

Rh(1,3-bis(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD) tetrafluoroborate, an unsymmetrical Rh-homoazallylcarbene: synthesis, X-ray structure and reactivity in carbonyl arylation and hydrosilylation reactions [☆]

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Abstract

The synthesis of novel Rh(1,3-bis(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD) tetrafluoroborate (**1**, COD = η^4 -1,5-cyclooctadiene) is described. The *N*-heterocyclic carbene acts as a bidentate ligand with the carbene coordinating to the Rh(I) center and an arene group acting as a homoazallyl ligand. **1** was used in various carbonyl arylation and hydrosilylation reactions allowing the formation of the desired products with unprecedented selectivity and efficiency. Thus, turn-over numbers (TONs) up to 2000 were achieved.

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Keywords: *N*-heterocyclic carbenes; Rhodium; Carbonyl arylation; Hydrosilylation

1. Introduction

N-heterocyclic carbenes (NHCs) [1–6] are currently among the most intensively investigated compounds since the corresponding transition metal complexes were found to possess good stabilities and high activities in various catalytic processes [7–14]. Recently, our group [15–21] reported on novel NHC complexes of Ag (I), Pd (II), Rh (I), Ir (I), and Ru (II) based on 1,3-*R*₂-3,4,5,6-tetrahydropyrimidin-2-ylidenes (R = mesityl, 2-

propyl). For carbonyl arylation and hydrosilylation reactions the novel NHC-complexes MX(1,3-*R*₂-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD) (M = Rh, Ir; X = Cl, Br; R = 2-Pr, mesityl; COD = η^4 -1,5-cyclooctadiene) have been used and were found to possess excellent activity [20,21]. However, inspired by fruitful discussions in course of the *International Symposium on Homogeneous Catalysis (ISHC)* in Munich, 2004, we were interested whether the corresponding cationic complexes would allow for even enhanced reactivity and/or selectivity in these reactions. Based on the finding that Rh(CF₃COO)(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD) (**2**) was the most active metal complex in comparison to all other analogues investigated, we aimed on the synthesis of Rh(1,3-bis(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene) tetrafluoroborate (**1**). In the following, its synthesis,

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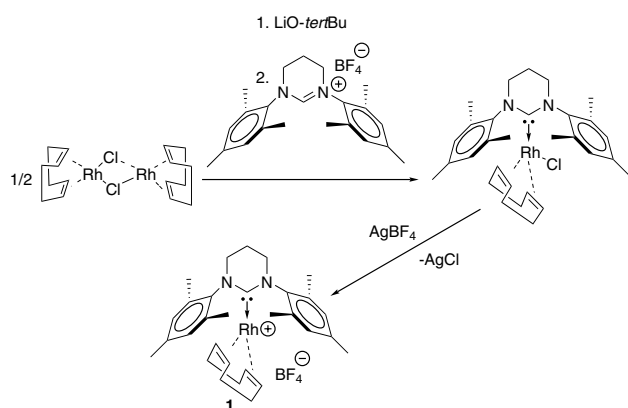
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solid state structure and reactivity in carbonyl arylation and hydrosilylation reactions is described.

2. Results and discussion

2.1. Synthesis and X-ray structure of compound **1**

1,3-Dimesityl-3,4,5,6-tetrahydropyrimidinium tetrafluoroborate was reacted with $[\text{RhCl}(\text{COD})]_2$ to yield $\text{RhCl}(1,3\text{-bis}(2,4,6\text{-trimethylphenyl})\text{-}3,4,5,6\text{-tetrahydropyrimidin-2-ylidene})$ ($\text{COD} = \eta^4\text{-}1,5\text{-cyclooctadiene}$) [17,18], which was subsequently reacted with silver tetrafluoroborate to yield $\text{Rh}(1,3\text{-bis}(2,4,6\text{-trimethylphenyl})\text{-}3,4,5,6\text{-tetrahydropyrimidinium})$ tetrafluoroborate (**1**, Scheme 1). **1** crystallizes in the orthorhombic space group $Pbca$, $a = 1560.31(4)$, $b = 1589.84(3)$, $c = 4790.4(1)$, $\alpha = \beta = \gamma = 90^\circ$, $Z = 16$ with two molecules in the asymmetric unit. These two molecules possess basically identical conformation with only incremental differences in the coordination of the cyclooctadienes (Fig. 1). Relevant structural data, bond angles, and distances are summarized in Tables 1 and 2.



Scheme 1. Synthesis of Rh-complex **1**.

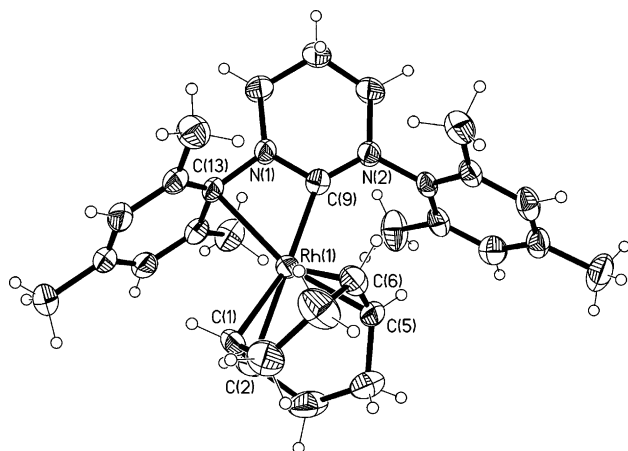


Fig. 1. X-ray structure of compound **1**.

Table 1
Crystal data and structure refinement for **1**

1	
Mol formula	$\text{C}_{30}\text{H}_{40}\text{BF}_4\text{N}_2\text{Rh}$
fw	618.36
Cryst syst	orthorhombic
Space group	$Pbca$ (No. 61)
a (pm)	1560.31(4)
b (pm)	1589.84(3)
c (pm)	4790.4(1)
Unit cell dimensions	
α ($^\circ$)	90
β ($^\circ$)	90
γ ($^\circ$)	90
Vol (nm^3)	11.8833(5)
Z	16
Temp (K)	233(2)
Density (calcd.) (Mg/m^3)	1.383
Abs coeff (mm^{-1})	0.621
Color, habit	orange prism
No. of rflns with $I > 2\sigma(I)$	6016
Goodness-of-fit on F^2	1.020
R indices $I > 2\sigma(I)$	$R_1 = 0.0408$ $\omega R^2 = 0.0786$

The crystal structure of **1** shows some interesting features. The distance $\text{Rh}(1)\text{-C}(9)$ is 204.0(4) pm, somewhat shorter than the one found in **2** (206.5(8)) [21]. However, the cationic Rh-center is stabilized by a homoallyl bonding to the arene, as evidenced by a comparably short distance $\text{Rh}(1)\text{-C}(13)$ of 237.7(4) pm. In due consequence, the angle $\text{N}(1)\text{-C}(9)\text{-Rh}(1)$ is reduced to $101.5(3)^\circ$, compared to $119.6(5)^\circ$ in **2** [21]. The distances $\text{Rh}(1)\text{-C}(5)$, $\text{Rh}(1)\text{-C}(6)$, $\text{Rh}(1)\text{-C}(1)$,

Table 2
Bond lengths (pm) and angles ($^\circ$) for **1**

$\text{Rh}(1)\text{-C}(9)$	204.0(4)
$\text{Rh}(1)\text{-C}(6)$	209.6(5)
$\text{Rh}(1)\text{-C}(5)$	211.9(5)
$\text{Rh}(1)\text{-C}(2)$	222.5(5)
$\text{Rh}(1)\text{-C}(1)$	223.9(5)
$\text{Rh}(1)\text{-C}(13)$	237.7(4)
$\text{N}(2)\text{-C}(9)\text{-Rh}(1)$	139.7(3)
$\text{N}(1)\text{-C}(9)\text{-Rh}(1)$	101.5(3)
$\text{C}(9)\text{-Rh}(1)\text{-C}(6)$	96.06(18)
$\text{C}(9)\text{-Rh}(1)\text{-C}(5)$	102.06(19)
$\text{C}(6)\text{-Rh}(1)\text{-C}(5)$	38.28(19)
$\text{C}(9)\text{-Rh}(1)\text{-C}(2)$	163.7(2)
$\text{C}(6)\text{-Rh}(1)\text{-C}(2)$	96.2(2)
$\text{C}(5)\text{-Rh}(1)\text{-C}(2)$	81.3(2)
$\text{C}(9)\text{-Rh}(1)\text{-C}(1)$	158.8(2)
$\text{C}(6)\text{-Rh}(1)\text{-C}(1)$	81.4(2)
$\text{C}(5)\text{-Rh}(1)\text{-C}(1)$	88.99(19)
$\text{C}(2)\text{-Rh}(1)\text{-C}(1)$	35.11(19)
$\text{C}(9)\text{-Rh}(1)\text{-C}(13)$	62.20(17)
$\text{C}(6)\text{-Rh}(1)\text{-C}(13)$	132.82(18)
$\text{C}(5)\text{-Rh}(1)\text{-C}(13)$	163.32(18)
$\text{C}(2)\text{-Rh}(1)\text{-C}(13)$	115.37(19)
$\text{C}(1)\text{-Rh}(1)\text{-C}(13)$	104.31(18)

Rh(1)–C(2) are 211.9(5), 209.6(5), 223.9(5) and 222.5(5) pm, respectively, are significantly longer than the Rh–COD distances found in **2** (208.2(8), 209.3(8), 216.6(11) and 219.5(11) pm, respectively). To the best of our knowledge, this is the only example of an originally symmetrical carbene forming an unsymmetrical homoazallylcarbene-complex of Rh(I) in the solid state. In contrast to these findings, the room temperature ^1H and ^{13}C NMR solution spectrum of **1**, recorded either in THF- d_8 or CDCl_3 does not show any further additional coordination of the arene ligand. In due consequence, both mesityl groups are chemically and magnetically equivalent. Since Herrmann et al. were able to identify the unsymmetrical structure of $\text{Cr}(\text{CO})_4(\text{C}(\text{N}-(2\text{-Pr})_2)_2)$ [22], we recorded a spectrum at -60°C in CDCl_3 . However, it was identical to the one obtained at room temperature, indicating a symmetrical structure.

2.2. Catalytic activity of compound **1** in carbonyl arylation reactions

Excellent summaries on both the synthesis and use of transition metal NHC complexes have been given elsewhere [7,8,10,23,24]. In terms of carbonyl arylation reactions (Scheme 2), originally reported by Miyaoura et al. [25,26], Rh(III) (NHC) complexes have been used by Fürstner [27], the use of Rh(I) (NHC) complexes has been reported by our group [20].

As already briefly mentioned particularly the use of **2** gave raise to arylation reactions with TONs up to 1200 [20]. With one exception (Table 3, entry 5), the use of **1** under conditions identical to the ones reported previously gave raise to enhanced turn-over numbers, exceeding the previously reported ones up to a factor of 3.

Important enough, the reactivity of **1** is by far higher than the one observed with other cationic Rh(I) and Rh(III) complexes, respectively [28]. In terms of product selectivity, no changes were observed in the reaction of 2-hydroxybenzeneboronic acid with an aldehyde, resulting exclusively in the formation of the thermodynamically favored 2-hydroxy-ketone. The same accounts for the reaction of arylboronic acids with cyclohex-2-en-1-one, proceeding exclusively via 1,4-addition to yield the corresponding ketone. However, different selectivity was observed in reactions involving electron-poor aryl

aldehydes (Table 3, entries 1, 5 and 7). Significant amounts of the ketone were formed in these reactions. Apparently, the cationic, electron deficient complex **1** favors the catalytic oxidation of the corresponding secondary alcohols formed in course of the reaction.

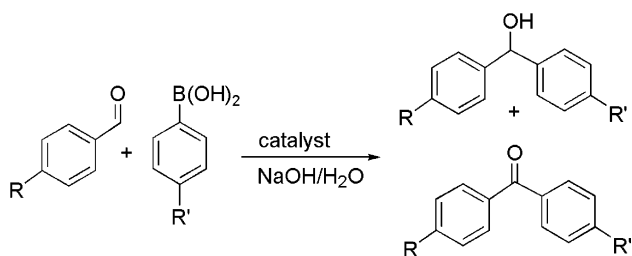
2.3. Catalytic activity of compound **1** in hydrosilylation reactions

Hydrosilylation (or hydrosilation) reactions involve the addition of inorganic or organic silicon hydrides to multiple bonds such as alkyne, alkene, ketoxime and carbonyl groups (Scheme 3). For hydrosilylations promoted by transition metal complexes, as is the case in the present report, the (modified) Chalk–Harrod mechanism [29,30] is still the generally accepted one, however, other mechanisms have been suggested recently [31–33]. Among the various transition metals most commonly employed in hydrosilylation reactions [33–37], Rh is certainly a prominent one. Various NHC complexes of Rh have been used so far, however, with the exception of **2** [21], Rh-1,3- R_2 -imidazol-2-ylidenes (R = mesityl, etc.) have been used almost exclusively [10,12,38–47]. In comparison to **2**, the new cationic catalyst **1** shows some interesting features. As can be deduced from Table 4, entries 1–7 and 8–10, respectively, both the reactivity and selectivity of novel **1** in the hydrosilylation of alkynes and 1-alkenes, respectively, is comparable to the one of **2**. However, increased reactivity is observed in the hydrosilylation of cyclohex-2-en-1-one (Table 4, entries 11–12). TONs twice as high as found with **2**, yet identical selectivity were observed. Thus, as for **2**, reactions catalyzed by **1** proceeded again selectively via 1,4-addition ($\text{C}=\text{O}$ hydrosilylation) to produce the corresponding silylethers. Finally, **1** can be used in the $\text{C}=\text{O}$ hydrosilylation of aldehydes and ketones (Table 4, entries 13–15), resulting in the formation of the corresponding silylethers.

3. Experimental

All manipulations were performed under a nitrogen atmosphere in a glove box (MBraun LabMaster 130) or by standard Schlenk techniques. Purchased starting materials were used without any further purification. Pentane and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl under nitrogen. Methylene chloride was distilled from calcium hydride.

NMR data were obtained at 300.13 MHz for proton and 75.74 MHz for carbon in the indicated solvent at 25°C on a Bruker Spectrospin 300 and are listed in parts per million downfield from tetramethylsilane for proton and carbon. Coupling constants are listed in Hz. IR spectra were recorded on a Mattson Instruments Galaxy Series FT-IR 3000. Elemental analyses were carried out



Scheme 2. Carbonyl arylation reactions.

Table 3
Arylation of carbonyl compounds with Rh(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD) BF₄

#	Educt	Product	Mol% cat. (yield)	TON ^a	Alcohol:Ketone ^a
1	4-F-Benzaldehyde/2-Thienylboronic acid		0.05 (52)	1040 (760)	12:88 (71:29)
2	4-F-Benzaldehyde/4-MeO-Benzeneboronic acid		0.05 (65)	1300 (950)	99:1 (100:0)
3	2-OH-Benzaldehyde/4-MeO-Benzeneboronic acid		0.05 (35) ^b	700 (375)	0:100 (0:100)
4	Cyclohex-2-en-1-one/4-MeO-Benzeneboronic acid		0.05 (33) ^b	660 (590)	0:100 (0:100)
5	4-F-Benzaldehyde/4-Me-Benzeneboronic acid		0.05 (40)	800 (1230)	0:100 (100:0)
6	2-OH-Benzaldehyde/4-Methylbenzeneboronic acid		0.05 (30) ^b	600 (420)	0:100 (0:100)
7	4-F-Benzaldehyde/4-Vinylbenzeneboronic acid		0.05 (68)	1360 (1230)	77:23 (100:0)
8	2-OH-Benzaldehyde/4-Vinylbenzeneboronic acid		0.05 (53) ^b	1060 (340)	0:100 (0:100)
9	Benzaldehyde/4-Methoxybenzeneboronic acid		0.05 (50)	1000	98:2

Reaction time: 8 h, $T = 80\text{ }^{\circ}\text{C}$.

^a Values in brackets are the one reported for **2** [20].

^b Reaction time: 20 h.

Table 4
Hydrosilylation of unsaturated compounds with Rh(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD) BF₄

#	Educt	Product	Mol% cat. (yield)	β -trans (%) ^b	β -cis (%) ^b	α (%) ^{a,b}	TON ^b
1	Diphenylacetylene/Triethylsilane		0.05 (69)	–	–	–	1380 (780)
2	Phenylacetylene/Triethylsilane		0.05 (30)	62	11	27	600
3	Trimethylsilylacetylene/Trimethoxysilane		0.05 (18)	77 (77)	0 (0)	23 (23)	360 (210)
4	Phenylacetylene/Dichlormethylsilane		0.05 (38)	53 (46)	28 (38)	19 (16)	760 (810)
5	1-Hexyne/Triethylsilane		0.05 (53)	56 (61)	8 (11)	36 (27)	1060 (890)
6	1-Hexyne/Triphenylsilane		0.05 (9)	0 (0)	92 (99)	8 (1)	180 (340)
7	1-Hexyne/Dichlormethylsilane		0.05 (36)	100 (100)	0 (0)	0 (0)	720 (900)
8	Styrene/Triethylsilane		0.05 (40)	–	–	–	800 (460)
9	1-Hexene/Triethylsilane		0.05 (36)	–	–	–	720 (180)
10	1-Octene/Triethylsilane		0.05 (12)	–	–	–	240(100)
11	Cyclohex-2-en-1-one/Triethylsilane		0.05 (100)	–	–	–	2000(1000)
12	Cyclohex-2-en-1-one/Triphenylsilane		0.04 (36)	–	–	–	900(310)

(continued on next page)

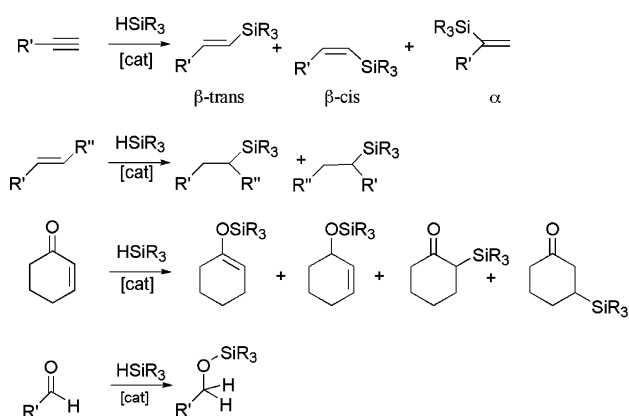
Table 4 (continued)

#	Educt	Product	Mol% cat. (yield)	β -trans (%) ^b	β -cis (%) ^b	α (%) ^{a,b}	TON ^b
13	4-Chloroacetylaldehyde/ Triethylsilane		0.05 (17)	–	–	–	340(300)
14	Benzaldehyde/Triethylsilane		0.05 (17)	–	–	–	340
15	4-F-Benzaldehyde/Triethylsilane		0.05 (37)	–	–	–	740

Reaction time: 12 h, $T = 80\text{ }^{\circ}\text{C}$.

^a Different positional numbers for the substituents according to Scheme 2 apply.

^b Values in brackets are the one reported for **2** [21].



Scheme 3. Hydrosilylation reactions.

at the Mikroanalytisches Labor, Anorganisch-Chemisches Institut, TU München, Germany.

3.1. *Rh*(1,3-bis(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydropyrimidinium)(COD) tetrafluoroborate (**1**)

RhCl(1,3-bis(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydropyrimidinium)(COD) (40.6 mg, 72 μmol) was dissolved in 1 mL of THF, the solution was cooled and silver tetrafluoroborate (14.0 mg, 72 μmol), dissolved in 3 mL of THF, was added slowly. The mixture was stirred at room temperature for 1 h. The mixture was filtered through celite, which was washed twice with THF (0.5 mL each). The solution was dried in vacuo yielding an orange-yellow powder (quantitative conversion). A crystal of **1** suitable for X-ray analysis was obtained by cooling a concentrated THF solution to $-40\text{ }^{\circ}\text{C}$ for several days. FT-IR (KBr, cm^{-1}): 2938 (m), 2919 (m),

2884 (m), 2831 (w), 1603 (w), 1537 (s), 1480 (s), 1456 (w), 1435 (w), 1380 (w), 1336 (m), 1308 (m), 1207 (w), 1085 (s), 1058 (s), 963 (w), 862 (w), 519 cm^{-1} (w); ¹H-NMR (CDCl_3) δ 6.93 (br s, 4H, aromatic H), 3.37 (t, 4H, NCH_2 , ³ $J(\text{H,H}) = 5.71$), 3.34 (m, 2H, CH_{COD}), 2.67 (m, 2H, CH_{COD}), 2.49 (br s, 12H, mesityl-ortho- CH_3), 2.35 (quint, 2H, CH_2 , ³ $J(\text{H,H}) = 5.71$), 2.27 (br s, 6H, mesityl-para- CH_3), 2.17–1.88 (m, 4H, CH_2 COD), 1.69–1.53 ppm (m, 4H, CH_2 COD); ¹³C NMR (CDCl_3) δ 174.4 (d, NCN, ¹ $J(^{103}\text{Rh},^{13}\text{C}) = 35.3$), 141.6, 137.2, 131.0, 127.9 (s, aromatic C), 99.7 (d, CH_{COD} , ¹ $J(^{103}\text{Rh},^{13}\text{C}) = 7$), 70.7 (d, CH_{COD} , ¹ $J(^{103}\text{Rh},^{13}\text{C}) = 15$), 49.2 (s, NCH_2), 33.6 (s), 27.6 (s), 21.5 (br), 21.2 (br) (CH_2 , mesityl- CH_3), 18.8 (br, CH_2 COD). Elemental Anal. Calcd. for $\text{C}_{30}\text{H}_{40}\text{BF}_4\text{N}_2\text{Rh}$: C, 58.27; H, 6.52; N, 4.53. Found: C, 57.71; H, 6.38; N, 4.37%.

3.2. Standard procedure for the reaction of an arylboronic acid with a carbonyl compound

The catalyst (for the amount refer to Table 3) and arylboronic acid (0.53 mmol) were dissolved in DME (2.2 mL). Tetradecane (0.7 equiv. with respect to the arylboronic acid) as an internal standard as well as the carbonyl compound (1 equiv. with respect to the arylboronic acid), sodium hydroxide (2 equiv. with respect to the arylboronic acid) and water (0.6 mL) were added. The mixture was stirred at $80\text{ }^{\circ}\text{C}$ until no further conversion was monitored by GC–MS. Yields and turn over numbers (TONs) were determined by GC–MS using both the conversion of the educts and the peak areas of standard solutions of the products. Isolation and properties of the products is described elsewhere [20,21].

3.3. Standard procedure for hydrosilylation reactions

The catalyst (for the amount refer to Table 4) was dissolved in DME (2 mL). Tetradecane (100 μ L) was added as an internal standard followed by the silane (0.50 mmol) and the unsaturated compound (alkyne-, alkene- or carbonyl compound, 0.50 mmol). The mixture was stirred at 80 °C until no further conversion was monitored by GC–MS. Yields and turn over numbers (TONs) were determined by GC–MS using both the conversion of the educts and the peak areas of standard solutions of the products. Isolation and properties of the products is described elsewhere [20,21]. For the alkyne compounds the ratio of the product isomers was determined by integration of the GC–MS peaks. These were correlated with the results taken from NMR-measurements.

For NMR-measurements, the solvent of the reaction mixture was removed in vacuo and the residue was taken up in CDCl_3 . Integration of the olefinic region provided the ratio of the product isomers of the reaction of an alkyne compound with a silane. Concerning the reaction of the α,β -unsaturated carbonyl compound with a silane, the 1,4-addition was confirmed by NMR, the lack of olefinic proton-signals and the appearance of a singlet around 5 ppm.

3.4. X-ray measurement and structure determination of **1**

Data collection was performed on a Nonius Kappa CCD equipped with graphite-monochromatized Mo $K\alpha$ -radiation ($\lambda = 0.71073 \text{ \AA}$) and a nominal crystal to area detector distance of 55 mm. Intensities were integrated using DENZO and scaled with SCALEPACK [48]. Several scans in ϕ and ω direction were made to increase the number of redundant reflections, which were averaged in the refinement cycles. This procedure replaces in a good approximation an empirical absorption correction. The structures were solved with direct methods SHELXS86 and refined against F^2 SHELXL97 [49]. The function minimized was $\sum[w(F_o^2 - F_c^2)^2]$ with the weight defined as $w^{-1} = [\sigma^2(F_o^2) + (xP)^2 + yP]$ and $P = (F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic displacement parameters. Positions of hydrogen atoms were calculated except for those at the double bonds of COD, which were refined isotropically with bond restraints ($d = 0.95 \text{ \AA}$).

4. Summary

In summary, we have developed a new cationic Rh (I) catalyst based on a novel *N*-heterocyclic carbene (1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene), suitable for carbonyl arylation and hydrosilylation reactions. The new cationic compound exceeds other active Rh

(I) catalysts based on the same *N*-heterocyclic carbene in activity up to a factor of 3. In addition, different selectivities are observed. Particularly in hydrosilylation reactions of α,β -unsaturated ketones, one can now perform chemo- and regioselective reactions with both the new catalyst **1** and the parent compound **2**.

Acknowledgement

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Appendix A. Supplementary data

The crystallographic data for **1** have been deposited with the CCDC-No. 248426, and on the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2004.11.057.

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