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Structural characterization and catalytic activity of the rhodium–carbene complex $Rh(PPh_3)_2(IMes)Cl$ (IMes = bis(1,3-(2,4,6-trimethylphenyl)imidazol-2-ylidene)

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Abstract

The rhodium–carbene complex $Rh(PPh_3)_2(IMes)Cl$ (**2**) is an active catalyst for the hydroboration of simple olefins at room temperature. The reactivity of **2** was also tested in the methylenation of aldehydes. The crystal structure of **2** is also reported.

Keywords: Structural characterization; Catalytic activity; Rhodium–carbene complexes

1. Introduction

The $Rh(PPh_3)_3Cl$ (**1**) complex (Wilkinson's catalyst) is well known as an active homogeneous catalyst for olefin hydrogenation [1], hydrosilylation [2] and hydroboration [3]. Other rhodium [3b,4a,4b] and cationic iridium complexes [3b,4c,4d] bearing bulky phosphines as ligands have also proven to be active catalysts for directed alkene hydroboration and hydrogenation. Very recently, complex **1** has been found active in the methylenation of aldehydes using trimethylsilyldiazomethane in the presence of triphenylphosphine and 2-propanol [5].

Imidazole-2-ylidenes (N-heterocyclic carbenes, NHC) [6] represent an alternative to the widely utilized phosphine ligands [7] in homogenous catalysis. Studies performed by us and others have demonstrated that replacement of bulky phosphines by NHC (Fig. 1) such as IMes (IMes = bis(1,3-(2,4,6-trimethylphenyl)imidazol-2-ylidene), IPr (IPr = bis(1,3-(2,6-diisopropylylphenyl)imidazol-2-ylidene), or SIMes (SIMes = 1,3-(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene) can result in enhanced catalytic performance over phosphine-bearing analogues in various catalytic transformations which include metal-mediated C–C cross coupling reactions [8], amination of aryl chlorides [9], hydroformylation [10], and olefin metathesis [11]. Rhodium–carbene complexes have been extensively studied by Lappert et al. [12]. However, there are few reports on the catalytic acitvity of rhodium–carbene complexes in rhodium-mediated processes [10,12c].

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 $Rh(PPh_3)_3Cl$ (**1**) [9] for olefin hydroboration and hydrogenation as well as for aldehyde methylenation when a PPh_3 ligand is replaced with the more donating IMes. We now report the catalytic activity of the previously synthesized $Rh(PPh_3)_2(IMes)Cl$ (**2**) [10] for olefin activation and methylenation of aldehydes as well as its crystal structure.

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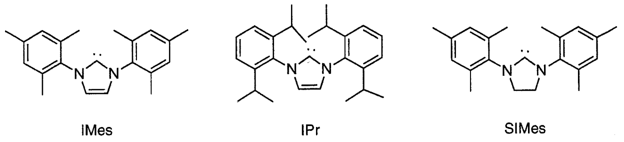
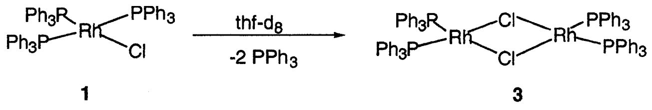


Fig. 1. Selected N-heterocyclic carbenes.

2. Results and discussion

2.1. Thermal stability of Rh(PPh$_3$)$_2$(IMes)Cl (**2**)

Complex **2** was synthesized according to the literature procedure [10] by a simple ligand exchange reaction of Rh(PPh$_3$)$_3$Cl (**1**) with IMes in toluene. Since we had observed improved thermal stability of a ruthenium olefin metathesis system when IMes was affixed to the metal center [11a], the hope was that improved thermal stability would also result for **2**. To monitor the effect the ligand displacement might have on the catalyst activity was one important goal of this study. Upon heating a THF-d_8 solution of **2** at 65 °C for 24 h, no phosphine dissociation nor decomposition occurs, indicating the high thermal stability of complex **2**. In contrast, the ^{31}P-NMR spectrum of a THF-d_8 solution of **1** indicated that heating resulted in the labilization of one phosphine ligand and the stabilization of the dimeric complex [(Rh(PPh$_3$)$_2$Cl]$_2$ (**3**) (Eq. (1)). While kinetic studies [13] indicate the presence of a Rh(PPh$_3$)$_2$Cl species in a pre-equilibrium leading to dimer formation, heating Rh(PPh$_3$)$_2$(IMes)Cl (**2**) in THF-d_8 does not lead to the corresponding [Rh(PPh$_3$)-(IMes)Cl]$_2$ dimer formation, indicating a higher stability of the monomeric form. To unequivocally establish the structure of **2**, single-crystal X-ray diffraction studies were performed on crystals grown from slow diffusion of hexanes into saturated dichloromethane solution of **2**.



(1)

2.2. X-ray analysis of **2**

The ORTEP diagram of **2** is presented in Fig. 2 and selected crystallographic data and bond lengths and angles are given in Tables 1 and 2. As shown in the ORTEP (Fig. 2), **2** adopts a distorted square-planar coordination geometry around the rhodium center (sum of bond angles around Rh is 360.565°, with two inequivalent phosphine ligands *cis* and *trans* to IMes (bond length Rh–P (*cis*-IMes) = 2.0527 Å and Rh–P (*trans*-IMes) = 2.3053 Å). Replacing a triphenylphosphine ligand in **1** with the more nucleophilic, and therefore more donating IMes, results in small changes in Rh–Cl and Rh–P bond distances (Table 2) [14]. This suggests that the *trans*-influence of PPh$_3$ and IMes are similar. This observation is further supported by similar ^{31}P coupling constants of Rh(PPh$_3$)$_3$Cl (**1**) ($J_{P-P} = 38$ Hz) and Rh(PPh$_3$)$_2$(IMes)Cl (**2**) ($J_{P-P} = 39$ Hz).

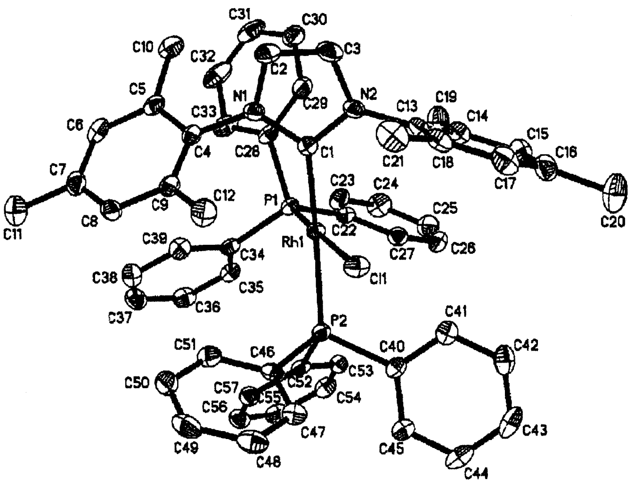


Fig. 2. ORTEP of Rh(PPh$_3$)$_2$(IMes)Cl (**2**) with ellipsoids drawn at 50% probability.

Table 1
Crystallographic data for Rh(PPh$_3$)$_2$(IMes)Cl (**2**)

	2
Empirical formula	$C_{57}H_{54}ClN_2P_2Rh$
Formula weight	967.32
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	19.9449(11)
b (Å)	11.2340(6)
c (Å)	22.0168(12)
α (°)	90.00
β,(°)	105.5890(10)
γ (°)	90.00
V (Å^3)	4751.6(4)
Z	4
D_{calc} (Mg m^{-3})	1.352
Reflections collected	94 242
Independent reflections	18 134 [$R_{int} = 0.0585$]
Refined parameters	784
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0272$, $wR_2 = 0.0480$
R indices (all data)	$R_1 = 0.0629$, $wR_2 = 0.0499$

To ascertain whether this simple substitution of IMes for one PPh$_3$ in **1** could lead to significant catalytic behavior differences, the role of **2** in a number of catalytic transformations was investigated.

2.3. Catalytic hydroboration

The catalytic performance of **2** in the hydroboration of 1-hexene by catecholborane was investigated and compared to the activity of related active complexes for

Table 2
Selected bond lengths (Å) and angles (°) for $Rh(PPh_3)_2(IMes)Cl$ (**2**), and $Rh(PPh_3)_3Cl$ (**1**) [14]

	2		**1** [14]
Bond lengths			
Rh–C(1)(carbene)	2.0527(14)	Rh–P(1) (*c* to Cl)	2.322, 2.335
Rh–P(1)(*c*-carbene)	2.2158(4)	Rh–P(1)(*t* to Cl)	2.212
Rh–P(2)(*t*-carbene)	2.3053(4)		
Rh–Cl	2.3941(4)	Rh–Cl	2.377
Bond angles			
P(1)(*c*-carbene)–Rh–C(carbene)	98.43(4)		
P(2)(*t*-carbene)–Rh–C(carbene)	164.10(4)		
P(1)–Rh–P(2)	96.238(15)		
C(1)–Rh–Cl	85.71(4)		
P(1)–Rh–Cl	173.835(15)		
P(2)–Rh–Cl	80.187(13)		

both hydroboration (**3**) and hydrogenation 4a4d[15]. These results are presented in Table 3. Although the hydroboration of olefins can be performed with hydroborating reagents such as 9-BBN or catecholborane, these reaction require elevated temperatures and long reaction times [3b] (Table 3, entry 1). However, the hydroboration reaction of simple olefins in the presence of rhodium-based catalysts takes place at room temperature [3b]4a4b with relatively short reaction time. The hydroboration mediated by **2** was performed using 1 mol% of catalyst in 2 ml of CH_2Cl_2. The catalytic activity of complex **2** is comparable to that displayed by Wilkinson's catalyst (Table 3, entries 2 and 3), with predominant formation of the anti-Markovnikov linear product. For comparison purposes, cationic iridium complexes $[Ir(COD)(SIMes)(Py)]PF_6$ [11e] and $[Ir(COD)(PCy_3)(Py)]PF_6$ [11a,11b,11c,11d], usually active for olefin hydrogenation, also led to high conversions of this reaction in 24 h. The mechanism for rhodium-mediated hydroboration is said to involve two separate manifolds, one involving initial ligand (PPh_3) loss and the second one involving initial oxidative-addition of the borane without prior ligand dissociation [3c,16]. The similar activities displayed by **1** and **2** and the less facile triphenylphosphine dissociation observed for **2** would suggest the initial oxidative addition manifold might be the preferred mode of activation in the hydroboration mediated by **2**.

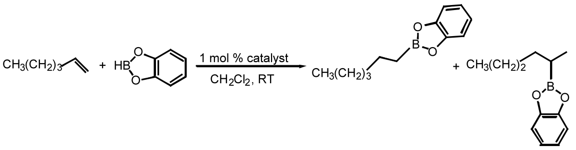
2.4. Catalytic hydrogenation

Using a similar protocol, we wished to compare the catalytic activity of compound **2** to the Wilkinson and Crabtree catalysts under hydrogenation conditions (ambient temperature and pressure of hydrogen) (Table 4). As expected, complex **2** yields lower conversions of the hydrogenated product compared to the very active Crabtree [11e] or Crabtree-type iridium catalysts [11e]. The lower catalytic activity may be explained in terms of the higher stability with respect to phosphine dissociation, since phosphine dissociation (followed by olefin insertion) is required in order to obtain a coordinatively unsaturated species during the catalytic cycle.

2.5. Catalytic olefination

The catalytic activity of **2** was also tested in the olefination reaction using trimethylsilyldiazomethane, 2-propanol and triphenylphosphine. In contrast to reactions mediated by **1**, the methylenation of hydrocinnamaldehyde proceeded very slowly at room temperature with **2** (entries 1 and 7). Only 20% of the desired terminal olefin was observed after 24 h, with some 10% of various by-products and 70% of starting material. Changing the solvent to dichloromethane did not improve the conversion, as the reaction was completely inhibited in this solvent (entry 8). These results clearly illustrate that the rhodium–carbene complex **2** is less

Table 3
Hydroboration of 1-hexene with catecholborane using various catalysts



Entry	Catalyst	Time (hrs)	Linear	Branched	Yield (%) [a,b]
1	9-BBN/ 68° C	8	< 99 [c]		< 99 [3b]
2	$Rh(PPh_3)_3Cl$ (**1**)	1	99	1	100
3	$Rh(IMes)(PPh_3)_2Cl$ (**2**)	1	99	1	95
4	$[Ir(COD)(SIMes)(Py)]PF_6$	24	< 99		92
5	$[Ir(COD)(Pcy_3)(Py)]PF_6$	24	< 99		92

[a] Reaction conditions: 1 mol% catalyst, 1 mmol 1-hexene, 2 ml CH_2Cl_2, 1.1 mmol catecholborane.
[b] GC yield, average of two runs.
[c] The product is 1-(9-BBN-)-hexane.

Table 4
Hydrogenation of cyclohexene using various catalysts [a]

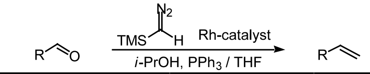
Catalyst	Time (h)	*T* (°C)	Yield (%) [a,b]
$[Ir(COD)(PCy_3)(Py)]PF_6$	< 0.5	RT	100 [11e]
$[Ir(COD)(SIMes)(Py)]PF_6$	2	RT	100 [11e]
$Rh(PPh_3)_3Cl$ (**1**)	24	RT	8
$Rh(IMes)(PPh_3)_2Cl$ (**2**)	24	RT	9
$Rh(PPh_3)_3Cl$ (**1**)	24	45	36
$Rh(IMes)(PPh_3)_2Cl$ (**2**)	24	45	18

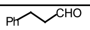
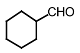
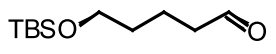
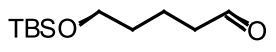
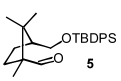
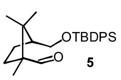
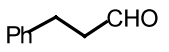
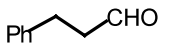
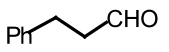
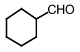
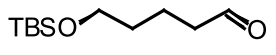
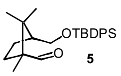
[a] Reaction conditions: 1 mol% catalyst, 1 mmol cyclohexene, 5 ml CH_2Cl_2, 1 atm H_2.
[b] GC yield, average of two runs.

potent at mediating the formation of methylenetriphenylphosphorane from trimethylsilyldiazomethane, triphenylphosphine and 2-propanol at room temperature than its $Rh(PPh_3)_3Cl$ (**1**) parent.

The higher thermal stability displayed by **2**, compared to **1**, suggested that improved catalytic conversions might be possible for **2** at higher temperatures. Indeed, when the reaction was carried out at 50 °C using complex **2**, the terminal olefin derived from hydrocinnamaldehyde was obtained in an 88% yield after 6 h (entry 9). Similar results were obtained with cyclohexanecarboxaldehyde, which produced the terminal olefin quantitatively at 50 °C with **2** (entry 10). We have also tested the catalytic activity of **1** and **2** with substrates that exhibit lower rate of conversion, such as **4** and **5**. The terminal alkenes of aldehydes **4** and **5** were produced, respectively in 91% after 8 h and in 79% after 7 h using Wilkinson's catalyst at room temperature. Both catalysts exhibit comparable activity at 50 °C with aldehyde **4** and **5** leading to 80– > 98% of the corresponding alkene after 2 h. Complex **2** was slightly more efficient with aldehyde **4** whereas **1** provided slightly superior yields with substrate **5**. Early mechanistic work shows the rhodium-catalyzed olefination catalytic cycle to involve the association of the trimethylsilyldiazomethane with the rhodium catalyst through nitrogen coordination [17]. This suggests that PPh_3 ligand dissociation may have a major effect on the relative catalytic activity of both rhodium catalysts. Indeed, we observed an induction period (ca. 30–45 min) when the olefination reaction was carried out with the carbene complex **2** at 50 °C that could be explained by phosphine dissociation and formation of an active species. As a control experiment, complex **2** was premixed with trimethylsilyldiazomethane in THF and stirred for 30 min at room temperature, thus favoring ligand exchange; triphenylphosphine, 2-propanol and the aldehyde were then added. Under those conditions, we observed the formation of the terminal olefin at 25 °C, with a maximal conversion of 57% [18]. This experiment clearly suggests that there is an initial activation of the catalyst with trimethylsilyldiazomethane and that might be responsible for the observed induction period once the trimethylsilyldiazomethane is added at the end. As for the hydrogenation reaction, the PPh_3 ligand dissociation seems to have a major effect contributing to the increased activity of **1** over that displayed by **2** in rhodium-catalyzed olefination (Table 5).

Table 5
Olefination of aldehydes using various catalysts [a]



Entry	Catalyst	Aldehydes	Time (hrs)	T (°C)	yield (%)[a,b]
1	$Rh(PPh_3)_3Cl$ (**1**)		<0.5	RT	100
2	$Rh(PPh_3)_3Cl$ (**1**)		1	RT	>98
3	$Rh(PPh_3)_3Cl$ (**1**)	 **4**	8	RT	91[c]
4	$Rh(PPh_3)_3Cl$ (**1**)	 **4**	2	50	92
5	$Rh(PPh_3)_3Cl$ (**1**)	 **5**	7	RT	79[c]
6	$Rh(PPh_3)_3Cl$ (**1**)	 **5**	2	50	89
7	$Rh(IMes)(PPh_3)_2Cl$ (**2**)		24	RT	20
8	$Rh(IMes)(PPh_3)_2Cl$ (**2**)		24	RT	0[d]
9	$Rh(IMes)(PPh_3)_2Cl$ (**2**)		6	50	88
10	$Rh(IMes)(PPh_3)_2Cl$ (**2**)		6	50	>98
11	$Rh(IMes)(PPh_3)_2Cl$(**2**)	 **4**	2	50	>98
12	$Rh(IMes)(PPh_3)_2Cl$(**2**)	 **5**	2	50	80

[a] The methylenation reaction was conducted using 1.4 equiv. Of $TMSCHN_2$, 1.1 equiv. Of 2-propanol, 1.1 equiv. Of triphenylphosphine and 2.5 mol% of Rh-catalyst in THF.[b] GC yield, average of two runs.[c] Isolated yield[5].[d] DCM was the solvent.

3. Conclusions

The replacement of one triphenylphosphine by a N-heterocyclic carbene in Wilkinson's catalyst results in a catalytic species displaying comparable activity towards olefin hydroboration. This catalyst displays lower activity with respect to iridium based Crabtree's and modified Crabtree's catalysts in catalytic hydrogenation of olefins at ambient pressure. The catalytic activity of **2** was virtually identical to that of $Rh(PPh_3)_3Cl$ (**1**) in the rhodium-catalyzed methylenation of aldehydes using trimethylsilyldiazomethane at 50 °C. Structural and thermal stability studies reveal that the replacement of one phosphine with IMes lowers the ease of displacement of the remaining coordinated triphenylphosphines. Investigations into the synthesis and catalytic uses of related rhodium–carbene complexes are ongoing.

4. Experimental

4.1. General considerations

All reactions were carried out under an atmosphere of dry Ar using standard Schlenk techniques or in a MBraun glovebox containing less than 1 ppm of oxygen and water. NMR spectra were recorded using Varian 400 or 300 MHz spectrometers. GC analyses were performed on a Hewlett-Packard HP 5890 II equipped with a FID and a HP-5 column. All reported yields for catalytic reactions were determined by GC.

4.2. Reagents

Substrates for catalysis were purchased from commercial suppliers and either used as received (solid compounds) or degassed prior to use by purging with Ar for 20–30 min. Dichloromethane was dried by passage through an alumina tower and stored in a glovebox. IMesHCl, IMes [19], [Ir(COD)(SIMes)-(Py)]PF_6 [11e] and $Rh(PPh_3)_2(IMes)Cl$ [10] were prepared according to the literature procedures.

4.3. Catalytic hydroboration

Catalyst (0.01 mmol), CH_2Cl_2 (2 ml), 1-hexene (1 mmol), catecholborane (1.1 mmol) were loaded into either a Schlenk tube or a scintillation vial fitted with a TFE/silicone liner and a screw cap inside a glove box. After removal from the glovebox the resulting yellow solution was stirred at room temperature for the indicated time. Reaction progress was monitored by analyzing aliquots by GC.

4.4. Catalytic hydrogenation

A solution of 0.01 mmol of metal catalyst and 1.0 mmol of cyclohexene in 5 ml of CH_2Cl_2 was loaded into a 50 ml scintillation vial equipped with a screw cap and TFE/silicone liner inside a glove box. The vial was then purged with hydrogen from a Schlenk line for 1 min. The reaction was allowed to stir under atmospheric pressure of hydrogen and the product formation was monitored by GC. In some cases, the catalytic solution was loaded into a Schlenk tube, purged with hydrogen three times, then allowed to stir in an oil bath at 45 °C for the indicated time.

4.5. Catalytic olefination

To a solution of metal catalyst (0.025 mmol) and PPh_3 (2.20 mmol) in THF (10 ml), was added 2-propanol (2.00 mmol) followed by the substrate (2.00 mmol). Then, $TMSCHN_2$ (2.80 mmol), was added to the resulting mixture. The mixture was stirred under Ar and product formation was monitored by GC.

4.6. X-ray diffraction measurements

Single crystals of **2** were obtained by diffusion of either hexanes into a solution of the complex in CH_2Cl_2. A single crystal was placed in a capillary tube and mounted on a Bruker SMART CCD X-ray diffractometer. Data were collected using Mo–K_α radiation at 150 K. The structures were solved using direct methods (SHELXS-86) and refined by full-matrix least-squares techniques. Crystallographic data can be found in Table 1 and selected bond distances and angles in Table 2.

5. Supplementary material

Details of the crystal structure determination for **2** are available. Crystallographic data for the structure analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 186952 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax (int. code): +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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