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Synthesis of novel rhodium-xylyl linked *N*-heterocyclic carbene complexes as hydrosilylation catalysts

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Reaction of *ortho*-xylylbis(*N*-2,4,6-trimethylbenzylimidazolinium); xylylbis(*N*-butylimidazolinium) and *para*-xylylbis(*N*-2,4,6-trimethylbenzylimidazolinium); xylylbis(*N*-butylimidazolinium) salts with KOBu^t and $[RhCl(COD)]_2$ yields *ortho*- and *para*-xylylbis{(*N*-alkylimidazolidin-2-ylidene)chloro(η^4-1,5-cyclooctadiene) rho dium(I)} complexes (2a–d). All compounds synthesized were characterized by elemental analysis and NMR spectroscopy, and the molecular structures of the 2a and 2d were determined by X-ray crystallography. Triethylsilane reacts with acetophenone derivatives in the presence of catalytic amount of the new rhodium(I)–carbene complexes (2a–d), to give the corresponding silylethers in good yields (83–99%). Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: *N*-heterocyclic carbene; xylylbis(imidazolinium) salts; hydrosilylation; rhodium

Introduction

Transition metal-based catalysis has gained lots of attention for diverse applications ranging from materials to pharmaceuticals.[1] The design of transition metal catalysts has to take into account several basic characteristics including high efficiencies and selectivities as well as economic and environmental considerations. The availability of catalysts to perform specific transformations is critical for both industry and academia. Over the years, the success of homogeneous catalysis can be attributed largely to the development of a diverse range of ligand frameworks that have been used to tune the behavior of a variety of metal-containing systems. Advances in ligand design have allowed not only for improvements of known processes in terms of scope, mildness and catalyst loadings, but also for the discovery of new selective reactions. Coordination chemistry directed towards catalysis has been boosted in recent years by the discovery of *N*-heterocyclic carbenes (NHCs) as powerful ligands.[2]

Since the synthesis and isolation of the first stable NHC by Arduengo *et al*.,[3] these species have emerged over the past decade as a group of efficient ligands for transition metal-based homogeneous catalysts. In some aspects these compounds can be viewed as phosphane surrogates,[4] the σ-donor ability of NHC ligands matching or improving that of the most basic phosphines. Additionally, NHC-based catalysts feature robust carbon–metal bonds that provide high thermal stability and low dissociation rates, and consequently better resistance against oxidation or leaching phenomena, making the use of ligand excess unnecessary.[5] These properties have led to a number of applications where NHC-based catalysts exhibit superior performance. Such NHC–metal complexes have been successfully utilized in cross-coupling reactions[6] and related processes, including hydrogenation,[7] hydroformylation,[8] hydrosilylation,[9] oxidation,[10] metathesis,[11] cycloisomerization of olefins,[12] the synthesis of furans[13] and for cyclopropanation reactions.[14]

We have previously reported the use of an *in situ* formed imidazolidin-2-ylidene, tetrahydropyrimidin-2-ylidene and tetrahydrodiazepin-2-ylidene/palladium(II) systems which exhibit high activity in various coupling reactions of aryl bromides and aryl chlorides. In order to obtain a more stable, efficient and active system, we also investigated benzo-annelated derivatives.[15] Recently our group reported that novel complexes of rhodium(I) based on 1,3-dialkyimidazolidin-2-ylidenes give good yields for the addition of phenylboronic acid to aldehydes.[16]

Hydrosilylation catalyzed by transition–metal complexes offers the most straightforward and atom-economic route to carbon–silicon and oxygen–silicon bond formations, which are important for organic synthesis and dendrimer and polymer chemistry.[17] Moreover, it is applied to the reduction of ketones to secondary alcohols.[18] In general, the term hydrosilylation is used to describe an addition reaction of hydrosilanes to double and triple bonds, and in the laboratory hydrosilylation is a very convenient method for the synthesis and arrangement of organosilicon compounds. The development of various hydrosilylation catalysts has already been summarized.[19]

Although, rhodium–carbene complexes have been extensively studied, there are few reports on the hydrosilylation reactions of rhodium–carbene complexes in rhodium-mediated

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processes.[9,20] Based on these findings and our continuing interest in developing more efficient and stable catalysts, we wished to examine whether we could influence the catalytic activity of *ortho*- and *para*-xylylbis{(*N*-alkylimidazolidin-2-ylidene)chloro(η^4-1,5-cyclooctadiene) rhodium(I)} complexes for the hydrosilylation of acetophenones. (Scheme 1).

We now report: (i) the straightforward preparation of new xylyl-linked imidazolinium salts (**1a–d**) and [RhCl(COD)(*o*-xylylbis{(*N*-alkylimidazolidin-2-ylidene)}] (**2a, b**) and [RhCl(COD)(*p*-xylylbis{(*N*-alkylimidazolidin-2-ylidene)}] (**2c, d**) complexes; and (ii) their efficient catalysis of the hydrosilylation of acetophenones.

Results and Discussion

Synthesis and spectroscopic characterization

Ortho- and *para*-xylylbis(*N*-alkylimidazolinium) salts (**1a–d)** are conventional NHC precursors. The xylene-bridged diimidazolinium salts (**1a–d)** were synthesized by reaction of *N*-alkylated imidazolidine derivatives with 1,2- or 1,4-di(chloromethyl)benzene in DMF (Scheme 2). After purification, the dimidazolinium salts **1a–d** were obtained in good yields of 86–94%. The salts are air- and moisture-stable both in the solid state and in solution. The structures of **1a–d** were determined by their characteristic spectroscopic data and elemental analyses (see the Experimental section).

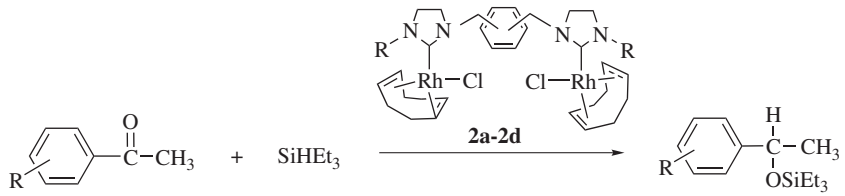
^{13}C NMR chemical shifts were consistent with the proposed structure; the imidinium carbon appeared as a typical singlet in the ^{1}H-decoupled mode at 158.8, 159.0, 157.6 and 158.7 ppm, respectively, for imidazolinium salts **1a–d**. The ^{1}H NMR spectra of the imidazolinium salts further supported the assigned structures; the resonances for C(2)–H were observed as sharp singlets in the 9.96, 10.15, 8.87 and 10.15 ppm, respectively, for **1a–d**. The IR data for imidazolinium salts **1a–d** clearly indicate the presence of the -C═N- group with ν (C═N) at 1656, 1653, 1646 and 1651 cm^{-1}, respectively, for **1a–d**. The NMR and IR values are similar to those found for other 1,3-dialkylimidazolinium salts.[19]

The dimidazolinium salts (**1a–d**) were initially deprotonated in THF with KOBu^t according to Lappert's procedure.[21] Very likely the free dicarbenes were obtained, and these reacted with $[RhCl(COD)]_2$ in boiling toluene for 2 h, affording the expected carbene–rhodium complexes (**2a–d**) good yields of 78–92% (Scheme 3). Each rhodium compound was fully characterized by ^{1}H and ^{13}C NMR; FT-IR, elemental analysis and molecular structures of the **2a** and **2d** were determined by X-ray crystallography.

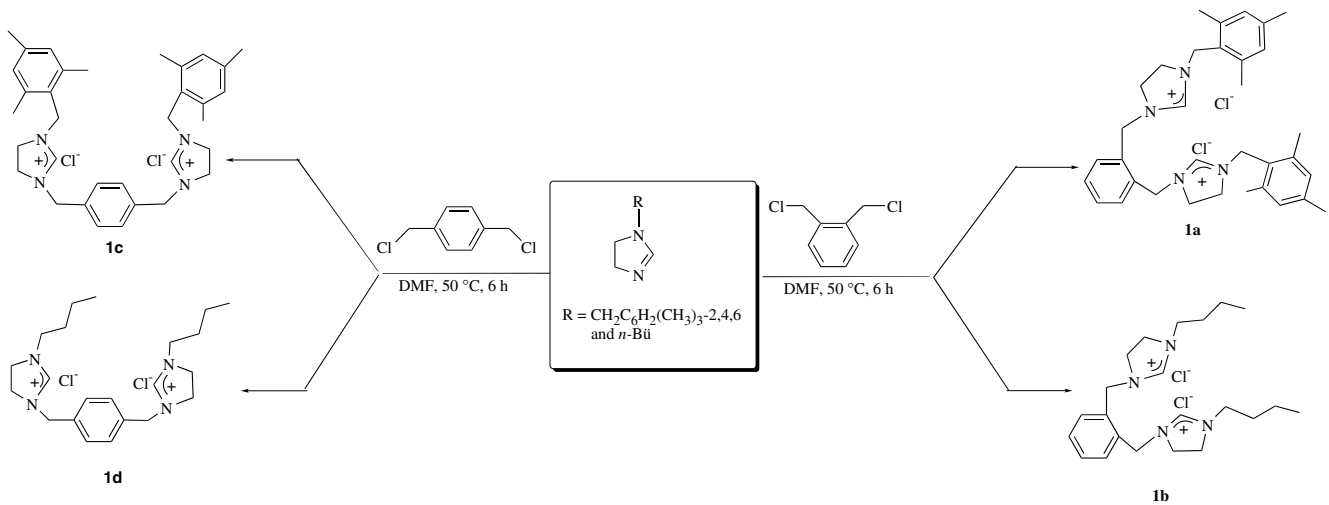
The rhodium complexes exhibit a characteristic $\upsilon_{(NCN)}$ band typically[22] at 1496–1506 cm^{-1}. ^{13}C chemical shifts, which provide a useful diagnostic tool for metal carbene complexes, show that C_{carb} is substantially deshielded. Values of $\delta(^{13}C_{carb})$ are in the range 212.5–214.0 ppm and are similar to those found in other carbene complexes. Coupling constants $J(^{103}Rh-^{13}C)$ for the new rhodium complexes (**2a–d**) are comparable with those found for carbene rhodium(I) complexes. These new complexes show typical spectroscopic signatures which are in line with those recently reported for [RhCl(COD)(1,3-dialkylimidazolin-2-ylidine)] complexes.[22]

Structural characterization of 2a and 2d

Yellow single crystals of **2a** and **2d** suitable for data collection were selected and data collection was performed on a STOE IPDS II diffractometer with graphite monochromated Mo-Kα radiation at 296 K. The structures were solved by direct-methods using



Scheme 1.



Scheme 2. Synthesis of bisimidazolinium salts (**1a–d**).

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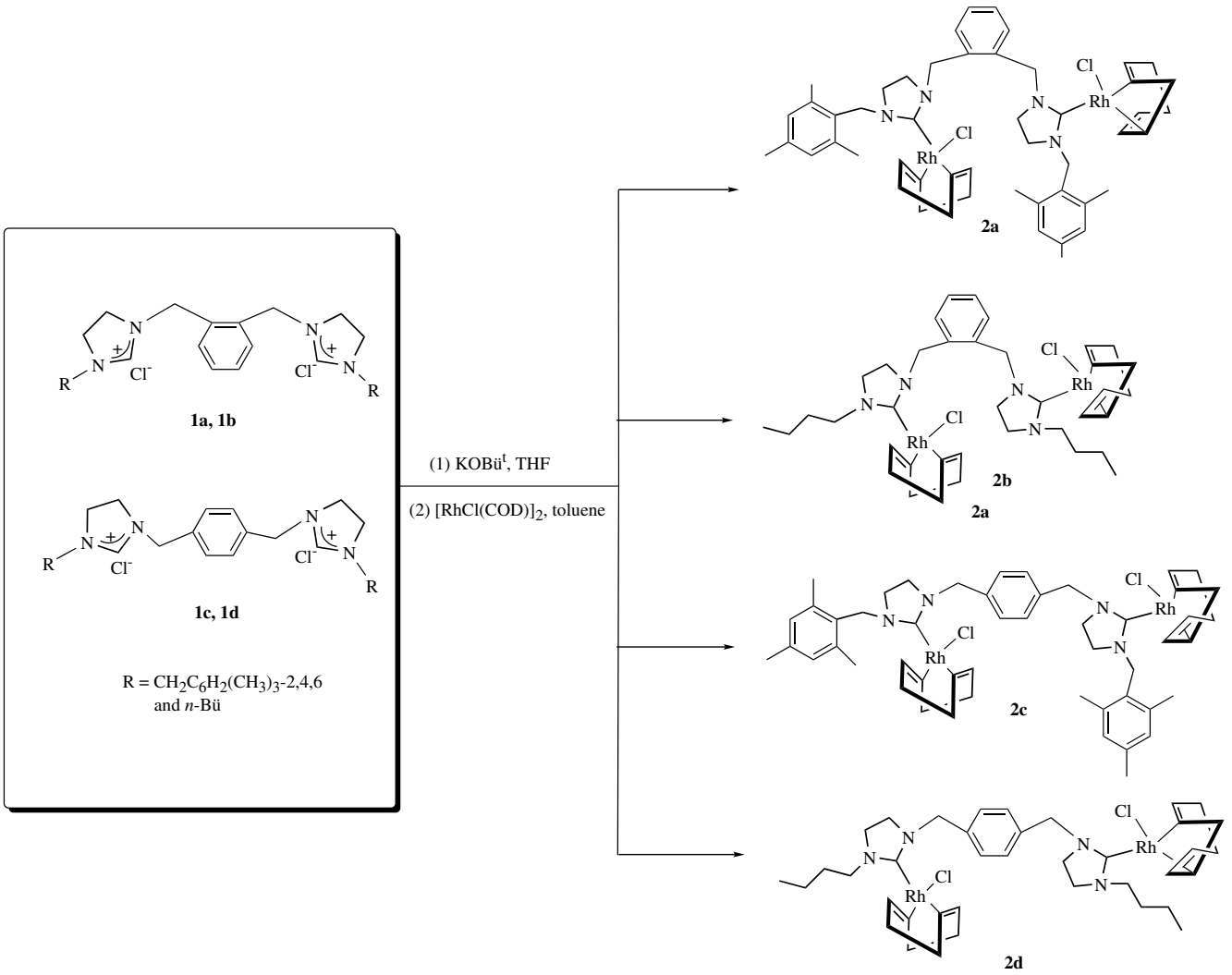

Scheme 3. Synthesis of rhodium–carbene complexes (**2a–d**).

SHELXS-97[23] and refined by full-matrix least-squares methods on F^2 using SHELXL-97[24] from within the WINGX[25,26] suite of software. All non-hydrogen atoms were refined with anisotropic parameters. Hydrogen atoms bonded to carbon were placed in calculated positions (C–H = 0.93–0.98 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. The crystal of **2d** used for the intensity data collection was a non-merohedral twin with two reciprocal lattices differently oriented according to the twofold rotation axis (100), giving rise to double diffraction spot sets. The two data sets of the twin parts were integrated separately and then scaled to give the combined data set. However, because the partially overlapped reflections could not be satisfactorily integrated separately, they were discarded, leading to a data completeness of only slightly over 48%. Molecular diagrams were created using ORTEP-III.[27] Geometric calculations were performed with Platon.[28]

Hydrosilylation of acetophenone derivatives

Hydrosilylation reactions involve the addition of inorganic or organic silicon hydrides to multiple bonds such as alkyne, alkene, ketoxime and carbonyl groups. Metal complexes are able to catalyze the hydrosilylation reaction of organic substrate under mild conditions and are very attractive for many process.

Rhodium–xylene bridged diimidazolidin-2-ylidene complexes (**2a–d**) have been found to be active catalysts for the hydrosilylation of acetophenone derivatives. The catalyst showed high activity for the addition of triethylsilane to acetophenone, even with low catalyst loading. *N*-heterocyclic carbene complexes displayed higher catalytic activity than the corresponding carbene complexes.[20a] All reactions were carried out without any special need for inert conditions, since the catalysts used proved to be fairly stable under oxygen-containing atmospheres, even at high temperatures. The results are summarized in Table 1. Under those conditions, acetophenone, 2-methoxyacetophenone, 3-methoxyacetophenone, and 4-methoxyacetophenone react very cleanly with triethylsilane in goods yields (Table 1, entries 4, 7, 11 and 15). These results are in agreement with other reports on rhodium–carbene catalyzed hydrosilylation of carbonyl compounds.[20a]

Among the materials used, **2c** showed better activity than others. The reason for this could be explained in terms of steric hindrance and chemical activity of the carbene–metal center, which is fortified with the R-group.

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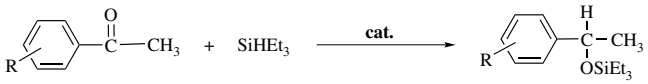
Table 1. Hydrosilylation of acetophenone derivatives by Rh-NHC complexes



Entry	Catalyst	R	Yield[a] (%)
1	**2a**	H	83
2	**2b**	H	85
3	**2c**	H	88
4	**2d**	H	86
5	**2a**	2-OCH_3	93
6	**2b**	2-OCH_3	96
7	**2c**	2-OCH_3	97
8	**2d**	2-OCH_3	95
9	**2a**	3-OCH_3	90
10	**2b**	3-OCH_3	90
11	**2c**	3-OCH_3	93
12	**2d**	3-OCH_3	88
13	**2a**	4-OCH_3	90
14	**2b**	4-OCH_3	93
15	**2c**	4-OCH_3	99
16	**2d**	4-OCH_3	97

[a] *Reaction conditions*: 1.0 mmol of acetophenone, 1.25 mmol of triethylsilane, 0.025 mmol% (based on ketone) **2a**–**d**. Purity of compounds is checked by GC and yield are based on ketone. Temperature 80 °C, 2 h.

Conclusions

From readily available starting materials, such as *ortho*-xylylbis(*N*-alkylimidazolinium) and *para*- xylylbis(*N*-alkylimidazolinium) salts four novel rhodium–carbenes (**2a–d**) have been prepared and characterized. A number of the complexes (**2a, 2d**) have been characterized by single-crystal X-ray diffraction studies. Also, we have investigated the hydrosilylation activity of novel rhodium–NHC complexes for acetophenone derivatives resulting in the formation of the corresponding silylethers. Studies on the reactivity of the new complexes, extension of the methodology to other transition metals and the synthesis of other functionalized *N*-heterocyclic carbene ligands with a variety of other donor functionalities is under way.

Experimental

Materials

All reactions for the preparation of **1** and**2** were carried out under Ar in flame-dried glassware using standard Schlenk-type flasks. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Na/K alloy), CH_2Cl_2 (P_4O_{10}), hexane and toluene (Na). For flash chromatography a Merck silica gel 60 (230–400 mesh) was used. The complex $[RhCl(COD)]_2$ [29] and **1a–d** were prepared according to known methods.[21] All reagents were purchased from Aldrich Chemical Co.

Melting point determination

Melting point were determined in glass capillaries under air with an Electrothermal-9200 melting point apparatus.

IR spectroscopy

FT-IR spectra were recorded as KBr pellets in the range 400–4000 cm^{-1} on an ATI Unicam 1000 spectrometer.

NMR spectroscopy

^1H NMR and ^{13}C NMR spectra were recorded using a Varian As 400 Merkur spectrometer operating at 400 MHz (^1H) and 100 MHz (^{13}C) in $CDCl_3$ and DMSO-d_6 with tetramethylsilane as an internal reference. The NMR studies were carried out in high-quality 5 mm NMR tubes. Signals are quoted in parts per million as δ downfield from tetramethylsilane (δ 0.00) as an internal standard. Coupling constants (*J*-values) are given in hertz. NMR multiplicities are abbreviated as fallows: s = singlet, d = doublet, t = triplet, m = multiplet signal.

Gas chromatography

All reactions were monitored on a Agilent 6890N GC system by GC-FID with an HP-5 column of 30 m length, 0.32 mm diameter and 0.25 µm film thickness.

Column chromatography

Column chromatography was performed using silica gel 60 (70–230 mesh). Solvent ratios are given as v/v.

Elemental analyses

Elemental analyses were performed by Turkish Resarch Council (Ankara, Turkey) Microlab and Centre Régional de Mesures Physiques de l'Ouest, Université de Rennes.

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General procedure for the preparation of the bisimidazolinium salts (1a–d)

To a solution of 1-alkylimidazoline (10 mmol) in DMF (10 ml) was added slowly 1,2- or 1,4-di(chloromethyl)benzene (5 mmol) at 25 °C and the resulting mixture was stirred at 50 °C for 6 h. Diethyl ether (15 ml) was added to obtain a white crystalline solid which was filtered off. The solid was washed with diethyl ether (3 × 15 ml), and dried under vacuum. The crude product was recrystallized from EtOH–Et_2O.

***o*-Xylylbis(*N*-2,4,6-trimethylbenzylimidazolidinium) dichloride, 1a**

Yield: 2.64 g (91%); m.p. 231–232 °C; $\nu_{(CN)}$ = 1656 cm^{-1}. Anal. calcd for $C_{34}H_{44}N_4Cl_2$: C, 70.45; H, 7.65; N, 9.67. Found: C, 70.51; H, 7.62; N, 9.74%. ^{1}H NMR (399.9 MHz, $CDCl_3$) δ = 9.96 (s, 2H, NC*H*N), 7.32–7.23 (m, 4H, *o*-$CH_2C_6H_4CH_2$), 6.85 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 5.34 (s, 4H, *o*-$CH_2C_6H_4CH_2$), 4.87 [s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 3.79 (s, 8H, NCH_2CH_2N), 2.34 [s, 12H, $CH_2C_6H_2(CH_3)_3$-2,6], 2.23 [s, 6H, $CH_2C_6H_2(CH_3)_3$-4]. ^{13}C NMR (100.5 MHz, $CDCl_3$) δ = 158.8 (NCHN), 132.7, 129.8 and 129.6 (*o*-$CH_2C_6H_4CH_2$), 139.1, 138.2, 129.9 and 125.7[$CH_2C_6H_2(CH_3)_3$-2,4,6], 49.9 (*o*-$CH_2C_6H_4CH_2$), 46.7 [$CH_2C_6H_2(CH_3)_3$-2,4,6], 48.2 and 47.9 (NCH_2CH_2N), 21.2 [$CH_2C_6H_2(CH_3)_3$-4], 20.4 [$CH_2C_6H_2(CH_3)_3$-2,6].

***o*-Xylylbis(*N*-*n*-butylimidazolidinium)dichloride, 1b**

Yield: 1.84 g (86%); m.p. 99–100 °C; $\nu_{(CN)}$ = 1653 cm^{-1}. Anal. calcd for $C_{22}H_{36}N_4Cl_2$: C, 61.82; H, 8.49; N, 13.11. Found: C, 61.85; H, 8.42; N, 13.19%. ^{1}H NMR (399.9 MHz, $CDCl_3$) δ = 10.15 (s, 2H, NC*H*N), 7.34–7.25 (m, 4H, *o*-$CH_2C_6H_4CH_2$), 5.38 (s, 4H, *o*-$CH_2C_6H_4CH_2$), 4.02 and 3.86 (m, 8H, NCH_2CH_2N), 3.54 (t, J = 7.2 Hz, 4H, $CH_2CH_2CH_2CH_3$), 1.66 (quint, J = 7.2 Hz, 4H, $CH_2CH_2CH_2CH_3$), 1.35 (sept, J = 7.2 Hz, 4H, $CH_2CH_2CH_2CH_3$), 0.93 (t, J = 7.2 Hz, 6H, $CH_2CH_2CH_2CH_3$). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ = 159.0 (NCHN), 132.6, 129.9 and 129.6 (*o*-$CH_2C_6H_4CH_2$), 49.9 (*o*-$CH_2C_6H_4CH_2$), 48.9 and 48.8 (NCH_2CH_2N), 48.2 ($CH_2CH_2CH_2CH_3$), 29.5 ($CH_2CH_2CH_2CH_3$), 19.9 ($CH_2CH_2CH_2CH_3$), 13.7 ($CH_2CH_2CH_2CH_3$).

***p*-Xylylbis(N-2,4,6-trimethylbenzylimidazolidinium) dichloride, 1c**

Yield: 2.72 g (94%); m.p. 316–317 °C; $\nu_{(CN)}$ = 1646 cm^{-1}. Anal. calcd for $C_{34}H_{44}N_4Cl_2$: C, 70.45; H, 7.65; N, 9.67. Found: C, 70.54; H, 7.58; N, 9.60%. ^{1}H NMR (399.9 MHz, DMSO-d_6) δ = 8.87 (s, 2H, NC*H*N), 7.44 (s, 4H, *p*-$CH_2C_6H_4CH_2$), 6.95 [s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 4.72 (s, 4H, *p*-$CH_2C_6H_4CH_2$), 4.66 [s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 3.74(m, 8H, NCH_2CH_2N), 2.31 [s, 12H, $CH_2C_6H_2(CH_3)_3$-2,6], 2.25 [s, 6H, $CH_2C_6H_2(CH_3)_3$-4]. ^{13}C NMR (100.5 MHz, DMSO-d_6) δ = 157.6 (NCHN), 134.8 and 129.8 (*p*-$CH_2C_6H_4CH_2$), 138.4, 138.3, 129.3 and 126.7 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 50.66 (*p*-$CH_2C_6H_4CH_2$), 45.9 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 48.6 and 48.1 (NCH_2CH_2N), 21.1 [$CH_2C_6H_2(CH_3)_3$-4], 19.9 [$CH_2C_6H_2(CH_3)_3$-2,6].

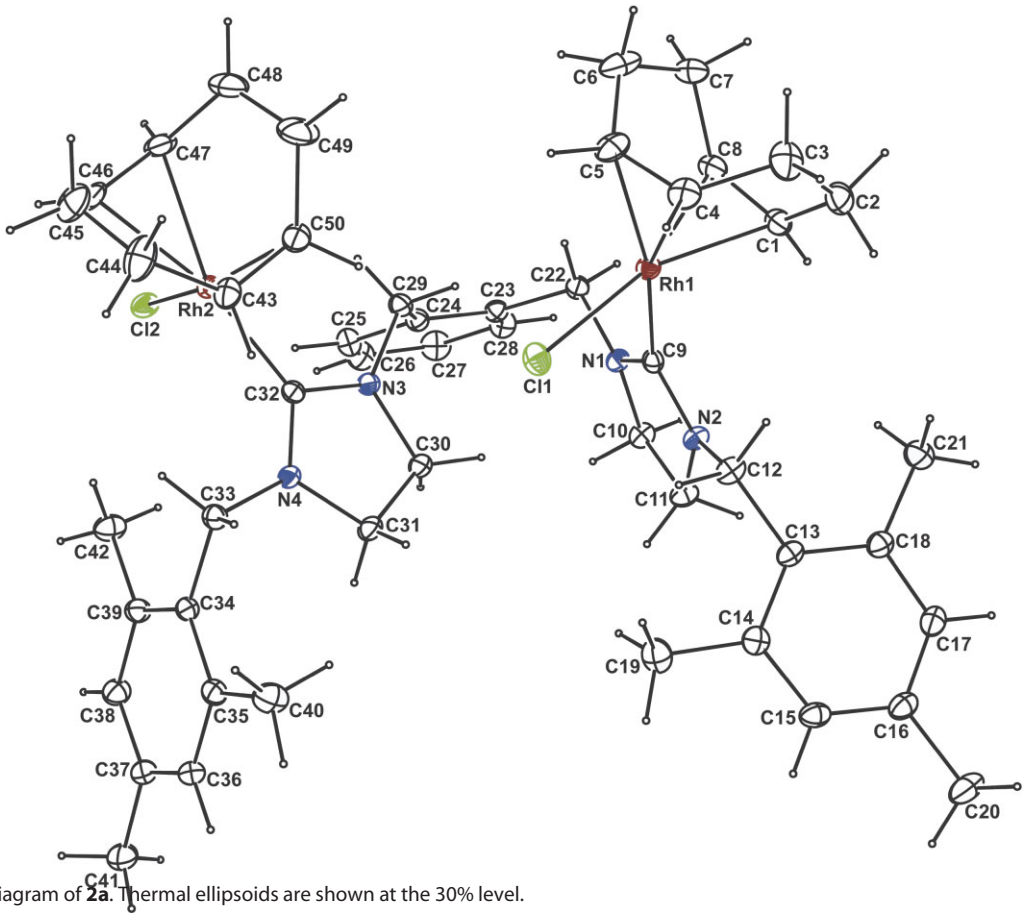

Figure 1. ORTEP diagram of **2a**. Thermal ellipsoids are shown at the 30% level.

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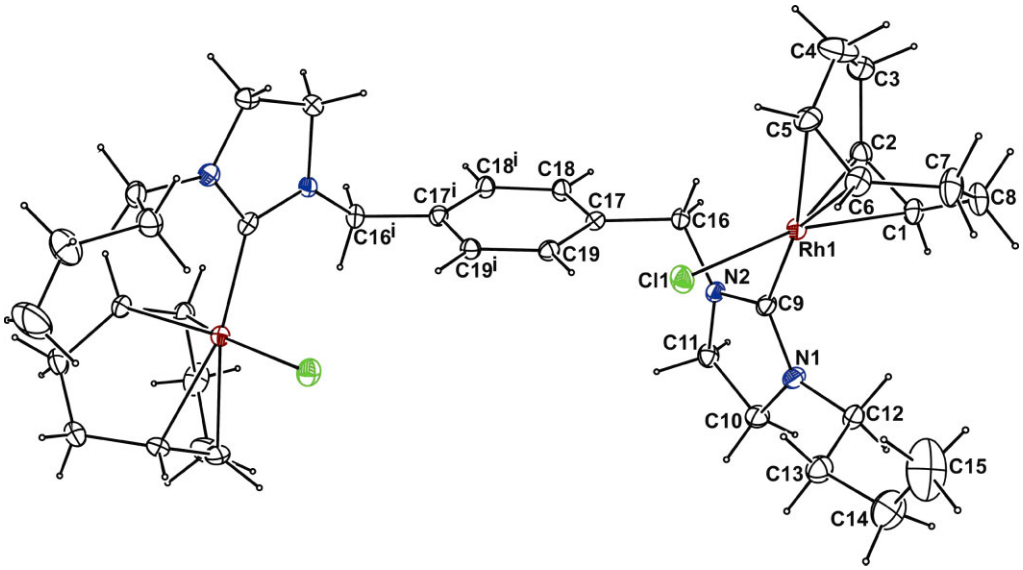

Figure 2. ORTEP diagram of **2d**. Thermal ellipsoids are shown at the 30% level. Symmetry code: (i) $-x+1, y, -z+3/2$.

p-Xylylbis(*N*-*n*-butylimidazolidinium)dichloride, 1d

Yield: 1.92 g (90%); m.p. 253–254 °C; $\nu_{(CN)} = 1651\ cm^{-1}$. Anal. calcd for $C_{22}H_{36}N_4Cl_2$: C, 61.82; H, 8.49; N, 13.11. Found: C, 61.77; H, 8.56; N, 13.09%. ^1H NMR (399.9 MHz, $CDCl_3$) δ = 10.15 (s, 2H, NC*H*N), 7.39 (s, 4H, *p*-$CH_2C_6H_4CH_2$), 4.84 (s, 4H, *p*-$CH_2C_6H_4CH_2$), 3.90 (m, 8H, NCH_2CH_2N), 3.52 (t, $J = 7.3$ Hz, 4H, $CH_2CH_2CH_2CH_3$), 1.60 (quint, $J = 7.3$ Hz, 4H, $CH_2CH_2CH_2CH_3$), 1.30 (sept, $J = 7.3$ Hz, 4H, $CH_2CH_2CH_2CH_3$), 0.87 (t, $J = 7.3$ Hz, 6H, $CH_2CH_2CH_2CH_3$). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ = 158.7 (NCHN), 134.0, 130.0 and 129.6 (*p*-$CH_2C_6H_4CH_2$), 51.5 (*p*-$CH_2C_6H_4CH_2$), 48.8 and 48.2 (NCH_2CH_2N), 48.4 ($CH_2CH_2CH_2CH_3$), 29.5 ($CH_2CH_2CH_2CH_3$), 19.8 ($CH_2CH_2CH_2CH_3$), 13.8 ($CH_2CH_2CH_2CH_3$).

General procedure for the preparation of the rhodium-carbene complexes (2a–d)

A solution of deprotonated bisimidazolinium (**1a–d**) according to the Lappert procedure[21] (1 mmol) and $[RhCl(COD)]_2$ (1 mmol) in toluene (15 ml) were heated under reflux for 2 h. Upon cooling to room temperature, yellow-orange crystals of **2a–d** were obtained. The crystals were filtered, washed with diethyl ether (3 × 15 ml) and dried under vacuum. The crude product was recrystallized from CH_2Cl_2–Et_2O.

o-Xylylbis{(*N*-2,4,6-trimethylbenzylimidazolidin-2-iliden)chloro(η^4-1,5-cyclooctadiene)rhodium(I)}, 2a

Yield: 0.849 g (85%); m.p. 248–249 °C; $\nu_{(CN)} = 1496\ cm^{-1}$. Anal. calcd for $C_{50}H_{66}N_4Cl_2Rh_2$: C, 60.07; H, 6.65; N, 5.60. Found: C, 60.15; H, 6.71; N, 5.68%. ^1H NMR (399.9 MHz, $CDCl_3$) δ = 7.61 and 7.34 (m, 4H, *o*-$CH_2C_6H_4CH_2$), 6.89 and 6.88 [s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 5.91 and 5.79 (d, $J = 15$ Hz, 2H, *o*-$CH_2C_6H_4CH_2$), 5.59 and 5.53 [d, $J = 14.1$ Hz, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 5.34 and 5.29 (d, $J = 12$ Hz, 2H, *o*-$CH_2C_6H_4CH_2$), 5.18 and 5.14 [d, $J = 10.2$ Hz, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 5.09–4.90 (m, 4H, CH_{COD}), 3.66 (m, 4H, CH_{COD}), 3.51–2.96 (m, 8H, NCH_2CH_2N), 2.49 and 2.41 [s, 12H, $CH_2C_6H_2(CH_3)_3$-2,6], 2.44–2.32 (m, 8H, CH_{2COD}), 2.29 and 2.28 (s, 6H, $CH_2C_6H_2(CH_3)_3$-4), 1.98 (m, 8H, CH_{2COD}). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 214.0 (d, $J = 46.5$ Hz, $C_{carbene}$), 138.2, 137.6, 134.7, 129.6, 129.2. 128.9 and 128.3 [$CH_2C_6H_2(CH_3)_3$-2,4,6 and *o*-$CH_2C_6H_4CH_2$], 99.36, 99.03, 68.9 and 68.0 (d, $J = 6.0$, 6.75, 14.25 and 15 Hz respectively CH_{COD}), 51.7 (*o*-$CH_2C_6H_4CH_2$), 48.4 [$CH_2C_6H_2(CH_3)_3$-2,4,6], 47.8 and 47.4 (NCH_2CH_2N), 33.5, 32.8, 28.8 and 28.3 (CH_{2COD}), 20.9 [$CH_2C_6H_2(CH_3)_3$-4], 20.7 [$CH_2C_6H_2(CH_3)_3$-2,6].

o-Xylylbis{(*N*-*n*-butylimidazolidin-2-iliden)chloro(η^4-1,5-cyclooctadiene)rhodium(I)}, 2b

Yield: 0.661g (78%), m.p. 137–138 °C, $\nu_{(CN)} = 1505\ cm^{-1}$. Anal. calcd for $C_{38}H_{58}N_4Cl_2Rh_2$: C, 53.85; H, 6.90; N, 6.61. Found: C, 53.94; H, 6.82; N, 6.55%. ^1H NMR (399.9 MHz, $CDCl_3$) δ = 7.57 and 7.31 (m, 4H, *o*-$CH_2C_6H_4CH_2$), 5.85 and 5.82 (d, $J = 14.0$ Hz, 14.4 Hz, respectively, 2H, *o*-$CH_2C_6H_4CH_2$), 5.18 and 5.14 (d, $J = 6$ Hz, 5.6 Hz, respectively, 2H, *o*-$CH_2C_6H_4CH_2$), 4.97 (m, 4H, CH_{COD}), 4.39 and 3.89 (m, 4H, NCH_2CH_2N), 3.56–3.22 (m, 12H, NCH_2CH_2N, CH_{COD} and $CH_2CH_2CH_2CH_3$), 2.38–2.25 (m, 8H, CH_{2COD}), 1.94–1.75(m, 8H, CH_{2COD}), 1.63–1.44 (m, 8H, $CH_2CH_2CH_2CH_3$), 1.03 (t, $J = 7.2$ Hz, 6H, $CH_2CH_2CH_2CH_3$). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 213.2 (d, $J = 46.5$ Hz, $C_{carbene}$), 135.0, 134.9, 129.8, 129.6, 128.6 and 128.5 (*o*-$CH_2C_6H_4CH_2$), 99.3, 98.9, 98.6 (d, $J = 6.9$ Hz, CH_{COD}), 68.9, 68.8, 68.4(d, $J = 6.1$, 6.9 and 14.5 Hz, respectively, CH_{COD}), 51.6 and 51.5 (*o*-$CH_2C_6H_4CH_2$), 50.9 ($CH_2CH_2CH_2CH_3$), 48.5 and 48.1 (NCH_2CH_2N), 33.5, 33.2, 33.1, 32.6, 29.2, 29.1, 28.9 and 28.8 (CH_{2COD}), 30.8 ($CH_2CH_2CH_2CH_3$), 20.5 ($CH_2CH_2CH_2CH_3$), 14.2 ($CH_2CH_2CH_2CH_3$).

p-Xylylbis{(N-2,4,6-trimethylbenzylimidazolidin-2-iliden)chloro(η^4-1,5-cyclooctadiene) rhodium(I)}, 2c

Yield: 0.889 g (89%); m.p. 254–255 °C; $\nu_{(CN)} = 1497\ cm^{-1}$. Anal. calcd for $C_{50}H_{66}N_4Cl_2Rh_2$: C, 60.07; H, 6.65; N, 5.60. Found: C, 60.01; H, 6.58; N, 5.69%. ^1H NMR (399.9 MHz, $CDCl_3$) δ = 7.45 (s, 4H, *p*-$CH_2C_6H_4CH_2$), 6.86 [s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 5.54, 5.50, 5.25 and 5.11 [d, $J = 5.6$, 6.0, 14.4 and 14.0 Hz, respectively, 8H, *p*-$CH_2C_6H_4CH_2$ and $CH_2C_6H_2(CH_3)_3$-2,4,6], 5.01–4.96 (m, 4H, CH_{COD}), 3.52 (m, 4H, CH_{COD}), 3.09 (m, 8H, NCH_2CH_2N), 2.47 (m, 8H, CH_{2COD}), 2.34 [s, 12H, $CH_2C_6H_2(CH_3)_3$-2,6], 2.29 [s, 6H, $CH_2C_6H_2(CH_3)_3$-4], 1.92 (m, 8H, CH_{2COD}). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 213.9 (d, $J = 46.5$ Hz, $C_{carbene}$), 138.5, 137.9, 129.5, 129.1

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Table 2. Crystal data and summary of X-ray data collection for complexes **2a** and **2d**

	2a	2d
Empirical formula	$C_{50}H_{64}Cl_2N_4Rh_2$	$C_{38}H_{58}Cl_2N_4Rh_2$
Formula weight	997.77	847.60
Temperature(K)	296	296
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	C2/c
Unit cell dimensions		
a (Å)	13.1664(4)	32.442(3)
b (Å)	15.2553(5)	7.6753(4)
c (Å)	23.4416(7)	15.1425(13)
α (deg)	90.00	90.00
β (deg)	90.00	91.944(7)
γ (deg)	90.00	90.00
Volume (Å^3)	4708.4(3)	3768.3(5)
Z	4	4
Calculated density (mg m^{-3})	1.408	1.494
Absorption coefficient (mm^{-1})	0.852	1.050
F(000)	2064	1752
Crystal size (mm)	0.27 × 0.25 × 0.24	0.50 × 0.267 × 0.130
θ range for data collection (deg)	1.33–27.17	1.26–25.53
Independent reflection	9246	1703
Collected reflection	61 632	11 573
Absorption correction	Integration	Integration
T_{min}	0.7938	0.6989
T_{max}	0.8592	0.8709
R_{int}	0.0473	0.0471
θ_{max}(deg)	25.99	25.52
h	−16 to 16	−38 to 38
k	−18 to 18	−9 to 9
l	−28 to 28	−18 to 18
Refinement method	Full-matrix least-squares on F^2	
$wR(F^2)$	0.0629	0.0773
Goodness-of-fit on F^2	0.931	0.970
Final *R* indices [$I > 2\sigma(I)$]	0.028	0.031
R indices (all data)	0.036	0.041
$(\Delta/\sigma)_{max}$	0.016	0.000
$\Delta\rho_{max}$ (e Å^{-3})	0.403	0.218
$\Delta\rho_{min}$ (e Å^{-3})	−0.372	−0.427

Table 3. $\pi\cdots$ ring interactions

C···H(I)	Cg(J)	H···Cg (Å)	C–H···Cg (deg)
	2a		
C30···H30A	Cg(9)	2.9608	142.78
C6···H6A	Cg(21)^{i}	3.1003	140.77
C22···H22A	Cg(19)^{ii}	3.0269	163.20
C28···H28	Cg(19)^{ii}	3.1265	142.03
C36···H36	Cg(20)^{iii}	3.1073	133.60
C42···H42C	Cg(19)^{iv}	3.1874	156.67
	2d		
C13···H13A	Cg(10)^{ii}	2.9430	147.90
C13···H13A	Cg(10)^{iii}	2.9430	147.90

2a: Cg(19), C13–C14–C15–C16–C17–C18; Cg(20), C23–C24–C25–C26–C27–C28; Cg(21), C34–C35–C36–C37–C38–C39. Symmetry codes: $^{(i)}$ $-x+1/2, -y, z+1/2$; $^{(ii)}$ $x-1/2, -y+1/2, -z+1$; $^{(iii)}$ $-x, y+1/2, -z+1/2$; $^{(iv)}$ $-x, y-1/2, -z+1/2$.
2d: Cg(10), C17–C18–C19–C17A^{i} –C18A^{i} –C19A.^{i} Symmetry codes: $^{(i)}$ $-x+1, y, -z+3/2$; $^{(ii)}$ $-x, -y+2, -z$; $^{(iii)}$ $x, -y+2, z-1/2$.

[$CH_2C_6H_2(CH_3)_3$-2,4,6], 136.3 and 128.8 (*p*-$CH_2C_6H_4CH_2$), 99.4 (d, J = 4.7 Hz, CH_{COD}), 69.3 and 67.4 (d, J = 14.4 and 14.5 Hz, respectively, CH_{COD}), 55.3 and 55.2 (*p*-$CH_2C_6H_4CH_2$), 48.4 and 48.2 [$CH_2C_6H_2(CH_3)_3$-2,4,6], 47.6 and 47.5 (NCH_2CH_2N), 33.4, 32.8, 28.5 and 28.3 (CH_{2COD}), 21.1 [$CH_2C_6H_2(CH_3)_3$-4], 20.9 [$CH_2C_6H_2(CH_3)_3$-2,6].

p-Xylylbis{(*N*-*n*-butylimidazolidin-2-iliden)chloro(η^4-1,5-cyclooctadiene)rhodium(I)}, 2d

Yield: 0.779 g (92%); m.p. 238–239 °C; $\nu_{(CN)}$ = 1506 cm^{-1}. Anal. calcd for $C_{38}H_{58}N_4Cl_2Rh_2$: C, 53.85; H, 6.90; N, 6.61. Found: C, 53.78; H, 6.82; N, 6.53%. ^{1}H NMR (399.9 MHz, $CDCl_3$) δ = 7.45 (s, 4H, *p*-$CH_2C_6H_4CH_2$), 5.53, 5.45, 5.22 and 5.14 (d, J = 14.7 Hz, 4H, *p*-$CH_2C_6H_4CH_2$), 4.98 (m, 4H, CH_{COD}), 4.36 and 3.90 (m, 4H, NCH_2CH_2N), 3.52–3.25 (m, 12H, NCH_2CH_2N, CH_{COD} and $CH_2CH_2CH_2CH_3$), 2.38–2.29 (m, 8H, CH_{2COD}), 1.93 (m, 8H, CH_{2COD}), 1.80–1.43 (m, 8H, $CH_2CH_2CH_2CH_3$), 1.04 (t, J = 7.2 Hz, 6H, $CH_2CH_2CH_2CH_3$). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 212.5 (d, J = 46.5 Hz, $C_{carbene}$), 136.2 and 128.7 (*p*-$CH_2C_6H_4CH_2$), 99.0, 98.9 (d, J = 6.75 and 6.0 Hz, respectively, CH_{COD}), 68.4, 68.1 (d, J = 15 Hz, CH_{COD}), 54.5 (*p*-$CH_2C_6H_4CH_2$), 50.5 ($CH_2CH_2CH_2CH_3$), 48.3 and 47.7 (NCH_2CH_2N), 32.9, 32.7, 28.8 and 28.6 (CH_{2COD}), 30.6 ($CH_2CH_2CH_2CH_3$), 20.2 ($CH_2CH_2CH_2CH_3$), 14.0 ($CH_2CH_2CH_2CH_3$).

General procedure for rhodium–carbene catalyzed addition of acetophenone to triethylsilane

Acetophenone (1 mmol), triethylsilane (1.25 mmol) and rhodium carbene catalyst (0.025 mol% based on ketone) were introduced into a Schlenk tube. The resulting mixture was heated for 2 h at 80 °C, cooled to ambient tempareture and purified by flash chromatography (hexane–ethyl acetate, 10 : 1). Analysis of the reaction product was carried out by NMR spectroscopy and GC.

X-ray structural analyses of 2a and 2d

Crystals of **2a** and **2d** suitable for X-ray analysis were obtained from a dichloromethane solution layered with diethyl ether. Figures 1 and 2 show the molecular structure of 2a and **2d**, respectively. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 2; $\pi\cdots$ ring interactions are shown in Table 3.

Supplementary material

Crystallographic data for the structures reported in this paper have been deposid with the Cambridge Crystallographic Data Center: CCDC-631654 and -631655 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre, www.ccdc.cam.ac.uk/data_request/cif.

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