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Bis-N-heterocyclic carbene ruthenium(II) carbonyl complexes: Synthesis, structural characterization and catalytic activities in transfer hydrogenation of ketones

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ABSTRACT

In this contribution, the synthesis and characterization of eight ruthenium(II) carbonyl complexes supported by chelating alkane-bridged bis-N-heterocyclic carbene ligands are reported. The products obtained are analyzed using infrared and NMR spectroscopies. The molecular structures of four metal complexes were determined by X-ray crystallography, which exhibit the six-coordinate octahedral geometry with two carbene carbon atoms from the bidentate Bi-NHCs, two carbonyl groups and two chlorine atoms in the trans(Cl)–cis(CO) configuration. All these complexes show catalytic activities in transfer hydrogenation of ketones.

1. Introduction

There have been considerable investigations on the syntheses of transition-metal N-heterocyclic carbene (NHC) complexes and their catalytic applications in organometallic chemistry. So far many efficient NHC-based catalysts have been developed for a wide range of transformation reactions [1]. The majority of NHC ligands used are monodentate. The chelating N-heterocyclic carbenes (NHCs) are likely to be useful in organometallic synthesis and catalysis, which would provide a new dimension in the preparation of new catalysts because it yields the metal complexes with usually high thermal and air stabilities [1f,g].

Many reports have emerged in recent years concerning bidentate alkane-bridged bis-NHC ligands [2]. Most of the metal complexes containing bis-NHCs employ them as chelating ligands at a single metal, although some have been reported in which the bis-NHCs group bridges metal atoms [2]. For example, Jia et al. [2a] have reported the synthesis of binuclear half-sandwich iridium and rhodium carbene complexes containing 1,2-dichalcogenolato carborane or carbonato ligands. Mata et al. [2b] and Leung et al. [2c] have observed that the bis-NHCs coordinate to a Rh(I) center in either a chelating or a bridging 2:1 (metal:bis-NHC) fashion, depending on the length of the linker between the two azole groups and the steric size of N-substituents.

Despite the rich catalytic applications of ruthenium complexes, the Ru bis-N-heterocyclic carbene complexes applied in catalysis is restricted to those complexes with pyridine-bridged pincer ligands [3]. They showed considerable catalytic activities in transfer hydrogenations of ketone [3a], oxidation of olefins [3b], and metathesis of olefins [3c]. There are few reports of ruthenium complexes containing alkane-bridged bis-NHC ligands [4]. Poyatos et al. [4a,b] have prepared several η^6-arene ruthenium complexes with chelating bis-NHC. Marshall et al. [4c] have synthesized ruthenium(II) benzylidene complexes of the chiral chelating bis-NHC. Although ruthenium(II) carbonyl complexes are well known and have shown many applications [5], to the best of our knowledge, no ruthenium(II) carbonyl complex containing a chelating bis-NHC with an alkane bridge has been reported. In this paper, we describe the preparation of the mononuclear bidentate ruthenium(II) carbonyl complexes with the bis-NHCs that contain $(CH_2)_n$ linkers ($n = 1–4$). Influence of the different linker lengths on the catalytic activities of these complexes in transfer hydrogenation of ketones has been studied.

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2. Results and discussion

2.1. Synthesis of ruthenium complexes

The bis(imidazolium) salts were prepared in high yields by the reactions of *n*-butylimidazole or *n*-benzylimidazole with the corresponding dibromoalkanes (e.g., dibromomethane, 1,2-dibromoethane, 1,3-dibromopropane, and 1,4-dibromobutane) according to the literature methods [2a,b,f]. The transmetallation route using a silver N-heterocyclic carbene complex has proved to be a very useful procedure in the preparation of metal–NHC complexes [6]. In the current work, this procedure was employed to prepare ruthenium(II) carbonyl complexes **1a–4a** and **1b–4b** by a two-step process (see Scheme 1). Reacting the bis(imidazolium) salts $\mathbf{L_{1a}}$–$\mathbf{L_{4a}}$, $\mathbf{L_{1b}}$–$\mathbf{L_{4b}}$ with an excess of Ag_2O in dichloromethane (for R = ^{n}Bu) or methanol (for R = Bn) afforded the corresponding silver N-heterocyclic carbene complexes *in situ*, which were then treated with $[Ru(CO)_2Cl_2]_n$ in dichloromethane to afford the desired complexes **1a–4a** and **1b–4b**. The products were purified by column chromatography (dichloromethane/methanol (40:1)). All these complexes are very soluble in CH_3OH and CH_2Cl_2, but insoluble in diethyl ether and hydrocarbon solvents. These complexes are stable in the solid state in the air.

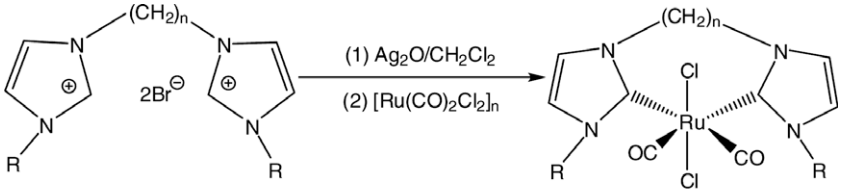
It should be noted that only one type of mononuclear ruthenium(II) complex with the chelating ligands was obtained with the $(-CH_2)_n$ linkers (*n* changing from 1 to 4). In contrast, the types of the Rh complexes with those bis-NHCs in either a chelating or a bridging 2:1 (metal:bis-NHC) fashion, have been obtained depending on the length of the linker [2b,c]. Attempts to prepare the analogues complexes with the bulky ^{t}Bu substituents in N-atom of imidazole under identical reaction conditions failed to yield the desired products.

All the compounds have been characterized by NMR, IR and elemental analyses. The chelating character of the bis-NHC ligands can be deduced from NMR spectroscopy by comparing with the spectra of the well characterized metal complexes [2]. In complexes **1a–4a** and **1b–4b**, only one set of ^{1}H and ^{13}C signals was observed for the two half molecules, indicating that the two halves are symmetry-related. The ^{1}H NMR spectra of **1a–4a** and **1b–4b** do not exhibit a signal at δ 9–10, where the NC*H*N proton of the imidazolium group was usually found, suggesting the coordination of the carbene carbon in bis-NHC ligands to the ruthenium atoms. The ^{13}C{H} NMR spectra of these complexes show resonances for the carbonyl carbon atoms at δ 196–198, similar to those of $[Ru(L)Cl_2(CO)_2]$ (L = bpy, bipy, dmbpy, $(PR_3)_2$) [5]. The ^{13}C{H} NMR signals for the carbene carbon atoms (δ 171–180) located in the characteristic range reported for the carbene carbon atoms of bis-NHCs metal complexes [5]. The IR spectra of complexes **1a–4a** and **1b–4b** show two ν (CO) absorptions at 2030–2040 and 1960–1970 cm^{-1}, similar to those of $[Ru(L)Cl_2(CO)_2]$ (L = bpy, bipy, dmbpy, $(PR_3)_2$) [5].

2.2. Molecular structures of *1a, 3a, 4a* and *3b*

The molecular structures of **1a**, **3a**, **4a**, and **3b** are displayed in Figs. 1–4, respectively. The crystallographic data for **1a**, **3a**, **4a** and **3b** are given in Table 1, and selected bond lengths and angles are given in Table 2.

The ORTEP drawings of **1a**, **3a**, **4a** and **3b** in Figs. 1–4 show that the coordination geometry around the ruthenium atom is a slightly distorted octahedron with carbon atoms from the chelating bis-NHC, two chloride atoms occupying mutually *trans* positions, and two CO groups locating *trans* to the carbene carbon, respectively. The Ru–$C_{carbene}$ distances (Ru1–C1 and Ru1–C2) ranged from 2.10



Scheme 1. Synthesis of Ru(II) carbonyl complexes **1a**–**4a** and **1b**–**4b**.

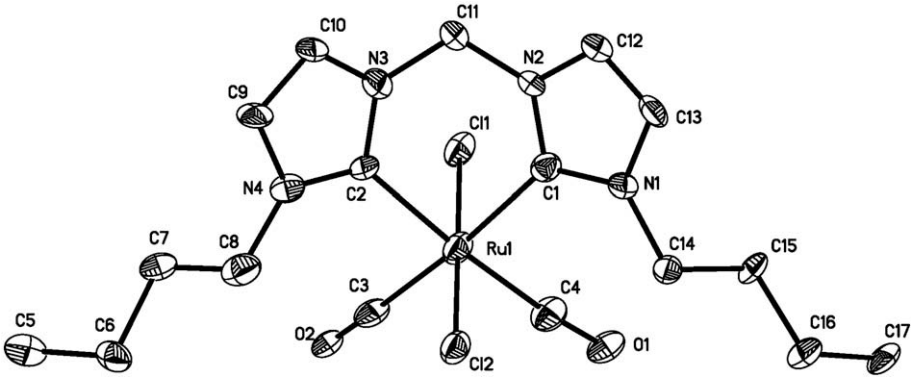


Fig. 1. Molecular structure of complex **1a** showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity.

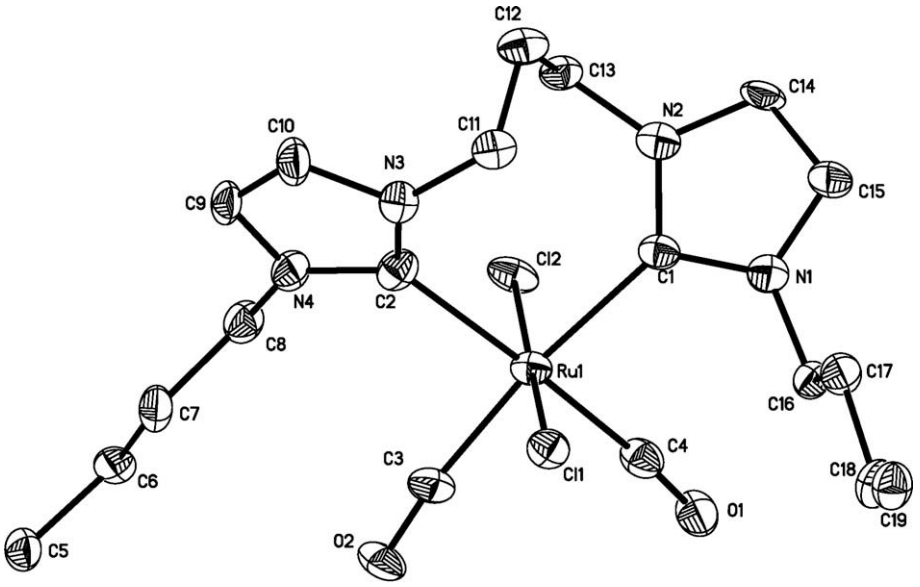


Fig. 2. Molecular structure of complex **3a** showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity.

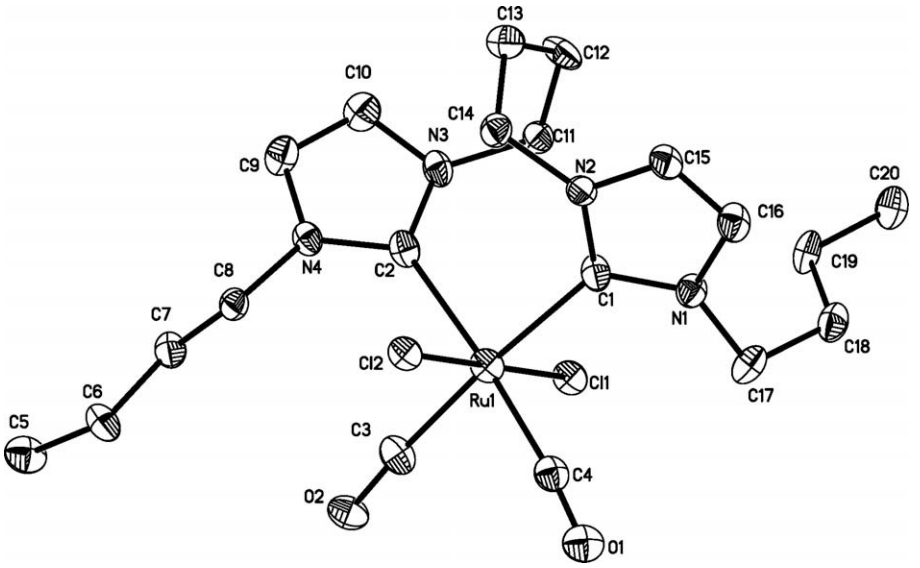


Fig. 3. Molecular structure of complex **4a** showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity.

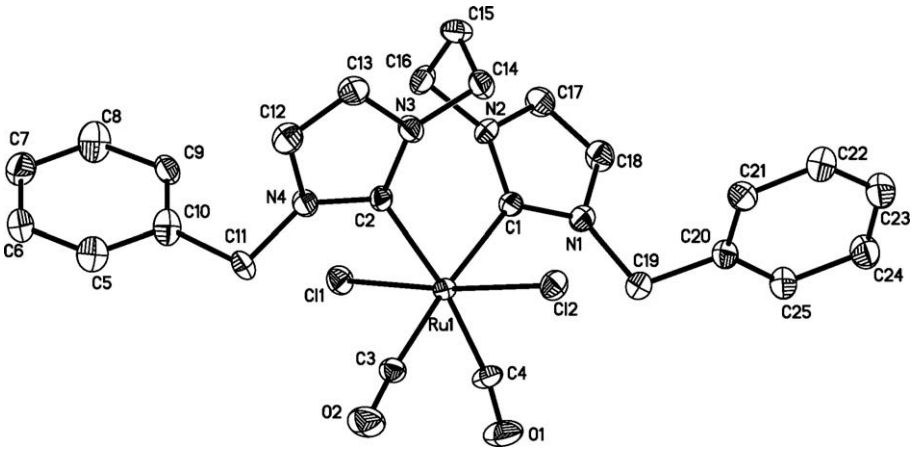


Fig. 4. Molecular structure of complex **3b** showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity.

Table 1
Summary of crystallographic data for **1a**, **3a**, **4a** and **3b**.

Compound	1a	3a	4a	3b
Formula	$C_{17}H_{24}Cl_2N_4O_2Ru$	$C_{19}H_{28}Cl_2N_4O_2Ru$	$C_{20}H_{30}Cl_2N_4O_2Ru$	$C_{25}H_{24}Cl_2N_4O_2Ru$
Formula weight	488.37	516.42	530.45	584.45
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*P*2(1)/*c*	*P*2(1)/*c*	*P*2(1)/*c*	*P*2(1)/*c*
a (Å)	7.7934(9)	11.986(3)	12.7794(9)	8.2681(9)
b (Å)	21.378(3)	14.657(4)	14.9518(10)	20.236(2)
c (Å)	13.4990(16)	13.586(3)	13.3881(9)	15.638(2)
β (°)	109.549(8)	106.611(4)	113.602(1)	102.313(1)
V (Å^3)	2119.4(5)	2287.2(10)	2344.1(3)	2556.3(5)
Z	4	4	4	4
T (K)	291(2)	291(2)	291(2)	291(2)
Radiation (Mo Ka)	0.71073	0.71073	0.71073	0.71073
Absorption coefficient (mm^{-1})	1.010	0.940	0.919	0.852
θ Range for data collection (°)	1.86/26.00	2.09/26.00	1.70/26.00	1.67/26.00
Data/restraints/parameters	4157/0/237	4481/0/255	4607/0/264	5019/0/ 307
Reflections collected	12 729	12 063	12 646	13 657
Reflections unique	4157	4481	4607	5019
R_{int}	0.025	0.029	0.037	0.043
Maximum and minimum transmission	0.80 and 0.70	0.82 and 0.77	0.82 and 0.79	0.82 and 0.84
Goodness-of-fit (GOF) on F^2	1.209	1.123	1.069	1.000
$R_1/wR_2[I > 2\sigma(I)]$	0.0562/0.0688	0.0376/0.0902	0.0453/0.1004	0.0451/0.0818
R_1/wR_2 (all data)[a]	0.0815/0.0718	0.0451/0.0920	0.0589/0.1030	0.0628/0.0838
Largest peak and hole (e/Å)	0.872/−0.663	0.285/−0.733	0.337/−0.811	0.996/−0.967

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table 2
Selected bond lengths (Å) and angles (°) for complexes **1a**, **3a**, **4a** and **3b**.

	1a	3a	4a	3b
Bond lengths				
Ru1–C1	2.107(4)	2.140(3)	2.160(3)	2.155(4)
Ru1–C2	2.138(4)	2.157(3)	2.152(4)	2.151(3)
Ru1–Cl1	2.4069(12)	2.4485(9)	2.4189(8)	2.4170(9)
Ru1–Cl2	2.4161(12)	2.4244(9)	2.4272(8)	2.4282(9)
Ru1–C3	1.914(5)	1.912(3)	1.896(4)	1.904(4)
Ru1–C4	1.919(5)	1.908(3)	1.883(4)	1.904(4)
C3–O2	1.128(5)	1.129(4)	1.134(4)	1.120(4)
C4–O1	1.156(5)	1.100(4)	1.140(4)	1.129(4)
Bond angles				
C3–Ru1–C1	175.35(17)	172.89(13)	175.71(16)	175.16(14)
C3–Ru1–C4	90.23(19)	85.64(14)	85.86(16)	85.52(16)
C4–Ru1–C1	93.49(18)	87.63(12)	89.87(15)	90.06(15)
C3–Ru1–C2	94.25(17)	90.99(14)	90.01(15)	88.47(15)
C4–Ru1–C2	175.46(18)	175.13(13)	175.74(14)	172.21(15)
C1–Ru1–C2	81.99(16)	95.88(12)	94.26(14)	96.10(13)
C3–Ru1–Cl1	86.60(14)	87.87(10)	86.48(11)	95.87(11)
C4–Ru1–Cl1	88.67(14)	96.08(11)	92.54(11)	86.63(12)
C1–Ru1–Cl1	90.70(11)	90.60(8)	93.25(9)	85.82(9)
C2–Ru1–Cl1	90.88(13)	87.30(8)	88.25(9)	89.06(9)
C3–Ru1–Cl2	92.98(14)	95.22(10)	93.82(11)	89.23(11)
C4–Ru1–Cl2	91.21(14)	87.33(11)	87.19(11)	95.64(12)
C1–Ru1–Cl2	89.72(11)	86.72(8)	86.42(9)	89.23(9)
C2–Ru1–Cl2	89.27(13)	89.48(8)	92.04(9)	89.23(9)
Cl1–Ru1–Cl2	179.57(4)	175.58(3)	179.58(3)	174.57(4)
Ru1–C3–O2	167.4(4)	172.9(3)	175.8(4)	175.0(4)
Ru1–C4–O1	174.0(4)	172.2(3)	174.2(3)	171.1(4)

to 2.16 Å, typical for those found in Ru–NHC complexes [3,4]. It is interesting to find that the Ru–$C_{carbene}$ bond become longer with increasing of the $(CH_2)_n$ linker length from **1a** (2.107(4), 2.138(4) Å), **3a** (2.140(3), 2.157(3) Å) to **4a** (2.160(3), 2.152(4) Å). Considering the same electronic donacity of the carbene carbon atoms in **1a**–**4a**, the lengthening of Ru–$C_{carbene}$ could be due to the geometric constraints imposed by the growing chain-bridge on chelating rings. The Ru–CO bond lengths (Ru1–C3 and Ru1–C4) become increasingly shorter from **1a** (1.914(5), 1.919(5) Å), **3a** (1.912(3), 1.908(3) Å) to **4a** (1.896(4), 1.883(4) Å). The Ru–CO bond lengths in these complex are in the range of 1.8–1.9 Å, similar to those reported in the other ruthenium(II) carbonyl complexes [5]. The Ru–Cl (Ru1–Cl1 and Ru1–Cl2) bond lengths observed in these compounds fall in the range 2.41–2.44 Å, similar to those of $[Ru(L)Cl_2(CO)_2]$ (L = bpy, bipy, dmbpy, $(PR_3)_2$) [5]. The C–O (C3–O2 and C4–O1) bond lengths in these complexes are in the normal range of 1.10–1.15 Å [5].

The bond angles Ru1–C3–O2 and Ru1–C4–O1 are in the range of 170–180°. The $C_{carbene}$–Ru–$C_{carbene}$ (C1–Ru1–C2) bond angles of complex **1a** (81.99(16)°) is much smaller than those of the other complexes **3a** (95.88(12)°), **4a** (94.26(14)°) and **3b** (96.10(13)°), which is due to the occurrence of six-membered chelating ring in complex **1a** in contrast with eight- or nine-membered chelating rings in complexes **3a, 3b**, and **4a**.

2.3. Catalytic transfer hydrogenation of ketones

Many ruthenium complexes have been found to be the active catalysts for transfer hydrogenation reactions [7]. Only few ruthe-

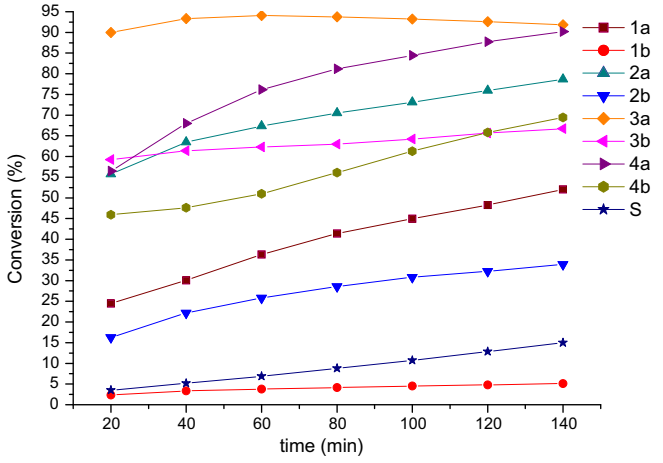
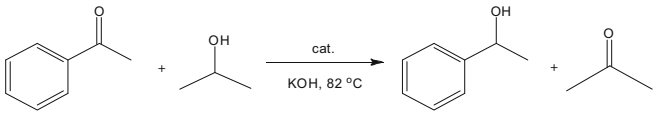


Fig. 5. Conversion versus reaction time of the catalytic transfer hydrogenation of acetophenone. *Experimental conditions:* 4 μmol of catalyst (**1a**–**4a** and **1b**–**4b**), 0.2 mmol of KOH, 4 mmol of acetophenone, solvent ^{i}PrOH (10 mL), *T* = 355 K. S = $[Ru(CO)_2Cl_2]_n$.

nium–NHC complexes, however, have been reported to be the catalysts for this transformation [8]. The ruthenium(II) carbonyl complexes **1a**–**4a** and **1b**–**4b** were thus studied as the catalysts for transfer hydrogenation of ketone. In the meantime, the ruthenium precursor $[Ru(CO)_2Cl_2]_n$ was examined under the same reaction conditions in order to investigate the role of the bis-N-heterocyclic carbene ligand.

The reduction of acetophenone to 1-phenylethanol by 2-propanol was used as the model reaction to explore the catalytic behavior for complexes **1a**–**4a** and **1b**–**4b** using 2-propanol as hydrogen donor in the presence of base (Eq. (1)). The catalytic experiments were carried out using 4.0 mmol of substrate ketone, 4 μmol of ruthenium complex catalyst, 0.2 mmol of KOH, 10 mL of ^{i}PrOH, with a catalyst/base/substrate (Cat/Base/S) ratio of 1:50:1000. A base solution in ^{i}PrOH was added to a ^{i}PrOH solution containing the catalyst and the substrate, which was kept at 82 °C. The conversion of the product was monitored by GC and the time-dependent conversions were followed (Fig. 5).



(1)

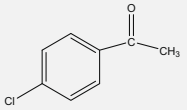
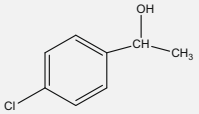
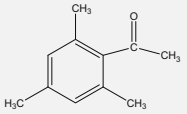
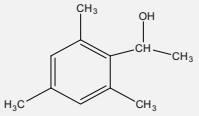
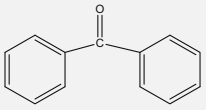
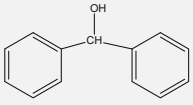
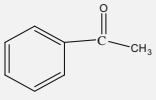
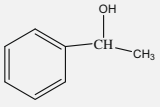
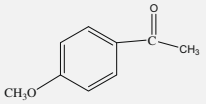
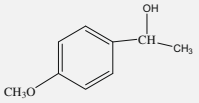
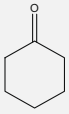
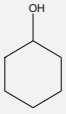
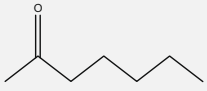
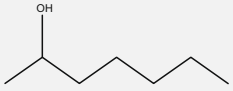
Fig. 5 shows that all the complexes except **1b** are much more active than ruthenium precursor $[Ru(CO)_2Cl_2]_n$, suggesting that the presence of most of the chelating bis-N-heterocyclic carbene ligand is beneficial for the transfer hydrogenation of ketone. The catalytic activity of **1a**–**4a** (R = ^{n}Bu) is better than the respective complexes **1b**–**4b** (R = Bn) with the order **1a** > **1b**; **2a** > **2b**; **3a** > **3b**; **4a** > **4b**.

It was found that **3a** is the most active catalyst among all of these complexes. The length of $-CH_2$ linker between two N-heterocyclic carbene also influences the catalytic activity of the complexes. The sequence of the activity is **3a** > **4a** > **2a** > **1a** > **S** (S = $[Ru(CO)_2Cl_2]_n$) and **3b** > **4b** > **2b** > **1b** > **S**. When the length of $-CH_2$ linker n = 3, the complex shows the best activity.

Since complex **3a** was found to be the most efficient catalyst in transfer hydrogenation of acetophenone, we decided to further explore its catalytic potentials in the reduction of other aryl and alkyl ketones with the reaction condition similar to those used in the transfer hydrogenation of acetophenone (Table 3). It was found that **3a** is efficient in transfer hydrogenation of cyclohexanone to cyclohexanol (99.67% after 2 h, entry 6), 4-chloroacetophenone to 4-chloroacetophenol (98.00% conversion after 6 h, entry 1), 2-heptanone to 2-heptanol (92.82% after 6 h, entry 7), moderate active in the case of diphenylketone (72.84% after 6 h, entry 3), 4-methoxyacetophenone (84.41% conversion after 6 h, entry 5), but shows a poor activity in reduction of 2,4,6-trimethylacetophenone (27.21% after 6 h, entry 2). These different catalytic activities may be attributed to the electronic and steric effects of the substituents on the ketones.

Some Ru–NHC [8] and Ir–NHC complexes [9] have been demonstrated to be the effective catalysts for the transfer hydrogenation of ketones. It should be noted that these catalytic studies were carried out under different reaction conditions and even with different substrates and bases. Compound **1a** had achieved turnover frequencies of 260 h^{-1} for transfer hydrogenation of acetophenone after 2 h, larger than the most closely related ruthenium(II) carbonyl chlorides complexes with pyridine-functionalized N-heterocyclic carbenes trans(Cl)- and cis(Cl)-Ru(Py-NHC)$Cl_2(CO)_2$

Table 3
Catalytic transfer hydrogenation of ketones using complex **3a**.[a]

Entry	Ketone	Alcohol	Conversion % (h)[b]
1			98.00 (6)
2			27.21 (6)
3			72.84 (6)
4			91.8 (40 min)
5			84.41 (6)
6			99.67 (2)
7			92.82 (6)

[a] *Experimental condition:* reactions were carried out at 82 °C; acetophenone (4 mmol), complex **3a** (4 μmol), KOH (0.2 mmol) in 2-propanol (10 mL); ketone/Ru/KOH = 1000/1/50.
[b] The conversion was determined by GC analysis.

(Py-NHC = 3-*n*-butyl-1-picolylimidazol-2-ylidene) [8c]. However, compound **1b** (TOF = 25.59 h^{-1}) is in the same order of magnitude found in trans(Cl)- and cis(Cl)-[Ru(Py-NHC)Cl_2(CO)$_2$] [Py-NHC = 3-benzyl-1-picolylimidazol-2-ylidene] [8c]. The turnover frequencies of **3a** is 498 h^{-1} for the hydrogenation of cyclohexanone after reaction for 2 h, which is much lower than that observed for [(CO-D)Ir(NHC)Br] (NHC = 1,3-dipropylbenzimidazol-2-ylidene, TOF = 6000 h^{-1}) reported by Hahn et al. [9a].

In order to determine the fate of carbonyl ligand in the catalytic reaction, we have attempted to probe if the carbonyl ligand still existed in the coordination sphere of ruthenium for the catalytic reduction of acetophenone with **3a**. After the catalytic reaction, the reaction mixture was evaporated to give a solid. The IR spectra of the isolated solids showed the absence of carbonyl ligand around the ruthenium atom, indicating the carbonyl group did not survive under the reaction conditions. The active catalytic species apparently do not contain the carbonyl group. It is thus reasonable to assume that complexes **1a**–**4a** and **1b**–**4b** just acted as precursors to the active catalysts.

3. Conclusions

The present work describes the synthesis and catalytic properties of a series of ruthenium(II) carbonyl complexes with bis-N-heterocyclic carbenes, where the substituent group of the azole ring are ^{n}Bu and Bn. The molecular structures of the bis-carbene complexes here indicate that the bis-NHC ligand is chelated to the metal atom and these complexes exhibit the trans(Cl)–cis(CO) configuration. These complexes are found to be efficient catalysts in transfer hydrogenation of ketones.

4. Experimental

4.1. General comments

Unless otherwise noted, all reactions and manipulations were performed under a dry nitrogen atmosphere using a standard Schlenk technique. The solvents were purified using standard methods and degassed before use. Methanol was dried over Mg/I_2, dichloromethane was dried over P_2O_5 and then distilled under nitrogen. Other chemicals were purchased from commercial source and used without further purification. The following starting materials were prepared according to the literature methods: [$RuCl_2(CO)_2$]$_n$ [5b], methylenebis(*N*-*n*-butylimidazolium) dibromide (**L$_{1a}$**) [2f], ethylenebis(*N*-*n*-butylimidazolium) dibromide (**L$_{2a}$**) [2a], trimethylenebis(*N*-*n*-butylimidazolium) dibromide (**L$_{3a}$**) [2a], tetramethylenebis(*N*-*n*-butylimidazolium) dibromide (**L$_{4a}$**) [2a], methylenebis(*N*-benzylimidazolium) dibromide (**L$_{1b}$**) [2f], ethylenebis(*N*-benzylimidazolium) dibromide (**L$_{2b}$**) [2f], trimethylenebis(*N*-benzylimidazolium) dibromide (**L$_{3b}$**) [2f], and tetramethylenebis(*N*-benzylimidazolium) dibromide (**L$_{4b}$**) [2f].

Elemental analyses were performed in an Elementar Vario ELIII elemental analyzer. NMR measurements were obtained in $CDCl_3$ or DMSO-d_6 on a Bruker AM-500 spectrometer. Chemical shifts are given in parts per million for ^{1}H and ^{13}C NMR. The IR spectra were recorded on a Bruker Vector 22 spectrophotometer with KBr pellets in the 4000–400 cm^{-1} region. The GC analyses of the catalytic mixture were performed on a Shimadzu GC-2010.

4.2. General procedures

A suspension of the appropriate bis(imidazolium) dibromide (0.5 mmol) and silver oxide (1.0 mmol) in 30 ml of dichloromethane (for R = ^{n}Bu) or methanol (for R = Bn) was stirred at room temperature for 2 h. Then, the mixture was filtered through Celite and treated with [$RuCl_2(CO)_2$]$_n$ (0.5 mmol) when R = ^{n}Bu. For R = Bn, the solvent MeOH was removed and replaced by 30 ml of CH_2Cl_2 and treated with [$RuCl_2(CO)_2$]$_n$ (0.5 mmol). The mixture was stirred at room temperature for 12 h, to give a precipitate. The suspension was filtered through Celite to remove the silver halide, and the solution was concentrated under reduced pressure. The product was purified by column chromatography using silica gel. Elution with dichloromethane/methanol (40:1) afforded the separation of a yellow band that contained the desired product, which was obtained as yellow powder after the volatiles were removed. Recrystallisation from methanol gave pure product suitable for elemental analysis and crystals suitable for X-ray diffraction (**1a**, **3a**, **4a**, and **3b**).

4.2.1. Methylenebis(N-n-butylimidazol-2-ylidene)dichlorodicarbonylruthenium (*1a*)

Yield: 0.18 g, 75%. *Anal.* Calc. for $C_{17}H_{24}Cl_2N_4O_2Ru$: C, 41.81; H, 4.95; N, 11.47. Found: C, 41.63; H, 4.86; N, 11.51%. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 7.63 (d, 2H, $^3J_{H-H}$ = 1.2 Hz, NC*H*), 7.58 (d, 2H, $^3J_{H-H}$ = 1.2 Hz, NC*H*), 6.48 (br, 2H, NCH_2N), 4.32 (m, 4H, NCH_2CH$_2$CH$_2$CH$_3$), 1.87 (m, 4H, NCH$_2$CH_2CH$_2$CH$_3$), 1.42 (m, 4H, NCH$_2$CH$_2$CH_2CH$_3$), 0.96 (t, 6H, $^3J_{H-H}$ = 7.3 Hz, NCH$_2$CH$_2$CH$_2$CH_3). ^{13}C{H} NMR (DMSO-d_6, 125.7 MHz): δ 196.0 (*C*O), 176.2 (*N*CN), 123.1 (*N*CH), 121.9 (*N*CH), 62.3 (NCH$_2$N), 50.5 (NCH$_2$CH$_2$CH$_2$CH$_3$), 33.9 (NCH$_2$CH$_2$CH$_2$CH$_3$), 20.3 (NCH$_2$CH$_2$CH$_2$CH$_3$), 14.5 (NCH$_2$CH$_2$CH$_2$CH$_3$). IR (KBr, cm^{-1}): ν (CO) 2039 and 1977.

4.2.2. Ethylenebis(N-n-butylimidazol-2-ylidene)dichlorodicarbonylruthenium (*2a*)

Yield: 0.20 g, 80%. *Anal.* Calc. for $C_{18}H_{26}Cl_2N_4O_2Ru$: C, 43.03; H, 5.22; N, 11.15. Found: C, 42.93; H, 5.06; N, 11.09%. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 7.74 (s, 2H, NC*H*), 7.63 (s, 2H, NC*H*), 5.06 (s, 4H, NCH_2CH_2N), 4.59 (m, 4H, NCH_2CH$_2$CH$_2$CH$_3$), 1.96 (m, 4H, NCH$_2$CH_2CH$_2$CH$_3$), 1.55 (m, 4H, NCH$_2$CH$_2$CH_2CH$_3$), 1.11 (t, 6H, $^3J_{H-H}$ = 7.0 Hz, NCH$_2$CH$_2$CH$_2$CH_3). ^{13}C{H} NMR (DMSO-d_6, 125.7 MHz): δ 198.0 (*C*O), 171.5 (*N*CN), 125.9 (*N*CH), 124.1 (*N*CH), 51.5 (NCH$_2$CH$_2$N), 50.7 (NCH$_2$CH$_2$CH$_2$CH$_3$), 34.3 (NCH$_2$CH$_2$CH$_2$CH$_3$), 20.0 (NCH$_2$CH$_2$CH$_2$CH$_3$), 14.4 (NCH$_2$CH$_2$CH$_2$CH$_3$). IR (KBr, cm^{-1}): ν (CO) 2039 and 1975.

4.2.3. Trimethylenebis(N-n-butylimidazol-2-ylidene)dichlorodicarbonylruthenium (*3a*)

Yield: 0.21 g, 80%. *Anal.* Calc. for $C_{19}H_{28}Cl_2N_4O_2Ru$: C, 44.19; H, 5.46; N, 10.85. Found: C, 44.11; H, 5.49; N, 10.81%. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 7.62 (s, 2H, NC*H*), 7.44 (s, 2H, NC*H*), 4.60 (m, 2H, NC*H*HCH$_2$C*H*HN), 4.41 (m, 2H, NCH*H*CH$_2$CH*H*N), 3.98 (m, 4H, NCH_2CH$_2$CH$_2$CH$_3$), 1.89 (m, 4H, NCH$_2$CH_2CH$_2$CH$_3$), 1.67 (m, 2H, NCH$_2$CH_2CH$_2$N), 1.44 (m, 4H, NCH$_2$CH$_2$CH_2CH$_3$), 0.95 (t, 6H, $^3J_{H-H}$ = 7.3 Hz, NCH$_2$CH$_2$CH$_2$CH_3). ^{13}C{H} NMR (DMSO-d_6, 125.7 MHz): δ 197.7 (*C*O), 176.4 (*N*CN), 123.4 (*N*CH), 123.3(*N*CH), 51.5 (NCH$_2$CH$_2$CH$_2$N), 45.7 (NCH$_2$CH$_2$CH$_2$CH$_3$), 35.1 (NCH$_2$CH$_2$CH$_2$N), 34.0 (NCH$_2$CH$_2$CH$_2$CH$_3$), 20.2 (NCH$_2$CH$_2$CH$_2$CH$_3$), 14.6 (NCH$_2$CH$_2$CH$_2$CH$_3$). IR (KBr, cm^{-1}): ν (CO) 2033 and 1966.

4.2.4. Tetramethylenebis(N-n-butylimidazole-2-ylidene) dichlorodicarbonylruthenium (*4a*)

Yield: 0.22 g, 80%. *Anal.* Calc. for $C_{20}H_{30}Cl_2N_4O_2Ru$: C, 45.28; H, 5.70; N, 10.56. Found: C, 44.98; H, 5.41; N, 10.38%. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 7.65 (s, 2H, NC*H*), 7.55 (s, 2H, NC*H*), 4.64 (m, 2H, NC*H*HCH$_2$CH$_2$C*H*HN), 4.44 (m, 2H, NCH*H*CH$_2$CH$_2$CH*H*N), 4.37 (m, 2H, NC*H*HCH$_2$CH$_2$CH$_3$), 3.63 (m, 2H, NCH*H*CH$_2$CH$_2$CH$_3$), 1.95 (m, 2H, NCH$_2$C*H*HC*H*HCH$_2$N), 1.87 (m, 4H, NCH$_2$CH_2CH$_2$CH$_3$), 1.45 (m, 4H, NCH$_2$CH$_2$CH_2CH$_3$), 1.08 (m, 2H, NCH$_2$CH*H*CH*H*CH$_2$N), 0.96 (t, 6H, $^3J_{H-H}$ = 7.4 Hz, NCH$_2$CH$_2$CH$_2$CH_3). ^{13}C{H} NMR (DMSO-d_6, 125.7 MHz): δ 197.5 (*C*O), 176.7 (*N*CN), 123.5 (*N*CH), 123.0 (*N*CH), 51.1 (NCH$_2$CH$_2$CH$_2$CH$_2$N), 46.9 (NCH$_2$CH$_2$CH$_2$CH$_3$),

34.2($NCH_2CH_2CH_2CH_3$), 22.6 ($NCH_2CH_2CH_2CH_2N$), 20.1 ($NCH_2CH_2CH_2CH_3$), 14.6 ($NCH_2CH_2CH_2CH_3$). IR (KBr, cm^{-1}): ν (CO) 2035 and 1970.

4.2.5. Methylenebis(benzylimidazol-2-ylidene) dichlorodicarbonylruthenium (**1b**)

Yield: 0.10 g, 40%. *Anal.* Calc. for $C_{23}H_{20}Cl_2N_4O_2Ru$: C, 49.65; H, 3.62; N, 10.07. Found: C, 49.23; H, 3.73; N, 9.79%. ^{1}H NMR (DMSO-d_6): δ 7.68 (d, J_{H-H} = 1.5 Hz, 2H, NC*H*); 7.23 (d, J_{H-H} = 1.5 Hz, 2H, NC*H*); 7.42 (m, 4H, 2,6-H of phenyl), 7.39 (m, 2H, 4-H of phenyl), 7.27 (m, 4H, 3,5-H of phenyl), 5.76 (br, 6H, NCH_2N and CH_2Ph); ^{13}C{H} NMR (DMSO-d_6, 125.7 MHz): δ 196.9 (*C*O); 177.2 (*C*N); 137.3, 129.1, 128.3, 127.8 (C_6H_6), 123.2 (*C*H), 122.1 (*C*H); 62.1 (NCH_2N), 53.4 (CH_2Ph). IR (KBr, cm^{-1}): ν (CO) 2044 and 1986.

4.2.6. Ethylenebis(benzylimidazol-2-ylidene) dichlorodicarbonylruthenium (**2b**)

Yield: 0.12 g, 42%. *Anal.* Calc. for $C_{24}H_{22}Cl_2N_4O_2Ru$: C, 50.53; H, 3.89; N, 9.82. Found: C, 50.67; H, 3.68; N, 9.63%. ^{1}H NMR (DMSO-d_6): δ 7.49 (d, J_{H-H} = 1.5 Hz, 2H, NC*H*); 7.14 (d, J_{H-H} = 1.5 Hz, 2H, NC*H*); 7.40 (m, 4H, 2,6-H of phenyl), 7.33 (m, 2H, 4-H of phenyl), 7.24 (m, 4H, 3,5-H of phenyl), 5.80 (s, 4H, CH_2Ph); 5.02 (s, 4H, NCH_2CH_2N). ^{13}C{H} NMR ($CDCl_3$, 125.7 MHz): δ 196.2 (*C*O); 173.5 (*C*H); 138.1, 129.0, 128.9, 128.1 (C_6H_6), 127.9 (*C*H), 123.2 (*C*H); 54.7 (CH_2Ph), 49.5 (NCH_2CH_2N). IR (KBr, cm^{-1}): ν (CO) 2041 and 1986.

4.2.7. Trimethylenebis(benzylimidazol-2-ylidene) dichlorodicarbonylruthenium (**3b**)

Yield: 0.15 g, 50%. *Anal.* Calc. for $C_{25}H_{24}Cl_2N_4O_2Ru$: C, 51.38; H, 4.14; N, 9.59. Found: C, 51.11; H, 3.87; N, 9.70%. ^{1}H NMR (DMSO-d_6): δ 7.47 (s, 2H, NC*H*); 7.10 (s, 2H, NC*H*); 7.40 (m, 4H, 2,6-H of phenyl), 7.35 (m, 2H, 4-H of phenyl), 7.35 (d, 4H, 3,5-H of phenyl); 6.14 (d, 2H, C*H*HPh), 5.58 (d, 2H, CH*H*Ph); 4.17 (m, 2H, NC*H*HCH$_2$C*H*HN), 4.09 (m, 2H, NCH*H*CH$_2$CH*H*N); 1.75 (s, 2H, $NCH_2CH_2CH_2N$). ^{13}C{H} NMR (DMSO-d_6, 125.7 MHz): δ 196.2 (*C*O); 178.9 (*C*N); 137.1, 129.4, 129.3, 128.7 (C_6H_6), 123.4 (*C*H), 121.9 (*C*H); 56.2 (CH_2Ph), 46.2 ($NCH_2CH_2CH_2N$), 34.9 ($NCH_2CH_2CH_2N$). IR (KBr, cm^{-1}): ν (CO) 2032 and 1963.

4.2.8. Tetramethylenebis(benzylimidazole-2-ylidene)dichlorodicarbonylruthenium (**4b**)

Yield: 0.17 g, 50%. *Anal.* Calc. for $C_{26}H_{26}Cl_2N_4O_2Ru$: C, 52.18; H, 4.38; N, 9.36. Found: C, 51.84; H, 4.65; N, 9.44%. ^{1}H NMR (DMSO-d_6): δ 7.58 (s, 2H, NC*H*); 7.16 (s, 2H, NC*H*); 7.43 (m, 4H, 2,6-H of phenyl), 7.35 (m, 2H, 4-H of phenyl), 7.31 (m, 4H, 3,5-H of phenyl); 6.15 (d, 2H, C*H*HPh), 5.66 (d, 2H, CH*H*Ph); 4.60 (d, 2H, NC*H*HCH$_2$CH$_2$C*H*HN), 3.80 (d, 2H, NCH*H*CH$_2$CH$_2$CH*H*N); 2.04 (d, 2H, NCH$_2$C*H*HC*H*HCH$_2$N), 1.15 (d, 2H, NCH$_2$CH*H*CH*H*CH$_2$N). ^{13}C{H} NMR ($CDCl_3$, 125.7 MHz): δ 195.9 (*C*O); 179.3 (*C*N); 137.3, 129.3, 129.1, 128.6 (C_6H_6), 122.9 (*C*H), 121.9 (*C*H); 55.7 (CH_2Ph), 47.3 ($NCH_2CH_2CH_2CH_2N$), 22.7 ($NCH_2CH_2CH_2CH_2N$). IR (KBr, cm^{-1}): ν (CO) 2040 and 1975.

4.3. General procedure for the catalytic hydrogen transfer studies

The procedure used follows standard literature methods [7]. The hydrogen-transfer catalysis experiments were carried out in Schlenk glassware.

Organic substrate ketone (4.0 mmol), catalyst ruthenium complex (4 μmol) was dissolved in 8 ml of ^{i}PrOH in a Schlenk tube. The solution was freeze–pump–thaw degassed before the reaction started. Then, the solution was allowed to warm to 82 °C for 30 min under nitrogen. By addition of 2 ml of 0.1 mol L^{-1} KOH in ^{i}PrOH, the reaction starts immediately. The reaction progress was monitored by GC analysis.

4.4. X-ray structure determination of complexes **1a**, **3a**, **4a** and **3b**

Crystal data and details of data collection and refinements of **1a**, **3a**, **4a** and **3b** are given in Table 1. Diffraction data were collected on a Bruker SMART Apex II CCD diffractometer using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation and collected for absorption using SADABS program [10]. The structures were solved by direct methods and refined on F^2 against all reflections by full-matrix least-squares methods with SHELXTL (version 6.10) program [11]. The hydrogen atoms in these compounds were positioned geometrically and refined in the riding-model approximation. All non-hydrogen atoms were refined with anisotropic thermal parameters.

Acknowledgments

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Appendix A. Supplementary material

CCDC 722254, 722255, 722256 and 723250 contain the supplementary crystallographic data for **1a**, **3a**, **4a** and **3b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.11.015.

References

[1] (a) F.E. Hahn, M.C. Jahnke, Angew. Chem., Int. Ed. 47 (2008) 3122;
(b) W.A. Herrmann, Angew. Chem., Int. Ed. 41 (2002) 1290;
(c) S.T. Liddle, I.S. Edworthy, P.L. Arnold, Chem. Soc. Rev. 36 (2007) 1732;
(d) O. Kühl, Chem. Soc. Rev. 36 (2007) 592;
(e) D. Bourissou, O. Guerret, F.P. Gabba, G. Bertrand, Chem. Rev. 100 (2000) 39;
(f) J.A. Mata, M. Poyatos, E. Peris, Coord. Chem. Rev. 251 (2007) 841;
(g) D. Pugh, A.A. Danopoulos, Coord. Chem. Rev. 251 (2007) 610.
[2] (a) W.-G. Jia, Y.-F. Han, G.-X. Jin, Organometallics 27 (2008) 6035;
(b) J.A. Mata, A.R. Chianese, J.R. Miecznikowski, M. Poyatos, E. Peris, J.W. Faller, R.H. Crabtree, Organometallics 23 (2004) 1253;
(c) C.H. Leung, C.D. Incarvito, R.H. Crabtree, Organometallics 25 (2006) 6099;
(d) M. Albrecht, J.R. Miecznikowski, A. Samuel, J.W. Faller, R.H. Crabtree, Organometallics 21 (2002) 3596;
(e) K. Öfele, W.A. Herrmann, D. Mihalios, M. Elison, F. Herdtweck, T. Priermeier, P. Kiprof, J. Organomet. Chem. 498 (1995) 1;
(f) M.G. Gardiner, A.W. Herrmann, C.-P. Reisinger, J. Schwarz, M. Spiegler, J. Organomet. Chem. 572 (1999) 239;
(g) R.E. Douthwaite, D. Haüssinger, M.L.H. Green, P.J. Silcock, P.T. Gomes, A.M. Martins, A.A. Danopoulos, Organometallics 18 (1999) 4584;
(h) K.D. Wells, M.J. Ferguson, R. McDonald, M. Cowie, Organometallics 27 (2008) 691;
(i) F.E. Hahn, M. Foth, J. Organomet. Chem. 585 (1999) 241;
(j) F.E. Hahn, L. Wittenbecher, D.L. Van, R. Fröhlich, Angew. Chem., Int. Ed. 39 (2000) 541;
(k) F.E. Hahn, T. von Fehren, L. Wittenbecher, R. Frohlich, Z. Naturforsch., Teil B 59 (2004) 541.
[3] (a) A.A. Danopoulos, S. Winston, W.B. Motherwell, Chem. Commun. (2002) 1376;
(b) M. Poyatos, J.A. Mata, E. Falomir, R.H. Crabtree, E. Peris, Organometallics 22 (2003) 1110;
(c) J.A. Wright, A.A. Danopoulos, W.B. Motherwell, R.J. Carroll, S. Ellwood, J. Organomet. Chem. 691 (2006) 5204.
[4] (a) M. Poyatos, E. Mas-Marzá, M. Sanaú, E. Peris, Inorg. Chem. 43 (2004) 793;
(b) M. Poyatos, W. McNamara, C. Incarvito, E. Clot, E. Peris, R.H. Crabtree, Organometallics 27 (2008) 2128;
(c) C. Marshall, M.F. Ward, W.T.A. Harrison, J. Organomet. Chem. 690 (2005) 3970.
[5] (a) J. van Slageren, F. Hartl, D.J. Stufkens, D.M. Martino, H. van Willigen, Coord. Chem. Rev. 208 (2000) 309;
(b) B.D. Klerk-Engels, H.-W. Frühauf, K. Vrieze, H. Kooijman, A.L. Spek, Inorg. Chem. 32 (1993) 5528;

(c) C.F.J. Barnard, J.A. Daniels, J. Jeffery, R.J. Mawby, J. Chem. Soc., Dalton Trans. (1976) 953;
(d) D. Mulhern, Y. Lan, S. Brooker, J.F. Gallagher, H. Görls, S. Rau, J.G. Vos, Inorg. Chim. Acta 359 (2006) 736;
(e) T.-J.J. Kinnunen, M. Haukka, T.A. Pakkanen, J. Organomet. Chem. 654 (2002) 8;
(f) S. Chardon-Noblat, P. Da Costa, A. Deronzier, M. Haukka, T.A. Pakkanen, R. Ziessel, J. Electroanal. Chem. 490 (2000) 62;
(g) N.A. Bokach, M. Haukka, P. Hirva, M. Fatima, C.G. Da Silva, V.Y. Kukushkin, A.J.L. Pombeiro, J. Organomet. Chem. 691 (2006) 2368;
(i) V. Lehtovuori, P. Myllyperkiö, J. Linnanto, C. Manzoni, D. Polli, G. Cerullo, M. Haukka, J. Korppi-Tommola, J. Phys. Chem. B 109 (2005) 17538;
(j) S. Luukkanen, P. Homanen, M. Haukka, T.A. Pakkanen, A. Deronzier, S. Chardon-Noblat, D. Zsoldos, R. Ziessel, Appl. Catal. A: Gen. 185 (1999) 157;
(k) N.A. Bokach, M. Haukka, P. Hirva, M. Fatima, C.G. Da Silva, Y.V. Kukushkin, A.J.L. Pombeiro, J. Organomet. Chem. 691 (2006) 2368.
[6] I.J.B. Lin, C.S. Vasam, Coord. Chem. Rev. 251 (2007) 642.
[7] (a) A.D. Zotto, W. Baratta, M. Ballico, E. Herdtweck, P. Rigo, Organometallics 26 (2007) 5636;
(b) G. Zassinovich, G. Mestroni, S. Gladiali, Chem. Rev. 92 (1992) 1051;
(c) R. Noyori, S. Hashiguchi, Acc. Chem. Res. 30 (1997) 97;
(d) J.E. Bäckvall, J. Organomet. Chem. 652 (2002) 105.
[8] (a) W. Baratta, J. Schutz, E. Herdtweck, W.A. Herrmann, P. Rigo, J. Organomet. Chem. 690 (2005) 5570;
(b) P.L. Chiu, H.M. Lee, Organometallics 24 (2005) 1692;
(c) Y. Cheng, H.-J. Xu, J.-F. Sun, Y.-Z. Li, X.-T. Chen, Z.-L. Xue, Dalton Trans. (2009) 7132.
[9] (a) F.E. Hahn, C. Holtgrewe, T. Pape, M. Martin, E. Sola, L.A. Oro, Organometallics 24 (2009) 2203;
(b) H. Türkmen, T. Pape, F.E. Hahn, B. Cetinkaya, Organometallics 27 (2008) 571;
(c) I. Kownacki, M. Kubicki, K. Szubert, B. Marciniec, J. Organomet. Chem. 693 (2008) 321;
(d) J.-F. Sun, F. Chen, B.A. Dougan, H.-J. Xu, Y. Cheng, Y.-Z. Li, X.-T. Chen, Z.-L. Xue, J. Organomet. Chem. 694 (2009) 2096.
[10] G.M. Sheldrick, Program for Multi-Scan Absorption Correction, University of Göttingen, Germany, 2000.
[11] G.M. Sheldrick, Program for Crystal Structure Solution and Refinement, University of Göttingen, Germany, 2000.