Synthesis, Reactivity, Crystal Structures and Catalytic Activity of New Chelating Bisimidazolium-Carbene Complexes of Rh

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A series of new bridging, chelating and pincer *N*-heterocyclic carbenes of Rh^{I} and Rh^{III} have been obtained under mild conditions. The compounds have been fully characterised and their crystal structures determined. The chelate-pincer coordination of the ligands means that the stability of these compounds is significantly greater than other carbene complexes of Rh. The compounds have been tested in catalytic reactions such as hydrogen transfer from alcohols to ketones, and hydrosilylation of terminal olefins and alkynes; they show a high activity for both processes.

Introduction

The number of synthetic applications of homogeneous catalysts has increased enormously during the last three decades. Highly active and selective catalysts have been prepared to activate a large variety of bonds, thus providing efficient methods to obtain new products with important industrial and pharmaceutical applications. However, homogeneous catalysts are far from being widely used in industrial processes, mainly due to their low chemical and thermal stability and to their low potential to provide recyclable systems. With this in mind, recent research in this area has focused mainly on the search for new methods for the synthesis of stable, effective and recyclable catalysts, since this would combine both economic and environmental benefits.

Homogeneous organometallic catalysis has long depended on phosphane ligands.[1,2] Despite their effectiveness in controlling reactivity and selectivity, phosphane catalysts require air-free handling to prevent the oxidation of the ligand and are subject to P−C activation at elevated temperatures.[3] As an alternative to the use of phosphanes, *N*-heterocyclic carbenes are currently being used in the design of new homogeneous catalysts.[4] The chemical versatility of these compounds and their easy access provide methods to obtain ligands with tunable steric and electronic properties. The precursor imidazolium salts are often easier to obtain than phosphanes, but their coordination to the metal often requires harsh preactivation conditions, in most cases needing the addition of strong bases such as *n*BuLi.[5,6] Once bound to the metal, however, monodentate carbenes are often reactive and undergo decomposition processes that can reduce the catalytic efficiency at high temperatures.

In order to improve the stability of the carbene-imidazolium compounds we[7−10] and others,[6,11−17] have reported a series of compounds whose stability is entropically improved by the chelate effect. In this sense, a series of bis-chelate and pincer-bis-carbene compounds have been reported, providing catalysts which resist higher temperatures than other classical homogeneous catalysts.

Most of the tridentate pincer CNC bis-carbene ligands reported so far are Pd-based and have been used in catalytic C-C bond formation reactions (Heck, Suzuki, Sonogashira).[9,10,15] Due to the high thermal stability of these catalysts, traditionally inert bonds such as C−Cl are readily activated providing the highest turnover numbers reported to date in the Heck C−C coupling.[9] Pincer CNC ligands have also allowed the preparation of recyclable heterogeneous catalysts which have also been effectively used in the Heck C−C coupling reaction.[18]

Despite their obvious potential applications, the use of bis-carbene chelate or pincer ligands with other metals is limited to a few papers reporting Rh[7] and Ru[13] complexes whose catalytic applications were envisaged.

Based on our previous findings, we now report the synthesis and reactivity of a series of CNC-bis-carbene complexes of Rh^{I} and Rh^{III}. The crystal structures of several of the reported compounds are described. We also report the

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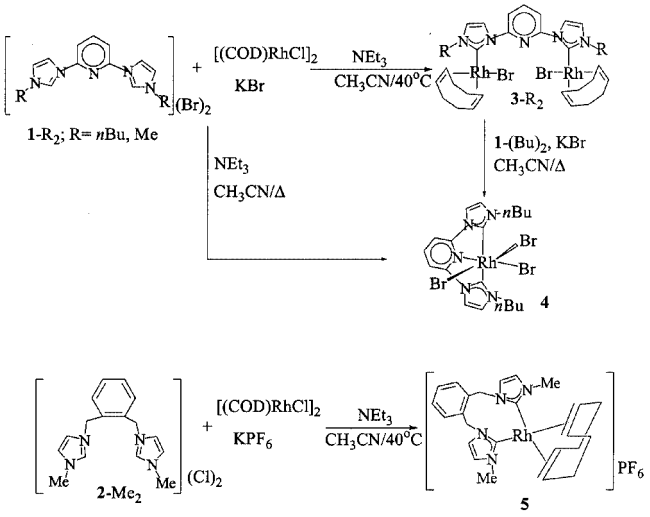
catalytic applications of our compounds toward the hydrosilylation of terminal olefins and alkynes, and hydrogen transfer between alcohols and ketones.

Results and Discussion

Synthesis and Reactivity of the Compounds

In order to obtain the new Rh compounds, we used the ligand precursors **1**-R_2 [9] (R = Me, Bu) and **2**-Me_2. The preactivation of the ligand (deprotonation) was performed with NEt_3, since we have previously found that this base affords good results under mild reaction conditions. As metal complex we used $[RhCl(COD)]_2$.

Scheme 1 shows the general method for the synthesis of complexes **3**, **4** and **5**. The reaction of $[RhCl(COD)]_2$ with **1**-R_2 allowed the synthesis, in high yield, of two different compounds, depending on the reaction conditions used. Under inert conditions, using a Rh/**1**-R_2 molar ratio of 1:1, compound **3** was obtained (65−80% yield). The complex **3**-Bu_2 was recently obtained and fully characterized in our group,[19] and **3**-Me_2 has very similar spectroscopic features[19] allowing for the obvious differences derived from changing the two Bu wingtips by two methyl groups. The more relevant NMR spectroscopic features arise from the fact that the twofold symmetry of the ligand is maintained upon coordination, and that the ^{13}C NMR spectrum of the complex shows Rh−C coupling ($^1J_{Rh,C}$ = 49.2 Hz, δ = 184.8 ppm), which confirms that metallation of the ligand has occurred.



Scheme 1

The synthesis of **4** can proceed both from $[RhCl(COD)]_2$ and from **3** (Scheme 1). The mechanism of this reaction is not well understood, but it looks as if the oxidation of the starting Rh^I complex is the first step in the reaction, which is why aerating the initial CH_3CN solution increases the reaction yields. In fact, when the reaction is carried out under a completely inert atmosphere, much lower yields are obtained, and most of the starting $[RhCl(COD)]_2$ complex is recovered, together with the Rh^I complex **3**, which can be considered as a reaction intermediate in the synthesis of **4**. KBr is added to the reaction medium in order to favour the formation of the perbrominated complex, although in most occasions mixtures of the Cl and Br complexes were still obtained. In the absence of KBr, mixtures of [Rh(CNC-Bu_2)Br_3] and *trans*-[Rh(CNC-Bu_2)Br_2Cl] were obtained, which we could not separate by conventional methods (i.e. column chromatography, crystallization, etc.).

The ^1H NMR spectrum of **4** shows the typical pattern of the bis-carbene ligand coordinated in the pincer form, very similar to that of related Pd complexes.[9,10] In the ^{13}C NMR spectrum, the carbene signal is observed as a doublet at δ = 177.5 ppm with a coupling constant that is diagnostic for Rh binding ($^1J_{Rh,C}$ = 33.7 Hz).

In order to confirm that **3** is in fact a reaction intermediate in the synthesis of **4**, we reacted **3**-Bu_2 with an equimolar amount of **1**-Bu_2 in refluxing CH_3CN, with the formation of **4** in almost quantitative yield (Scheme 1). We still do not have a satisfactory explanation for the oxidation step from **3**-Bu_2 to **4**, although we have observed that aerated solvents provide better yields. A possible explanation for this process may be the oxidation of traces of Br^- to Br_2 by dioxygen, with the subsequent oxidative addition of Br_2 to **3**. Further studies on this matter are being carried out in more detail.

All attempts to coordinate **1**-Bu_2 and **1**-Me_2 to Rh^I in the pincer form were unsuccessful. Although all these attempts were with $[RhCl(COD)]_2$, we believe that any other Rh^I starting compound would have given us similar results. Reduction of the corresponding Rh^{III} species was unsuccessful, with decomposition of the compound and the formation of unknown species.

We also wanted to see whether a chelating bis-carbene coordination to Rh^I was possible, since all attempts made so far have resulted in the oxidation to Rh^{III}, both in the results that we now present and in our previous work.[7] With this aim in mind, we tried to coordinate the ligand precursor **2**-Me_2, made from direct reaction of dichloro-*o*-xylene and methylimidazole. The reaction of **2**-Me_2 with $[RhCl(COD)]_2$ in CH_3CN in the presence of NEt_3 yielded compound **5** in high yield (85%). The synthesis of **5** occurs without the formation of any Rh^{III} species, which could support the idea that prior oxidation of the halide (in this case Cl^- to Cl_2 obviously would be not possible) by air is needed for the oxidation of Rh^I to Rh^{III}. Evidence for the chelate coordination of the bis-carbene ligand comes again from NMR spectroscopy, which shows that the imidazole rings are symmetry related. The metallation of the ligand is confirmed by the presence of a doublet (δ = 180.8 ppm; $^2J_{Rh,C}$ = 52.6 Hz) in the ^{13}C NMR spectrum. The coordination sphere of the rhodium atom is completed by the presence of a molecule of 1,5-COD.

The molecular structures of **3**-Me_2, **4** and **5** were unambiguously confirmed by single crystal X-ray diffraction.

The molecular structure of **3**-Me_2 (Figure 1) is virtually identical to that of complex **3**-Bu_2 which we have published previously.[19] The compound consists of a dirhodium struc-

ture bridged by 2,6-bis(1-methyl imidazolylidene-3-yl)pyridine, with the nitrogen atom of the pyridine unbound. The geometry about each rhodium atom is pseudo-square-planar, with Rh−C_{imid} distances of 1.948(11) and 2.029(11) Å suggesting that these bonds have a major σ contribution with very little back-donation.

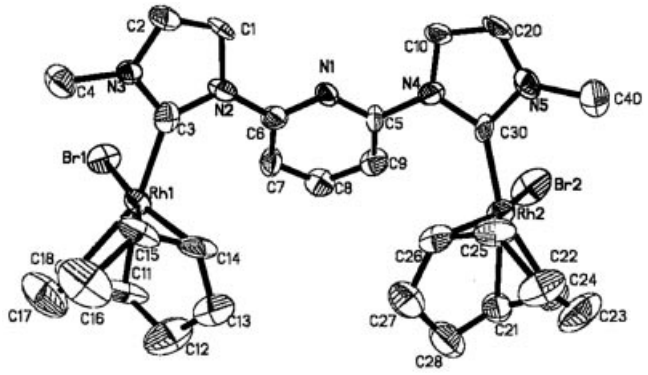


Figure 1. ORTEP diagram of **3**-Me_2 with 50% probability ellipsoids; hydrogen atoms omitted for clarity; selected bond lengths (Å) and angles (°): Rh(1)−C(3) 2.029(11), Rh(1)−C(15) 2.095(12), Rh(1)−C(14) 2.105(12), Rh(1)−C(11) 2.200(12), Rh(1)−C(18) 2.220 (11), Rh(1)−Br(1) 2.5172(17), Rh(2)−C(30) 1.948(11), Rh(2)−C(26) 2.101(11), Rh(2)−C(25) 2.157(12), Rh(2)−C(22) 2.189(11), Rh(2)−C(21) 2.216(11), Rh(2)−Br(2) 2.5169(18); C(3)−Rh(1)−Br(1) 87.7(3), C(30)−Rh(2)−Br(2) 90.2(3)

Figure 2 shows the molecular structure of complex **4**. The crystal contains a mixture of [Rh(CNC-Bu_2)Br_3] and *trans*-[Rh(CNC-Bu_2)Br_2Cl], and was refined with a 50% occupancy for each. The molecular structure shows the Rh atom in a distorted octahedral coordination, with a pincer-ligand bite angle of 79.9°. The imidazole and pyridine rings are virtually coplanar, and the two butyl groups point out of these planes. The Rh−C bond length (2.05 Å) is slightly longer than that obtained for a similar *cis*-chelate rhodium(III) bis-carbene reported in our group (1.99 Å),[7] due to the mutual trans influence.

The molecular diagram of **5** is shown in Figure 3. The structure shows the Rh atom in a distorted square-planar coordination with a chelate bite angle of 90.55°. The Rh−C bond lengths of 2.03 and 2.05 Å are similar to those of compound **3**, implying that the Rh−C bond has a major σ contribution. To the best of our knowledge, this is the first Rh^I chelate-bis-carbene complex reported so far.

Catalytic Hydrosilylation

Hydrosilylation of multiple bonds represents a useful class of catalytic processes for the functionalization of organic molecules. Vinylsilanes, which are widely used intermediates for organic synthesis, can be efficiently prepared by transition-metal-catalyzed addition of silanes to alkynes. Most of the recent efforts in the study of catalytic hydrosilylation concern the design of new and efficient catalysts that enable the preparation of both (*Z*)- and (*E*)-alkenylsilanes independently.[20−25] For this reason, the number of reports regarding mechanistic studies in order to rationalize the factors affecting the selectivity of this reaction have increased over the last few years.[20,22,25−27] In view of the compounds that we report in this paper, we thought that catalytic hydrosilylation could be a good test of the catalytic potential of these new complexes. Our Rh^I complexes (**3**-Me_2, **3**-Bu_2 and **5**) display all the structural and chemical requirements for this catalytical system, and could throw some light onto the reaction process.

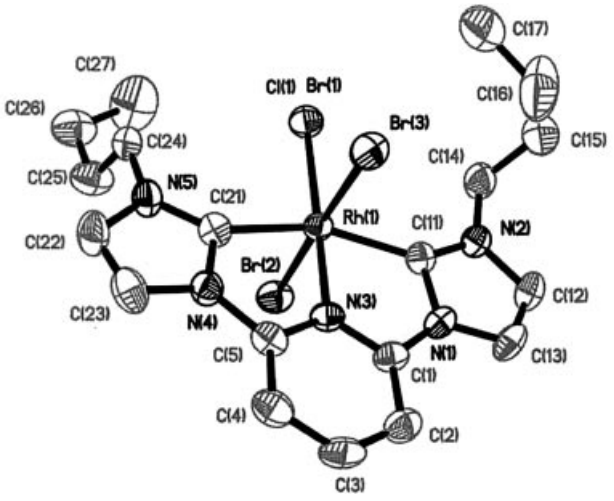


Figure 2. ORTEP diagram of **4** with 50% probability ellipsoids; hydrogen atoms omitted for clarity; selected bond lengths (Å) and angles (°): Rh(1)−N(3) 1.969(4), Rh(1)−C(21) 2.045(5), Rh(1)−C(11) 2.055(5), Rh(1)−Br(1) 2.4382(12), Rh(1)−Br(3) 2.4922(12); N(3)−Rh(1)−C(27) 78.7(2), N(3)−Rh(1)−C(11) 78.9(2)

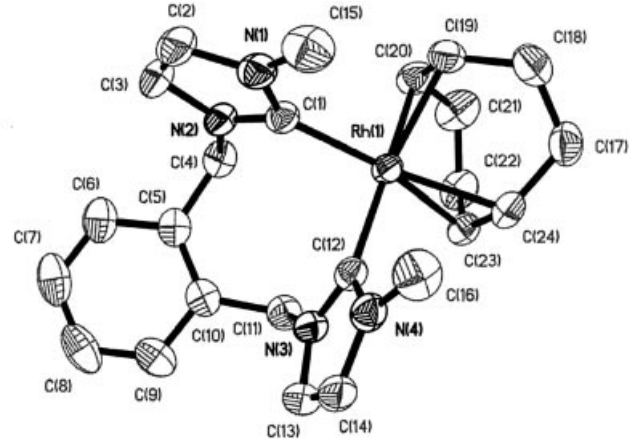


Figure 3. ORTEP diagram of **5** with 50% probability ellipsoids; hydrogen atoms omitted for clarity; selected bond lengths (Å) and angles (°): Rh(1)−C(12) 2.027(3), Rh(1)−C(1) 2.050(3), Rh(1)−C(23) 2.193(3), Rh(1)−C(19) 2.199(3), Rh(1)−C(24) 2.222(3), Rh(1)−C(20) 2.225(3); C(12)−Rh(1)−C(1) 90.55(11), C(19)−Rh(1)−C(24) 80.57(12), C(23)−Rh(1)−C(20) 80.95(12)

Table 1 shows the catalytic results for the hydrosilylation of several terminal alkynes with $HSi(OEt)_3$ and $HSiMe_2Ph$. All the 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 reactions were carried out in $CDCl_3$ at 60 °C, with 1 mol % catalyst. For all the reactions studied, all the catalysts used give a mixture of the β-(*E*),

Table 1. Hydrosilylation of alkynes

Entry[a]	RC≡CH	$HSiR_3$	Catalyst	Time (h)	*E*/*Z*/α	Yield (%)
1	PhC≡CH	$HSiMe_2Ph$	**3**-Me_2	72	83/0/17	95
2	PhC≡CH	$HSiMe_2Ph$	**3**-Bu_2	24	33/50/17	95
3	PhC≡CH	$HSiMe_2Ph$	**5**	72	80/11/9	100
4	PhC≡CH	$HSi(OEt)_3$	**3**-Me_2	72	57/30/13	92
5	PhC≡CH	$HSi(OEt)_3$	**3**-Bu_2	72	50/33/17	90
6	PhC≡CH	$HSi(OEt)_3$	**5**	72	66/26/8	85
7	*n*BuC≡CH	$HSiMe_2Ph$	**3**-Me_2	24	61/39/0	95
8	*n*BuC≡CH	$HSiMe_2Ph$	**3**-Bu_2	72	64/35	100
9	*n*BuC≡CH	$HSiMe_2Ph$	**5**	72	68/32/0	100
10	*n*BuC≡CH	$HSi(OEt)_3$	**3**-Me_2	24	50/50/0	70
11	*n*BuC≡CH	$HSi(OEt)_3$	**3**-Bu_2	72	50/50	50
12	*n*BuC≡CH	$HSi(OEt)_3$	**5**	72	61/39	100

[a] 0.077 mmol of alkyne, 0.085 mmol of silane. and 1% mol catalyst used in $CDCl_3$. T = 60 °C. Yields determined by ^1H NMR spectroscopy.

β-(*Z*) and α-isomers, although the β-(*E*) isomer is preferred in all cases where the process is carried out for long reaction times (72 h). In most metal-catalyzed hydrosilylations, the regioselectivity is affected by factors such as types of alkynes and silanes, catalyst, solvent or temperature. However, it has been reported that cationic Rh complexes catalyze the hydrosilylation of alkynes to give the β-(*E*)-vinylsilanes as the major products, while neutral Rh complexes show a higher preference to yield the β-(*Z*) ones.[20,28−30] Since initially we did not see this tendency for the neutral complexes, we decided to follow the reaction more carefully, and study how the isomer ratio evolves with time (Figure 4).

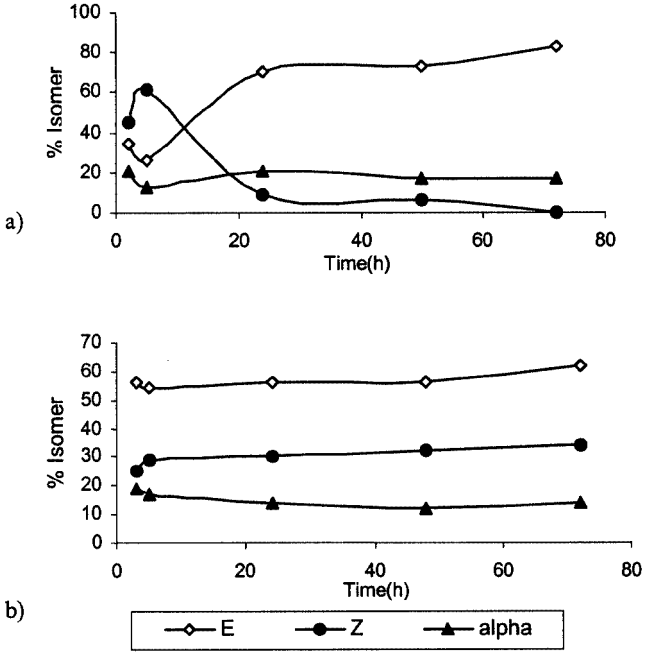


Figure 4. Reaction profiles for the hydrosilylation reactions of phenylacetylene by using **3**-Me_2 (1 mol % ratio) with: (a) $HSiMe_2Ph$, and (b) $HSi(OEt)_3$; percentage of isomer relative to molar fraction ($E + Z + \alpha = 100$)

As seen from Figure 4a, the reaction of phenylacetylene with $HSiMe_2Ph$ using **3**-Me_2 as catalyst starts by showing a higher preference for the β-(*Z*) isomer. As the reaction proceeds, there is a conversion from the (*Z*)- to the (*E*)-isomer, until total conversion into the (*E*)-isomer is achieved. A similar behavior is observed for the *n*BuC≡CH/$HSiMe_2Ph$ system with both neutral catalysts. These results confirm that the rate of isomerization of the initially preferred (*Z*)-isomer to the thermodynamically more stable (*E*)-isomer competes with the hydrosilylation process. The fact that no (*Z*)-vinylsilane is observed at the end of the reaction probably implies that the isomerization occurs via a reversible addition of the (*Z*) product in the last step of the reaction mechanism rather than a change in the selectivity of the catalyst due to a modification of its nature during the reaction.[20,27] When $HSi(OEt)_3$ is used, there is a clear preference for the (*E*)-isomer from the start of the reaction, and no (*Z*)-(*E*) conversion is observed with time (Figure 4b).

For the cationic catalyst **5**, the tendency to produce the (*E*)-vinylsilane isomer is observed from the beginning of the reaction. A higher selectivity for the (*E*)-isomer is obtained when $HSiMe_2Ph$ is used instead of $HSi(OEt)_3$.

These results are in agreement with other reports on rhodium-catalyzed alkyne-hydrosilylation reactions, in which a mixture of isomers is always obtained.[31] $[Rh(nbd)(dppe)_2]PF_6$ gives no β-(*Z*) isomer, although some α-isomer is formed.[22]

The relative efficiencies of these Rh complexes as olefin hydrosilylation catalysts were compared by means of a standard reaction of styrene with $HSi(OEt)_3$ and $HSiMe_2Ph$ (Table 2). No induction periods were observed, and the formation of the silylated compounds proceeded without detectable by-products by NMR spectroscopy. As seen from the results shown in Table 2, there is a predominant tendency to yield the linear (terminal) phenethyl isomer. The cationic complex **5** has a better ability to yield the mentioned isomer, displaying higher selectivities.

It is difficult to determine whether the neutral dimetallic precatalysts **3**-Me_2 and **3**-Bu_2 remain dimetallic under the reaction conditions of the hydrosilylation process. In fact, we cannot exclude that the compounds evolve to a stable Rh^{III} species with the chelate carbene bound and a Rh^{I} compound without carbene, which could be the true cata-

Table 2. Hydrosilylation of styrene

Entry[a]	$HSiR_3$	Catalyst	Time (h)	Linear/ branched	Yield (%)
1	$HSiMe_2Ph$	**3**-Me_2	48	82/18	88
2	$HSiMe_2Ph$	**3**-Bu_2	24	65/35	78
3	$HSiMe_2Ph$	**5**	72	90/10	100
4	$HSi(OEt)_3$	**3**-Me_2	72	55/45	20
5	$HSi(OEt)_3$	**3**-Bu_2	24	56/44	70
6	$HSi(OEt)_3$	**5**	72	85/25	80

[a] 0.077 mmol of olefin, 0.085 mmol of silane and 1% mol catalyst used in $CDCl_3$. T = 60 °C. Yields determined by ^1H NMR spectroscopy.

lytic species. However, according to our previous results on the hydroformylation of olefins,[19] we have observed that **3**-Me_2 and **3**-Bu_2 do not decompose to mononuclear species under the harsh conditions required for hydroformylation, thus suggesting that the complexes may maintain their dinuclear nature under the much milder conditions used in hydrosilylation.

Catalytic Hydrogen Transfer

The pseudo-octahedral Rh^{III} complex fulfills the electronic and structural requirements to catalyze the hydrogenation of the C=O groups of ketones via hydrogen transfer from *i*PrOH/KOH. The reactions are slow at room temperature, but proceed at very good rates at 80 °C. Again, the high stability of **4** allowed us to run all the reactions under non-inert conditions, with solvents used as purchased and in the absence of any precautions concerning the presence of air or moisture. As seen from the data shown in Table 3, the hydrogenation rates of the aromatic ketones are significantly higher than those shown for the aliphatic ones. The catalytic activity of this compound is similar to that reported by us for another Rh^{III} bis-carbene complex,[7] although in that case aliphatic ketones were hydrogenated faster than the aromatic ones.

In order to check whether incubation of the catalyst is important for this system we studied the reaction profiles of the hydrogen transfer to the three ketones used. As seen in Figure 5, the reaction profile is a sigmoid curve for the acetophenone case, indicating that a preactivation period of 3−4 h is necessary only for this substrate. This result is also observable for the reaction performed with 6×10^{-3} mol % catalyst (not shown in Figure 5). We still do not have a satisfactory explanation for this observation, although further studies are being carried out.

Transfer hydrogenation to alkenes failed with our catalyst, which in fact allows chemoselective reduction of C=O bonds in conjugated enones.

Table 3. Selected results for catalytic hydrogenation transfer of ketones with **4** as catalyst

Entry[a]	Substrate	Time (h)	Catalyst (mol %)	TON	TOF
1	Cyclohexanone	7	0.06	1322	189
2	Cyclohexanone	24	0.06	1322	55
3	Acetophenone	7	0.06	500	71
4	Acetophenone	24	0.06	1107	46
5	Acetophenone	6	0.006	3500	583
6	Benzophenone	7	0.06	1357	194
7	Benzophenone	24	0.06	1357	57
8	Benzophenone	3	0.006	3636	1212
9	Benzophenone	7	0.006	6450	921
10	Benzophenone	24	0.006	10580	441

[a] 2 mmol of substrate, 10 mL 0.1 M KOH in *i*PrOH T = 80 °C. Yields determined by ^{1}H NMR spectroscopy. TON = mol product/mol catalyst. TOF = mol product/(mol catalyst × hour).

Conclusion

We have obtained new bis-carbene complexes of Rh^{I} and Rh^{III}, and complex **4** is the first CNC-pincer complex of Rh described to date. The synthetic methods that we have described provide high yields under mild conditions, and establish a new method of activating bis-imidazolium salts in order to perform their coordination to metal complexes. The complexes obtained have been tested in the catalytic hydrosilylation of alkynes and olefins, and in the hydrogen transfer from alcohols to ketones; they show high catalytic activity. All in all, we have shown that a new family of Rh bis-carbene complexes can be easily obtained, providing a new and versatile class of catalysts whose properties deserve to be exploited.

Experimental Section

General Remarks: NMR spectra were recorded on Varian Innova 300 MHz and 500 MHz spectrometers, with $CDCl_3$ or [D_6]DMSO as solvents. The ligand precursors **1**-R_2 [7] (R = Me, *n*Bu) and the complex **3**-Bu_2 [19] were prepared according to literature methods. All other reagents are commercially available and were used as received.

Synthesis of [*o*-(CH_3-imid-CH_2)$_2$Ph](Cl)$_2$ (2): A mixture of α,α′-dichloro-*o*-xylene (2 g, 11.2 mmol) and *N*-methylimidazole (1.93 mL, 22.4 mmol) was heated at 150 °C for 12 h. The resulting solid was then washed with CH_2Cl_2 and filtered, yielding pure **2** (95%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 9.61 (s, 2 H, NC*H*N), 7.92 (s, 2 H, imid), 7.84 (s, 2 H imid), 7.48 (2 H, Ph), 7.38 (2 H, Ph), 5.82 (s, 4 H, CH_2), 3.92 (s, 6 H, CH_3) ppm. $C_{16}H_{20}Cl_2N_4$

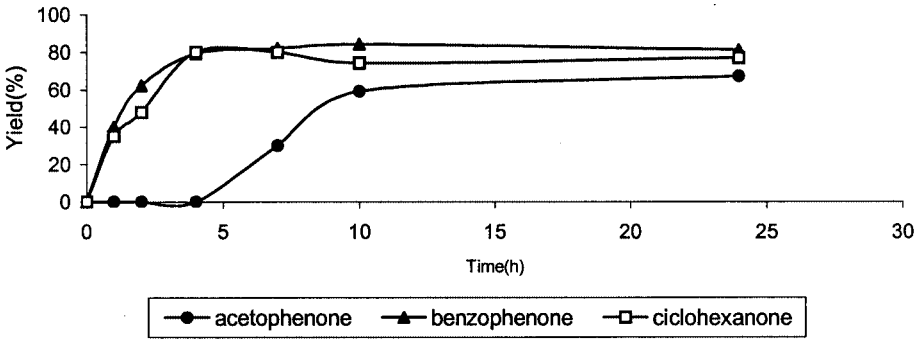


Figure 5. Reaction profile for the hydrogen-transfer reaction; 80 °C and 0.06 mol % catalyst (**4**)

(339.0): calcd. C 56.6, H 5.89, N 16.52; found C 56.2, H 5.67, N 16.87.

Synthesis of [(COD)RhBr]$_2$(μ-CNC-Me$_2$) (3-Me$_2$) and [(COD)RhBr]$_2$(μ-CNC-Bu$_2$) (3-Bu$_2$): A mixture of [RhCl(COD)]$_2$ (200 mg, 0.41 mmol), **1**-Me$_2$ (327 mg, 0.82 mmol), KBr (300 mg) and NEt$_3$ (0.5 mL, 3.5 mmol) was heated at 45 °C for 12 h in CH_3CN. The reaction mixture was filtered and the solvent was eliminated under vacuum. The resulting solid was redissolved in CH_2Cl_2 and the solution was transferred to a chromatography column. Elution with CH_2Cl_2 separated a minor yellow band that contained [RhCl(COD)]$_2$. Further elution with a gradient of CH_2Cl_2/acetone (10:1) allowed the separation of a major yellow band that contained **3**-Me$_2$ (yield 80%). $C_{29}H_{37}Br_2N_5Rh_2$ (820.9): calcd. C 42.42, H 4.51, N 8.53; found C 42.1, H 4.49, N 8.59.

[(COD)RhBr]$_2$(CNC-Me$_2$), (3-Me$_2$): ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 10.05 (d, $^2J_{H,H}$ = 8.1 Hz, pyridine-*H*), 8.28 (t, $^2J_{H,H}$ = 8.0 Hz, pyridine-*H*), 7.80 (imidazole-H), 6.99 (imidazole-*H*), 4.21 (s, 6 H, NCH_3) ppm. ^{13}C NMR ([D$_6$]DMSO, 300 MHz): δ = 184.8 (d, $^2J_{Rh-C}$ = 49.2 Hz, N*C*N), 149.8 (C_{ipso}), 139.7 (C_{ortho}), 123.1 (im-C), 123 (C_{meta}), 116.2 (im-C), 98.8, 97.5, 70.2 (COD), 39.6 (CH_3), 29.8, 29.3 (COD) ppm.

Synthesis of Rh(CNC-Bu$_2$)Br$_3$ (4): A mixture of [RhCl(COD)]$_2$ (200 mg, 0.41 mmol), **1**-Bu$_2$ (400 mg, 0.82 mmol), KBr (300 mg) and NEt$_3$ (0.5 mL, 3.6 mmol) was refluxed in 10 mL of CH_3CN for 12 h. During this time the solvent was aerated several times by bubbling a steam of air through the reaction medium. The reaction mixture was filtered and the solvent of the filtrate was removed under vacuum. The crude solid was redissolved in CH_2Cl_2 and the solution was transferred to a column chromatography. Elution with CH_2Cl_2 separated a minor yellow band that contained [RhCl(COD)]$_2$. Further elution with a gradient of CH_2Cl_2/acetone (10:1) afforded the separation of an orange band containing **4** (yield 53%). Complex **4** can also be obtained from **3** as follows: a mixture of **3**-Bu$_2$ (100 mg, 0.12 mmol), **1**-Bu$_2$ (59 mg, 0.12 mmol), KBr (100 mg) and NEt$_3$ (150 μL) was refluxed in CH_3CN for 5 h. After this time the workup was similar to that described above (yield 62%).

Rh(CNC-Bu$_2$)Br$_3$ (4): ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 8.54 (d, $^3J_{H,H}$ = 1.5 Hz, 2 H, imidazole−*H*), 8.39 (t, $^3J_{H,H}$ = 7.8 Hz, 1 H, pyridine−*H*), 8.04 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, pyridine−*H*), 7.77 (d, $^3J_{H,H}$ = 1.5 Hz, 2 H, imidazole−*H*), 4.77 (t, 4 H, N*C*H_2CH$_2$CH$_2$CH$_3$), 2.48 (quintet, 4 H, NCH$_2$*C*H_2CH$_2$CH$_3$), 1.89 (sextet, 4 H, NCH$_2$CH$_2$*C*H_2CH$_3$), 0.88 (t, 6 H, NCH$_2$CH$_2$CH$_2$*C*H_3) ppm. ^{13}C NMR ([D$_6$]DMSO, 300 MHz): δ = 177.5 (d, $^1J_{Rh,C}$ = 33.7 Hz, N*C*N), 152.5 (C_{ipso}), 144.51 (C_{ortho}), 124.97 (im-C), 118.54 (C_{meta}), 108.44 (im-C), 50.39 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 33.70 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 20.02 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 14.68 (CH$_2$CH$_2$CH$_2$*C*H$_3$) ppm. $C_{19}H_{25}Br_{2.5}Cl_{0.5}N_5Rh$ (643.85): calcd. C 35.42, H 3.88, N 10.87; found C 35.42, H 4.11, N 10.07.

Synthesis of [Rh(COD)(C∧C)]PF$_6$ (5): A mixture of [RhCl(COD)]$_2$ (200 mg, 0.41 mmol), **2**-Me$_2$ (275 mg, 0.82 mmol), KCl (400 mg) and NEt$_3$ (0.5 mL, 3.5 mmol) was heated at 45 °C for 12 h in CH_3CN. The reaction mixture was filtered and washed with CH_2Cl_2, and the solvent was then eliminated under vacuum. The crude solid was redissolved in CH_2Cl_2 and the solution was transferred to a chromatography column. Elution with CH_2Cl_2 separated a minor yellow band that contained [RhCl(COD)]$_2$. The solution was eluted with a gradient of CH_2Cl_2/acetone/KPF_6 allowing the separation of a major yellow band that contained **5** (yield 85%).

[Rh(COD)(C∧C)]PF$_6$ (5): ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.84 (m, 2 H, phenylene-*H*), 7.55 (d, 2 H, imidazole-*H*), 7.40 (m, 2 H, phenylene-H), 7.19 (d, imidazole-*H*), 6.48 (d, 2 H, NCH_2), 5.12 (d, 2 H, NCH$_2$) ppm. ^{13}C NMR ([D$_6$]DMSO, 300 MHz): δ = 180.8 (d, $^2J_{Rh,C}$ = 52.6 Hz, N*C*N), 136.4 (C_{ortho}, phenylene), 132.4 (C, phenylene), 129.7 (C, phenylene), 124.3 (im-C), 121.9 (im-C), 90.2, 88.9 (COD), 51.3 (CH_2), 39.2 (CH_3), 31.0 (COD) ppm. $C_{24}H_{30}F_6N_4PRh$ (621.9): calcd. C 46.32, H 4.82, N 9.02; found C 46.7, H 4.73, N 8.82.

Hydrosilylation of 1-Alkynes and Olefins with Silanes. General Procedure: In a 5 mm NMR tube, *n*BuC≡CH or PhC≡CH (0.077 mmol), silane [HSi(OEt)$_3$ or HSiMe$_2$Ph, 0.085 mmol] and a catalytic amount of **3**-Me$_2$, **3**-Bu$_2$ or **5** (1 mol %, 7.7×10^{-5} mmol) were dissolved in $CDCl_3$ (0.5 mL). The mixture was kept at 60 °C by immersion in a hot oil bath. The progress of the reaction was monitored by ^{1}H NMR spectroscopy, according to the data of the products obtained from the literature.[28,30]

Hydrogen-Transfer Catalysis: A mixture of the ketone (2 mmol), KOH (10 mL, 0.2 M in *i*PrOH) and a suspension of **4** (0.06% or 0.006% mol vs. substrate) in CH_2Cl_2 was heated to reflux. After the desired reaction times, aliquots were extracted from the reaction vessel and added to an NMR tube containing 0.5 mL of $CDCl_3$. Yields were determined by ^{1}H NMR spectroscopy.

X-ray Diffraction Studies: Single crystals of **3**-Me$_2$, **4** and **5** were mounted on a glass fiber in a random orientation. Crystal data are summarized in Table 4. Data collection was performed at room temperature on a Siemens Smart CCD diffractometer using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) with a nominal crystal-to-detector distance of 4.0 cm. A hemisphere of data was collected based on three ω-scan runs (starting with ω = −28°) at φ values of 0°, 90° and 180° with the detector at 2θ = 28°. After each of these runs, frames (606, 435 and 230) were collected at 0.3° intervals and 30 s per frame. Space group assignment was based on systematic absences, E statistics and successful refinement of the structures. The structures were solved by direct methods with the aid of successive difference Fourier maps and were refined using the SHELXTL 5.1 software package.[32] All non-hydrogen were refined anisotropically. Hydrogen atoms were assigned to ideal positions and refined using a riding model. Details of the data collection, cell dimensions and structure refinement are given in Table 4. The diffraction frames were integrated using the SAINT[33] package and corrected for absorption with SADABS.[34]

CCDC-194088 (**3**), -194089 (**4**) and -194090 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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Table 4. Crystallographic data

	3-Me_2	**4**	**5**
Empirical formula	$C_{29}H_{37}Br_2N_5Rh_2$	$C_{19}H_{25}Br_{2.50}Cl_{0.50}N_5Rh$	$C_{24}H_{30}F_6N_4PRh$
Molecular mass	821.28	643.85	622.40
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	14.635(5)	12.777(4)	12.717
b (Å)	10.547(4)	10.882(4)	13.849
b (Å)	19.842(7)	16.432(5)	14.887
α	90°	90°	90°
β	99.015(9)°	103.653(7)°	100.097(5)°
γ	90°	90°	90°
V (Å)^3	3024.8(19)	2220.2(12)	2581.4(12)
Z	4	4	4
Density (calculated)	1.803 Mg/m^3	1.926 Mg/m^3	1.602 Mg/m^3
Absorption coefficient	3.760 mm^{-1}	5.344 mm^{-1}	0.788 mm^{-1}
Reflections collected	24380	10540	20616
Goodness-of-fit on F^2	0.855	1.039	1.058
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0677$ $wR2 = 0.1863$	$R1 = 0.0323$, $wR2 = 0.0753$	$R1 = 0.0414$, $wR2 = 0.1026$

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