Journal of Organometallic Chemistry 696 (2011) 687–692

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Bridge functionalized bis-N-heterocyclic carbene rhodium(I) complexes and their application in catalytic hydrosilylation

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ARTICLE INFO

Article history:
Received 2 July 2010
Received in revised form
20 September 2010
Accepted 22 September 2010
Available online 1 October 2010

Keywords:
N-Heterocyclic carbene
Bridge functionalization
Rhodium
Hydrosilylation (hydrosilation)

ABSTRACT

A series of chelating bridge functionalized bis-*N*-heterocyclic carbenes (NHC) complexes of rhodium (I) were prepared by reacting the corresponding imidazolium salts with $[Rh(COD)Cl]_2$ in an *in-situ* reaction. For the *N*-methyl substituted complex with a PF_6-anion an X-ray crystal structure was exemplary obtained. All complexes were spectroscopically characterized and tested for the hydrosilylation of acetophenone.

1. Introduction

NHC metal complexes [1–4] have found widespread applications in a multitude of catalytic transformations such as Heck-, Suzuki- and Sonogashira reactions, aryl amination or metathesis [5], in carbon monoxide/ethylene copolymerization [6] and hydrosilylation [7]. *N*-heterocyclic carbenes as ligands in organometallic complexes act as strong σ-donors and weak π-acceptors. In many cases NHC complexes are air- and moisture stable and show high thermal stability. Especially chelating bis-NHC complexes of Pd and Pt exhibit extreme thermal and moisture stable complexes, leading to remarkable catalytic properties [8].

In recent years the interest in "green" environmentally benign chemistry has been continuously increasing. In this context, the immobilization of NHC metal complexes on insoluble supports to facilitate their reuse and recycling is emerging as a preferable alternative for the application of homogeneous catalysis, which usually requires energy intensive processes to separate the catalyst from the product [9]. In order to achieve immobilization more easily a functional group is attached to the complexes to allow a connection to the surface. Ligands with tethered hydroxy groups have been successfully utilized for the immobilization of other catalysts before [10], usually accounting for quite low leaching [11]. This concept was applied to synthesize novel hydroxy-functionalized bridged bis-carbene complexes.

2. Experimental

Unless otherwise stated, all reactions were performed under a dry argon atmosphere using standard Schlenk techniques. Solvents and substrates were dried by standard procedures, distilled under an argon atmosphere and stored over molecular sieves. 1,3-dibromo-propane-2-ol was purchased from Acros and used without further purification. ^{1}H, $^{13}C\{^{1}H\}$, ^{19}F and ^{31}P-NMR spectra were recorded on a JEOL-JMX-GX 400 MHz spectrometer at 25 °C. ^{1}H-NMR peaks are assigned as singlet (s), doublet (d), triplet (t), multiplet (m). Mass spectrometric measurements were performed on a Finnigan MAT 90 spectrometer using the FAB technique. Elemental analyses were performed in the Microanalytical Laboratory at the TU München. Compounds **1a**–**3a** were prepared according to a modified literature procedure. The spectroscopic date of compounds **1a** and **3a** identical to those reported in the literature [12].

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doi:10.1016/j.jorganchem.2010.09.049

2.1. General procedure for bridged bis-imidazoliumbromide salts (**1a**–**3a**)

In an ACE pressure tube 25 mmol 1-*R*-imidazole (R = methyl, isopropyl, benzyl) and 10 mmol 1,3-dibromo-propane-2-ol are dissolved in 5 ml THF at room temperature. After stirring the solution over night, the reaction mixture is heated for 72 h at 100 °C. After cooling to room temperature the reaction solution is filtered off and the precipitate washed twice with 5 ml THF. Drying under reduced pressure leaves compound **1**–**3** as off-white solids.

2.1.1. 1,1′-(2-Hydroxy-1,3-propanediyl)bis[3-isopropyl-1H-imidazolium]dibromid **2a**

Yield: 96%.^{1}H-NMR(400 MHz, 298 K, d_6-DMSO): δ = 9.28 (2H, s, NC*H*N), 7.94 (2H, S, NC*H*), 7.78 (2H, S, NC*H*), 5.95 (1H, d, $^3J_{H\text{-}OH}$ = 5.6 Hz, O*H*), 4.67 (2H, sept, CH_{iPr}), 4.40 (2H, d, ^3J = 13.6 Hz, CH_2), 4.25 (1H, m, C*H*), 4.12 (2H, dd, ^2J = 8 Hz, ^3J = 13.6 Hz, CH_2), 1.46 (12H, d, CH_3). ^{13}C{^{1}H}-NMR(100 MHz, 298 K, d_6-DMSO): δ = 135.4 (NCHN), 123.1 (NCH), 120.3 (NCH), 67.5 (*C*-H), 52.2 (CH_{iPr}), 51.9 (NCH_2) 22.2 (CH_3). MS (FAB): *m*/*z* (%): 356.9 (40, [M-Br]$^+$), 277.0 (34, [M-2xBr]$^+$). Anal. Calc for $C_{37}H_{52}Br_2N_4O$: C 41.11; H 5.98; N 12.79. Found: C 40.64; H 6.09; N 12.65%.

2.2. General procedure for the PF_6-Salts (**1b**–**3b**)

The corresponding bromine salts **1a**–**3a** were dissolved in a minimum amount of water and added to a saturated solution of KPF_6 in water. The precipitated imidazolium hexafluorophosphate salts are filtered off, washed with water and diethylether and dried under vacuum yielding the imidazolium salts **1b**–**3b**.

2.2.1. 1,1′-(2-Hydroxy-1,3-propanediyl)bis[3-methyl-1H-imidazolium]di(hexafluorophosphate)**1b**

Yield: 51%. ^{1}H-NMR(400 MHz, 298 K, d_6-Aceton): δ = 9.00 (2H, s, NC*H*N), 7.72 (4H, d, NC*H*), 5.50 (1H, d, O*H*), 4.71 (2H, d, NCH_2), 4.56 (1H, m, C*H*), 4.42 (2H, dd, CH_2), 4.07 (6H, s, NCH_3). ^{13}C{^{1}H}-NMR(100 MHz, 298 K, d_6-Aceton): δ = 138.0 (NCHN), 124.6 (NCH), 124.0 (NCH), 69.2 (*C*-H), 53.1 (NCH_2) 36.5 (NCH_3). ^{31}P{^{1}H}-NMR(161 MHz, 298 K, d_6-Aceton): δ = − 130.5 to − 158.0. MS (FAB): *m*/*z* (%): 367 (75, [M-PF_6]$^+$), 221 (100, [M-2xPF_6]$^+$). Anal. Calc for $C_{11}H_{18}F_{12}N_4OP_2$*2KBr: C 17.61; H 2.42; N 7.47. Found: C 17.84; H 2.42; N 7.33%.

2.2.2. 1,1′-(2-Hydroxy-1,3-propanediyl)bis[3-isopropyl-1H-imidazolium]di(hexafluorophosphate) **2b**

Yield: 59%.^{1}H-NMR(400 MHz, 298 K, d_6-Aceton): δ = 9.21 (2H, s, NC*H*N), 7.89 (2H, d, NC*H*), 7.77 (2H, d, NC*H*), 5.91 (1H, s, O*H*), 4.67 (2H, sept, CH_{iPr}), 4.48 (2H, d, NCH_2), 4.26 (1H, m, C*H*), 4.17 (2H, dd, CH_2), 1.48 (12H, s, NCH_3). ^{31}P{^{1}H}-NMR(161 MHz, 298 K, d_6-Aceton): δ = − 131.0 to − 157.0. Anal. Calc for $C_{15}H_{26}F_{12}N_4OP_2$*1/2 KBr: C 28.70; H 4.17; N 8.92. Found: C 28.79; H 4.32; N 8.93%.

2.2.3. 1,1′-(2-Hydroxy-1,3-propanediyl)bis[3-benzyl-1H-imidazolium]di(hexafluorophosphate) **3b**

Yield: 75%.^{1}H-NMR(400 MHz, 298 K, d_6-Aceton): δ = 9.17 (2H, s, NC*H*N), 7.75 (2H, d, NC*H*), 7.48 (2H, d, NC*H*), 7.43 (10H, m, H_{Ar}), 5.58 (5H s, br, 1H-OH + 4H-CH_2-Ph), 4.69 (2H, d, NCH_2), 4.53 (1H, m, C*H*), 4.41 (2H, dd, CH_2).^{31}P{^{1}H}-NMR(161 MHz, 298 K, d_6-Aceton): δ = − 130.0 to − 158.0. MS (FAB): *m*/*z* (%): 518.5 (100, [M-PF_6]$^+$), 373 (72, [M-2xPF_6]$^+$). Anal. Calc for $C_{23}H_{26}F_{12}N_4OP_2$: C 41.58; H 3.94; N 8.43. Found: C 41.52; H 3.85; N 8.49%.

2.3. Synthesis procedure for the BPh_4-Salt **3c**

The corresponding bromine salt **3a** was suspended in acetone and a saturated solution of $KBPh_4$ in acetone was added. After a few minutes a precipitate yields in the corresponding tetraphenylborate salt. The solid was filtered off and washed with water, diethylether and pentane and dried under vacuum to yield the imidazolium salt **3c** in 72%.

2.3.1. 1,1′-(2-Hydroxy-1,3-propanediyl)bis[3-benzyl-1H-imidazolium]di(tetraphenylborate) **3c**

^{1}H-NMR(400 MHz, 298 K, d_6-Aceton): δ = 8.77 (2H, s, NC*H*N), 7.57 (4H, s, NC*H*), 7.40 (20H, d, H_{Ar}), 6.89 (20H, m, H_{Ar}),6.75 (10H, m, H_{Ar}), 5.39 (4H, s, NCH_2-Ph), 4.42 (2H + 1H, m, NCH_2 + C*H*), 4.20 (dd, 2H, NCH_2). MS (FAB): *m*/*z* (%): 693 (15, [M-BPh_4]$^+$), 373 (60, [M-2x BPh_4]$^+$). Anal. Calc for $C_{23}H_{26}B_2N_4O$*1/2 KBr: C 79.52; H 6.20; N 5.22. Found: C 79.62; H 6.13; N 4.98%.

2.4. General procedure for the chelating bis(NHC)-Rh(I) complexes (**4**–**7**)

NaH and $[Rh(COD)Cl]_2$ were each dissolved in ethanol and the solutions were combined and stirred for 30 min at room temperature. The clear, yellow solution was added via canula to the hexafluorophosphate salts (complexes **4**–**6**) respectively tetraphenylborate salt (complex **7**) was added and the mixture was stirred for 16 h. After reaction, ethanol was removed under vacuum and the complexes were extracted with dichloromethane. Recrystallization from a saturated DCM-solution with diethylether yields in the rhodium complexes **4**–**7** as yellow solids. Crystals suitable for X-ray diffraction studies of complex **4** could be obtained by slowly diffusion of pentane into a dichloromethane solution of complex **4**.

2.4.1. $[Rh(Me\text{-}Im)_2(COD)](PF_6)$ **4**

Yield: 30%. ^{1}H -NMR(400 MHz, 298 K, d_2-DCM): δ = 6.97 (2H, d, NC*H*), 6.77 (2H, d, NC*H*), 4.97 (2H, d, NCH_2), 4.54 (4H, m, CH_2-COD), 4.44 (1H, m, C*H*), 4.30 (2H, dd, NCH_2), 3.89 (6H, s, NCH_3), 2.45 (4H, m, CH_2-COD), 2.25 (4H, m, CH_2-COD). ^{13}C{^{1}H}-NMR(100 MHz, 298 K, d_2-DCM): δ = 183.2 C_{Carben}, 125.5 (NCH), 121.6 (NCH), 90.3 (COD), 67.0 (*C*-H), 55.9 (NCH_2), 35.1 (NCH_3), 30.9 (COD). ^{31}P{^{1}H}-NMR(161 MHz, 298 K, d_2-DCM): δ = − 130.5 to − 158.0. MS (FAB): *m*/*z* (%): 431 (100, [M-PF_6]$^+$), 323 (70, [M-PF_6-COD]$^+$). Anal. Calc for $C_{19}H_{28}F_6N_4OPRh$: C 39.60; H 4.90; N 9.72. Found: C 39.18; H 4.70; N 9.30%.

2.4.2. $[Rh\ (^iPr\text{-}Im)_2(COD)](PF_6)$ **5**

Yield: 45%. ^{1}H-NMR(400 MHz, 298 K, d_2-DCM): δ = 7.29 (2H, d, NC*H*), 6.75 (2H, d, NC*H*), 5.11 (2H, d, NCH_2 + 1H C*H*), 4.84 (2H, sept., CH_{iPr}), 4.55 (4H, m, CH_2-COD), 4.13 (2H, dd, NCH_2), 2.38 (4H, m, CH_2-COD), 2.21 (4H, m, CH_2-COD), 1.37 (12H, d, CH_3). ^{13}C{^{1}H}-NMR (100 MHz, 298 K, d_2-DCM): δ = 179.7 C_{Carben}, 125.4 (NCH), 115.8 (NCH), 90.1 (COD), 65.0 (*C*-H), 59. 6 (*C*-H), 52.4 (NCH_2), 30.9 (COD), 23.8 (CH_3). MS (FAB): *m*/*z* (%): 487 (100, [M-PF_6]), 379 (100, [M-PF_6-COD]). Anal. Calc for $C_{23}H_{36}F_6N_4OPRh$: C 43.68; H 5.74; N 8.86. Found: C 43.12; H 6.12; N 8.72%.

2.4.3. $[Rh(Bn\text{-}Im)_2(COD)](PF_6)$ **6**

Yield: 28%. ^{1}H-NMR(400 MHz, 298 K, d_2-DCM): δ = 7.35 (6H, m, H_{Ar}), 7.11 (2H, d, NC*H*), 6,83 (4H, m, H_{Ar}), 6.64 (4H, d, NC*H*), 5.64 (2H, d, Ph-NCH_2), 5.12 (2H, d, Ph-NCH_2), 4.86 (1H, m, C*H*), 4.64 (4H, m, CH_2-COD + NCH_2), 4.48 (4H, m, CH_2-COD + NCH_2), 2.47 (4H, m, CH_2-COD), 2.25 (4H, m, CH_2-COD). MS (FAB): *m*/*z* (%): 582 (100, [M-PF_6]$^+$), 474 (81, [M-PF_6-COD]$^+$). Anal. Calc for $C_{31}H_{36}F_6N_4OPRh$: C 51.11; H 4.91; N 7.46. Found: C 50.27; H 4.98; N 7.69%.

2.4.4. $[Rh(Bn\text{-}Im)_2(COD)](BPh_4)$ **7**

Yield: 37%. ^{1}H-NMR(400 MHz, 298 K, d_6-Aceton): δ = 7.37 (20H, m, H_{Ar}), 7.04 (2H, s, NC*H*), 7.05 (10H, m, H_{Ar}), 7.04 (2H, s, NC*H*), 5.58 (4H, s, NCH_2-Ph), 4.77 (2H + 1H, m, NCH_2 + C*H*), 4.57 (4H, m, CH_2-COD), 4.35 (dd, 2H, NCH_2), 2.44 (4H, m, CH_2-COD), 2.24 (4H, m,

CH_2-COD). MS (FAB): *m/z* (%): 583 (100, $[M\text{-}BPh_4]^+$), 475 (90, $[M\text{-}BPh_4\text{-}COD]^+$). Anal. Calc for $C_{55}H_{56}BN_4ORh$*1/2 DCM: C 70.52; H 6.08; N 5.93. Found: C 69.94; H 6.39; N 5.15%.

2.5. Catalysis–hydrosilation of 4-fluoro-acetophenone

4-fluoro-acetophenone (0.504 mmol) and the rhodium complex (0.02 mmol) in 0.3 mL solvent (DCM, THF or DCE) were stirred for 10 min. Diphenylsilane (0.765 mmol) was added and the mixture stirred at 25 °C (60 °C) and monitored by ^{19}F-NMR spectroscopy.

2.6. Single crystal X-ray structure determination of compound **4**

Crystal data and details of the structure determination are presented in Tables 1 and 2. Suitable single-crystals for the X-ray diffraction study were grown with standard cooling techniques. Crystals were stored under perfluorinated ether and fixed on the top of a glass fiber. Preliminary examination and data collection were carried out on an area detecting system (BRUKER AXS, APEX II, κ-CCD; FR591 rotating anode) and graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The unit cell parameters were obtained by full-matrix least-squares refinements during the scaling procedure. Data collection was performed at 123 K (OXFORD CRYOSYSTEMS cooling device). The crystal was measured with a couple of data sets (five runs; 3065 frames) in rotation scan modus ($\Delta\varphi/\Delta\omega = 0.50°$; dx = 35 mm). Intensities were integrated and the raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure for latent decay and absorption effects. The structure was solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. Methyl hydrogen atoms were calculated as a part of rigid rotating groups, with $d_{C-H} = 0.98$ Å and $U_{iso(H)} = 1.5U_{eq(C)}$. All other hydrogen atoms were placed in ideal positions and refined using a riding model, with methylene, methine and aromatic d_{C-H} distances of 0.99 Å, 1.00 Å and 0.95 Å, respectively, and $U_{iso(H)} = 1.2U_{eq(C)}$. The hydrogen atom of the hydroxyl group was calculated as a part of a rigid rotating group, with d_{O-H} = 0.84 Å and $U_{iso(H)} = 1.2U_{eq(O)}$. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2-F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err < 0.001. The final residual electron density maps showed no remarkable features. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography. All calculations were performed with the WINGX system, including the programs PLATON, SHELXL-97, and SIR92 [13].

Table 1
Selected bond distances (Å) and angles (°) for compound **4**.

Bond distance (Å)	
Rh–C1	2.030(5)
Rh–C10	2.042(6)
Rh–Cg1[a]	2.100
Rh–Cg2[a]	2.082
C6–O1	1.418(7)
Bond angle (°)	
C1–Rh–C10	83.6(2)
C1–Rh–Cg1[a]	176.9
C1–Rh–Cg2[a]	96.0
C10–Rh–Cg1[a]	93.4
C10–Rh–Cg2[a]	178.8
Cg1–Rh–Cg2[a]	87.0
N1–C1–N2	104.2(4)
C5–C6–O1	111.1(4)
C7–C6–O1	107.7(4)
C5–C6–C7	118.4(5)
N3–C10–N4	104.9(5)

[a] Cg is defined as the midpoint of the double bonds Cg1: C12=C13, and Cg2: C16=C17, resp.

Table 2
Crystallographic data for compound **4**.

	4
Formula	$C_{19}H_{28}F_6N_4OPRh$
Fw	576.33
Color/habit	Yellow/fragment
Crystal dimensions (mm^3)	0.20 × 0.25 × 0.46
Crystal system	Monoclinic
Space Group	$P2_1/c$ (no. 14)
a (Å)	14.2479(6)
b (Å)	12.6485(5)
c (Å)	13.6367(6)
β (°)	114.119(2)
V ($Å^3$)	2242.99(17)
Z	4
T (K)	123
D_{calcd} (g cm^{-3})	1.707
μ (mm^{-1})	0.902
F(000)	1168
θ Range (°)	1.57–25.31
Index ranges (*h*, *k*, *l*)	− 16/+ 17, ± 15, ± 16
No. of rflns. collected	60597
No. of indep. rflns./R_{int}	4083/0.021
No. of obsd. rflns. ($I > 2\sigma(I)$)	3957
No. of data/restraints/params	4083/0/291
R_1/wR_2 ($I > 2\sigma(I)$)[a]	0.0488/0.1141
R_1/wR_2 (all data)[a]	0.0504/0.1154
GOF (on F^2)[a]	1.160
Largest diff. peak and hole (e $Å^{-3}$)	+ 1.06/- 0.86

[a] $R_1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2]\}^{1/2}$; $GOF = \{\Sigma[w(F_o^2-F_c^2)^2]/(n\text{-}p)\}^{1/2}$.

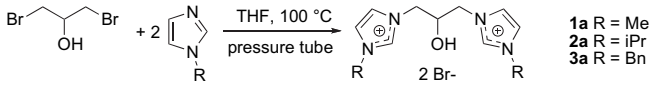
3. Results and discussion

Herein we describe a series of new bridged Rh(I)(bis-NHC)X complexes with a hydroxy functionality in the bridge. As it can be seen in the crystal structure, the hydroxy group does not coordinate to the metal center, being free for reaction with a linker group on a solid support, e.g. a polymer such as Wang-resin or inorganic silica materials such as MCM-41 for use in heterogeneous catalysis. In order to examine whether the newly introduced functional group would affect the catalytic activity, all complexes were examined as catalysts for homogeneous hydrosilylation reaction of acetophenone with diphenylsilane.

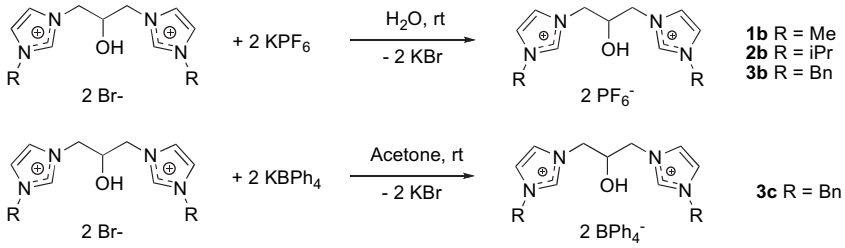
3.1. Synthesis and characterization

The hydroxy-functionalized imidazolium salts **1a**–**3a** were prepared by reaction of 1,3-dibromo-propane-2-ol with the corresponding *N*-subsituted imidazoles in THF in a pressure tube (Scheme 1) [12]. All bromine salts are soluble in polar solvents such as methanol and dimethylsulfoxide. They are stable both under air and in the presence of moisture, however compound **2a** is very hygroscopic and should be stored under an argon atmosphere.

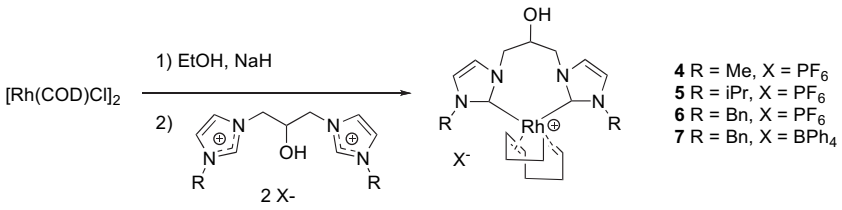
The formation of compounds **1a-3a** was verified by the appearance of the NC*H*N peak at around 9 ppm in the ^{1}H-NMR spectra and the peak at around 137 ppm in the ^{13}C-NMR spectra which are in the typical range for the NC*H*N-proton of imidazolium salts. An X-ray structure of **1a** has been obtained [12].



Scheme 1. Synthesis of the bis-imidazolium salts 1a–3a.



Scheme 2. Anion exchange reaction.



Scheme 3. Syntheses of the Rh(I) NHC complexes **4**–**7**.

The anion exchange from bromine salts to the corresponding hexafluorophosphate salts was carried out by mixing an aqueous solution of the bromine salt with a saturated aqueous solution of KPF_6 (Scheme 2). The PF_6-salts precipitate instantly from the solution. The formation of the hexafluorophosphate ligand salts was verified by FAB mass spectrometry, elemental analysis and the septet signal around – 140 ppm in the ^{31}P-NMR spectra. The exchange of the bromide anions by tetraphenylborate anions was achieved by reaction of the bromine salts with $KBPh_4$ in acetone (Scheme 2) yielding compound **3c**. The formation of compound **3c** was verified by FAB-MS, elemental analysis and NMR spectroscopy.

The rhodium(I) complexes **4**–**6** were prepared starting from [Rh(COD)Cl]$_2$ and two equivalents of the corresponding PF_6-imidazolium salts **1b**–**3b** (Scheme 3) at room temperature under an argon atmosphere. The *in-situ* synthesis of [Rh(COD)(OEt)]$_2$ in the presence of NaH in ethanol resulted in a colour change from orange to bright yellow. Afterwards, the PF_6-salt was added to the suspension and stirred over night. A yellow precipitate formed and the solution was filtered off. After extraction with DCM and precipitation after addition of pentane the Rh-bis-NHC complexes **4**–**6** were obtained as yellow crystals. All complexes are air- and moisture stable and soluble in DCM, THF, acetone and 1,2-dichloroethane. They are stable in the presence of water, but not soluble. The synthesis of complex **7** was carried out in the same way starting from tetraphenylborate salt **3c**.

The formation of the carbene complexes was established by the absence of the carbon peak at around 137 ppm and the peak for the 2*H*-imidazolium proton in the ^{1}H-NMR spectra δ (^{1}H) = 9 ppm and by the presence of a doublet peak at δ (^{13}C) ~ 180 ppm, which can be assigned to the 2*C*-imidazol-2-ylidene (carbene) carbons of the complexes **4**–**7** with a typical Rh-C coupling constant of ca. 50 Hz. The structure of **4** was determined by X-ray crystallography and is shown in Fig. 1. As for related bis-carbene complexes a boat conformation could be established [14] with a non-coordinating hydroxy group pointing away from the metal center.

To the best of our knowledge no other bis-carbene rhodium(I) complex with a hydroxy functionality directly bonded on a bridging atom has been characterized and described before.

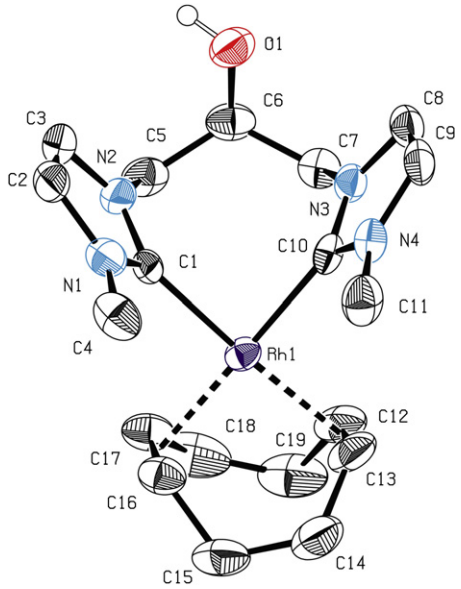


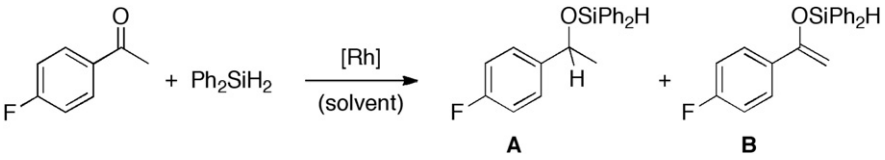
Fig. 1. ORTEP style plot of the cationic part of compound **4** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity except the hydroxyl hydrogen atom.

3.2. Catalysis

The hydrosilylation of ketones or aldehydes leading to silyl ethers is a useful and experimentally relatively straightforward transformation, as protected alcohols can be produced directly from carbonyl compounds. The newly synthesized rhodium complexes were tested with a catalyst loading of 2 mol % in homogeneous hydrosilylation of acetophenone with diphenylsilane yielding silylether **A** and silylenolether **B** [15]. The substrate acetophenone was replaced by 4-fluoroacetophenone in order to conveniently monitor the reaction progress *in-situ* by ^{19}F-NMR spectroscopy, to avoid taking samples and the associated workup and to circumvent the problem of overlapping integrals as observed in the ^{1}H-NMR spectra. The results are summarized in Table 3. For a better comparison of the relative catalyst activities the time-conversion curves are shown in Fig. 2.

With different wingtip groups Me - complex **4** (entry 1), ^{i}Pr - complex **5** (entry 3) and Bn - complex **6** (entry 5) a roughly 10% higher selectivity can be seen for the sterically more demanding ^{i}Pr and Bn groups. A five to ten times higher TOF is achieved for ^{i}Pr (entry 3). However, even after long reaction times of 15 h and 24 h, Me and Bn groups to not go to full conversion under these reaction

Table 3
Results for the hydrosilylation of 4-fluoro-acetophenone.



entry	[Rh]	R	X^-	T [°C]	solvent	time [h]	conv. [%]	A [%]	B [%]	TOF [h^{-1}]
1	**4**	Me	PF_6	25	DCM	15	73	51	49	15
2	**4**	Me	PF_6	60	DCE	4	100	63	37	30
3	**5**	^{i}Pr	PF_6	25	DCM	2	100	66	34	70
4	**5**	^{i}Pr	PF_6	25	THF	4	100	40	60	55
5	**6**	Bn	PF_6	25	DCM	24	81	64	36	5
6	**7**	Bn	BPh_4	25	DCM	50 min	100	72	28	70

Reaction conditions: 2 mol % catalyst, 0.504 mmol of 4-fluoro-acetophenone, 0.756 mmol of diphenylsilane, 0.3 ml dichloromethane (entry 2: 1,2-dichloroethane DCE). Conversions were determined by ^{19}F-NMR spectroscopy. No spectroscopic evidence was found for defluorination, nor the formation of other products than A and B. TOFs have been calculated from at the maximal slope of the time-conversion curve.

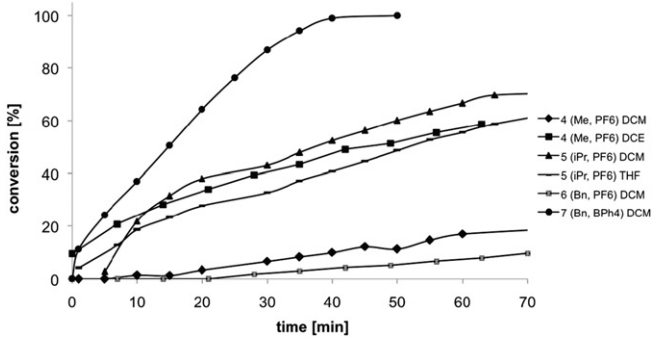


Fig. 2. Time-conversion curves of the hydrosilylation reaction.

conditions. Using complex **4** as catalyst at 25 °C, a TOF of 15 h^{-1} is achieved and a conversion of 73% after 15 h (entry 1). A temperature increase from room temperature to 60 °C increases the turnover frequencies up to 30 h^{-1} and complete conversion is achieved after 4 h reaction time (entry 2). A solvent dependent selectivity can be noted. Using complex **5** in DCM as solvent, a TOF of 70 h^{-1} is achieved and a product selectivity of 66% for the silylated alcohol **A** (entry 3) could be reached. Application of the same complex in THF as solvent leads to a reverse product selectivity, TOF is 55 h^{-1} (entry 4). For complex **6**, with a PF_6-anion and **7**, with a BPh_4 anion, a clear influence of the anion can be observed. Complex **6** displays a TOF of 5 h^{-1} and even after 24 h no complete conversion can be obtained (entry 5). Using complex **7** under the same conditions leads to full conversion after only 50 min with a TOF of 70 h^{-1} (entry 6).

Considering these results, we found that besides reaction temperature and solvent, both the wingtip groups and the anion play a important role in this hydrosilylation reaction. The observed turnover frequencies are within the range of previously described catalysts for hydrosilylation reactions of acetophenone [16]. All complexes show high activities under mild conditions and in future work the immobilization of these compounds will be tested.

4. Conclusion

The synthesis and structural characterization of Rh(I) complexes is reported. Investigations of the performance of these novel rhodium NHC complexes in homogeneous hydrosilylation of acetophenone show good activities. The hydroxy functionality present in these complexes appears to be applicable for immobilization on supporting materials for applications as immobilized catalysts. Related immobilized complexes of palladium have been successfully used in Suzuki-Miyaura cross coupling reactions. Investigations with respect to the synthesis and catalytic performance of such immobilized compounds are currently under way in our labs.

Acknowledgements

We gratefully acknowledge Dr. Monica Carril and Serena L.M. Goh for helpful discussions. This work was supported by Universität Bayern e. V. (Ph.D. fellowship for N.B.J.) and the Wacker Insitut für Silicium Chemie-Wacker AG (Ph.D. fellowship for M.P.H). We further thank the International Graduate School of Science and Engineering (IGSSE) for financial support.

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