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PAPER

Preparation of a series of Ru(II) complexes with *N*-heterocyclic carbene ligands for the catalytic transfer hydrogenation of aromatic ketones†

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The reaction of $[RuCl_2(p\text{-cymene}]_2$ with Ag–*N*-heterocyclic carbene (NHC) complexes yields a series of [(*p*-cymene)Ru(NHC)] complexes (**2a–f**). All synthesised compounds were characterized by elemental analysis, NMR spectroscopy and the molecular structure of **2a** was determined by X-ray crystallography. All complexes have been tested as catalysts for the transfer hydrogenation of aromatic ketones, showing excellent activity in this reaction.

Introduction

N-heterocyclic carbenes (NHC) have emerged as a useful class of ligands in the development of homogeneous organic and organometallic catalysts. They have proven an alternative to tertiary phosphines in homogeneous catalysis, because of the strong σ-donating and negligible π-accepting character, NHCs can form stable bonds with various metals from main group to transition metals in different oxidation states and stabilize catalytically active intermediates.[1,2] The last few decades have witnessed an extensive exploration of metal-NHC complexes as catalysts for a wide variety of organic transformations including olefin metathesis,[3] hydrosilylation,[4] hydroformylation,[5] hydrogenation,[6] copolymerization,[7] furan synthesis,[8] C–C[9] and C–N[10] coupling reactions and asymmetric transformations.[11]

Transfer hydrogenation is the addition of hydrogen to an unsaturated molecule by a reagent other than H_2. Typically a sacrificial reagent (hydrogen donor) such as 2-propanol together with a strong base and a Ru, Rh or Ir catalyst are used. Transfer hydrogenation generates few by-products, avoids hazardous reagents, and uses readily available and benign starting materials such as carbonyl compounds, imines, alkenes and alkynes.[12] Transfer hydrogenation is preferred for large-scale industrial use in the hope of developing a greener process by reducing waste production and energy use and lowering toxicity.[13] Recently, research has also been devoted to the synthesis of functionalized ligands containing NHC moieties, in order to modify the ligand properties and catalytic activities.[14] The first application of NHC complexes for the transfer hydrogenation reaction was reported by Nolan in 2001.[15] With regard to transfer hydrogenations different carbene or carbene-phosphane systems containing Rh,[16] Ir[16,17] Ru[18] and Ni[19] have been reported.

Recently, our research group has focused on *N*-heterocyclic carbene derivative ligands and their metal complexes as synthesis, characterization and catalytic activity.[20] We have also reported the application of imidazolidin-2-ylidene ruthenium complexes and benzimidazolidin-2-ylidene ruthenium complexes in transfer hydrogenation of aromatic ketones.[21] In this article, the new imidazolidinium salts that are precursors to these NHC ligands are readily synthesized and the subsequent formation of complexes of Ag–NHC has proved facile. The reaction of the Ag–NHC complexes with $[RuCl_2(p\text{-cymene})]_2$ in dichloromethane afforded the Ru-NHC complexes (**2a–2f**). All synthesized compounds were characterized by ^{1}H NMR, ^{13}C NMR, IR and elemental analysis techniques which support the proposed structures. The molecular and crystal structure of dichloro-[1,3-bis(2-methylbenzyl)imidazolidin-2-ylidene](*p*-cymene)ruthenium(II) complex was determined by single crystal X-ray diffraction technique. Further, the synthesized complexes have been effectively used as catalyst in transfer hydrogenation of ketones in the presence of isopropanol and KOH as base.

Results and discussion

Synthesis of imidazolidinium salts

A series of new symmetrical 1,3-dialkyl-imidazolidinium salts (**1**) were prepared according to known methods[22] and were conventional NHC precursors. The symmetrical NHC precursors were prepared according to general reaction pathway depicted in Scheme 1. Treatment of ethylenediamine with 2 equivalents of aromatic aldehyde in methanol at room temperature led to the

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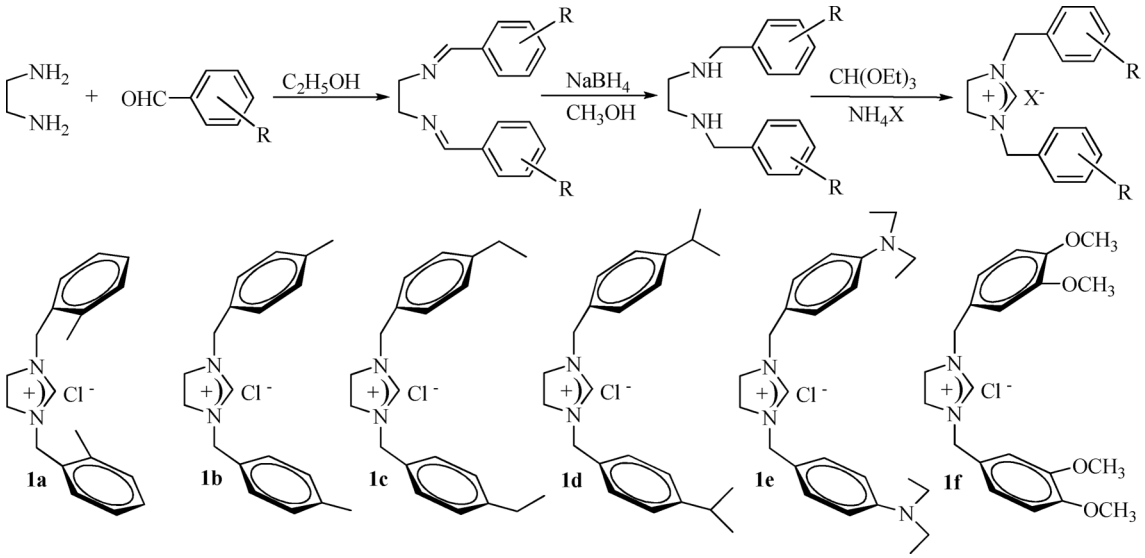
‡ Dedicated to Prof. Dr Christian Bruneau on the occasion of his 60th birthday.



Scheme 1 Preparation of imidazolidinium salts.

formation of the corresponding diimine. Their reduction with sodium borohydride in methanol, followed by treatment with triethylorthoformate in the presence of ammonium chloride with continuous elimination of ethanol led to the formation of the expected imidazolidinium chlorides in excellent yields.

The imidazolidinium salts were isolated as colourless solids in very good yields and fully characterized by ^{1}H and ^{13}C NMR, and IR spectroscopies, elemental analyses, and their melting points were determined (see experimental section). The ^{1}H NMR spectra of the imidazolidinium salts further supported the assigned structures; the resonances for acidic C(2)-H were observed as sharp singlet at the 9.06, 10.51, 10.39, 10.61, 8.32 and 10.65 ppm respectively for **1a–f**. The positions of the methyl groups on the benzyl rings have also a strong influence on the chemical shift of the proton. For the imidazoldinium salts **1a**, there is shielding due to the *ortho* methyl groups, so the chemical shift is observed singlet at the 9.06 ppm. Whereas the 4-substitution pattern in **1b** leads to 10.51 ppm. ^{13}C NMR chemical shifts were consistent with the proposed structure; the imino carbon appeared as a typical singlet in the ^{1}H-decoupled mode in the 158.6, 158.5, 158.4, 158.6, 156.2 and 158.8 ppm respectively for imidazolidinium salts (**1a–f**). The IR data for imidazolidinium salts **1a–f** clearly indicate the presence of the –C═N– group with a ν(C═N) vibration at 1660, 1669, 1661, 1669, 1653 and 1646 cm^{-1} respectively for **1a–f**. The NMR values are similar to those found for other imidazolidinium salts.[20b,23] The salts are air- and moisture stable both in the solid state and in solution.

Preparation of ruthenium–carbene complexes 2a–f

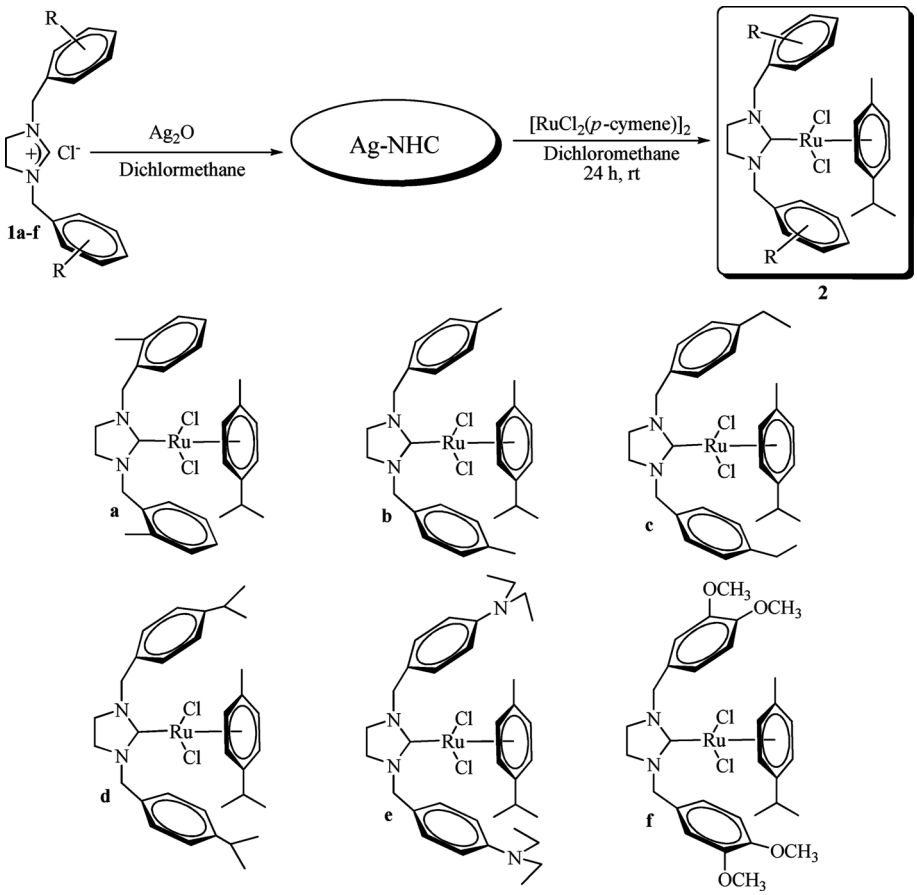
The complexation protocols in NHC chemistry are mainly based on the following routes: i) the complexation of the free, preisolated NHC with metal; ii) *in situ* deprotonation of the azolium salt by base, either exogenous or embedded in the metal precursor, and subsequent metal-complexation; iii) use of basic Ag_2O to generate a Ag–NHC complex, followed by the NHC transfer to a late transition metal *via* transmetallation.[24] Recently, CuI–NHC complexes have been shown to transfer NHC to Au, Pd and Ru.[25] Several other procedures have also been developed in recent years.[26]

The procedure involving Ag–NHC carbene, generated by treatment of imidazolium salt with Ag_2O is probably one of the most general methods, because it generates an air stable intermediate under mild reaction-conditions, thus allowing an easy access to a wide range of transition metal complexes. It is often used successfully when other methods fail.[27] The use of Ag–NHC complexes as carbene transfer reagents provides in many cases a convenient way to overcome the difficulties arising from using strong bases, inert atmospheres, and complicated workups. This method was used for the preparation of complexes **2a–2f**. Firstly, we examined the formation of variously substituted NHC–Ag complexes having two alkyls on the NHC moiety. All these NHC–Ag compounds were obtained in high yields.[28] The isolated Ag-complex prepared from **1a–1f** and Ag_2O were converted into the red brown monocarbene Ru–NHC complexes (**2a–2f**) in high yields (Scheme 2). The air and moisture-stable ruthenium carbene complexes (**2a–f**) were soluble in solvents such as dichloromethane, chloroform, toluene, and tetrahydrofurane and insoluble in non-polar solvents.

The complexes **2a–f**, which are very stable in the solid state have been characterized by analytical and spectroscopic techniques. Ruthenium complexes exhibit a characteristic $\upsilon_{(NCN)}$ band typically at 1495, 1515, 1497, 1492, 1498 and 1515 cm^{-1} respectively for **2a–2f**.[29] ^{13}C chemical shifts provide a useful diagnostic tool for this type of metal carbene complex. The chemical shifts for the carbon atom fall in the 206.6–209.7 ppm and are similar to those found in other ruthenium–carbene complexes. These complexes show typical spectroscopic signatures, which are in line with those recently reported for other [$RuCl_2$(NHC)(arene)] complexes.[29]

Catalytic transfer hydrogenation of ketones

Transition-metal catalyzed transfer hydrogenation using 2-propanol as a hydrogen source has become an efficient method in organic synthesis as illustrated by several useful applications reported in recent years.[12–19] The reaction conditions for this

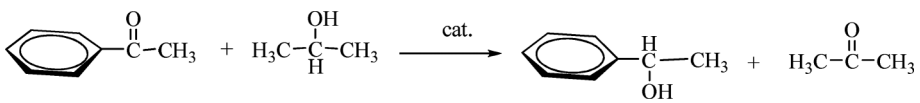


Scheme 2 General preparation of Ru–NHC complexes.

important process are economic, relatively mild and environmentally friendly. The volatile acetone product can also be easily removed to shift an unfavorable equilibrium. Owing to its efficiency in the transfer hydrogenation of acetophenone derivatives, ruthenium(II) complexes (**2a–2f**) were further investigated by transfer hydrogenation of various methyl aryl ketones.

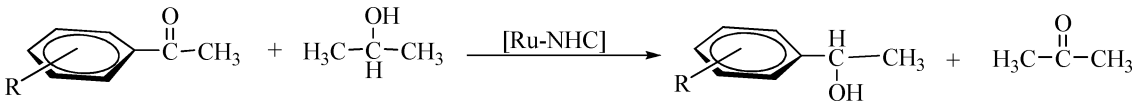
The ruthenium(II) complexes **2a–2f** catalyzed the reduction of ketones to the corresponding alcohols *via* hydrogen transfer from 2-propanol with KOH as the promoter. As the starting point, the performance of the catalysts in the transfer hydrogenation were screened by using acetophenone as a model substrate (eqn (1)).

In a typical experiment the preformed, isolated crystalline catalyst (0.01 mmol) was dissolved in 2-propanol. After the catalysts had completely dissolved, acetophenone (1.00 mmol) and a base (4 mmol) were added and the reaction was performed at 80 °C. The reactions were conducted at a substrate/catalyst/base (S/C/base) molar ratio of 1 : 0.01 : 4. In the transfer hydrogenation reaction, the base facilitates the formation of ruthenium alkoxide by abstracting proton from the alcohol and subsequently alkoxide undergoes β-elimination to give ruthenium hydride, which is an active species in this reaction. Since the base facilitates the formation of a ruthenium alkoxide by abstracting the proton from isopropanol, different bases were used as promoters in the transfer hydrogenation of ketones. Acetophenone was kept as a test substrate and allowed it to react in isopropanol with catalytic quantities of complex **2** in the presence of different bases like Cs_2CO_3, K_2CO_3, NaOH, KOH, *t*-BuOK and NaOAc. It has been observed that NaOH and KOH are shown to have good conversions when compared to the Cs_2CO_3, K_2CO_3, *t*-BuOK and NaOAc in the hydrogenation reactions. The stronger the base the higher the conversion rate, NaOAc (51%) < K_2CO_3(58%) < Cs_2CO_3(61%) < *t*-BuOK(82%) < NaOH (91%) < KOH(97%). As in the previous study the best results were obtained with KOH.[21c] Hence, it is decided that base KOH is the best compromise between optimum reaction rate in isopropanol and reaching 97% conversion for acetophenone within 1 h. In the absence of a base no transfer hydrogenation of the ketones was observed. Under the reaction conditions complex **2b** proved to be the most effective catalyst relative to **2a**, **2c**, **2d**, **2e** and **2f**. The reduction of acetophenone with **2b** was completed within 1 h reaching 97%. In contrast, acetophenone was reduced within 1 h using **2a**, **2c**, **2d**, **2e** and **2f** with 94, 96, 94, 96 and 90% conversion, respectively (Table 1, entries 1–6). Also, we tried this reaction at 30 min. However, the



(1)

Table 1 Transfer hydrogenation of ketones catalyzed by **2a–f**



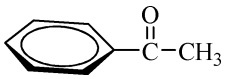
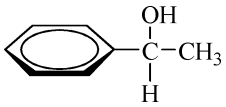
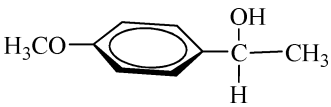
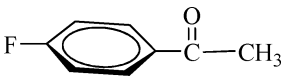
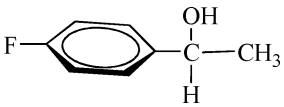
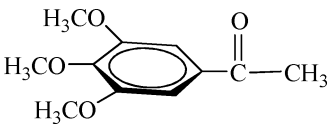
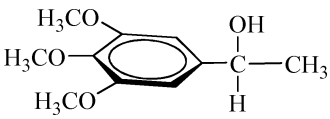
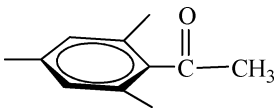
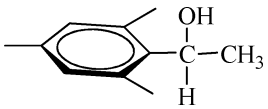
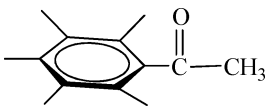
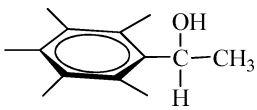
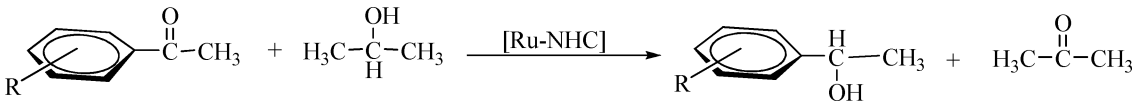
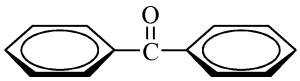
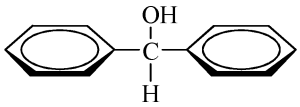
Entry	Cat.	Substrate	Product	Yield (%)
1	**2a**			94
2	**2b**			97
4	**2c**			96
4	**2d**			94
5	**2e**			96
6	**2f**			90
7	**2a**			75[a]
8	**2b**			82[a]
9	**2c**			72[a]
10	**2d**			69[a]
11	**2e**			76[a]
12	**2f**			68[a]
13	**2a**			92
14	**2b**			94
15	**2c**			92
16	**2d**			90
17	**2e**			91
18	**2f**			90
19	**2a**			94
20	**2b**			98
21	**2c**			95
22	**2d**			94
23	**2e**			92
24	**2f**			95
25	**2a**			92
26	**2b**			90
27	**2c**			91
28	**2d**			89
29	**2e**			90
30	**2f**			91
31	**2a**			63
32	**2b**			68
33	**2c**			61
34	**2d**			67
35	**2e**			68
36	**2f**			60
37	**2a**			—
38	**2b**			—
39	**2a**			91

Table 1 (*Contd.*)



Entry	Cat.	Substrate	Product	Yield (%)
40	**2b**			95
41	**2c**			91
42	**2d**			92
43	**2e**			93
44	**2f**			90

Reaction conditions: 1.0 mmol substrate, ^{i}PrOH (10 mL), KOH (4 mmol), Ru–NHC (0.01 mmol), 80 °C, 1 h. Purity of compounds is checked by GC and GC-MS and yields are based on ketones. Yields were determined by GC.[a] Reaction time is 30 min.

yields lower than 1 h, for example the reduction of acetophenone with **2b** was completed within 30 min 82% (Table 1, entries 7–12).

A variety of ketones were transformed to the corresponding secondary alcohols. Typical results are shown in Table 1. Under those conditions *p*-methoxyacetophenone, *p*-fluoroacetophenone and 3,4,5-trimethoxyacetophenone react very cleanly and in good yields with 2-propanol (Table 1, entries 14, 20, and 25). The presence of electron withdrawing (F) or electron donating (OCH_3) substituents on acetophenone (Table 1, entries 16, 20, and 26) has a significant effect on the reduction of ketones to their corresponding alcohols. The maximum conversion of 4-fluoroacetophenone to corresponding alcohol was achieved over a period of 1 h (Table 1, entry 20).

The conversion of ketones with bulky substituents on the aromatic ring was not observed or slightly decreased. For example, when 2,4,6-trimethylbenzyl-methyl ketone was used conversion decreased (Table 1, entries 31–36) and when ketone with pentamethyl on aromatic ring was used in the transfer hydrogenation, conversion was not observed (Table 1, entries 37–38). The ruthenium complexes also catalyzed the transfer hydrogenation of benzophenone very effectively (Table 1, entries 39–44). Among the tested complexes, the complex **2b** is highly efficient in the transfer hydrogenation of ketone to secondary alcohol. Also, in our previous work, reaction time was chosen as 12 h and AgOTf was used for the activation of Ru–(NHC) complexes. However in this present work AgOTf is not used and the reaction time is lowered to 1 h and higher conversion is obtained as compared with our previous results.[21a,b]

Conclusions

From readily available starting materials, such as 1,3-dialkylimidazoldinium salts, six [$RuCl_2$(*p*-cymene)(1,3-dialkylimidazolidin-2-ylidene)] complexes (**2a–f**) have been prepared by transmetallation from Ag–NHC complexes. Complex **2a** has been characterized by single crystal X-ray diffraction studies. The efficiency of complexes **2a–f** as catalyst precursors for the transfer hydrogenation of ketones has been established.

Experimental section

All reactions for the preparation imidazolidinium salts (**1**) and ruthenium-(NHC) complexes (**2**) were carried out under argon in flame-dried glassware using standard Schlenk techniques. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: Et_2O (Na/K alloy), CH_2Cl_2 (P_4O_{10}), hexane, toluene (Na). All reagents were purchased from Aldrich Chemical Co. Melting points were determined in glass capillaries under air with an Electrothermal-9200 melting point apparatus. FT-IR spectra were recorded as KBr pellets in the range 400–4000 cm^{-1} on a ATI UNICAM 1000 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded using a Varian AS 400 Merkur spectrometer operating at 400 MHz (^{1}H), 100 MHz (^{13}C) in $CDCl_3$ and DMSO-d_6 with tetramethylsilane as an internal reference. All reactions were monitored on a Agilent 6890 N GC system by GC-FID with a HP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness. Column chromatography was performed using silica gel 60 (70–230 mesh). Elemental analyses were performed by Turkish Research Council (Ankara, Turkey) Microlab.

General preparation of 1,3-dialkylimidazolidinium salts

The aromatic aldehyde (20 mmol) and the ethylenediamine (10 mmol) were stirred overnight in methanol. The diimine was collected as a white solid, filtrated and recrystallized in an alcohol/ether mixture. The diimine (10 mmol) was subsequently reduced by $NaBH_4$ (30 mmol) in CH_3OH (30 mL). The solution was then treated by 1 N HCl, and the organic phase was extracted with CH_2Cl_2 (3 × 30 mL). After drying over $MgSO_4$ and evaporation, the diamine was isolated as a solid. The diamine was then treated in a large excess of triethyl orthoformate (50 mL) in the presence of 10 mmol of NH_4Cl at 110 °C in a distillation apparatus until the removal of ethanol ceased. Upon cooling to RT a colourless solid precipitated, which was collected by filtration and dried under vacuum. The crude product was recrystallized from absolute ethanol to give colourless needles and the solid was washed with diethyl ether (2 × 10 mL) and dried under vacuum.

1,3-Bis(2-methylbenzyl)imidazolidinium chloride, 1a

Yield: 4.43 g; 90%; m.p.: 169–170 °C; $\nu_{(CN)}$: 1660 cm^{-1}. ^1H NMR (δ, $CDCl_3$): 2.30 (s, 6H, $CH_2C_6H_4(CH_3)$-2), 3.73 (s, 4H, NCH_2CH_2N), 4.72 (s, 4H, $CH_2C_6H_4(CH_3)$-2), 7.23–7.33(m, 8H, $CH_2C_6H_4(CH_3)$-2), 9.06 (s, 1H, NC*H*N). $^{13}C\{H\}$NMR (δ, $CDCl_3$): 19.3 ($CH_2C_6H_2(CH_3)$-2), 48.7 (NCH_2CH_2N), 49.7 ($CH_2C_6H_4(CH_3)$-2), 127.0, 129.3, 129.9, 131.4, 132.4 and 137.5 ($CH_2C_6H_4(CH_3)$-2), 158.6 (NCHN). Anal. Calcd. for $C_{19}H_{23}N_2Cl$: C,72.48; H, 7.36; N, 8.90. Found: C, 72.54; H, 7.47; N, 8.90%.

1,3-Bis(4-methylbenzyl)imidazolidinium chloride, 1b

Yield: 3,87 g; 82%; m.p: 227–228 °C; $\nu_{(CN)}$: 1669 cm^{-1}. ^1H NMR (δ, $CDCl_3$): 2.30 (s, 6H, $CH_2C_6H_4(CH_3)$-4), 3.71 (s, 4H, NCH_2CH_2N), 4.79 (s, 4H, $CH_2C_6H_4(CH_3)$-4), 7.13 and 7.25 (d, J = 7.8 Hz, 8H, $CH_2C_6H_4(CH_3)$-4), 10.51 (s, 1H, NC*H*N). $^{13}C\{H\}$NMR (δ, $CDCl_3$): 21.2 ($CH_2C_6H_2(CH_3)$-4), 47.5 (NCH_2CH_2N), 51.6 ($CH_2C_6H_4(CH_3)$-4), 128.8, 129.5, 129.9, 138.9 ($CH_2C_6H_4(CH_3)$-4), 158.5 (NCHN). Anal. Calcd. for $C_{19}H_{23}N_2Cl$: C,72.48; H, 7.36; N, 8.90. Found: C, 72.52; H, 7.40; N, 8.92%.

1,3-Bis(4-ethylbenzyl)imidazolidinium chloride, 1c

Yield: 4,52 g; 88%; m.p: 243–244 °C; $\nu_{(CN)}$: 1661 cm^{-1}. ^1H NMR (δ, $CDCl_3$): 1.12 (t, J = 7.5 Hz, 6H, $CH_2C_6H_4(CH_2CH_3)$-4), 2.56 (q, J = 7.5 Hz, 4H, $CH_2C_6H_4(CH_2CH_3)$-4), 3.68 (s, 4H, NCH_2CH_2N), 4.73 (s, 4H, $CH_2C_6H_4(CH_2CH_3)$-4), 7.07 and 7.22 (d, J = 7.8 Hz, 8H, $CH_2C_6H_4(CH_2CH_3)$-4), 10.39 (s, 1H, NC*H*N). $^{13}C\{H\}$NMR (δ, $CDCl_3$): 15.4 ($CH_2C_6H_2(CH_2CH_3)$-4), 28.5 ($CH_2C_6H_2(CH_2CH_3)$-4), 47.5 (NCH_2CH_2N), 51.9 ($CH_2C_6H_4(CH_2CH_3)$-4), 128.7, 128.9, 129.7, 145.2 ($CH_2C_6H_4(CH_2CH_3)$-4), 158.4 (NCHN). Anal. Calcd. for $C_{21}H_{27}N_2Cl$: C,73.56; H, 7.94; N, 8.17. Found: C, 73.61; H, 7.90; N, 8.21%.

1,3-Bis(4-i-propylbenzyl)imidazolidinium chloride, 1d

Yield: 4,34 g; % 78; m.p.: 246–247 °C; $\nu_{(CN)}$: 1669 cm^{-1}. ^1H NMR (δ, $CDCl_3$): 1.90 (d, J = 6.9 Hz, 12H, $CH_2C_6H_4(CH(CH_3)_2)$-4), 2.89 (h, J = 6.9 Hz, 2H, $CH_2C_6H_4(CH(CH_3)_2)$-4), 3.74 (s, 4H, NCH_2CH_2N), 4.73 (s, 4H, $CH_2C_6H_4(CH(CH_3)_2)$-4), 7.18 and 7.29 (d, J = 5.1 Hz, 8H, $CH_2C_6H_4(CH(CH_3)_2)$-4), 10.61 (s, 1H, NC*H*N). $^{13}C\{H\}$NMR (δ, $CDCl_3$): 23.8 ($CH_2C_6H_2(CH(CH_3)_2)$-4), 33.8 ($CH_2C_6H_2(CH(CH_3)_2)$-4), 47.5 (NCH_2CH_2N), 52.0 ($CH_2C_6H_4(CH(CH_3)_2)$-4), 127.3, 128.9, 129.9, 149.8 ($CH_2C_6H_4(CH_3)$-4), 158.6 (NCHN). Anal. Calcd. for $C_{23}H_{31}N_2Cl$: C,74.47; H, 8.42; N, 7.55. Found: C, 74.41; H, 8.70; N, 7.61%.

1,3-Bis(4-diethylaminobenzyl)imidazolidinium chloride, 1e

Yield: 3.40 g; 79%; m.p.: 113–115 °C; $\nu_{(CN)}$: 1653 cm^{-1}. ^1H NMR (δ, $CDCl_3$): 1.15 (t, J = 7.05 Hz, 12H, $CH_2C_6H_4N(CH_2CH_3)_2$-4), 3.36 (q, J = 6.9 Hz, 8H, $CH_2C_6H_4N(CH_2CH_3)_2$-4), 3.74 (s, 4H, NCH_2CH_2N), 4.52 (s, 4H, $CH_2C_6H_4N(CH_2CH_3)_2$-4), 6.62 and 7.11 (d, J = 8.7 Hz, 8H, $CH_2C_6H_4N(CH_2CH_3)_2$-4), 8.32 (s, 1H, NC*H*N). $^{13}C\{H\}$NMR (δ, $CDCl_3$): 12.5 ($CH_2C_6H_2N(CH_2CH_3)_2$-4), 44.3 ($CH_2C_6H_2N(CH_2CH_3)_2$-4), 47.5 (NCH_2CH_2N), 52.0 ($CH_2C_6H_4N(CH_2CH_3)_2$-4), 111.8, 118.2, 130.3, 148.1 ($CH_2C_6H_4N(CH_2CH_3)_2$-4), 156.2 (NCHN). Anal. Calcd. for $C_{25}H_{37}N_4Cl$: C, 67.99; H, 8.69; N, 13.06. Found: C, 67.89; H, 8.91; N, 13.05%.

1,3-Bis(3,4-dimethoxybenzyl)imidazolidinium chloride, 1f

Yield: 4,95 g; 81%; m.p: 403–404 °C; $\nu_{(CN)}$: 1646 cm^{-1}. ^1H NMR (δ, $CDCl_3$): 3.72 (s, 4H, NCH_2CH_2N), 3.84 (s, 6H, $CH_2C_6H_3(OCH_3)_2$-3), 3.91 (s, 6H, $CH_2C_6H_3(OCH_3)_2$-4), 4.77 (s, 4H, $CH_2C_6H_3(OCH_3)_2$-3,4), 6.78–7.11(m, 6H, $CH_2C_6H_3(OCH_3)_2$-3,4), 10.65 (s, 1H, NC*H*N). $^{13}C\{H\}$NMR (δ, $CDCl_3$): 47.3 (NCH_2CH_2N), 55.9 ($CH_2C_6H_3(OCH_3)_2$-3), 56.5 ($CH_2C_6H_3(OCH_3)_2$-4), 52.8 ($CH_2C_6H_3(OCH_3)_2$-3,4), 111.1, 112.1, 121.5, 124.9, 129.6, 149.7 ($CH_2C_6H_3(OCH_3)_2$-3,4), 158.8 (NCHN). Anal. Calcd. for $C_{21}H_{27}N_2ClO_4$: C,61.99; H, 6.69; N, 6.88. Found: C, 61.73; H, 6.64; N, 6.92%.

General procedure for the preparation of the ruthenium–NHC complexes (2a–f)

The ruthenium complexes were prepared by means of Ag-carbene transfer method developed by Wang and Lin.[30] The silver monocarbene complexes, which should subsequently serve as a carbene-transfer agent, were synthesized by the reaction of Ag_2O with 2 equiv. of salts (**1**) in CH_2Cl_2 at ambient temperature. The formulation of Ag–NHC was determined by elemental analyses and spectroscopic techniques.[28] We conveniently reacted Ag–NHC with $[RuCl_2(p\text{-cymene}]_2$ in dark condition and the mixture was allowed to stir for 24 h at room temperature. The solution was filtered through Celite, and the solvent was removed under vacuum to afford the product as a red-brown powder. The crude product was recrystallized from dichloromethane : diethyl ether (1 : 2) at room temperature.

Dichloro-[1,3-bis(2-methylbenzyl)imidazolidin-2-ylidene](*p*-cymene)ruthenium(II), 2a

Yield: 0,33 g; 69%; m.p: 225–227 °C; $\upsilon_{(CN)}$ = 1495 cm^{-1}. ^1H NMR (δ, $CDCl_3$): 1.21 (d, J = 7.2 Hz, 6H, $p\text{-}CH_3C_6H_4CH(CH_3)_2$), 1.94 (s, 3H, $p\text{-}CH_3C_6H_4CH(CH_3)_2$), 2.35 (s, 6H, $CH_2C_6H_4(CH_3)$-2), 2.56 (h, J = 7.2 Hz, 1H, $p\text{-}CH_3C_6H_4CH(CH_3)_2$), 3.46–3.61 (m, 4H, NCH_2CH_2N), 4.84 ve 5.59 (d, J = 15.6 Hz, 4H, $CH_2C_6H_4(CH_3)$-2), 5.11 ve 5.33 (d, J = 6.3 Hz, 4H, $p\text{-}CH_3C_6H_4CH(CH_3)_2$)), 7.23–7.41 (m, Hz, 8H, $CH_2C_6H_4(CH_3)$-2). $^{13}C\{H\}$NMR (δ, $CDCl_3$): 17.9 ($p\text{-}CH_3C_6H_4CH(CH_3)_2$), 19.3 ($CH_2C_6H_4(CH_3)$-2), 22.5 ($p\text{-}CH_3C_6H_4CH(CH_3)_2$), 30.58 ($p\text{-}CH_3C_6H_4CH(CH_3)_2$), 49.4 ($NCH_2CH_2N$), 52.7 ($CH_2C_6H_4(CH_3)$-2), 84.8, 85.2, 96.2, 106.3 ($p\text{-}CH_3C_6H_4CH(CH_3)_2$), 126.3, 127.1, 130.8, 135.8 ($CH_2C_6H_4(CH_3)$-2), 209.7 (Ru–C_{carb}). Anal. Calcd for $RuC_{29}H_{36}N_2Cl_2$: C, 59.58; H, 6.21; N, 4.79; found: C, 59.60; H, 6.21; N, 4.78%.

Dichloro-[1,3-bis(4-methylbenzyl)imidazolidin-2-ylidene](*p*-cymene)ruthenium(II), 2b

Yield: 0,33 g; 69%; m.p: 230–231 °C; $\upsilon_{(CN)}$ = 1515 cm^{-1}. ^1H NMR (δ, $CDCl_3$): 1.29 (d, J = 6.9 Hz, 6H, $p\text{-}CH_3C_6H_4CH(CH_3)_2$), 2.17 (s, 3H, $p\text{-}CH_3C_6H_4CH(CH_3)_2$), 2.91 (h, J = 6.9 Hz, 1H, $p\text{-}CH_3C_6H_4CH(CH_3)_2$), 2.34 (s, 6H, $CH_2C_6H_4(CH_3)$-4), 3.38–3.53 (m, 4H, NCH_2CH_2N), 4.88 (d, J = 6.9 Hz, 2H, $CH_2C_6H_4(CH_3)$-4) and 5.37 (m, 2H, $CH_2C_6H_4(CH_3)$-4), 5.17 and 5.43 (d, J = 6 Hz, 4H, $p\text{-}CH_3C_6H_4CH(CH_3)_2$), 7.17 and

7.31 (d, J = 8.1 Hz, 8H, $CH_2C_6H_4(CH_3)$-4). $^{13}C\{H\}$NMR (δ, $CDCl_3$): 18.8 (p-$CH_3C_6H_4CH(CH_3)_2$), 21.4 ($CH_2C_6H_2(CH_3)_3$-4), 22.6 (p-$CH_3C_6H_4CH(CH_3)_2$), 30.7 (p-$CH_3C_6H_4CH(CH_3)_2$), 48.8 (NCH_2CH_2N), 55.6 ($CH_2C_6H_4(CH_3)$-4), 83.7, 85.7, 97.6, 108.2 (p-$CH_3C_6H_4CH(CH_3)_2$), 127.8, 129.4, 134.1, 137.3 ($CH_2C_6H_4(CH_3)$-4), 208.1 (Ru–C_{carb}). Anal. Calcd. for $RuC_{29}H_{36}N_2Cl_2$: C, 59.58; H, 6.21; N, 4.79; found: C, 59.62; H, 6.23; N, 4.75%.

Dichloro-[1,3-bis(4-ethylbenzyl)imidazolidin-2-ylidene](*p*-cymene)ruthenium(II), 2c

Yield: 0.33 g; % 65; m.p: 206–207 °C; $\upsilon_{(CN)}$ = 1497 cm^{-1}. ^1H NMR (δ, $CDCl_3$): 1.24 (t, J = 7.5 Hz, 6H, $CH_2C_6H_4(CH_2CH_3)$-4), 1.28 (d, J = 6.9 Hz, 6H, p-$CH_3C_6H_4CH(CH_3)_2$), 2.17 (s, 3H, p-$CH_3C_6H_4CH(CH_3)_2$), 2.65 (q, J = 7.5 Hz, 4H, $CH_2C_6H_4(CH_2CH_3)$-4), 2.90 (h, J = 6.9 Hz, 1H, p-$CH_3C_6H_4CH(CH_3)_2$), 3.55–3.97 (m, 4H, NCH_2CH_2N), 4.92 and 5.33 (d, J = 15 Hz, 4H, $CH_2C_6H_4(CH_2CH_3)$-4) 5.17 and 5.44 (d, J = 6 Hz, 4H, p-$CH_3C_6H_4CH(CH_3)_2$), 7.19 and 7.34 (d, J = 7.8 Hz, 8H, $CH_2C_6H_4(CH_2CH_3)$-4). $^{13}C\{H\}$NMR (δ, $CDCl_3$): 15.6 ($CH_2C_6H_4(CH_2CH_3)$-4), 18.8 (p-$CH_3C_6H_4CH(CH_3)_2$), 22.6 (p-$CH_3C_6H_4CH(CH_3)_2$), 30.7 (p-$CH_3C_6H_4CH(CH_3)_2$), 48.8 (NCH_2CH_2N), 55.6 ($CH_2C_6H_4(CH_2CH_3)$-4), 83.7, 85.7, 97.6, 108.0 (p-$CH_3C_6H_4CH(CH_3)_2$), 127.8, 128.2, 134.3, 143.6 ($CH_2C_6H_4(CH_2CH_3)$-4), 208.1 (Ru–C_{carb}). Anal. Calcd. for $RuC_{31}H_{40}N_2Cl_2$: C, 60.78; H, 6.58; N, 4.57; found: C, 60.81; H, 6.64; N, 4.58%.

Dichloro-[1,3-bis(4-i-propylbenzyl)imidazolidin-2-ylidene](*p*-cymene)ruthenium(II), 2d

Yield: 0,36 g; % 71; m.p: 226–227 °C; $\upsilon_{(CN)}$ = 1492 cm^{-1}. ^1H NMR (δ, $CDCl_3$): 1.26 (t, J = 7.2 Hz, 12H, $CH_2C_6H_4(CH(CH_3)_2)$-4), 1.28 (d, J = 7.8 Hz, 6H, p-$CH_3C_6H_4CH(CH_3)_2$), 2.17 (s, 3H, p-$CH_3C_6H_4CH(CH_3)_2$), 2.95 (h, J = 6.9 Hz, 3H, $CH_2C_6H_4(CH(CH_3)_2)$-4 and p-$CH_3C_6H_4CH(CH_3)_2$), 3.46 (m, 4H, NCH_2CH_2N), 4.97 and5.31 (m, 4H, $CH_2C_6H_4(CH(CH_3)_2)$-4) 5.17 and 5.44 (d, J = 6 Hz, 4H, p-$CH_3C_6H_4CH(CH_3)_2$), 7.23 and 7.34 (d, J = 8.1 Hz, 8H, $CH_2C_6H_4(CH(CH_3)_2)$-4). $^{13}C\{H\}$NMR (δ, $CDCl_3$): 18.8 (p-$CH_3C_6H_4CH(CH_3)_2$), 22.6 (p-$CH_3C_6H_4CH(CH_3)_2$), 24.0 ($CH_2C_6H_2(CH(CH_3)_2)$-4), 30.7 (p-$CH_3C_6H_4CH(CH_3)_2$), 33.8 $CH_2C_6H_2(CH(CH_3)_2)$-4), 48.8 (NCH_2CH_2N), 55.6 ($CH_2C_6H_4(CH_3)$-4), 83.7, 85.8, 97.6, 108.0 (p-$CH_3C_6H_4CH(CH_3)_2$), 126.7, 127.7, 134.4, 148.2 ($CH_2C_6H_4(CH(CH_3)_2)$-4), 208.2 (Ru–C_{carb}). Anal. Calcd. for $RuC_{33}H_{44}N_2Cl_2$: C, 61.86; H, 6.92; N, 4.37; found: C, 61.81; H, 6.95; N, 4.41%.

Dichloro-[1,3-bis(4-diethylaminobenzyl)imidazolid-2-ylidene](*p*-cymene)ruthenium(II), 2e

Yield: 0,280 g; 70%; m.p: 199–201 °C; $\upsilon_{(CN)}$ = 1498 cm^{-1}. ^1H NMR (δ, $CDCl_3$): 1.17 (t, J = 7.2 Hz, 12H, $CH_2C_6H_4N(CH_2CH_3)_2$-4), 1.31 (d, J = 7.2 Hz, 6H, p-$CH_3C_6H_4CH(CH_3)_2$), 2.19 (s, 3H, p-$CH_3C_6H_4CH(CH_3)_2$), 2.94 (h, J = 7.2 Hz, 1H, p-$CH_3C_6H_4CH(CH_3)_2$), 3.36 (q, J = 7.2 Hz, 8H, $CH_2C_6H_4N(CH_2CH_3)_2$-4), 3.51–3.67 (m, 4H, NCH_2CH_2N), 4.77–5.16 (m, 2H, $CH_2C_6H_4(CH_3)_2$-4), 5.19 ve 5.46 (d, J = 6.3 Hz, 4H, p-$CH_3C_6H_4CH(CH_3)_2$), 6.66 ve 7.20 (d, J = 12.9 Hz, 8H, $CH_2C_6H_4(CH_3)_2$-4). $^{13}C\{H\}$NMR (δ, $CDCl_3$): 12.5 ($CH_2C_6H_4N(CH_2CH_3)_2$-4), 18.8 (p-$CH_3C_6H_4CH(CH_3)_2$), 22.7 (p-$CH_3C_6H_4CH(CH_3)_2$), 30.71 (p-$CH_3C_6H_4CH(CH_3)_2$), 44.35 ($CH_2C_6H_4N(CH_2CH_3)_2$-4), 48.59 (NCH_2CH_2N), 55.31 ($CH_2C_6H_4(CH_3)$-4), 83.5, 85.6, 86.6, 97.6 (p-$CH_3C_6H_4CH(CH_3)_2$), 147.3, 129.1, 123.4, 111.8 ($CH_2C_6H_4(CH_3)_2$-4). 206.6 (C_{carb}). Anal. Calc. For $RuC_{29}H_{36}N_2Cl_2$: C, 59.58; H, 6.21; N, 4.79; found: C, 59.60; H, 6.21; N, 4.78%.

Dichloro-[1,3-bis(3,4-dimethoxybenzyl)imidazolidin-2-ylidene](*p*-cymene)ruthenium(II), 2f

Yield: 0.34 g; % 63; m.p: 202–203 °C; $\upsilon_{(CN)}$ = 1515 cm^{-1}. ^1H NMR (δ, $CDCl_3$): 1.34 (d, J = 6.9 Hz, 6H, p-$CH_3C_6H_4CH(CH_3)_2$), 2.24 (s, 3H, p-$CH_3C_6H_4CH(CH_3)_2$), 3.03 (h, J = 6.9 Hz, 1H, p-$CH_3C_6H_4CH(CH_3)_2$), 3.54–3.91 (m, 4H, NCH_2CH_2N), 3.89 (s, 6H, $CH_2C_6H_3(OCH_3)_2$-4), 3.90 (s, 6H, $CH_2C_6H_3(OCH_3)_2$-4), 4.63 and 5.56 (d, J = 14.4 Hz, 4H, $CH_2C_6H_3(OCH_3)_2$-3,4) 5.12 and 5.47 (d, J = 6 Hz, 4H, p-$CH_3C_6H_4CH(CH_3)_2$), 6.82–7.22 (m, 6H, $CH_2C_6H_4(OCH_3)_2$-3,4). $^{13}C\{H\}$NMR (δ, $CDCl_3$): 19.0 (p-$CH_3C_6H_4CH(CH_3)_2$), 22.6 (p-$CH_3C_6H_4CH(CH_3)_2$), 30.8 (p-$CH_3C_6H_4CH(CH_3)_2$), 48.8 (NCH_2CH_2N), 55.9 ($CH_2C_6H_3(OCH_3)_2$-3), 56.1 ($CH_2C_6H_3(OCH_3)_2$-4), 53.4 ($CH_2C_6H_3(OCH_3)_2$-3,4), 82.3, 86.7, 98.2, 109.4 (p-$CH_3C_6H_4CH(CH_3)_2$), 110.7, 111.9, 120.0, 129.4, 148.6, 149.3 ($CH_2C_6H_3(OCH_3)_2$-3,4), 207.8 (Ru–C_{carb}). Anal. Calcd. for $RuC_{31}H_{40}N_2Cl_2O_4$: C, 55.03; H, 5.96; N, 4.14; found: C, 54.99; H, 5.98; N, 4.10%.

General procedure for the transfer hydrogenation of ketones

Under an inert atmosphere a mixture containing ketones (1 mmol), the ruthenium catalyst, **2a–2f**, (0.01 mmol) and KOH (4 mmol) was heated to reflux in 10 mL of *i*-PrOH for 1 h. The solvent was then removed under reduced pressure and product distribution was determined by ^1H-NMR spectroscopy and GC and GC-MS.

Structural characterization of 2a

Crystal of **2a** suitable for X-ray analysis was obtained from a dichloromethane solution layered with diethyl ether. The single-crystal X-ray data were collected on a STOE diffractometer with an IPDS II image plate detector Mo-Kα radiation λ = 0.71069 Å. The structure was solved by direct-methods using SHELXS-97[31] and refined by full-matrix least-squares methods on F^2 using SHELXL-97[32] from within the WINGX[33,34] suite of software. The crystal was very small and thin and so the reflection intensities were too low. So, the observed/unique data ratio (23%) of data was not as desired. The absorption correction applied is also not as good as expected due to the smallness of the crystal and the absorption coefficient of Ru is large. This causes also additional unsuitability for the R_{int} and Goof parameters. Some C atoms show a large displacement parameter and the direction of motion between these atoms was restrained (DELU instruction in SHELXL97). The parameters for data collection and structure refinement of complex **2a** are listed in Table 2. All non-hydrogen atoms were refined with anisotropic parameters. Hydrogen atoms bonded to carbon were placed in calculated positions (C–H = 0.93–0.97 Å) and treated using a riding model with U = 1.2 times the U value of the parent atom for CH, CH_2 and CH_3. Molecular diagrams were created

Table 2 Parameters for data collection and structure refinement of **2a**

Empirical formula	$C_{62}H_{82}Cl_4N_4ORu_2$
Formula weight	1243.26
T/K	296
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	15.5879(8)
b/Å	13.1132(5)
c/Å	30.0461(16)
α (°)	90
β (°)	91.148(4)
γ (°)	90
V/Å^3	6140.4(5)
Z	4
ρ_{calcd}/Mgm^{-3}	1.345
μ/mm^{-1}	0.71
F(000)	2584
Crystal size/mm	0.08 × 0.05 × 0.02
θ Range for data collection/°	1.3–26.0
Reflections collected	41355
Independent reflection	11549
R_{int}	0.273
Max./min. transmission	0.915 and 0.986
Data/restraints/parameters	11549/10/649
Goodness-of-fit on F^2	0.66
R_1 ($I > 2\sigma(I)$)	0.060
wR_2 ($I > 2\sigma(I)$)	0.071
R_1 (all data)	0.279
wR_2 (all data)	0.123
$\Delta\rho_{max./min.}$/e Å^{-3}	0.33 and –0.55

Table 3 Hydrogen-bond parameters (Å, °)

D–H···A	D–H	H···A	D···A	D–H···A
C4–H4B···Cl4	0.97	2.34	3.240 (14)	153
C6–H6···Cl2[a]	0.93	2.70	3.572 (17)	156
C6–H6···N4	0.93	2.59	2.920 (19)	102
C12–H12B···Cl3	0.97	2.63	3.253 (13)	122
C14–H14···N3	0.93	2.55	2.879 (16)	101
C22–H22···Cl3[b]	0.93	2.66	3.524 (12)	154
C31–H31A···Cl4	0.97	2.78	3.415 (13)	123
C33–H33B···Cl2	0.97	2.60	3.326 (12)	132
C35–H35···Cl2	0.93	2.79	3.605 (12)	147
C41–H41A···Cl1	0.97	2.64	3.276 (13)	124
C47–H47···N1	0.93	2.54	2.864 (19)	101
C53–H53···Cl1[c]	0.93	2.69	3.531 (12)	151
C56–H56···Cl2	0.98	2.83	3.394 (16)	118

Symmetry codes:[a] x, y – 1, z; [b] –x + 1, –y + 1, –z + 1; [c] –x, –y + 2, –z + 1.

using ORTEP-III.[35] Geometric calculations were performed with PLATON.[36] Fig. 1 shows the molecular structure of **2a**.

The molecules are linked into sheets by a combination of three C–H···Cl hydrogen bonds (Table 3). Atom C22 in the reference molecule acts as a hydrogen-bond donor, *via* H22, to atom Cl3^{ii}, so forming a centrosymmetric $R_2^2(8)$[37] ring centred at (1/2, 1/2, 1/2). Similarly, atom C53 in the reference molecule acts as a hydrogen-bond donor, *via* H53, to atom Cl1^{iii}, so forming a centrosymmetric $R_2^2(8)$ ring centred at (0, 1, 1/2). The combination of C–H···Cl hydrogen bonds generate a chain of rings running parallel to the *ab* plane (Fig. 2).

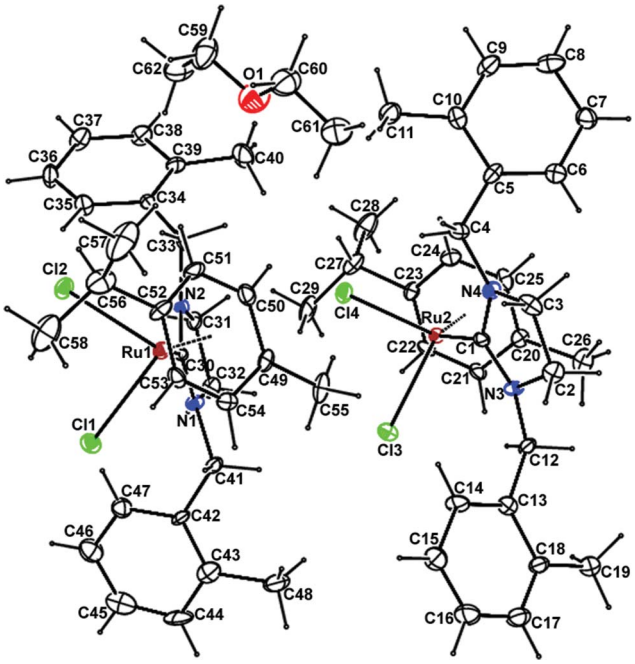


Fig. 1 ORTEP drawing of complex **2a** showing 30% probability thermal ellipsoids. Selected bond lengths [Å]:Ru1–C30 = 2.018(13), Ru1–Cl1 = 2.417(3), Ru1–Cl2 = 2.424(4), C1–N3 = 1.346(14), C1–N4 = 1.350(14), C2–C3 = 1.507(17), Ru2–C1 = 2.026(14), Ru2–Cl13 = 2.416(3), Ru2–Cl14 = 2.430(4), C30–N1 = 1.348(13), C30–N2 = 1.361(13), C31–C32 = 1.516(15); angles [°]: C30–Ru1–Cl1 = 88.1(3), C30–Ru1–Cl2 = 89.3(4), N1–Ru1–C30 = 130.2(9), N2–C30–Ru1 = 127.1(9), N1–C30–N2 = 102.7(10), N1–C41–C42 = 113.0(10), Cl3–Ru1–Cl14 = 83.38(12), C54–C53–Ru1 = 68.6(7), C1–Ru2–Cl14 = 92.4(4), C1–Ru2–Cl13 = 89.6(4), N4-Ru2–C1 = 125.9(10), N3–Ru2–C1 = 128.1(10), N3–C1–N4 = 105.7(12), N3–C12–C13 = 116.4(11), Cl1–Ru1–Cl2 = 84.06(12), C22–C21–Ru2 = 76.2(9).

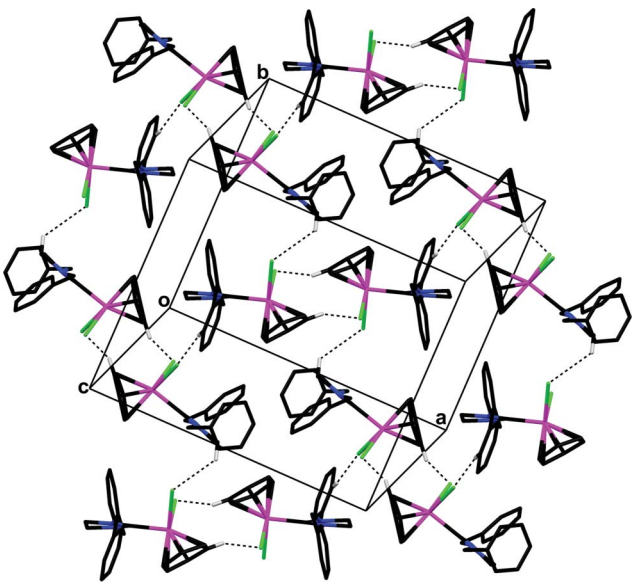


Fig. 2 Packing arrangement of the molecules in the unit cell.

Supplementary material

CCDC-828989 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.†

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