (substrate/KOH/complex ratio of 1000:1000:1). It is clear that when working with KOH concentrations of 0.2 M the effect of our complexes is very

small and other conditions must be chosen. We think that these studies must be taken into account before performing reactions of transfer hydrogenation in the presence of KOH.

Table 3. Transfer hydrogenation of benzophenone with KOH without Ru complexes.^[a]

[KOH] [mol·L ⁻¹]	Mol KOH [500 mol substrate]	Yield [b] [%]
0.004	10	0
0.006	15	2
0.008	20	3
0.016	40	7
0.04	100	10
0.1	250	36
0.2	500	68
0.3	750	88

[a] Conditions: 2 mmol of benzophenone, 10 mL of *i*PrOH, reflux (82 °C). [b] Yield of diphenylmethanol after 13 h.

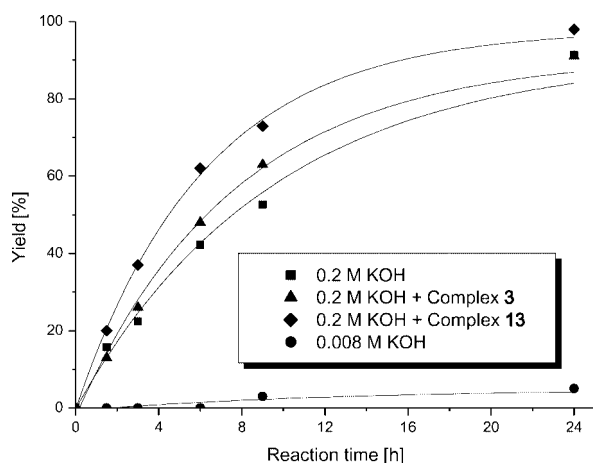


Figure 8. Yield of diphenylmethanol against time for the hydrogenation of benzophenone. Conditions: 2 mmol of benzophenone, 10 mL of *i*-PrOH, reflux (82 °C), 0.004 mmol precatalyst (when applicable).

Considering these results we decided to study the behaviour of our different derivatives with a base concentration of 0.008 M and a substrate/KOH/complex ratio of 500:20:1. The yields and the turnover frequencies evaluated at 20% conversion (TOF₂₀) are reflected in Table 4. The conversion for the TOF number was chosen in order to minimise the influence on the rate of decreases in substrate concentration and increases in product concentration. Several clear conclusions can be drawn from the analysis of the results. (i) Better behaviour of the benzene derivatives (those with an odd number) against *p*-cymene complexes (even number) is observed (in some cases the differences are not large). (ii) The introduction of methyl substituents on the pyrazole rings has a dramatic and positive effect (compare runs 4/6, 5/7, 11/13 and 12/14). For example, in the case of complexes 4 and 6, the improvement is from 10 to 82% in the product yield (see Figure 9 to observe both effects). (iii) The introduction of a phenyl group at the benzyl carbon atom (compare runs 2/4 and 3/5) also increases the activity of the system. (iv) When the existence of functional groups on this ring is considered, a negative effect of the NH₂ (runs 4/15 and 5/16) or NO₂ groups (runs 4/11 and 5/12 for methylated

pyrazoles and runs 6/13 and 7/14 for nonmethylated pyrazoles) is observed. However, a large increase in the activity is observed when the OCH₃ group is introduced on the phenyl ring (runs 6/8 and 7/10). In all the experiments samples were taken at 1.5, 3, 6, 9 and 24 h (see Supporting Information for the corresponding data).

Table 4. Transfer hydrogenation of benzophenone with Ru precatalysts.^[a]

Run	Complex	NN ligand	TOF ₂₀ ^[b] [h ⁻¹]	Yield ^[c] [%]
1 ^[d]	—	—	—	5
2	1	bpz*m	35	62
3	2	bpz*m	25	61
4	3	bpz*mPh	62	97
5	4	bpz*mPh	31	82
6	5	bpzmPh	8	37
7	6	bpzmPh	—	10
8	7	bpzmArOCH ₃	125	90
9 ^[e]	7	bpzmArOCH ₃	125	82
10	8	bpzmArOCH ₃	50	90
11	9	bpz*mArNO ₂	18	60
12	10	bpz*mArNO ₂	15	60
13	11	bpzmArNO ₂	—	18
14	12	bpzmArNO ₂	—	8
15	13	bpz*mArNH ₂	45	74
16	14	bpz*mArNH ₂	29	66

[a] Conditions: 2 mmol of benzophenone, 0.004 mmol precatalyst, 10 mL of *i*PrOH, reflux (82 °C), 0.008 M in KOH, substrate/KOH/complex ratio of 500:20:1. [b] Catalyst turnover frequency at 20% conversion. [c] Yield of diphenylmethanol at 24 h of reaction. [d] No precatalyst was added. [e] 300 equiv. of Hg was added.

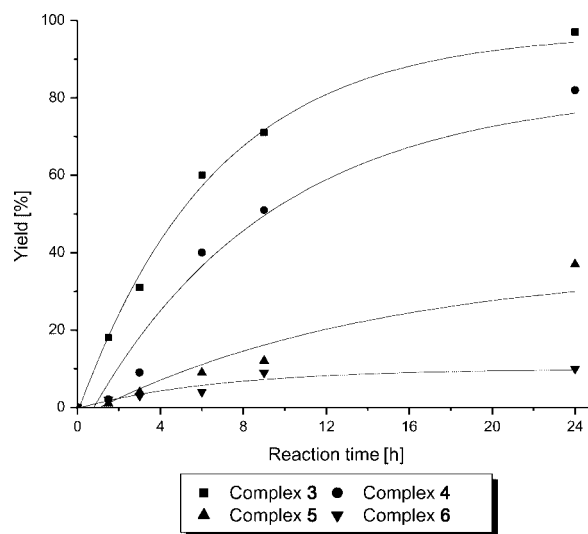


Figure 9. Yield of diphenylmethanol against time for the hydrogenation of benzophenone. Conditions: 2 mmol of benzophenone, 0.004 mmol precatalyst, 10 mL of *i*PrOH, reflux (82 °C), 0.008 M in KOH, substrate/KOH/complex ratio of 500:20:1.

We subjected complex 7 to the mercury drop test during the hydrogenation of benzophenone. Several authors^[24] found that the addition of excess metallic mercury (with respect to the metal complex) to the reaction mixture led to the amalgamation of the surface of a heterogeneous metal particle, thus poisoning it, but did not affect a homogeneous catalyst. When we added 300 equiv. of Hg(0) to the

reaction mixture at $t = 0$ min, the catalytic system only suffered a slight decrease in activity (compare runs 8/9), indicating the existence of a homogeneous system.

We also carried out a catalytic test with complex **7** (0.004 mmol), analysing samples at short times of 5, 10, 15, 30, 45 and 60 min. No induction period was observed. We also subjected complex **7** to a pretreatment of one hour, during which the precatalyst was heated at reflux in the presence of the base (base:7 = 20:1) prior to the addition of the substrate (2 mmol), and the outcome of the reaction was the same as that without this treatment.

The precatalysts are not active in the hydrogenation of styrene. Thus, they exhibit selectivity towards the ketone unsaturation.

According to previous mechanistic proposals,^[11a–11e] and considering the formulae and type of ligand present in our derivatives, the most plausible mechanism is that involving a monohydride intermediate generated after β elimination from an isopropoxide complex. In principle, the vacant coordination site necessary for the ketone coordination could be generated by partial decoordination of the nitrogenated ligand or by slippage of the arene moiety. Our study of the isomer interconversion and the fact that the methylated ligands that exhibit longer Ru–N distances have much higher activity point to the former possibility. Transfer of the hydride and reaction with 2-propanol will yield the dibenzyl alcohol.

More studies concerning the catalytic behaviour of these complexes are in progress. We will study complexes with the $\text{bpz}^*\text{PhOCH}_3$ ligand that predictably will give better results than those reported in Table 4 and we will also consider the possibility of obtaining ligands that have pyrazoles containing more bulky substituents. Other parameters such as the introduction of other functional groups on the phenyl ring and the use of asymmetric ligands will also be analysed.

Conclusions

New bis(pyrazol-1-yl)methane ligands containing different substituents on the central carbon atom have been synthesised using a new and safer methodology. Ru derivatives of the type $[\text{Ru}(\text{arene})\text{Cl}(\text{NN})]\text{BPh}_4$ (arene = benzene, *p*-cymene) have been synthesised from these ligands. The formation of two isomers is possible depending on the axial or equatorial disposition of the substituent on this carbon. The formation of only one isomer (axial) or a mixture of two (including their ratio) can be rationalised in terms of steric repulsions (effect of the methyl groups on the pyrazolyl rings or of the arene). A full NMR analysis was performed and a clear effect of the type of isomer on the chemical shifts of certain resonances was found. The structures of five derivatives were determined by X-ray diffraction. In four complexes the benzyl substituent is in the axial disposition and in one case in the equatorial disposition. A relationship between the dihedral angle formed by the planes of the two pyrazole rings and the substituent on these rings was found. The behaviour of the new derivatives in the

transfer hydrogenation of benzophenone in the presence of KOH was studied. The influence of the arene, the functional group on the phenyl ring and the substitution on the pyrazole ring has been evaluated. A marked positive effect of the methyl groups on the pyrazole rings and of the methoxy group on the phenyl ring has been found. The hydrogenation of benzophenone without the addition of a complex in the presence of KOH is possible and the effect of the base concentration has been analysed.

Experimental Section

General: All manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk techniques. Solvents were distilled from the appropriate drying agents and degassed before use. Elemental analyses were performed with a Thermo Quest FlashEA 1112 microanalyser. IR spectra were recorded as KBr pellets or Nujol solutions with a Perkin–Elmer PE 883 IR spectrometer and on a Shimadzu IRPrestige-21 IR spectrometer equipped with a Pike Technologies ATR. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded with a Varian Unity 500 spectrometer. Chemical shifts (ppm) are relative to TMS (^1H , ^{13}C NMR). ^1H – ^1H COSY spectra: standard pulse sequence with an acquisition time of 0.214 s, pulse width 10 ms, relaxation delay 1 s, number of scans 16, number of increments 512. For ^1H – ^{13}C *g*-HMBC and *g*-HMQC spectra the standard VARIAN pulse sequences were used (VNMR 6.1 C software). The spectra were acquired using 7996-Hz (^1H) and 25133.5-Hz (^{13}C) widths; 16 transients of 2048 data points were collected for each of the 256 increments. NOESY spectra were acquired using 8000-Hz width; 16 transients of 2048 data points were collected for each of the 256 increments; pulse time of 1 s and mixing time of 1 s. *o*-, *m*- and *p*- stand for *ortho*, *meta* and *para*. s, d, t and p stand for singlet, doublet, triplet and apparent for the NMR resonances. Unless otherwise stated, the $^{13}\text{C}\{^1\text{H}\}$ NMR signals are singlets. The ligands $\text{bpz}^*\text{m}^{[18]}$ and $\text{bpzmArOCH}_3^{[13c]}$ were prepared according to the methods described in the literature. For the preparation of the ligands bpzmPh and $\text{bpz}^*\text{mPh}^{[17]}$ the ketone bpz^*CO was synthesised as described below.

bpz^*CO : 3,5-Dimethylpyrazole (1.5 g, 15.6 mmol) was dissolved in thf (20 mL) and NEt_3 (2.13 mL) was added afterwards. Triphosgene, $\text{Cl}_3\text{COCOCCl}_3$ (772 mg, 2.60 mmol), was dissolved in thf (20 mL) and the resulting solution was added as quickly as possible to the initial one. After 16 h of stirring at room temperature, the white solid formed was filtered off and washed twice with thf. The thf fractions were combined and the solvent evaporated. The yellowish oil obtained was washed with pentane and a white solid was formed. The solid was recrystallised from toluene/hexane obtaining white crystals. Yield 1.4 g (80%).

bpzCO : The method was similar to that used for bpz^*CO . Amounts were as follows: pyrazole (1 g, 15.6 mmol), NEt_3 (2.13 mL) and triphosgene (772 mg, 2.60 mmol). bpzCO was obtained as a white solid. Yield 948.6 mg (75%).

$\text{bpz}^*\text{mArNO}_2$: bpz^*CO (500 mg, 2.29 mmol) and 2-nitrobenzaldehyde (346 mg, 2.29 mmol) were mixed in toluene (25 mL). After refluxing for 24 h, the yellowish solution was evaporated and the residue was washed with pentane (3×10 mL), obtaining a white solid of $\text{bpz}^*\text{mArNO}_2$. Yield 506.7 mg (68%). ^1H NMR (500 MHz, CDCl_3 , 298 K): $\delta = 2.08$ (s, 6 H, $\text{Me}^5\text{-Pz}$), 2.15 (s, 6 H, $\text{Me}^3\text{-Pz}$), 5.89 (s, 2 H, $\text{H}^4\text{-Pz}$), 6.60 (d, $J = 7.7$ Hz, 1 H, $\text{H}^3\text{-ArNO}_2$), 7.53 (td, $J = 7.7$, 1.5 Hz, 1 H, $\text{H}^5\text{-ArNO}_2$), 7.57 (td, $J = 7.7$, 1.5 Hz, 1 H, $\text{H}^4\text{-ArNO}_2$), 8.04 (dd, $J = 7.7$, 1.5 Hz, 1 H, $\text{H}^6\text{-ArNO}_2$), 8.22

(s, 1 H, H_a) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 298 K): δ = 11.16 (2 C, $\text{Me}^5\text{-Pz}$), 13.97 (2 C, $\text{Me}^3\text{-Pz}$), 71.57 (1 C, C_a), 107.22 (2 C, $C^4\text{-Pz}$), 122.25 (1 C, $C^6\text{-ArNO}_2$), 128.80 (1 C, $C^3\text{-ArNO}_2$), 129.78 (1 C, $C^5\text{-ArNO}_2$), 131.90 (1 C, $C^2\text{-ArNO}_2$), 133.86 (1 C, $C^4\text{-ArNO}_2$), 141.17 (2 C, $C^5\text{-Pz}$), 148.27 (1 C, $C^1\text{-ArNO}_2$), 148.76 (2 C, $C^3\text{-Pz}$) ppm. IR (KBr): $\tilde{\nu}$ = 1563 (CN); 1528, 1360, 1317 (NO) cm^{-1} .

bpzmArNO₂: The method was similar to that used for bpz*ArNO₂. Amounts were as follows: bpzCO (300 mg, 1.85 mmol) and 2-nitrobenzaldehyde (280 mg, 1.85 mmol). Yield 382.3 mg (62%). ^1H NMR (500 MHz, CDCl_3 , 298 K): δ = 6.38 (pt, J = 2.1 Hz, 2 H, $H^4\text{-Pz}$), 6.71 (dd, J = 7.3, 1.7 Hz, 1 H, $H^3\text{-ArNO}_2$), 7.52 (d, J = 2.2 Hz, 2 H, $H^5\text{-Pz}$), 7.57 (td, J = 7.6, 1.7 Hz, 1 H, $H^2\text{-ArNO}_2$), 7.62 (td, J = 7.6, 1.7 Hz, 1 H, $H^4\text{-ArNO}_2$), 7.63 (d, J = 1.7 Hz, 2 H, $H^3\text{-Pz}$), 8.11 (dd, J = 7.6, 1.9 Hz, 1 H, $H^6\text{-ArNO}_2$), 8.52 (s, 1 H, H_a) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 298 K): δ = 74.42 (1 C, C_a), 107.42 (2 C, $C^4\text{-Pz}$), 125.64 (1 C, $C^6\text{-ArNO}_2$), 129.40 (1 C, $C^3\text{-ArNO}_2$), 130.58 (1 C, $C^5\text{-ArNO}_2$), 130.92 (2 C, $C^5\text{-Pz}$), 131.79 (1 C, $C^2\text{-ArNO}_2$), 134.10 (1 C, $C^4\text{-ArNO}_2$), 141.44 (2 C, $C^3\text{-Pz}$), 147.52 (1 C, $C^1\text{-ArNO}_2$) ppm. IR (KBr): $\tilde{\nu}$ = 1580 (CN); 1526, 1350, 1312 (NO) cm^{-1} .

bpz*ArNH₂: bpz*ArNO₂ (745.1 mg, 2.29 mmol) was solved in toluene (30 mL) in a Fischer-Porter tube. A suspension of Pd/C (10%) catalyst (200 mg) in toluene (10 mL) was added to the initial solution. When the system was under dry oxygen-free nitrogen, hydrogen was introduced under pressure (about 3 kg·cm⁻²). After 5.5 h of reaction at room temperature, the suspension was filtered off in a column filled with Kieselguhr. The solution was evaporated, obtaining a bright yellow oil, which was left under vacuum overnight, and a pale yellow solid was obtained. After recrystallisation in toluene/pentane, colourless crystals were obtained. Yield: 491.8 mg (90%). ^1H NMR (500 MHz, CDCl_3 , 298 K): δ = 2.14 (s, 6 H, $\text{Me}^5\text{-Pz}$), 2.22 (s, 6 H, $\text{Me}^3\text{-Pz}$), 3.51 (br. s, 2 H, NH_2), 5.87 (s, 2 H, $H^4\text{-Pz}$), 6.42 (d, J = 7.8 Hz, 1 H, $H^3\text{-ArNH}_2$), 6.65 (d, J = 7.3 Hz, 1 H, $H^6\text{-ArNH}_2$), 6.68 (t, J = 7.6 Hz, 1 H, $H^4\text{-ArNH}_2$), 7.13 (t, J = 7.1 Hz, 1 H, $H^5\text{-ArNH}_2$), 7.40 (s, 1 H, H_a) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 298 K): δ = 11.93 (2 C, $\text{Me}^5\text{-Pz}$), 14.08 (2 C, $\text{Me}^3\text{-Pz}$), 72.58 (1 C, C_a), 107.19 (2 C, $C^4\text{-Pz}$), 116.48 (1 C, $C^6\text{-ArNH}_2$), 118.63 (1 C, $C^4\text{-ArNH}_2$), 121.53 (1 C, $C^2\text{-ArNH}_2$), 127.64 (1 C, $C^3\text{-ArNH}_2$), 129.88 (1 C, $C^5\text{-ArNH}_2$), 141.43 (2 C, $C^5\text{-Pz}$), 144.49 (1 C, $C^1\text{-ArNH}_2$), 148.96 (2 C, $C^3\text{-Pz}$) ppm. IR (KBr): $\tilde{\nu}$ = 3395, 3312 (NH_2); 1554 (CN) cm^{-1} .

[RuCl(benzene)(bpz*mPh)][BPh₄] (1): $[\text{RuCl}_2(\text{C}_6\text{H}_6)(\text{CH}_3\text{CN})]$ (93 mg, 0.32 mmol) and bpz*m (65.4 mg, 0.32 mmol) were mixed in MeOH (10 mL). After stirring for 12 h, a solution of NaBPh₄ (200 mg, 0.6 mmol) in MeOH (10 mL) was added to the initial orange solution, changing the colour to yellow. After 30 min, the solution was partially evaporated up to 5 mL and the solid obtained was filtered off. The light yellow solid was washed once with MeOH. The product was recrystallised from 1,2-dichloroethane/hexane. Yield 210.2 mg (89%). $\text{C}_{41}\text{H}_{42}\text{BClN}_4\text{Ru}\cdot\text{C}_2\text{H}_4\text{Cl}_2$ (837.11): calcd. C 61.70, H 5.54, N 6.69; found C 61.41, H 5.41, N 6.94. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 298 K): δ = 11.38 (2 C, $\text{Me}^5\text{-Pz}$), 15.76 (2 C, $\text{Me}^3\text{-Pz}$), 55.67 (1 C, C_a), 85.46 (6 C, C-benzene), 109.35 (2 C, $C^4\text{-Pz}$), 122.11 [4 C, $C_p\text{-Ph(BPh}_4\text{)}$], 125.81 [8 C, $C_m\text{-Ph(BPh}_4\text{)}$], 136.19 [8 C, $C_o\text{-Ph(BPh}_4\text{)}$], 142.99 (2 C, $C^5\text{-Pz}$), 156.28 (2 C, $C^3\text{-Pz}$), 164.31 [q, $J_{\text{C-}^{11}\text{B}}$ = 49.4 Hz, 4 C, $C_{\text{ipso}}\text{-Ph(BPh}_4\text{)}$] ppm. IR: $\tilde{\nu}$ = 1558 (CN) cm^{-1} .

[RuCl(*p*-cymene)(bpz*mPh)][BPh₄] (2): $[\text{RuCl}_2(\textit{p}\text{-cymene})]_2$ (128 mg, 0.21 mmol) and bpz*m (85.8 mg, 0.42 mmol) were stirred in MeOH (10 mL) for 12 h. Afterwards, a solution of MeOH (10 mL) with NaBPh₄ (200 mg, 0.6 mmol) was added to the initial reddish solu-

tion, obtaining a yellow suspension. The solution was partially evaporated up to 5 mL and the solid obtained was filtered off. The yellow solid was washed once with MeOH. The product was recrystallised from 1,2-dichloroethane/hexane. Yield 293.5 mg (88%). $\text{C}_{45}\text{H}_{50}\text{BClN}_4\text{Ru}\cdot\text{C}_2\text{H}_4\text{Cl}_2$ (893.22): calcd. C 63.20, H 6.09, N 6.27; found C 63.51, H 6.06, N 6.37. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 298 K): δ = 11.64 (2 C, $\text{Me}^3\text{-Pz}$), 16.02 (2 C, $\text{Me}^5\text{-Pz}$), 18.72 (1 C, Me-Tol), 22.77 (2 C, Me-*i*Pr), 31.87 (1 C, CH-*i*Pr), 56.01 (1 C, C_a), 81.71 (2 C, $\text{CH}^{2/2'}\text{-p-cym}$), 84.86 (2 C, $\text{CH}^{3/3'}\text{-p-cym}$), 99.74 (1 C, $C^4\text{-p-cym}$), 107.38 (1 C, $C^1\text{-p-cym}$), 109.75 (2 C, $C^4\text{-Pz}$), 122.29 [4 C, $C_p\text{-Ph(BPh}_4\text{)}$], 125.96 [8 C, $C_m\text{-Ph(BPh}_4\text{)}$], 136.52 [8 C, $C_o\text{-Ph(BPh}_4\text{)}$], 143.32 (2 C, $C^5\text{-Pz}$), 156.86 (2 C, $C^3\text{-Pz}$), 164.32 [q, $J_{\text{C-}^{11}\text{B}}$ = 49.4 Hz, 4 C, $C_{\text{ipso}}\text{-Ph(BPh}_4\text{)}$] ppm. IR: $\tilde{\nu}$ = 1560 (CN) cm^{-1} .

[RuCl(benzene)(bpz*mPh)][BPh₄] (3): The method was similar to that used for complex 1. Amounts were as follows: $[\text{RuCl}_2(\text{C}_6\text{H}_6)(\text{CH}_3\text{CN})]$ (93 mg, 0.32 mmol) and bpz*m (89.7 mg, 0.32 mmol). Complex 3 was obtained as a yellowish solid. The product was recrystallised from 1,2-dichloroethane/hexane. Yield 221.5 mg (85%). $\text{C}_{47}\text{H}_{46}\text{BClN}_4\text{ORu}\cdot 0.5\text{C}_2\text{H}_4\text{Cl}_2$ (863.73): calcd. C 66.75, H 5.60, N 6.49; found C 66.45, H 5.66, N 7.20. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_3COCD_3 , 298 K): δ = 10.98 (2 C, $\text{Me}^5\text{-Pz}$), 16.10 (2 C, $\text{Me}^3\text{-Pz}$), 68.78 (1 C, C_a), 86.31 (6 C, C-benzene), 109.61 (2 C, $C^4\text{-Pz}$), 121.63 [4 C, $C_p\text{-Ph(BPh}_4\text{)}$], 125.41 [8 C, $C_m\text{-Ph(BPh}_4\text{)}$], 125.56 (2 C, $C_o\text{-Ph}$), 130.25 (1 C, $C_p\text{-Ph}$), 130.282 (2 C, $C_m\text{-Ph}$), 136.38 [8 C, $C_o\text{-Ph(BPh}_4\text{)}$], 136.757 (1 C, $C^1\text{-Ph}$), 146.48 (2 C, $C^5\text{-Pz}$), 157.86 (2 C, $C^3\text{-Pz}$), 164.31 [q, $J_{\text{C-}^{11}\text{B}}$ = 49.4 Hz, 4 C, $C_{\text{ipso}}\text{-Ph(BPh}_4\text{)}$] ppm. IR: $\tilde{\nu}$ = 1558 (CN) cm^{-1} .

[RuCl(*p*-cymene)(bpz*mPh)][BPh₄] (4): The method was similar to that used for complex 2. Amounts were as follows: $[\text{RuCl}_2(\textit{p}\text{-cymene})]_2$ (128 mg, 0.21 mmol) and bpz*mPh (117.8 mg, 0.42 mmol). Complex 4 was obtained as an orange solid, which was washed once with MeOH. Yield 325.3 mg (89%). $\text{C}_{51}\text{H}_{54}\text{BClN}_4\text{Ru}\cdot\text{CH}_3\text{OH}$ (902.40): C 69.21, H 6.48, N 6.21; found C 69.13, H 6.45, N 6.23. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_3COCD_3 , 298 K): δ = 11.23 (2 C, $\text{Me}^5\text{-Pz}$), 16.44 (2 C, $\text{Me}^3\text{-Pz}$), 17.63 (1 C, Me-Tol), 21.76 (1 C, CH-*i*Pr), 22.38 (2 C, Me-*i*Pr), 66.62 (1 C, C_a), 82.20 (2 C, $\text{CH}^{2/2'}\text{-p-cym}$), 84.42 (2 C, $\text{CH}^{3/3'}\text{-p-cym}$), 101.97 (1 C, $C^4\text{-p-cym}$), 107.23 (1 C, $C^1\text{-p-cym}$), 109.93 (2 C, $C^4\text{-Pz}$), 121.58 [4 C, $C_p\text{-Ph(BPh}_4\text{)}$], 125.34 [8 C, $C_m\text{-Ph(BPh}_4\text{)}$], 126.23 (2 C, $C_o\text{-Ph}$), 130.13 (2 C, $C_m\text{-Ph}$), 130.35 (1 C, $C_p\text{-Ph}$), 135.99 (1 C, $C^1\text{-Ph}$), 136.41 [8 C, $C_o\text{-Ph(BPh}_4\text{)}$], 146.55 (2 C, $C^5\text{-Pz}$), 157.87 (2 C, $C^3\text{-Pz}$), 164.32 [q, $J_{\text{C-}^{11}\text{B}}$ = 49.4 Hz, 4 C, $C_{\text{ipso}}\text{-Ph(BPh}_4\text{)}$] ppm. IR: $\tilde{\nu}$ = 1566 (CN) cm^{-1} .

[RuCl(benzene)(bpzmPh)][BPh₄] (5): The method was similar to that used for complex 2. Amounts were as follows: $[\text{RuCl}_2(\text{C}_6\text{H}_6)(\text{CH}_3\text{CN})]$ (37.8 mg, 0.13 mmol) and bpzmPh (29.1 mg, 0.25 mmol). The yellow solid obtained was washed once with MeOH. The product was recrystallised from 1,2-dichloroethane/hexane. Yield: 161.1 mg (85%). $\text{C}_{43}\text{H}_{38}\text{BClN}_4\text{Ru}\cdot 0.5\text{C}_2\text{H}_4\text{Cl}_2$ (807.62): calcd. C 65.44, H 4.99, N 6.94; found C 65.88, H 4.88, N 7.08. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_3COCD_3 , 298 K): δ = 75.26 (1 C, C_a), 86.48 (6 C, C-benzene), 108.80 (2 C, $C^4\text{-Pz}$), 121.62 [4 C, $C_p\text{-Ph(BPh}_4\text{)}$], 125.36 (2 C, $C_o\text{-Ph}$), 125.42 [8 C, $C_m\text{-Ph(BPh}_4\text{)}$], 129.97 (2 C, $C_m\text{-Ph}$), 130.38 (1 C, $C_p\text{-Ph}$), 136.39 [8 C, $C_o\text{-Ph(BPh}_4\text{)}$], 130.67 (2 C, $C^5\text{-Pz}$), 150.98 (2 C, $C^3\text{-Pz}$), 164.29 [q, $J_{\text{C-}^{11}\text{B}}$ = 49.4 Hz, 4C, $C_{\text{ipso}}\text{-Ph(BPh}_4\text{)}$] ppm. IR: $\tilde{\nu}$ = 1577 (CN) cm^{-1} .

[RuCl(*p*-cymene)(bpzmPh)][BPh₄] (6): The method was similar to that used for complex 2. Amounts were as follows: $[\text{RuCl}_2(\textit{p}\text{-cymene})]_2$ (36.7 mg, 0.06 mmol) and bpzmPh (29.1 mg, 0.13 mmol) in MeOH (5 mL). Complex 6 was obtained as a light yellow solid,

which was washed once with MeOH. Yield: 95.3 mg (90%). $C_{47}H_{46}BClN_4Ru$ (814.25): calcd. C 69.33, H 5.69, N 6.88; found C 69.42, H 5.61, N 6.92. $^{13}C\{^1H\}$ NMR (125 MHz, CD_3COCD_3 , 298 K): δ = 17.80 (1 C, Me-Tol), 21.79 (1 C, CH-*i*Pr), 22.07 (2 C, Me-*i*Pr), 75.29 (1 C, C_a), 80.77 (2 C, $CH^{3/3'}$ -*p*-cym), 88.75 (2 C, $CH^{2/2'}$ -*p*-cym), 101.92 (1 C, C^4 -*p*-cym), 104.32 (1 C, C^1 -*p*-cym), 108.99 (2 C, C^4 -Pz), 121.58 [4 C, C_p -Ph(BPh₄)], 125.34 [8 C, C_m -Ph(BPh₄)], 125.70 (2 C, C_o -Ph), 130.05 (2 C, C_m -Ph), 130.49 (1 C, C_p -Ph), 136.41 [8 C, C_o -Ph(BPh₄)], 137.65 (2 C, C^5 -Pz), 149.96 (2 C, C^3 -Pz), 164.32 [q, $J_{C-^{11}B}$ = 49.4 Hz, 4 C, C_{ipso} -Ph(BPh₄)] ppm. IR: $\tilde{\nu}$ = 1577 (CN) cm^{-1} .

[RuCl(benzene)(bpzmArOCH₃)](BPh₄) (7): The method was similar to that used for complex 1. Amounts were as follows: $[RuCl_2(C_6H_6)(CH_3CN)]$ (37.8 mg, 0.13 mmol) and bpzmArOCH₃ (33.1 mg, 0.13 mmol) in MeOH (5 mL). Complex 7 was obtained as a yellow solid. Yield: 86.6 mg (83%). Ratio of isomers A/B = 4.8:1. $C_{44}H_{40}BClN_4ORu \cdot 0.5C_2H_4Cl_2$ (837.65): calcd. C 64.53, H 5.05, N 6.69; found C 64.58, H 5.09, N 6.58. Crystals for the X-ray structure determination were obtained from 1,2-dichloroethane/hexane. **Isomer A:** $^{13}C\{^1H\}$ NMR (CD_3COCD_3 , 125 MHz, 298 K): δ = 55.51 (1 C, Me-ArOCH₃), 73.30 (1 C, C_a), 86.61 (6 C, C-benzene), 108.12 (2 C, C^4 -Pz), 121.60 (4 C, C_p -Ph(BPh₄)), 125.36 [8 C, C_m -Ph(BPh₄)], 127.96 (1 C, C^3 -ArOCH₃), 136.39 [8 C, C_o -Ph(BPh₄)], 137.89 (2 C, C^5 -Pz), 150.53 (2 C, C^3 -Pz), 164.29 [q, $J_{C-^{11}B}$ = 49.4 Hz, 4 C, C_{ipso} -Ph(BPh₄)] ppm. **Isomer B:** $^{13}C\{^1H\}$ NMR (CD_3COCD_3 , 125 MHz, 298 K): δ = 87.04 (6 C, C-benzene), 121.60 [4 C, C_p -Ph(BPh₄)], 125.36 [8 C, C_m -Ph(BPh₄)], 136.39 [8 C, C_o -Ph(BPh₄)], 164.29 [q, $J_{C-^{11}B}$ = 49.4 Hz, 4 C, C_{ipso} -Ph(BPh₄)] ppm. IR: $\tilde{\nu}$ = 1580 (CN) cm^{-1} .

[RuCl(*p*-cymene)(bpzmArOCH₃)](BPh₄) (8): The method was similar to that used for complex 2. Amounts were as follows: $[RuCl_2(*p*-cymene)]_2$ (36.7 mg, 0.06 mmol) and bpzmArOCH₃ (33.1 mg, 0.13 mmol) in MeOH (5 mL). Complex 8 was obtained as a yellow solid. Yield: 56.1 mg (78%). Ratio of isomers A/B = 1.1:1. $C_{48}H_{48}BClN_4ORu$ (844.28): calcd. C 68.29, H 5.73, N 6.64; found C 68.25, H 5.77, N 6.68. Crystals for the X-ray structure determination were obtained from 1,2-dichloroethane/pentane. **Isomer A:** $^{13}C\{^1H\}$ NMR (125 MHz, CD_3COCD_3 , 298 K): δ = 17.73 (1 C, Me-Tol), 22.25 (2 C, Me-*i*Pr), 31.14 (1 C, CH-*i*Pr), 55.75 (1 C, Me-ArOCH₃), 73.73 (1 C, C_a), 84.77 (2 C, $CH^{2/2'}$ -*p*-cym), 85.94 (2 C, $CH^{3/3'}$ -*p*-cym), 105.64 (1 C, C^1 -*p*-cym), 108.65 (2 C, C^4 -Pz), 112.77 (1 C, C^6 -ArOCH₃), 121.43 (1 C, C^4 -ArOCH₃), 122.02 [4 C, C_p -Ph(BPh₄)], 125.75 [8 C, C_m -Ph(BPh₄)], 128.61 (1 C, C^3 -ArOCH₃), 133.05 (1 C, C^5 -ArOCH₃), 136.84 [8 C, C_o -Ph(BPh₄)], 138.39 (2 C, C^5 -Pz), 150.34 (2 C, C^3 -Pz), 158.23 (1 C, C^1 -ArOCH₃), 164.29 [q, $J_{C-^{11}B}$ = 49.4 Hz, 4 C, C_{ipso} -Ph(BPh₄)] ppm. **Isomer B:** $^{13}C\{^1H\}$ NMR (125 MHz, CD_3COCD_3 , 298 K): δ = 18.37 (1 C, Me-Tol), 22.21 (2 C, Me-*i*Pr), 31.72 (1 C, CH-*i*Pr), 85.46 (br. s, 4 C, $CH^{2/2'}$, $CH^{3/3'}$ -*p*-cym), 108.69 (2 C, C^4 -Pz), 122.02 [4 C, C_p -Ph(BPh₄)], 125.75 [8 C, C_m -Ph(BPh₄)], 135.48 (br. s, 3 C, C^5 -ArOCH₃, C^5 -Pz), 136.84 [9 C, C_o -Ph(BPh₄), C^6 -ArOCH₃], 164.29 [q, $J_{C-^{11}B}$ = 49.4 Hz, 4 C, C_{ipso} -Ph(BPh₄)] ppm. IR: $\tilde{\nu}$ = 1580 (CN) cm^{-1} .

[RuCl(benzene)(bpz*ArNO₂)](BPh₄) (9): The method was similar to that used for complex 1. Amounts were as follows: $[RuCl_2(C_6H_6)(CH_3CN)]$ (72.8 mg, 0.25 mmol) and bpz*ArNO₂ (81.3 mg, 0.25 mmol) in MeOH (10 mL). Complex 9 was obtained as a bright yellow solid. The product was recrystallised from 1,2-dichloroethane/hexane (X-ray crystals). Yield: 159.0 mg (74%). $C_{47}H_{45}BClN_5O_2Ru$ (859.25): calcd. C 65.70, H 5.28, N 8.15; found C 65.79, H 5.22, N 8.18. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 298 K): δ = 11.17 (2 C, Me³-Pz), 16.32 (2 C, Me⁵-Pz), 66.35 (1 C, C_a), 86.01 (6 C, C-benzene), 110.14 (2 C, C^4 -Pz), 121.60 [4 C, C_p -

Ph(BPh₄)], 125.22 (1 C, C^6 -ArNO₂), 125.35 [8 C, C_m -Ph(BPh₄)], 128.86 (1 C, C^2 -ArNO₂), 129.55 (1 C, C^3 -ArNO₂), 132.36 (1 C, C^4 -ArNO₂), 133.07 (1 C, C^5 -ArNO₂), 136.39 [8 C, C_o -Ph(BPh₄)], 149.29 (1 C, C^1 -ArNO₂), 164.29 [q, $J_{C-^{11}B}$ = 49.4 Hz, 4 C, C_{ipso} -Ph(BPh₄)] ppm. IR (Nujol): $\tilde{\nu}$ = 1563 (CN); 1542 (NO) cm^{-1} .

[RuCl(*p*-cymene)(bpz*ArNO₂)](BPh₄) (10): The method was similar to that used for complex 2. Amounts were as follows: $[RuCl_2(*p*-cymene)]_2$ (76.5 mg, 0.125 mmol) and bpz*ArNO₂ (81.3 mg, 0.25 mmol) in MeOH (10 mL). Complex 10 was obtained as a cream-coloured solid. The product was recrystallised from 1,2-dichloroethane/hexane (X-ray crystals). Yield: 178.5 mg (78%). $C_{51}H_{53}BClN_5O_2Ru \cdot 0.5C_2H_4Cl_2$ (964.84): calcd. C 64.73, H 5.75, N 7.26; found C 64.76, H 5.83, N 7.21. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, 298 K): δ = 12.00 (2 C, Me⁵-Pz), 17.35 (2 C, Me³-Pz), 18.51 (1 C, Me-Tol), 23.06 (2 C, Me-*i*Pr), 31.11 (1 C, CH-*i*Pr), 65.22 (1 C, C_a), 81.91 (2 C, $CH^{2/2'}$ -*p*-cym), 83.35 (2 C, $CH^{3/3'}$ -*p*-cym), 103.08 (1 C, C^4 -*p*-cym), 106.49 (1 C, C^1 -*p*-cym), 110.69 (2 C, C^4 -Pz), 121.67 [4 C, C_p -Ph(BPh₄)], 124.81 (1 C, C^6 -ArNO₂), 125.47 [8 C, C_m -Ph(BPh₄)], 126.61 (1 C, C^2 -ArNO₂), 129.16 (1 C, C^3 -ArNO₂), 132.62 (1 C, C^4 -ArNO₂), 133.54 (1 C, C^5 -ArNO₂), 136.11 [8 C, C_o -Ph(BPh₄)], 146.34 (2 C, C^5 -Pz), 148.35 (1 C, C^1 -ArNO₂), 159.21 (1 C, C^3 -Pz), 163.89 [q, $J_{C-^{11}B}$ = 49.4 Hz, 4 C, C_{ipso} -Ph(BPh₄)] ppm. IR (Nujol): $\tilde{\nu}$ = 1562 (CN); 1531 (NO) cm^{-1} .

[RuCl(benzene)(bpzmArNO₂)](BPh₄) (11): The method was similar to that used for complex 1. Amounts were as follows: $[RuCl_2(C_6H_6)(CH_3CN)]$ (72.8 mg, 0.25 mmol) and bpzmArNO₂ (67.3 mg, 0.25 mmol) in MeOH (10 mL). Complex 11 was obtained as a pale yellow solid. Ratio of isomers A/B = 4.2:1. The product was recrystallised from 1,2-dichloroethane/hexane. Yield: 162.6 mg (81%). $C_{43}H_{37}BClN_5O_2Ru \cdot 0.5C_2H_4Cl_2$ (852.62): calcd. C 61.98, H 4.61, N 8.21; found C 62.32, H 4.34, N 8.18. **Isomer A:** $^{13}C\{^1H\}$ NMR (125 MHz, CD_3COCD_3 , 298 K): δ = 72.41 (1 C, C_a), 86.41 (6 C, C-benzene), 108.98 (2 C, C^4 -Pz), 121.61 [4 C, C_p -Ph(BPh₄)], 125.36 [8 C, C_m -Ph(BPh₄)], 125.49 (1 C, C^6 -ArNO₂), 128.61 (1 C, C^2 -ArNO₂), 129.60 (1 C, C^3 -ArNO₂), 132.60 (1 C, C^4 -ArNO₂), 133.19 (1 C, C^5 -ArNO₂), 136.39 [8 C, C_o -Ph(BPh₄)], 139.07 (2 C, C^5 -Pz), 148.85 (1 C, C^1 -ArNO₂), 151.99 (2 C, C^3 -Pz), 164.56 [q, $J_{C-^{11}B}$ = 49.4 Hz, 4 C, C_{ipso} -Ph(BPh₄)] ppm. **Isomer B:** $^{13}C\{^1H\}$ NMR (125 MHz, CD_3COCD_3 , 298 K): δ = 72.00 (1 C, C_a), 87.08 (6 C, C-benzene), 108.47 (2 C, C^4 -Pz), 121.61 [4 C, C_p -Ph(BPh₄)], 125.36 [8 C, C_m -Ph(BPh₄)], 126.96 (1 C, C^6 -ArNO₂), 133.64 (1 C, C^3 -ArNO₂), 134.15 (1 C, C^5 -ArNO₂), 135.23 (1 C, C^4 -ArNO₂), 135.50 (2 C, C^5 -Pz), 136.39 [8 C, C_o -Ph(BPh₄)], 149.54 (2 C, C^3 -Pz), 164.56 [q, $J_{C-^{11}B}$ = 49.4 Hz, 4 C, C_{ipso} -Ph(BPh₄)] ppm. IR (Nujol): $\tilde{\nu}$ = 1579 (CN); 1530 (NO) cm^{-1} .

[RuCl(*p*-cymene)(bpzmArNO₂)](BPh₄) (12): The method was similar to that used for complex 2. Amounts were as follows: $[RuCl_2(*p*-cymene)]_2$ (76.5 mg, 0.125 mmol) and bpzmArNO₂ (67.3 mg, 0.25 mmol) in MeOH (10 mL). Complex 12 was obtained as a yellowish orange solid, as a mixture of the isomers. Yield: 139.6 mg (65%). Ratio of isomers A/B = 1.2:1. The product was recrystallised from 1,2-dichloroethane/hexane (X-ray crystals). $C_{47}H_{45}BClN_5O_2Ru$ (859.25): calcd. C 65.70, H 5.28, N 8.15; found C 65.62, H 5.19, N 8.21. **Isomer A:** $^{13}C\{^1H\}$ NMR (125 MHz, CD_3COCD_3 , 298 K): δ = 17.70 (1 C, Me-Tol), 21.97 (2 C, Me-*i*Pr), 30.51 (1 C, CH-*i*Pr), 72.25 (1 C, C_a), 81.26 (2 C, $CH^{2/2'}$ -*p*-cym), 88.13 (2 C, $CH^{3/3'}$ -*p*-cym), 102.52 (1 C, C^4 -*p*-cym), 103.69 (1 C, C^1 -*p*-cym), 109.16 (2 C, C^4 -Pz), 121.61 [4 C, C_p -Ph(BPh₄)], 125.47 [8 C, C_m -Ph(BPh₄)], 125.52 (1 C, C^6 -ArNO₂), 128.52 (1 C, C^2 -ArNO₂), 129.80 (1 C, C^3 -ArNO₂), 132.79 (1 C, C^4 -ArNO₂), 133.48 (1 C, C^5 -ArNO₂), 136.38 [8 C, C_o -Ph(BPh₄)], 139.04 (2 C, C^5 -Pz), 151.04 (2 C, C^3 -Pz), 149.05 (1 C, C^1 -ArNO₂), 164.29 [q, $J_{C-^{11}B}$ =

49.4 Hz, 4 C, C_{ipso} -Ph(BPh₄)] ppm. **Isomer B:** $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_3COCD_3 , 298 K): δ = 17.93 (1 C, Me-Tol), 21.97 (2 C, Me-*i*Pr), 30.97 (1 C, CH-*i*Pr), 71.93 (1 C, C_a), 83.39 (2 C, $\text{CH}^{2/2'}$ -*p*-cym), 87.03 (2 C, $\text{CH}^{3/3'}$ -*p*-cym), 102.58 (1 C, C^4 -*p*-cym), 105.32 (1 C, C^1 -*p*-cym), 108.64 (2 C, C^4 -Pz), 121.61 [4 C, C_p -Ph(BPh₄)], 121.79 (1 C, C^2 -ArNO₂), 125.47 [8 C, C_m -Ph(BPh₄)], 126.88 (1 C, C^6 -ArNO₂), 133.86 (1 C, C^3 -ArNO₂), 134.23 (1 C, C^4 -ArNO₂), 135.16 (1 C, C^5 -ArNO₂), 135.77 (2 C, C^5 -Pz), 136.38 [8 C, C_o -Ph(BPh₄)], 148.88 (2 C, C^3 -Pz), 150.76 (1 C, C^1 -ArNO₂), 164.29 [q, $J_{C-^{11}\text{B}}$ = 49.4 Hz, 4 C, C_{ipso} -Ph(BPh₄)] ppm. IR: $\tilde{\nu}$ = 1580 (CN), 1533 (NO) cm^{-1} .

[RuCl(benzene)(bpzm*ArNH₂)](BPh₄) (13):** The method was similar to that used for complex **1**. Amounts were as follows: [RuCl₂(C₆H₆)(CH₃CN)] (72.8 mg, 0.25 mmol) and bpz**m*ArNH₂ (73.8 mg, 0.25 mmol) in MeOH (10 mL). Complex **13** was obtained as a yellow solid. The product was recrystallised from 1,2-dichloroethane/hexane. Yield: 165.8 mg (80%). C₄₇H₄₇BClN₅Ru·0.5C₂H₄Cl₂ (878.75): calcd. C 65.61, H 5.62, N 7.97; found C 65.88, H 5.34, N 8.04. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl₃, 298 K): δ = 11.48 (2 C, Me³-Pz), 16.29 (2 C, Me⁵-Pz), 67.97 (1 C, C_a), 86.28 (6 C, C-benzene), 109.87 (2 C, C^4 -Pz), 119.08 (1 C, C^4 -ArNH₂), 119.35 (1 C, C^6 -ArNH₂), 121.45 [4 C, C_p -Ph(BPh₄)], 125.21 [8 C, C_m -Ph(BPh₄)], 127.64 (1 C, C^3 -ArNH₂), 130.98 (1 C, C^5 -ArNH₂), 136.24 [8 C, C_o -Ph(BPh₄)], 145.65 (1 C, C^1 -ArNH₂), 145.88 (2 C, C^5 -Pz), 157.97 (2 C, C^3 -Pz), 164.07 [q, $J_{C-^{11}\text{B}}$ = 49.4 Hz, 4 C, C_{ipso} -Ph(BPh₄)] ppm. IR: $\tilde{\nu}$ = 1562 (CN), 3464 (NH₂) cm^{-1} .

[RuCl(*p*-cymene)(bpzm*ArNH₂)](BPh₄) (14):** The method was similar to that used for complex **2**. Amounts were as follows: [RuCl₂(*p*-cymene)]₂ (76.5 mg, 0.125 mmol) and bpz**m*ArNH₂ (73.8 mg, 0.25 mmol) in MeOH (10 mL). Complex **14** was obtained as a reddish orange solid. Yield: 157.16 mg (71%). C₅₁H₅₅BClN₅Ru·1.5CH₃OH (933.44): calcd. C 67.56, H 6.59, N 7.50; found C 67.55, H 6.40, N 7.14. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl₃, 298 K): δ = 12.42 (2 C, Me⁵-Pz), 17.27 (2 C, Me³-Pz), 18.43 (1 C, Me-Tol), 23.22 (2 C, Me-*i*Pr), 30.79 (1 C, CH-*i*Pr), 67.28 (1 C, C_a), 83.01 (2 C, $\text{CH}^{2/2'}$ -*p*-cym), 83.81 (2 C, $\text{CH}^{3/3'}$ -*p*-cym), 102.14 (1 C, C^4 -*p*-cym), 107.56 (1 C, C^1 -*p*-cym), 110.76 (2 C, C^4 -Pz), 118.26 (1 C, C^2 -ArNH₂), 119.78 (1 C, C^4 -ArNH₂), 120.27 (1 C, C^6 -ArNH₂), 122.09 [4 C, C_p -Ph(BPh₄)], 125.86 [8 C, C_m -Ph(BPh₄)], 127.56 (1 C, C^3 -ArNH₂), 132.16 (1 C, C^5 -ArNH₂), 136.54 [8 C, C_o -Ph(BPh₄)], 145.30 (1 C, C^1 -ArNH₂), 145.06 (2 C, C^5 -Pz), 158.00 (2 C, C^3 -Pz), 164.37 [q, $J_{C-^{11}\text{B}}$ = 49.4 Hz, 4 C, C_{ipso} -Ph(BPh₄)] ppm. IR (Nujol): $\tilde{\nu}$ = 1562 (CN), 3467 (NH₂) cm^{-1} .

Hydrogen-Transfer Catalysis: A typical procedure for the catalytic hydrogen-transfer reaction is as follows. A mixture of benzophenone (368.1 mg, 2 mmol), KOH (10 mL, 0.008 M in *i*PrOH) and the catalyst (0.004 mmol) was heated to reflux under nitrogen. At the desired reaction times, aliquots were extracted from the reaction vessel, obtaining the yields by ^1H NMR spectroscopy.

X-ray Crystallography: A summary of crystal data collection and refinement parameters for all compounds is given in Table 1. The single crystals for **7A**·0.5C₂H₄Cl₂ and **8B** were mounted on a glass fibre and transferred to a Bruker X8 APPEX II CCD-based diffractometer equipped with a graphite-monochromated Mo- K_α radiation source (λ = 0.71073 Å). Data were integrated using the SAINT^[25] program and an absorption correction was performed with the program SADABS.^[26] The software package SHELXTL version 6.12^[27] was used for space group determination, structure solution and refinement by full-matrix least-squares methods based on F^2 . All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed using a “riding model” and included in the refinement at calculated positions.

Prismatic crystals of complexes **9**, **10**·0.5C₂H₄Cl₂ and **12A** were selected and mounted on a Bruker SMART-CCD area diffractometer. Intensities were collected with graphite-monochromated Mo- K_α radiation (λ = 0.71073 Å). Lorentz polarisation and absorption corrections were made.^[26] The structures were solved by direct methods, using the SHELXS computer program^[28] and refined by full-matrix least-squares method with the SHELX97 computer program.^[28] All hydrogen atoms were computed and refined using a riding model.

CCDC-631606 to -631610 contain the supplementary crystallographic data for complexes **7A**·0.5C₂H₄Cl₂, **8B**, **9**, **10**·0.5C₂H₄Cl₂ and **12A**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Tables S1 and S2 contain the ^1H NMR spectroscopic data and the results of the catalytic tests at different times, respectively.

Acknowledgments

Financial support from the Junta de Castilla-La Mancha-FEDER Funds (PBI-05-003) and the Spanish DGES/MCyT (CTQ2005-01430/BQU) is acknowledged.

- [1] S. Trofimenko, *Scorpionates, The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, 1999.
- [2] a) A. Caballero, M. C. Carrión, G. Espino, F. A. Jalón, B. R. Manzano, *Polyhedron* **2004**, *23*, 361–371; b) D. C. Wilson, J. H. Nelson, *J. Organomet. Chem.* **2003**, *682*, 272–289; c) B. A. Messerle, V. Tolhurst, P. Turner, *Eur. J. Inorg. Chem.* **2003**, *2*, 293–300; d) C. Zuccaccia, G. Bellachioma, G. Cardaci, A. Macchioni, *J. Am. Chem. Soc.* **2001**, *123*, 11020–11028; e) M. H. Huynh, J. M. Lasker, M. Wetzler, B. Mort, L. Szczepura, L. M. Witham, J. M. Cintron, A. C. Marschilok, L. J. Ackerman, R. K. Castellano, D. L. Jameson, M. R. Churchill, A. J. Jircitano, K. J. Takeuchi, *J. Am. Chem. Soc.* **2001**, *123*, 8780–8784; f) L. D. Field, B. A. Messerle, L. Soler, I. E. Buys, T. W. Hambley, *J. Chem. Soc. Dalton Trans.* **2001**, *13*, 1959–1965; g) M. Yamaguchi, T. Iida, T. Yamagishi, *Inorg. Chem. Commun.* **1998**, *1*, 299–301; h) A. Macchioni, G. Bellachioma, G. Cardaci, V. Gramlich, H. Rueegger, S. Terenzi, L. M. Venanzi, *Organometallics* **1997**, *16*, 2139–2145; i) F. A. Jalón, A. Otero, A. Rodríguez, M. Pérez-Manrique, *J. Organomet. Chem.* **1996**, *508*, 69–74; j) M. Fajardo, A. de la Hoz, E. Diez-Barra, F. A. Jalón, A. Otero, A. Rodríguez, J. Tejeda, D. Belletti, M. Lanfranchi, M. A. Pellinghelli, *J. Chem. Soc. Dalton Trans.* **1993**, *13*, 1935–1939.
- [3] a) S. Bhambri, D. A. Tocher, *Polyhedron* **1996**, 2763–2770; S. Bhambri, D. A. Tocher, *J. Chem. Soc. Dalton Trans.* **1997**, 3367–3372; b) S. Bhambri, A. Bishop, N. Kaltsoyannis, D. A. Tocher, *J. Chem. Soc. Dalton Trans.* **1998**, 3379–3390.
- [4] a) V. Rautenstrauch, X. Hoang-Cong, R. Churlaud, K. Abdur-Rashid, R. H. Morris, *Chem. Eur. J.* **2003**, *9*, 4954–4967; b) R. Noyori, T. Ohkuma, *Angew. Chem. Int. Ed.* **2001**, *40*, 40–73; c) H.-U. Blaser, C. Malan, B. Pugin, F. Spindler, H. Steiner, M. Studer, *Adv. Synth. Catal.* **2003**, *345*, 103–151.
- [5] a) K. Y. Ghebreyessus, J. H. Nelson, *J. Organomet. Chem.* **2003**, *669*, 48–56; b) R. K. Rath, M. Nethaji, A. R. Chakravarty, *Polyhedron* **2001**, *20*, 2735–2739; c) P. Braunstein, M. D. Fryzuk, F. Naud, S. J. Rettig, *J. Chem. Soc. Dalton Trans.* **1999**, 589–594; d) P. Braunstein, F. Naud, S. J. Rettig, *New J. Chem.* **2001**, *25*, 32–39; e) S. Ogo, T. Abura, Y. Watanabe, *Organometallics* **2002**, *21*, 2964–2969; f) M. T. Reetz, X. Li, *J. Am. Chem. Soc.* **2006**, *128*, 1044–1045.

- [6] a) T. Ohkuma, H. Ooka, S. Hashiguchi, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1995**, *117*, 7562–7563; b) A. Fujii, S. Hashiguchi, N. Uematsu, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1996**, *118*, 2521–2522; c) R. Noyori, S. Hashiguchi, *Acc. Chem. Res.* **1997**, *30*, 97–102; d) K.-J. Haack, S. Hashiguchi, A. Fujii, T. Ikariya, R. Noyori, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 285–288; e) T. Ohkuma, N. Utsumi, K. Tsutsumi, K. Murata, C. Sandoval, R. Noyori, *J. Am. Chem. Soc.* **2006**, *128*, 8724–8725.
- [7] a) M. Yamakawa, H. Ito, R. Noyori, *J. Am. Chem. Soc.* **2000**, *122*, 1466–1478; b) M. Yamakawa, I. Yamada, R. Noyori, *Angew. Chem. Int. Ed.* **2001**, *113*, 2900–2903; c) R. Noyori, M. Yamakawa, S. Hashiguchi, *J. Org. Chem.* **2001**, *66*, 7931–7944.
- [8] a) S. J. M. Nordin, P. Roth, T. Tarnai, D. A. Alonso, P. Brandt, P. G. Andersson, *Chem. Eur. J.* **2001**, *7*, 1431–1436; b) J. W. Faller, A. R. Lavoie, *Organometallics* **2002**, *21*, 3493–3495; c) M. Pastó, A. Riera, M. A. Pericàs, *Eur. J. Org. Chem.* **2002**, 2337–2341; d) K. Everaere, A. Mortreux, J. F. Carpentier, *Adv. Synth. Catal.* **2003**, *345*, 67–77; e) D. G. I. Petra, P. C. J. Kamer, P. W. N. M. Van Leeuwen, K. Goubitz, A. M. Van Loon, J. G. De Vries, H. E. Schoemaker, *Eur. J. Inorg. Chem.* **1999**, 2335–2341.
- [9] P. Pelagatti, M. Carcelli, F. Calbiani, C. Cassi, L. Elviri, C. Pelizzi, U. Rizzotti, D. Rogolino, *Organometallics* **2005**, *24*, 5836–5844.
- [10] a) D. Carmona, M. P. Lamata, L. A. Oro, *Eur. J. Inorg. Chem.* **2002**, 2239–2251; b) D. Carmona, M. P. Lamata, F. Viguri, I. Dobrinovich, F. J. Lahoz, L. A. Oro, *Adv. Synth. Catal.* **2002**, *344*, 499–502.
- [11] a) J. S. M. Samec, J.-E. Bäckvall, P. G. Anderson, P. Brandt, *Chem. Soc. Rev.* **2006**, *35*, 237–248; b) S. E. Clapham, A. Hadzovic, R. H. Morris, *Coord. Chem. Rev.* **2004**, *248*, 2201–2237; c) O. Pàmies, J.-E. Bäckvall, *Chem. Eur. J.* **2001**, *7*, 5052–5058; d) Y. R. S. Laxmi, J.-E. Bäckvall, *Chem. Commun.* **2000**, 611–612; e) J.-E. Bäckvall, *J. Organomet. Chem.* **2002**, *652*, 105–111; f) D. G. I. Petra, J. N. H. Reek, J.-W. Handgraaf, E. J. Meijer, P. Dierkes, P. C. J. Kamer, J. Brussee, H. E. Schoemaker, P. W. N. M. Van Leeuwen, *Chem. Eur. J.* **2000**, *6*, 2818–2829.
- [12] a) W. Baratta, J. Schütz, E. Herdtweck, W. A. Herrmann, P. Rigo, *J. Organomet. Chem.* **2005**, *690*, 5570–5575; b) W. Baratta, E. Herdtweck, K. Siega, M. Toniutti, P. Rigo, *Organometallics* **2005**, *24*, 1660; c) W. Baratta, G. Chelucci, S. Gladiali, K. Siega, M. Toniutti, M. Zanette, E. Zangrando, P. Rigo, *Angew. Chem. Int. Ed.* **2005**, *44*, 6214–6219.
- [13] a) N. Arroyo, F. Gómez-de la Torre, F. A. Jalón, B. R. Manzano, B. Moreno-Lara, A. M. Rodríguez, *J. Organomet. Chem.* **2000**, *603*, 174–184; b) M. C. Carrión, A. Díaz, A. Guerrero, F. A. Jalón, B. R. Manzano, A. Rodríguez, L. P. Rowena, J. C. Jeffery, *J. Organomet. Chem.* **2002**, *650*, 210–222; c) M. C. Carrión, A. Díaz, A. Guerrero, F. A. Jalón, B. R. Manzano, A. Rodríguez, *New J. Chem.* **2002**, *26*, 305–312.
- [14] M. C. Carrión, F. A. Jalón, I. López-Solera, B. R. Manzano, F. Sepúlveda, L. Santos, A. Rodríguez, M. Moreno, M. Martínez-Ripoll, *Can. J. Chem.* **2005**, *83*, 2106–2119.
- [15] E. Iengo, E. Zangrando, E. Baiutti, E. Alessio, *Eur. J. Inorg. Chem.* **2005**, 1019–1031.
- [16] A. J. Canty, R. T. Honeyman, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **1990**, *396*, 105–113.
- [17] a) K. I. The, L. K. Peterson, *Can. J. Chem.* **1973**, *51*, 422–426; b) K. I. The, L. K. Peterson, E. Kiehlmann, *Can. J. Chem.* **1973**, *51*, 2448–2451; c) L. K. Peterson, E. Kiehlmann, A. R. Sanger, K. I. The, *Can. J. Chem.* **1974**, *52*, 2367–2374.
- [18] J. Sebastian, P. Sala, J. Del Mazo, M. Sancho, C. Ochoa, J. Elguero, T. A. Fayet, M. C. Vertut, *J. Heterocycl. Chem.* **1982**, *19*, 1141–1145.
- [19] H. Günter, *NMR Spectroscopy: Basic Principles, Concepts and Applications in Chemistry*, 2nd ed., John Wiley and Sons, New York, **1995**.
- [20] G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, Oxford, **1997**.
- [21] a) C. Waalling, L. Bollyky, *J. Am. Chem. Soc.* **1964**, *86*, 3750–3752; b) A. Berkessel, T. J. S. Schubert, T. N. Müller, *J. Am. Chem. Soc.* **2002**, *124*, 8693–8698.
- [22] M. D. Le Page, B. R. James, *Chem. Commun.* **2000**, 1647–1648.
- [23] D. Amoroso, A. Jabri, G. P. A. Yap, D. G. Gusev, E. N. dos Santos, D. E. Fogg, *Organometallics* **2004**, *23*, 4047–4054.
- [24] a) D. R. Anton, R. H. Crabtree, *Organometallics* **1983**, *2*, 855–859; b) P. Foley, R. DiCosimo, G. M. Whitesides, *J. Am. Chem. Soc.* **1980**, *102*, 6713–6725; c) M. R. Eberhard, *Org. Lett.* **2004**, *6*, 2125–2128.
- [25] SAINT+ v7.12a. Area-Detector Integration Program, Bruker-Nonius AXS, Madison, WI, USA, **2004**.
- [26] G. M. Sheldrick, *SADABS version 2004/1. A Program for Empirical Absorption Correction*, University of Göttingen, Göttingen, Germany, **2004**.
- [27] SHELXTL-NT version 6.12. Structure Determination Package, Bruker-Nonius AXS, Madison, WI, USA, **2001**.
- [28] G. M. Sheldrick, *SHELXS-97, A Program for Solving Crystal Structures and Crystal Structure Refinement*, University of Göttingen, Germany, **1997**.

Received: March 7, 2007
Published Online: July 6, 2007