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Irreversible cleavage of a carbene–rhodium bond in Rh-*N*-heterocyclic carbene complexes: implications for catalysis

Daryl P. Allen [a], Cathleen M. Crudden [a,*], Larry A. Calhoun [b], Ruiyao Wang [a,1]

[a] *Department of Chemistry, Queen's University, Kingston, Ont., Canada K7L 3N6*
[b] *Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 6E2*

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Abstract

Despite the generally accepted belief that carbene–metal bonds are strong and do not dissociate, the reaction of Rh-*N*-heterocyclic carbene complexes with triphenylphosphine in dichloroethane was determined to take place via cleavage of the Rh–carbene bond. The products of this reaction are Wilkinson's catalyst and a bisimidazolium salt derived from reaction between dichloroethane and two equivalents of the carbene. The implications of this reaction for catalysis are significant since the carbene complex shows *lower* activity than Wilkinson's catalyst in hydrogenation reactions. In non-halogenated solvents, the catalyst shows higher stability, such that the rate of exchange with free phosphine could be measured, and was determined to be ca. 10 times slower than in Wilkinson's catalyst.

Keywords: *N*-heterocyclic carbene; Catalysis; Hydrogenation; Rhodium complex

1. Introduction

The use of *N*-heterocyclic carbenes (NHCs) as replacements for phosphines has provided some significant improvements over traditional phosphine-based ligands [1]. The most commonly employed *N*-heterocyclic carbene, 1,3-bis (2,4,6-trimethylphenyl)-imidazol-2-ylidene (IMes), and its congeners are considered to be equivalent to strongly electron rich phosphines such as PCy_3, but with the added benefits of increased catalyst stability [2] and decreased ligand lability [1]. Significant studies of the stoichiometric reactivity of isolated carbene complexes are now beginning to accompany the numerous catalytic studies of these species [3]. Cavell and co-workers [4] have clearly demonstrated that carbene ligands can suffer decomposition by reductive elimination and both C–H and C–C activation of the 2,4,6-trimethylphenyl substituents have been reported [5]. Two reports of equilibration of the carbene–metal complexes with free carbene have recently appeared [6], which, along with early results from Lappert's lab [7], challenge the commonly held view that carbenes are substitutionally inert [8]. We report herein the irreversible displacement of a carbene ligand from rhodium complexes which leads to the formation of a completely different species, *with higher catalytic activity*. These findings have significant implications for catalysis, since the transformation of a carbene complex into a simple phosphine-containing species can lead to incorrect assumptions regarding the activity of the original carbene-ligated complex. At the same time, our studies shed light on a debate in the literature over the reactivity of *N*-heterocyclic carbenes with halogenated hydrocarbons such as dichloroethane and dichloromethane [9].

* Corresponding author. Tel.: +613 5336755; fax: +613 5336669.
E-mail address: cruddenc@chem.queensu.ca (C.M. Crudden).
[1] Author to whom correspondence concerning X-ray crystallography should be addressed.

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2. Results and discussion

2.1. NMR studies of phosphine dissociation

Building on the seminal work of Lappert and co-workers [10] and Herrmann and Kocher [11], we recently introduced an analog of Wilkinson's catalyst (**1**) in which one of the phosphines was replaced by an *N*-heterocyclic carbene ligand (**2**) [12]. Carbonyl complex **3** was prepared by treating **2** with carbon monoxide (Scheme 1). The resulting CO complexes can be handled in air and they are robust enough to be purified by chromatography on silica gel. Carbonyl complex (**3**) was found to be more active and more selective than $[ClRh(CO)(PPh_3)_2]$ in the hydroformylation of vinyl arenes [12]. Lebel and co-workers [13a] examined the activity of **2a** in several catalytic reactions, and found that in methenylation reactions [13b] the carbene complex was significantly less active and also displayed an induction period.

Unlike the large majority of $[ClRh(PAr_3)_2L]$ type complexes, rhodium complex **2** has the phosphines arranged in a *cis*-fashion in both solution and solid states [14,15]. Since the carbene is believed to be a strong σ-donor, dissociation of the *trans*-phosphine, which is important for the catalytic activity of such complexes, should be facilitated. Contrary to these expectations, when we examined the exchange of free phosphine with bound phosphine in a selective inversion transfer experiment, we found that the *dissociation of the trans-phosphine in **2a** and **2b** is slower than in **1alb*** by at least an order of magnitude [16].

The results obtained in our inversion transfer experiments are described in Table 1. At room temperature, carbene complexes **2a**, **2b** and **3** showed *no evidence of exchange* even though Wilkinson's complex (**1a**) and the tolyl version (**1b**), were found to exchange with free phosphine at a rate of 0.3 s^{-1} at 25 °C [17]. Upon heating to 50 °C or greater, catalysts **2a** and **2b** did undergo slow exchange, but **3** did not exchange with free phosphine even at 80 °C. At 50 °C, **2b** undergoes exchange with free phosphine (3 eq., 0.13 M) at a rate of 0.35 s^{-1}. Only the upfield signal assigned to the phosphine *trans* to the carbene was affected, indicating that exchange occurred exclusively into this position [18]. At 60 °C, the rate of exchange was determined to be 0.91 s^{-1} (average of eight runs). With a constant concentration of **2b**, increasing the amount of free P(*p*-tolyl)$_3$ to 50 equivalents gave an exchange rate of 0.90 s^{-1}, indicating that the exchange is likely dissociative (compare entries 2 and 3).

Table 1
Phosphine exchange in complex **2b**[a]

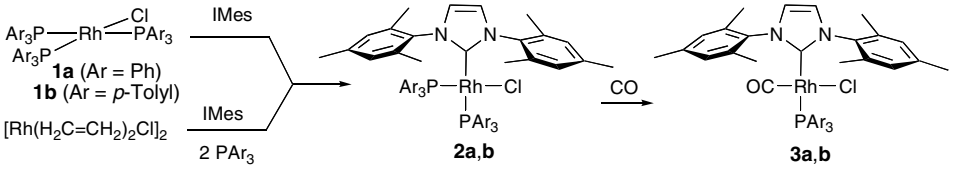
Entry	Equivalents of PR_3	Temperature (°C)	Exchange rate (s^{-1})
1	5.6	50	0.35
2	5.5	60	0.90
3	50.4	60	0.90
4	23.3	60	1.00
5	6.4	60	0.85
6	3.8	60	0.95
7	3.5	60	0.89
8	7.5	60	0.95
9	19.3	60	0.87
10	3.6	70	2.40

[a] Exchange experiments carried out at the indicated temperature in dry distilled d_8-toluene, [**2b**] = 0.04 M using a delay time at least = $5 \times T_1$. Solutions were prepared in a glove box under argon and are in sealed tubes or NMR tubes fitted with J–Young valves. See supplementary material for full experimental details.

These results are in line with the recent reports of Grubbs et al. [19] who have shown that in Ru NHC complexes, dissociation of phosphine ligands is significantly decreased relative to the all phosphine systems. To the best of our knowledge, our results represent the only other study of the effect of *N*-heterocyclic carbene ligands on phosphine dissociation. Interestingly, despite the significant differences between the two systems, the effect of the NHC on the *trans*-phosphine is roughly equivalent.

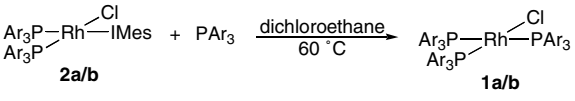
2.2. Stability of the Rh–NHC bond

During this study, the limited solubility of **2a** in aromatic solvents led us to examine several other solvents. Although dichloroethane appeared to be a good solvent at room temperature, upon heating to 60 °C to measure the rate of exchange, we observed the disappearance of signals attributed to **2a**, and the appearance of signals consistent with the formation of Wilkinson's catalyst (**1**) (Eq. (1))! Similar reactivity was observed for complex **2b**. Both complexes **2a** and **2b** were significantly more

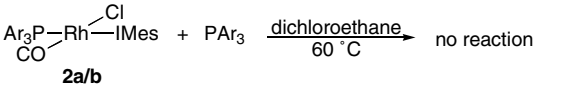


Scheme 1. Preparation of carbene complexes **2** and **3**.

stable in aromatic solvents such as toluene, although Wilkinson's complex does form after extended reaction times ($t_{1/2}$ = 3 weeks at 80 °C) [20]. Carbonyl complex **3** displayed enhanced stability relative to the more crowded and electron rich bisphosphine complexes **2**, with no evidence of decomposition or loss of the carbene ligand even after heating to 80 °C for 100 hrs in dichloroethane.



(1)



(2)

Although the formation of Wilkinson's complex appeared to be relatively clean at 60 °C, there were no signals apparent in the ^{1}H or ^{13}C NMR spectra of these reactions indicating the fate of the carbene. Visual inspection of the reactions showed that a fine precipitate had formed. NMR and mass spectroscopy of the solid material indicated that it was derived from IMes, and was dimeric in nature. Considering the possibility that this compound resulted from liberation of free carbene (**5**) and its subsequent reaction with solvent, we examined the reaction between free carbene and dichloroethane. Dissolving carbene IMes (**5**) in neat dichloroethane at 60 °C gave the same product in 77% isolated yield, the structure of which was confirmed by X-ray crystallographic analysis (Fig. 1, Eq. (3)). Dimer **6** likely results from a double S_N2 reaction between dichloroethane and two molecules of the carbene [21]. The remaining material was IMesHCl (18% yield, 95% mass balance). Remarkably, the reaction of free IMes and the decomposition of the Rh complex gave the same ratio of dimer to IMesHCl within experimental error. Selected crystallographic data and bond lengths for compound **6** are given in Tables 2 and 3.

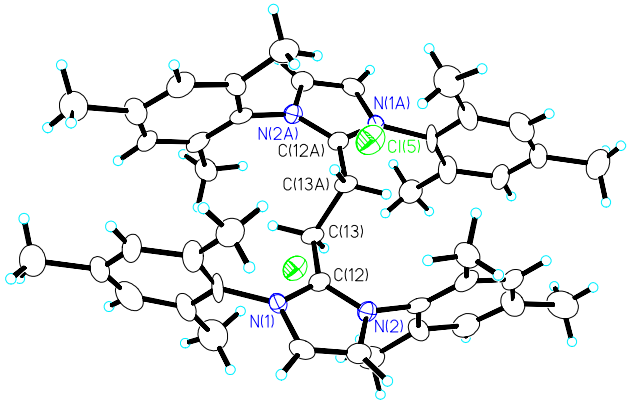


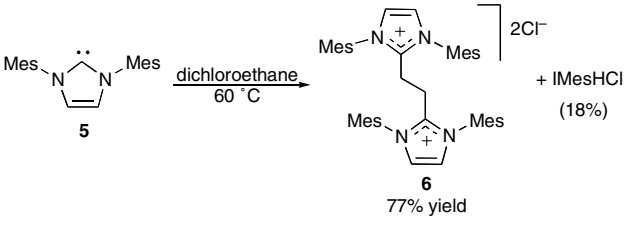
Fig. 1. X-ray structure of $[IMesCH_2CH_2IMes]^{2+}$ $2Cl^-$ (**6**).

Table 2
Crystal data and structure refinement for dication **6**

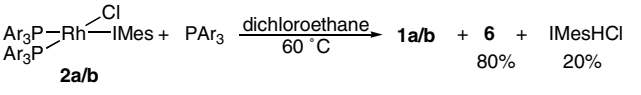
	6
Empirical formula	$C_{52}H_{68}Cl_{10}N_4$ ($C_{44}H_{52}Cl_2N_4 \cdot 2(CH_2)_2Cl_2$)
Formula weight	1103.60
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.266(4)
b (Å)	11.294(5)
c (Å)	14.482(6)
α (°)	100.908(7)
β (°)	105.297(7)
γ (°)	94.929(6)
V (Å^3)	1420.6(10)
Z	1
D_{calc} (Mg/m^3)	1.290
Reflections collected	9519
Independent reflections	6243 (R_{int} = 0.341)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6243/0/416
Goodness-of-fit on F^2	0.921
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0689, wR_2 = 0.1675
R indices (all data)	R_1 = 0.1274, wR_2 = 0.1849

Table 3
Selected bond lengths (Å) and angles (°) for dimer **6**

	6
Bond lengths	
C(12)–C(13)	1.479(5)
C(13)–C(13A)	1.541(7)
N(1)–C(12)	1.348(4)
N(1)–C(10)	1.388(4)
N(2)–C(12)	1.340(4)
N(2)–C(11)	1.401(4)
C(10)–C(11)	1.331(5)
Bond angles	
C(12)–C(13)–C(13A)	111.0(3)
N(2)–C(12)–C(13)	127.4(3)
N(1)–C(12)–C(13)	125.5(3)
N(2)–C(12)–N(1)	107.1(3)
C(12)–N(1)–C(10)	108.8(3)
C(12)–N(2)–C(11)	109.4(3)
C(11)–C(10)–N(1)	108.2(3)
C(10)–C(11)–N(2)	106.5(3)
C(12)–N(2)–C(14)	126.1(3)
C(12)–N(1)–C(1)	127.1(3)



(3)



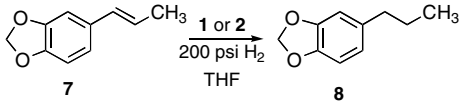
(4)

The stability of carbene complex **2b** was also examined in dichloromethane at 45 °C under inert atmosphere, since this is a more common solvent. Decomposition of complex **2b** and production of Wilkinson's catalyst was also observed. Interestingly, Lebel and co-workers [13a] noted that **2a** was active for the methenylation of aldehydes in THF, but completely inactive when methylene chloride was employed as the solvent. This result may be ascribed to decomposition of the carbene complex.

2.3. Catalytic studies

The hydrogenation of isosafrole (**7**) was examined employing carbene catalyst **2a** and Wilkinson's catalyst **1a** in THF (Eq. 5) [22,23]. At room temperature, catalyst **2a** gave a paltry 2 turnover per hour compared with 40 h^{-1} for Wilkinson's catalyst (**1a**) (Table 4, entries 1 and 2). At higher temperatures, the rate of both reactions increased, but the carbene catalyst was still inferior to Wilkinson's catalyst (50 TO/h for **2a** compared to 250 TO/h for **1a** at 60 °C), presumably because of the decreased rate of phosphine dissociation in the former catalyst, which is essential for catalyst activation in hydrogenations with **1a** [24]. The addition of CuCl, a known phosphine sponge, increases the activity significantly, indicating that phosphine dissociation is critical for the activity of the NHC complexes as well. The addition of one equiv. of CuCl per Rh, increased the activity of **2a** by a factor of 45 (compare entries 2 and 6). CuCl also increases the rate of reaction at 60 °C, but the most notable feature of Table 4 is the effect of dichloroethane at 60 °C. As shown in entry 7, the addition of dichloroethane to the reaction has an accelerating effect presumably by promoting the formation of Wilkinson's catalyst via Eq. (4). Thus the rate of reaction with **2a** increases from 50 TO/h at 60 °C in THF to 110 TO/h in THF with added dichloroethane (compare entries 4 and 7) [25]. This clearly illustrates the difficulty interpreting catalytic activity in solvents where catalyst stability is unknown.

Table 4
Hydrogenation activity of catalysts **1** and **2**[a]



7 **8** (5)

Entry	Catalyst	Temperature (°C)	Additive	TOF[b] (h^{-1})
1	**1**	25	–	40
2	**2a**	25	–	2
3	**1**	60	–	250
4	**2a**	60	–	50
5	**1**	25	CuCl	50
6	**2a**	25	CuCl	90
7	**2a**	60	$ClCH_2CH_2Cl$	110
8	**1**	60	CuCl	300
9	**2a**	60	CuCl	430

[a] Reactions were carried out in an autoclave, under 200 psi of H_2, with 0.75% catalyst, $[substrate]_{init} = 0.1$ M in dry, deoxygenated, distilled THF. Solutions were prepared in a glove box under argon.
[b] Turnover frequency per hour, measured after 30 min.

3. Conclusions

In conclusion, we have demonstrated that the IMes ligand in rhodium complexes **2a** and **b** is completely replaced by phosphine upon treatment with PAr_3 in dichloroethane at slightly elevated temperatures. The displaced carbene reacts with dichloroethane leading to alkylation of the solvent. The product distribution obtained from the reaction of free IMes with dichloroethane is identical to that obtained with the Rh complex, suggesting that the carbene is being displaced from the coordination sphere of rhodium prior to reaction. This reaction has significant implications for reactions involving carbene complexes, since loss of the carbene and formation of new species with greater catalytic activity may hamper the interpretation of results. Thus halogenated solvents such as dichloromethane and dichloroethane pose a threat to the integrity of certain carbene complexes as decomposition of the carbene ligand may occur to a significant extent by removing it from equilibration with the complexed form.

4. Experimental

4.1. General considerations

All the reactions were carried out in a dry Argon or nitrogen atmosphere using standard Schlenk techniques or in an Mbraun glovebox containing less than 1 ppm of oxygen and water. NMR spectra were recorded using Bruker 300, 400 or 500 MHz spectrometers. All reported TOFs were determined by ^1H NMR using hexamethylbenzene as an internal standard.

4.2. Reagents

All solvents were purified by standard procedure and degassed prior to use by 3 freeze/pump/thaw cycles. Isosafrole was purchased from commercial suppliers and distilled and degassed ($3 \times$ fpt) and stored cold in the glovebox. It was passed through a plug of activated basic alumina before each hydrogenation experiment. Wilkinson's catalysts was purchased commercially and used as received. IMesHCl [26], IMes [26], $RhCl((P\text{-}p\text{-}tolyl)_3)_3$ [27] were prepared according to literature procedures.

4.3. Preparation of $[(IMes)Rh(PPh_3)_2Cl]$ (**2a**)

In a 100 ml schlenk flask, IMes (**5**) (185.0 mg, 0.61 mmol) and Wilkinson's catalyst (**1a**) (522.0 mg, 0.56

mmol) were suspended in deoxygenated toluene (50 ml). The resulting purple suspension was stirred at ambient temperature for 16 h. The resulting brown solution was concentrated to ≈10 ml in total volume on the schlenk line and precipitation of a bright yellow powder could be affected by the addition of 40 ml of deoxygenated hexane. The solid was isolated via schlenk filtration and washed with deoxygenated hexane (3 × 15 ml). After drying under vacuum for 5 h, 472.5 mg (87%) of complex **2a** was isolated.

^{1}H NMR (300 MHz, C_6D_6) δ 1.76 (s, 6H), 2.43 (s, 6H), 2.82 (s, 6H), 6.32 (s, 2H), 6.86 (m, 22 H), 7.41 (m,12H).

^{13}C NMR (500 MHz, d_8-thf) δ 20.45, 21.57, 22.38, 124.20, 126.97 (d, $J = 9$ Hz), 127.54 (d, $J = 9$ Hz), 128.06, 128.89, 129.33, 130.37, 135.87 (br), 136.56, 136.78 (br), 138.18, 138.61, 138.90, 139.26, 139.59, 190.50 (ddd, $J_{C-Rh} = 115$ Hz, $J_{C-P(trans)} = 49$ Hz, $J_{C-P(cis)} = 14$ Hz).

^{31}P NMR (300 MHz, C_6D_6) δ 35.70 (dd, $J_{P-Rh} = 120$ Hz, $J_{P-P} = 40$ Hz), 48.78 (dd, $J_{P-Rh} = 207$ Hz, $J_{P-P} = 40$ Hz).

4.4. Preparation of [(IMes)Rh(P-p-tolyl$_3$)$_2$Cl] (**2b**)

In a 50 ml schlenk flask, IMes (**5**) (98 mg, 0.32 mmol) and RhCl((P-*p*-tolyl)$_3$)$_3$ (**1b**) (275.0 mg, 0.26 mmol) were dissolved in deoxygenated toluene (25 ml). The resulting orange solution was stirred at ambient temperature for 16 h. The volatiles were removed on the vacuum line from the resulting yellow solution. Then deoxygenated hexane (30 ml) was added and the residue was triturated against a counter flow of argon. This resulted in a fine yellow precipitate, which was isolated by schlenk filtration and washed with deoxygenated cold hexane (3 × 10 ml) to obtain 214 mg (78%) of **2b**.

^{1}H NMR (500 MHz, C_6D_6) δ 1.87 (s, 6H), 2.01 (s, 9H), 2.06 (s, 9H), 2.50 (s, 6H), 2.89 (s, 6H), 6.40 (s, 2H), 6.74 (m, 12H), 6.93 (s, 2H), 7.20 (s, 2H), 7.41 (br, 12H).

^{13}C NMR (600 MHz, C_6D_6) δ 20.52, 21.44, 21.62, 21.78, 22.76, 123.25, 127.77 (d, $J = 9$ Hz), 128.01 (br), 128.96, 130.31, 135.66, 135.70, 136.64 (br), 137.40, 137.69, 138.10, 139.03, 139.70, 191.66 (ddd, $J_{C-Rh} = 116$ Hz, $J_{C-P(trans)} = 49$ Hz, $J_{C-P(cis)} = 14$ Hz).

^{31}P NMR (500 MHz, C_6D_6) δ 34.26 (dd, $J_{P-Rh} = 120$ Hz, $J_{P-P} = 40$ Hz), 46.69 (dd, $J_{P-Rh} = 207$ Hz, $J_{P-P} = 40$ Hz).

4.5. Preparation of dication 6 from free IMes (**5**)

In a 35 ml pressure tube, IMes (**5**) (52 mg, 0.17 mmol) and deoxygenated 1,2-dichloroethane were mixed. The tube was sealed and the resulting orange solution was heated at 60 °C for 5 days. During this time, white needle like crystals formed while the solution color faded from bright orange, the light orange to a golden brown. The white crystals were collected by schlenk filtration and washed with deoxygenated hexane (3 × 10 ml). After drying under vacuum for 5 h, 46.5 mg (78%) of the dication was isolated as X-ray quality crystals.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 1.83 (s, 24H), 2.49 (s, 12H), 2.57 (s, 4H), 6.99 (s, 8H), 8.21 (s, 4H).

^{13}C NMR (500 MHz, CD_2Cl_2) δ 17.82 (s), 20.74 (s), 21.77 (s), 127.30 (s), 129.52 (s), 131.06 (s), 134.54 (s), 141.62 (s), 142.96 (s).

4.6. Preparation of dication 6 from Rh complex **2b**

In a schlenk NMR tube, Rh-complex **2b** (20 mg, 0.02 mmol), PPh_3 (16 mg, 0.06 mmol) and deoxygenated d_4-1,2-dichloroethane were mixed. The NMR tube was deoxygenated and held under vacuum and then flame sealed. The tube was then heated at 60 °C until no further signals were seen for the **2b**. At this time, the tube was taken into the glovebox and cracked. A small amount of white solid was isolated by filtration and washed with deoxygenated toluene (3 × 1 ml). This was pumped on under vacuum for 12 h. The yield of the dication was 11.4 mg (81%).

4.7. Typical NMR experiment for determination of exchange rate

NMR samples were prepared inside an Argon or Nitrogen filled glove box using tubes fitted with J–Young valves, or in flame sealed tubes. Rh complex **2b** was added into the NMR tube (31.5 mg, 0.03 mmol) along with excess phosphine (3–50 equivalents), and 0.75 ml of solvent. The T_1 of free phosphine and the phosphines in Rh complex **2** were measured at room temperature using the standard inversion recovery method, and a relaxation delay time of $5 \times T_1$ for the largest T_1 was employed for the inversion transfer experiments. The temperature was raised to the desired point, and allowed to equilibrate with the sample in the probe for 15 min before beginning the experiment.

The ^{31}P inversion transfer experiments were performed as follows: a 180° selective pulse was applied to the signal for free phosphine with the transmitter on resonance. Delay times of 0 s to $5 \times T_1$ were applied in increments followed by a 90° read pulse. The data were acquired successively in blocks of four transients at each delay time. The free-induction decays were zero-filled prior to Fourier transformation and a baseline correction routine was applied to the resulting spectra prior to integration of the phosphine signals. The exchange rate of bound and free phosphine was extracted by fitting the integration of these signals at increasing delay times to a two-site exchange model using either Bain's CIFIT program [28], or a programmable

spreadsheet. Error analysis of the calculated exchange rates was performed using the method of Bain and Cramer [28] to yield typical 95% confidence limits of ≈±15%.

4.8. Typical hydrogenation reaction

The Rh catalyst (**1** or **2a**) (0.01 mmol) and isosafrole (1.3 mmol) were loaded into a glassliner and dissolved in 7 ml of THF. This was then placed in a high pressure autoclave and assembled. The autoclave was filled and flushed three times with H_2 before it was finally pressurized to 200 psi. The autoclave was then allowed to stir for 30 min (either at rt or 60 °C). At this time the pressure was released and the autoclave was disassembled. All the contents were then transferred to a 50 ml rbf containing a known amount of hexamethylbenzene as an internal standard. The volatiles were removed under reduced pressure and the residue was analyzed by ^{1}H NMR to determine the % conversion and subsequent TOF.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 246782 for compound **5**. 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)336-033, or E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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[20] Trace amounts of water accelerate production of Wilkinson's catalyst dramatically. All of the experiments described herein are carried out in flame sealed NMR tubes prepared using standard Schlenk techniques and rigorously deoxygenated samples.

[21] Note that the course of this reaction has been debated in the literature. Kuhn has reported that tetramethylimidazol-2-ylidene reacts with $ClCH_2CH_2Cl$ to give 2-chloroimidazolium chloride [9a]. Junk and Jones observed a 50/50 mixture of IMesHBr and 2-bromoimidazolium bromide upon treatment of IMes with $BrCH_2CH_2Br$ [9b]. Since the C–Cl bond is stronger than the C–Br bond, they proposed that the abstraction of chlorine as reported by Kuhn was unreasonable, although it should be noted that different carbenes were employed in the two studies. In order to rule out the presence of 2-chloroimidazolium chloride resulting from Cl abstraction in our reaction, we prepared this compound by reaction of IMes with Cl_6C_2 [9b]. The positions of several of the protons are diagnostic and show definitively that this species is not present in the 60 °C reaction or in the 25 °C reaction. Since there is a considerable difference between the tetramethyl carbene Kuhn employed and IMes which we have employed, a difference in reactivity may be reasonable.

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