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Synthesis and characterization of a free phenylene bis(N-heterocyclic carbene) and its di-Rh complex: Catalytic activity of the di-Rh and CCC–NHC Rh pincer complexes in intermolecular hydrosilylation of alkynes

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Abstract

1,3-Bis(3-butylimidazolium-1-yl)benzene diiodide (**1**) was reacted with Li(2,2,6,6-tetramethylpiperidine) yielding the free bis-carbene, 1,3-bis(3-butylimidazol-2-ylidene-1-yl)benzene (**3**), which has been spectroscopically characterized. Combining the free bis-carbene with $[Rh(COD)Cl]_2$ yielded the corresponding di-Rh bis(N-heterocyclic carbene) complex (**4**) that was structurally characterized. The di-Rh bis-carbene complex was found to exhibit complex solution ^{13}C and ^{1}H NMR spectra that have been assigned as a mixture of diastereomers. The crystal structure of the di-Rh bis-carbene compound **4** was composed of a pair of enantiomeric atropisomers. The diastereomeric atropisomers were assigned as the source of the spectral complexities. The di-Rh di-carbene complex **4** and the CCC–NHC Rh pincer complex **2** were applied as catalysts in hydrosilylation reactions of terminal and internal alkynes. Both catalysts are highly active, regioselective, stereoselective, and chemoselective: terminal alkynes give predominantly the β-(*Z*) isomer and internal alkynes afford the β-(*E*) isomer in chloroform or benzene. One of the strongest attributes of the catalyst systems is that the results were achieved without exclusion of air and without purification of commercially available reagents.

Keywords: Free bis-carbene; Pincer complex; Hydrosilylation; N-heterocyclic carbene; Rhodium complex; Carbene complex

1. Introduction

The preparation of N-heterocyclic carbene complexes of transition metals was first reported in 1968 [1]. The synthetic difficulty of accessing the ligand motif hampered development of the field for many years [2]. In 1991, Arduengo reported the deprotonation of imidazolium salts to prepare the free carbene thus opening up a synthetic route to the ligand [3]. The remarkable ability of the imidazolium nucleus in stabilizing a carbene center at the C-2 position has been demonstrated by the isolation and X-ray crystal structure characterization of the free carbene [3,4], and by the preparation of their complexes with transition metals [5]. The field of N-heterocyclic carbene chemistry has exploded since that time and many new synthetic methods have been developed, and the applications of NHC ligands have multiplied [6].

We and several other groups have recently been engaged in the replacement of phosphines with NHC's in pincer complexes. Much new and interesting chemistry has resulted. Pincer complexes, especially PCP pincers, have been demonstrated to be useful catalysts for

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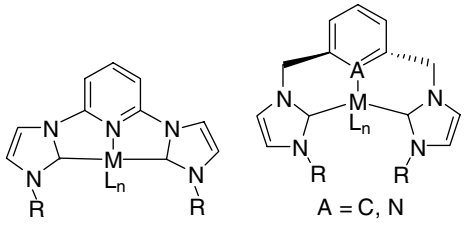
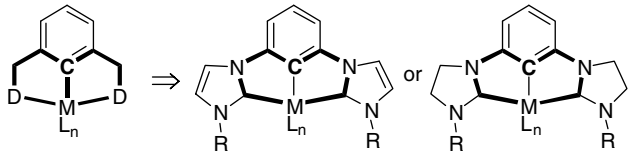
dehydrogenation of alkanes [7]. Very recently, a PCP pincer was designed to be even more electron rich, and it was found to be capable of oxidative addition of the N–H bond of ammonia [8]. The phosphines in pincer ligands have been replaced by NHC's to produce pincer architectures incorporating the carbene as the σ-donor. We were the first to report the CCC–NHC pincer architecture illustrated in Scheme 2, where the NHC architecture with a M–C bond at the central position has been directly mapped atom for atom onto the PCP pincer architecture [9]. Several different types of NHC pincer complexes have been reported and been extensively studied. These pincer NHC complexes have been demonstrated to be catalytically active for transfer hydrogenation, C–C coupling reactions in Heck and related chemistries, hydroformylation and the hydroamination of alkynes [10]. The synthetic routes to the known types of NHC pincer analogues illustrated in Scheme 1 are ligand and metal specific [11,12]. A generally applicable route to CCC–NHC pincer complexes has not been available until our recent report [9].

We have established the efficient one-pot synthesis of 1,3-bis(imidazol-1-yl)benzene followed by alkylation yielding bis(imidazolium) salts **1** [13], and we have recently reported an efficient metallation/transmetallation strategy to tris-activate imidazolium salt **1** in the preparation of CCC–NHC pincer complexes as illustrated in Scheme 3. Reaction with a Zr amido reagent activates all three C–H bonds generating the pincer architecture,



Scheme 1. Recently reported NHC pincer architectures.



Scheme 2. Atom mapping of pincer complexes onto a CCC–NHC architecture.

which was found to effectively transmetallate to late transition metals like Rh yielding CCC–NHC pincer complex **2** [9]. The ligand precursor **1** was also envisioned to position two mono(NHC) coordinated metals in proximity to one another for potential applications in bimetallic cooperativity [14]. We report here the synthesis and characterization of the free bis-carbene, its di-Rh complex, and comparison to the di-Rh and pincer complexes as catalysts for hydrosilylation reactions.

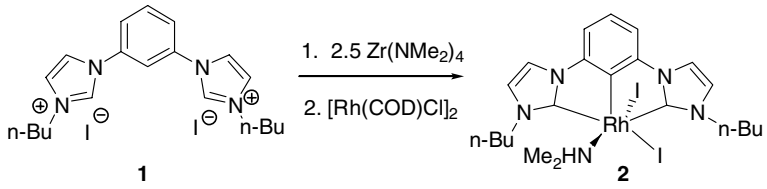
2. Results

2.1. Bimetallic rhodium N-heterocyclic carbene synthesis

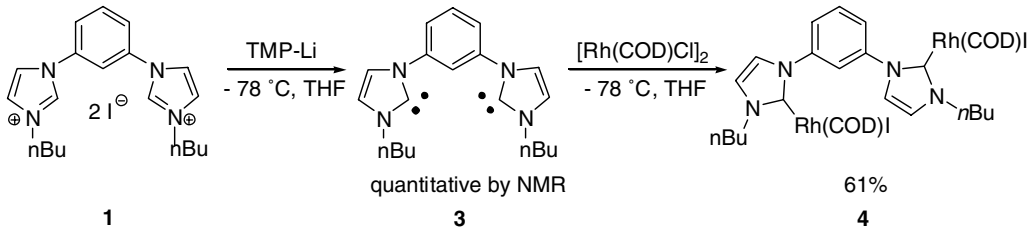
We first envisaged the synthesis of a novel electron-rich di-Rh bis-carbene complex based on the bis(imidazolium) salt **1** (Scheme 4). The imidazolium salt **1** was obtained by alkylating 1,3-bis(imidazol-1-yl)benzene according to the standard method employed in our laboratory [13]. The synthesis of a di-Rh bis-carbene complex from **1** would give a complex in which the two Rh atoms are in close proximity perhaps giving rise to enhanced reactivity due to cooperative effects. Thus, we sought a method for deprotonating the bis(imidazolium) salt **1** to form the free carbene and to subsequently metallate it with an appropriate Rh source.

Several standard bases that have been reported previously to produce NHC's were evaluated in THF at −78 °C by ^{13}C NMR spectroscopy analysis. Potassium hydride produced 0% conversion, and lithium hexamethyldisilazine yielded only 60% conversion. It was found that 1,3-bis(3-butylimidazol-1-yl)benzene diiodide **1** reacted with 2,2,6,6-(tetramethylpiperidine)lithium (TMP-Li) in THF-d_8 at −78 °C quantitatively yielding bis-carbene **3** as characterized by ^{1}H and ^{13}C NMR spectroscopy at −50 °C [5e,15]. The ^{1}H NMR signals for the iminium protons of **1** were no longer observed, and the ^{13}C NMR spectrum revealed a new peak at 201 ppm, which is characteristic of carbenes. The bis-carbene was not stable above −30 °C and decomposed to numerous unidentified products.

Bis-carbene **3** and $[Rh(COD)Cl]_2$ were reacted at −78 °C in situ to yield the di-Rh bis-carbene complex **4** as a yellow powder in 61% isolated yield [16]. The signal for the carbene carbon of **4** was doubled with peaks observed at δ 182.0 ($^{1}J_{Rh-C} = 49$ Hz) and δ 181.9



Scheme 3. Preparation of a CCC–NHC Rh pincer complex.



Scheme 4. Preparation of the carbene **3** and the di-Rh complex **4**.

($^1J_{Rh-C} = 49$ Hz), upfield relative to the free carbene and with the characteristic doublet from coupling to Rh. The ^{13}C and ^1H NMR spectra of compound **4** had a doubling of many of the observed peaks (vide infra). An exact mass determination indicated the corresponding parent ion $m/z = 998$ corroborating the formation of di-Rh bis-carbene **4**.

A X-ray quality single crystal of **4** was grown from a saturated toluene solution. The molecular structure was determined and is depicted in Fig. 1. The Rh(1)–C(2) and Rh(1′)–C(2′) bond distances are 2.020 and 2.015 Å. The structure reveals that Rh centers are in a square-planar environment. Selected geometric parameters are collected in Table 1. Details of data collection and solution of the X-ray crystal structure are listed in Table 2.

2.2. Catalytic hydrosilylation

Hydrosilylation is a powerful tool in organic synthesis. It is an atom-economical method of synthesis [17] and allows access to versatile silanes [18], which are important building blocks in organic chemistry [19]. However, the synthetic utility of addition of silanes to terminal alkynes is limited. As shown in Eq. (1), three isomeric vinylsilanes β-(*E*), β-(*Z*) and α may be formed in addition to dehydrosilylation [20]. The hydrosilylation of internal alkynes still gives β-(*E*) and β-(*Z*) isomers (Eq. (2)). Thus, a highly regio- and stereospecific synthesis is highly desirable, and a plethora of transition metal catalysts for this reaction have been developed.

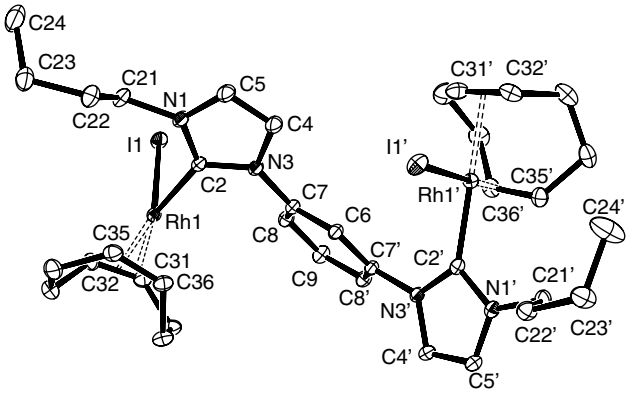


Fig. 1. ORTEP diagram of **4** (50% probability, hydrogen atoms are omitted for clarity).

Table 1
Selected bond distances (Å) and angles (°) for di-Rh bis-carbene complex **4**

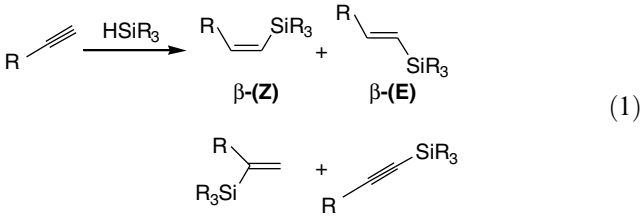
Distances (Å)	
Rh1–C2	2.0201(11)
Rh1–C31	2.1912(11)
Rh1–C32	2.2392(12)
Rh1–C35	2.1105(12)
Rh1–C36	2.1324(11)
Rh1–I1	2.68340(11)
Rh1′–C2′	2.0150(11)
Rh1′–C31′	2.2143(12)
Rh1′–C32′	2.2445(12)
Rh1′–C35′	2.1025(11)
Rh1′–C36′	2.1304(11)
Rh1′–I1′	2.67326(11)
N1–C2	1.3477(14)
N1–C21	1.4649(15)
N1–C5	1.3913(16)
C2–N3	1.3713(14)
N3–C7	1.4268(14)
N3–C4	1.3954(14)
N1′–C2′	1.3547(14)
N1′–C21′	1.4644(15)
N1′–C5′	1.3888(15)
C2′–N3′	1.3665(14)
N3′–C7′	1.4278(13)
N3′–C4′	1.3916(14)
Angles (°)	
N1–C2–Rh1	128.42(8)
N3–C2–Rh1	127.18(8)
C2–N3–C7	125.42(9)
C2–Rh1–I1	89.25(3)
C2–Rh1–C31	155.61(4)
C2–Rh1–C32	167.70(5)
C2–Rh1–C35	91.06(5)
C2–Rh1–C36	91.06(4)
C31–Rh1–C32	36.38(5)
C35–Rh1–C32	81.43(5)
C36–Rh1–C31	82.23(5)
C35–Rh1–C36	38.92(5)
N1′–C2′–Rh1′	128.76(8)
N3′–C2′–Rh1′	126.18(7)
C2′–N3′–C7′	124.17(9)
C2′–Rh1′–C31′	92.04(3)
C2′–Rh1′–C31′	158.56(5)
C2′–Rh1′–C32′	164.12(5)
C2′–Rh1′–C35′	87.53(5)
C2′–Rh1′–C36′	89.64(4)
C31′–Rh1′–C32′	35.98(5)
C35′–Rh1′–C32′	81.29(5)
C36′–Rh1′–C31′	81.54(5)
C35′–Rh1′–C36′	39.06(5)

Table 2
Crystallographic data for **4**

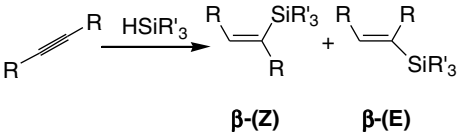
Empirical formula	$C_{36}H_{50}I_2N_4Rh_2$
Formula weight	998.42
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions	
a (Å)	14.0393(2)
b (Å)	16.9296(2)
c (Å)	31.2725(4)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	7432.84(17)
Z	8
Density (Mg/m^3)	1.784
Absorption coefficient (mm^{-1})	2.579
$F(000)$	3920
Crystal size (mm)	$0.45 \times 0.37 \times 0.26$
θ Range for data collection (°)	1.95–40.25
Index ranges	$-25 \leqslant h \leqslant 25$, $-30 \leqslant k \leqslant 30$, $-56 \leqslant l \leqslant 56$
Reflections collected	276 835
Independent reflections [R_{int}]	23 383 [0.0328]
Completeness to $\theta = 40.25°$	99.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.5481 and 0.3892
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	23383/0/449
Goodness-of-fit on F^2	1.033
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0227$, $wR_2 = 0.0543$

Over the past decade significant progress has been made in this area, and catalysts for regio- and stereocontrolled syntheses of vinylsilanes are now available [21]. Platinum catalysts were among the first ones investigated and typically lead to the β-(*E*) isomers [22]. Rhodium complexes were intensively studied, and it has been shown that neutral Rh complexes tend to form β-(*Z*) isomers [23], whereas cationic Rh complexes such as $[Rh(COD)_2]BF_4$ give the β-(*E*) compounds [18,24]. Stereodivergent syntheses of β-(*E*) and β-(*Z*) isomers were reported [25], and enantioselective hydrosilylation catalysts are available [26].

However, the regioselectivity and stereoselectivity of the hydrosilylation of alkynes still depends on several factors such as temperature, reaction time, substrates, additives and catalyst. In many cases, long reaction times and high temperatures are necessary and the exclusion of moisture and air is required. Thus, the search for generally applicable catalyst systems in this reaction is ongoing.



(1)



(2)

Hydrosilylation of multiple bonds catalyzed by metal complexes typically involves oxidative addition of the silane to the metal as the first step [27]. Therefore, we envisaged our new electron-rich di-Rh complex **4** as a potential hydrosilylation catalyst. Thus, complex **4** and for comparison the pincer Rh complex **2** were employed as catalysts for this reaction. Experiments were first conducted under conditions similar to those applied by Peris and co-workers [21e]. Dimethylphenylsilane (Me_2PhSiH), the alkyne, $CDCl_3$ and the catalyst (2–3.5 mol%) were combined in a screw-capped pressure vial and maintained at different temperatures. Schlenk techniques were not applied and neither was purification of starting materials performed. Conversion of the alkynes was ascertained by NMR spectroscopy, and product distributions were determined by comparison of ^1H and ^{13}C NMR data with literature values [20,23a,24a,25b,28]. The coupling constants for the vinylic protons are very indicative and range from 13 to 15 Hz for β-(*Z*), 18 to 20 Hz for β-(*E*) and ~2 Hz for α isomers. The results of the catalytic experiments are compiled in Table 3. In general and unlike previous reports, hydrosilylation of terminal and internal alkynes was successful. Most of the alkynes were quantitatively converted to the products in 2 h or less at 80 °C indicating the high activity of both catalysts. Switching the solvent to benzene gave similar results (entries 1, 7, 21).

The product distribution for the hydrosilylation of terminal alkynes shows in general a strong preference for the β-(*Z*)-alkene for both catalysts. This finding is consistent with earlier reports showing β-(*Z*)-selectivity for neutral Rh complexes [23]. Only *t*-Bu-acetylene gives mainly the β-(*E*) isomer. Internal alkynes are smoothly hydrosilylated and give predominantly the β-(*E*)-products. The stereoselectivities are good to excellent, and only small amounts of the α product were formed. In general, the pincer complex **2** shows somewhat better selectivity than the di-Rh complex **4**. The activities are comparable, as an experiment at room temperature revealed. Phenylacetylene was reacted with catalysts **2** or **4** with a catalyst load of 2 mol% based on Rh under otherwise the same conditions described in Table 3. ^1H NMR spectra of the crude product showed ~27% conversion for both catalysts after three hours, and the product distribution was similar to that reported in Table 3.

To demonstrate functional group compatibility, some experiments were conducted with alkyne-containing alcohols (entries 21–26). 5-Hexyne-1-ol (entries 21 and 22) was readily hydrosilylated and showed a similar product distribution as the other terminal alkynes.

Table 3
Catalytic hydrosilylation results[a]

Entry	Alkyne	Catalyst	Time (h)	Temp. (°C)	Conversion[b] (%)	β-(*E*)[c,d]	β-(*Z*)[c,d]	α[c,d]
1	PhC≡CH[e]	**4**	2	80	100	8	92	0
2	PhC≡CH	**2**	2	80	100	5	95	0
3	PhC≡CH	**2**	12	rt	87	5	95	0
4	$H_3C(CH_2)_2C$≡CH	**4**	2	80	100	10	82	8
5	$H_3C(CH_2)_2C$≡CH	**4**	16	rt	52	14	76	10
6	$H_3C(CH_2)_2C$≡CH	**2**	1	80	100	8	89	3
7	$H_3C(CH_2)_6C$≡CH[e]	**4**	2	80	100	16	80	4
8	$H_3C(CH_2)_6C$≡CH	**2**	2	80	100	11	83	6
9	$H_3C(CH_2)_7C$≡CH	**4**	2	80	100	9	84	7
10	$H_3C(CH_2)_7C$≡CH	**2**	1	80	100	8	88	4
11	$H_3C(CH_2)_7C$≡CH	**2**	18	80	100	9	86	5
12	*t*-BuC≡CH	**4**	18	60	100	80	10	10[f]
13	*t*-BuC≡CH	**2**	2	80	57	69	20	11[f]
14	PhC≡CPh	**4**	2	80	100	80	20	–
15	PhC≡CPh	**2**	12	60	100	89	11	–
16	EtC≡CEt	**4**	2	80	100	85	15	–
17	EtC≡CEt	**4**	20	80	100	85	15	–
18	EtC≡CEt	**2**	18	80	100	85	15	–
19	PrC≡CPr	**4**	2	80	100	79	21	–
20	PrC≡CPr	**2**	1.5	80	100	72	28	–[g]
21	$CH_2(OH)(CH_2)_3C$≡CH[e]	**4**	1.5	80	100	8	87	5
22	$CH_2(OH)(CH_2)_3C$≡CH	**2**	2	80	100	15	77	8
23	PrCH(OH)C≡CH	**4**	7	80	100	–	52[h]	–
24	PrCH(OH)C≡CH	**2**	6.5	80	100	–	71[h]	–
25	*c*-C_6H_{10}(C≡CH)(OH)[j]	**4**	7	45	100	69	10	21[i]
26	*c*-C_6H_{10}(C≡CH)(OH)[j]	**2**	2	80	100	73	15	12[i]

[a] Catalyst (2–3.5 mol%) and silane (1.1 equiv.) were mixed in $CDCl_3$ 10 min before addition of the alkyne (1 equiv).
[b] Conversion of the alkyne. The consumption of internal alkynes was confirmed by ^{13}C NMR.
[c] Determined by ^1H NMR of the crude reaction mixture.
[d] The percentages of β-(*Z*), β-(*E*), and α are in relation to each other only.
[e] In C_6D_6.
[f] ~40% hydrogenated product.
[g] ~15% hydrogenated product.
[h] No β-(*E*) and α-products were observed, other side products.
[i] ~20% hydrogenated product.
[j] 1-Ethynyl-1-cyclohexanol.

Hydrosilylation of 1-hexyne-3-ol and 1-ethynyl-1-cyclohexanol (entries 23–26) required longer reaction times for catalyst **4**, and the product distribution differs from the other terminal alkynes. No O-silylated products were detected.

Further experiments were conducted to better understand the selectivity of our Rh carbene catalysts. Hydrosilylations were conducted at room temperature to evaluate the temperature dependence of the catalytic activity and selectivity. The reaction occurs at room temperature also, but incomplete conversion was observed (see entries 3 and 5) without significant change in the product distribution. The stability of the product ratio over time was evaluated and established to be the result of kinetic control. Thus, we checked the *E*/*Z* ratio of the hydrosilylation of 1-decyne and 3-hexyne after 1 h and maintained the reaction mixture at 80 °C for 18 h (entries 10, 11, 16, and 17). The ratio did not change significantly, establishing that isomerization to the thermodynamically favored β-(*E*) product does not take place.

As reported before [25a], salt effects can dramatically change the selectivity of catalyst systems. Thus, several catalysis experiments were repeated with phenylacetylene under conditions as reported in Table 3 with the addition of LiCl, water, and *n*-Bu_4NBr. The results of these experiments are compiled in Table 4. Both catalysts, **2** and **4**, were found to produce different β-(*E*)/β-(*Z*) selectivity in the presence of additives. The most dramatic effect was observed in the hydrosilylation of phenylacetylene with added *n*-Bu_4NBr (entry 4). Exclusively the β-(*E*)-hydrosilylation product was observed, but nearly 50% of the phenylacetylene was converted to styrene. Addition of LiCl typically causes the catalysts to switch from producing predominantly the β-(*Z*) isomer with terminal alkynes (entries 1, 3, 5, and 7) to producing more of or predominantly the β-(*E*) isomer (compare to entries 2, 4, 6, and 8, respectively). Similar patterns were observed for *n*-Bu_4NBr. When water was added the amount of α-product increased. There was no significant salt effect observed when LiCl was added

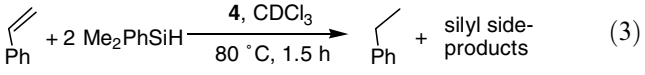
Table 4
Effect of additive on product selectivity[a]

Entry	Alkyne	Catalyst	β-(*E*)[b,c]	β-(*Z*)[b,c]	α[b,c]
1	PhC≡CH[d]	**4**	29	61	10
2	PhC≡CH	**4** + LiCl	55	35	10[e]
3	PhC≡CH[d]	**4** + LiCl/H_2O	40	43	17
4	PhC≡CH	**4** + NBu_4Br	100	0	0[f]
5	PhC≡CH[d]	**2**	5	95	0
6	PhC≡CH	**2** + LiCl	51	40	9
7	PhC≡CH[d]	**2** + LiCl/H_2O	37	43	20
8	PhC≡CH	**2** + NBu_4Br	56	43	3[e]
9	$H_3C(CH_2)_7C$≡CH[d]	**2**	8	88	4
10	$H_3C(CH_2)_7C$≡CH	**2** + LiCl	34	53	13
11	$H_3C(CH_2)_7C$≡CH	**2** + NH_4BuBr	33	32	35
12	$H_3C(CH_2)_7C$≡CH[d]	**4**	9	84	7
13	$H_3C(CH_2)_7C$≡CH	**4** + LiCl	16	73	11
14	$H_3C(CH_2)_7C$≡CH	**4** + NH_4BuBr	44	29	26
15	PrC≡CPr[d]	**4**	79	21	–
16	PrC≡CPr	**4** + LiCl	80	20	–
17	PrC≡CPr[d]	**2**	72	28	–
18	PrC≡CPr	**2** + LiCl	73	27	–

[a] Catalyst (2–3.5 mol%) and silane (1.1 equiv.) were mixed in $CDCl_3$ 10 min before addition to the alkyne (1 equiv.) and the corresponding salt (1 equiv.) followed by heating at 80 °C for 2.5 h.
[b] Determined by ^1H NMR spectroscopy of the crude reaction mixture. Average of two or three experiments.
[c] The percentages of (*Z*), (*E*), and α are in relation to each other only.
[d] In $CDCl_3$ without additive.
[e] ~20% hydrogenated product.
[f] ~50% hydrogenated product.

to reactions of internal alkynes (entries 9–12). Added salts have some influence on the selectivity of addition to terminal alkynes with catalysts **2** and **4**, therefore care should be taken to exclude ionic impurities.

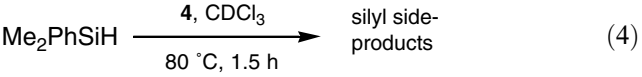
Hydrosilylation of styrene was not successful under the reaction conditions described in Table 3. However, careful analysis of the ^1H and ^{13}C NMR spectra of the reaction mixture revealed that ethylbenzene was formed; the silane had completely converted and ~50% of the styrene remained unreacted. When two equivalents of silane were employed, no more styrene starting material was left over. Thus, a hydrogen transfer from the silane to the alkene took place, giving rise to a process as shown in Eq. (3). A GC–MS analysis of the crude product mixture showed ethylbenzene and silane-containing byproducts such as $Me_2PhSiSiMe_2Ph$, Me_2PhSi–O–SiMe_2Ph and $Me_2PhSiCl$.



(3)

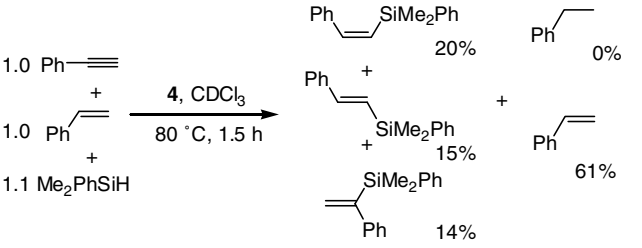
Hydrosilylation of carbonyls to give O-silylethers was not successful under the reaction conditions described above. Cyclohexanone or benzaldehyde was reacted under the conditions described in Table 3. The carbonyl starting materials were recovered, but the silane had been completely consumed. Presumably, a dehydrogenation of the silane in a reaction similar to that in Eq. (3) took place. Thus, we conclude that the dehydrogenation of the silane is a side reaction with our catalyst system with substrates that hydrosilylate slowly.

To examine the dehydrogenation of the silane, a control experiment was performed. Catalyst **4** and Me_2PhSiH were combined as illustrated in Eq. (4) without substrate under the conditions described in Table 3 for the catalytic experiments. ^1H NMR and GC–MS analysis showed that the silane was consumed. Silyl-containing byproducts similar to those of the reaction in Eq. (3) were observed by GC–MS. Thus dehydrogenative coupling of the silane took place, even without an appropriate hydrogen acceptor. It is not clear what happens to all of the hydrogen produced, but cyclooctene and cyclooctane were detected in the reaction mixture. Thus, the cyclooctadiene (COD) serves as a hydrogen acceptor.



(4)

Finally, the chemoselectivity of the hydrosilylation catalysts was evaluated in a competition experiment involving 1 equiv. of styrene and phenylacetylene and 1.1 equiv. of Me_2PhSiH. Combination with catalyst **2** or **4** under standard conditions as shown in Eq. (5) was observed to produce the corresponding vinylsilanes with a product distribution similar to that reported in Table 3. The styrene remained unreacted with catalyst **4**, and ~12% ethylbenzene had formed with catalyst **2**. Thus, hydrosilylation of alkynes in the presence of alkenes chemoselectively was achieved.



(5)

3. Discussion

3.1. Bimetallic rhodium N-heterocyclic carbene synthesis

The di-Rh bis-carbene system **4** that is reported is related to the 1,2-ethylene bridged analogue reported by Herrmann et al. [5e] and the 2,6-pyridylene bridged analogue reported by Peris and co-workers [21e]. The Rh(1)–Rh(1′) distance of 7.9 Å precludes a M–M bond and is similar to the di-Rh bis-carbene pyridyl bridged structure reported by Peris and co-workers [21e]. An analysis of Cambridge Crystallographic Database including the May 2005 release data revealed 127

examples of structurally characterized Rh–NHC bonds. The mean of the Rh–C bond distances was 2.023 Å with a population standard deviation of 0.035 Å. The maximum value reported was 2.111 Å, and the minimum was 1.914 Å. Evaluation of this data and comparison with our Rh–NHC bond distances of 2.0201(11) and 2.0150(11) reveal that the distances fall in the lower half of the reported bond distances between the first quartile value of 2.0115 Å and the second quartile value of 2.029 Å.

Apparently, hindered rotation of the aryl-NHC bond generates diastereomers at the axes of chirality in solution due to the steric bulk of the COD ligand, iodide, and the presence of the *ortho*-hydrogen resulting in the complex NMR spectra observed. Such an observation has not been reported for the ethylene or pyridylene bridged systems [5e,21e], thus the *ortho*-hydrogen and the halide have a significant impact on the dynamics of the system. The crystal structure contains the *R*,*R* and *S*,*S* enantiomeric pair related through a center of inversion. Quickly collecting a ^{13}C NMR spectrum upon dissolution of the crystals reveals a diastereomeric ratio of ~2:1, which is consistent with rapid equilibration. The assignment of the major isomer in solution as *rac* or *meso* has not been made, and the mixture is reported in Section 5.

3.2. Catalytic hydrosilylation

The activities of our carbene complexes **2** and **4** are high. Rh-based catalyst systems recently published by Peris and co-workers (24–72 h at 60 °C; 33–80% β-(*E*) selectivity for phenylacetylene) [21e] or Faller (2.5 h at 45 °C; 81–99% β-(*E*) selectivity for phenylacetylene) [18] show activities and selectivity which are comparable to our system. However, complexes **2** and **4** can be handled in air and no special treatment of solvents or substrates is necessary. Furthermore, they selectively hydrosilylate alkynes, making them an attractive alternative to established catalyst systems. The findings herein are consistent with the generally accepted mechanism of the hydrosilylation reaction of terminal alkynes involving Rh-containing catalysts proposed by Crabtree [28a] and Ojima et al. [23a].

The experiments with *t*-Bu-acetylene and the alkyne-containing alcohols nicely show the influence of steric effects. As described earlier, the bulky *t*-Bu substituent directs the silyl group in the β-(*E*)-configuration and some hydrogen transfer from the silane to the alkyne to give an alkene product was observed. In 1-hexyn-3-ol and 1-ethynyl-1-cyclohexanol (entries 23–26) the alkyne units are in α positions adjacent to secondary and tertiary carbon atoms making the hydrosilylation more difficult. The silyl group is directed to the β-(*E*) position and hydrogen transfer is promoted. Carbonyl compounds and alcohols are not converted to the corresponding silanes, and alkenes do not react in the presence of alkynes as shown in Eq. (5). Thus, the reported catalysts are selective for alkynes.

4. Conclusions

In conclusion, we performed the synthesis of the di-Rh bis-carbene complex **4** in a straightforward one-pot synthesis from readily available starting materials. Catalyst **4** and the analogous CCC–NHC pincer complex **2** were demonstrated to have high reactivity in hydrosilylation reactions. Hydrosilylations are highly regio- and stereospecific: terminal alkynes give β-(*Z*) isomers and internal alkynes lead to β-(*E*) isomers (65–89%). Therefore, the di-Rh complex **4** and pincer complex **2** are promising candidates for other catalytic applications requiring electron-rich metal centers. Further catalytic studies of these new complexes are ongoing.

5. Experimental

5.1. General considerations

For the ligand and complex synthesis, manipulations were carried out under an inert atmosphere of Ar with the use of standard Schlenk, vacuum line, and glove box techniques. Dry oxygen-free solvents were used. The deuterated chlorinated solvents were filtered through basic alumina before dissolving the samples. $[Rh(COD)Cl]_2$ was purchased from Strem Chemicals and was used as received. NMR spectra were recorded on Bruker Avance 300 (300.132 MHz) and Varian Inova (500.140 and 300.053 MHz) instruments. Chemical shifts reported are relative to tetramethylsilane, and were referenced by assigning the residual solvent peak (C_6D_5H to 7.16 ppm and $CHCl_3$ to 7.28 ppm). Reagents and solvents for the hydrosilylation reactions were used as received and reactions were performed in the air.

5.2. Synthesis of 1,3-bis(3-butylimidazolium-1-yl)benzene diiodide (*1*)

1,3-Bis(imidazol-1-yl)benzene (0.840 g, 4.00 mmol), 1-iodobutane (2.94 g, 16.0 mmol), and toluene (8 mL) were reacted in a sealed tube at 150 °C for 8 h. The suspension was then allowed to reach room temperature, and the contents were washed with THF (3 × 10 mL). The residue was dried under high vacuum to obtain **1** as a yellow colored solid (1.78 g, 77%): ^1H NMR ($CDCl_3$): δ 11.23 (s, 2H), 9.01 (s, 1H), 8.72 (s, $J = 2.1$ Hz, 2H), 8.24 (dd, $J = 8.1$ and 2.1 Hz, 2H), 7.77 (t, $J = 8.1$ Hz, 1H), 7.5 (s, 2H), 4.46 (t, $J = 8.0$ Hz, 4H), 2.06 (pseudo-quintet, $J = 8.0$ Hz, 4H), δ 1.49 (pseudo-sextet, $J = 7.5$ Hz, 4H), 1.05 (t,

$J = 7.5$ Hz, 6H); $^{13}C\{^1H\}$ (75 MHz, DMSO-d_6): δ 137.6, 133.7, 127.2, 125.4, 124.5, 122.9, 117.6, 51.2, 32.9, 20.7, 15.2.

5.3. Synthesis of 1,3-bis(3-butylimidazol-2-ylidene-1-yl)-benzene (*3*)

A mixture of 2,2,6,6-(tetramethylpiperidine)lithium salt (0.088 g, 0.6 mmol) and 1,3-bis(3-butylimidazolium-1-yl)benzene iodide (0.173 g, 0.3 mmol) was cooled to −78 °C and THF (3 mL) was added dropwise. The colorless suspension was allowed to react at −78 °C for 1 h. The $^{13}C\{^1H\}$ and ^1H NMR spectra of the resulting orange colored solution were recorded at −50 °C and showed quantitative conversion: ^1H NMR (THF-d_8): δ 8.20 (broad s, 1H), 7.95 (broad s, 2H), 7.82 (broad s, 2H), 7.56 (broad s, 3H), 4.32 (b, 4H), 1.85 (b, 4H), 1.63 (b, 4H), 0.96 (b, 6H); $^{13}C\{^1H\}$ (125 MHz, THF-d_8): δ 200.5, 142.7, 130.9, 122.4, 120.6, 115.9, 49.7, 31.8, 18.9, 14.4 .

5.4. Synthesis of bis(1,5-cyclooctadiene)diiodo[1,3-bis(3-butylimidazol-2-ylidene-1-yl)benzene]dirhodium(I) (*4*)

A mixture of 2,2,6,6-(tetramethylpiperidine)lithium salt (0.088 g, 0.6 mmol) and 1,3-bis(3-butylimidazolium-1-yl)benzene iodide (0.173 g, 0.3 mmol) was cooled to −78 °C and THF (3 mL) was added dropwise. The colorless suspension was kept at −78 °C for 1 h which afforded an orange colored solution. $[Rh(COD)Cl]_2$ (0.148 g, 0.297 mmol) dissolved in THF (7 mL) was added slowly. The reaction was then allowed to reach r.t. and stirred for another 3 h (with no change in the color). The reaction was concentrated and the solid was triturated with toluene and filtered to remove the residual solid. Pentane was added to the filtrate producing a powder that was removed by filtration. The filtrate was concentrated to obtain orange colored crystals (0.183 g, 61%). Single crystals of **4** were grown from a saturated solution of toluene. ^1H NMR (300.053 MHz, CD_2Cl_2): *Major isomer*: δ 9.02 (t, $J = 2.1$ Hz, 1H), 8.59 (dd, $J = 2.1$ and 8.1 Hz, 1H), 7.66 (d, $J = 2.1$ Hz, 1H), 7.14 (d, $J = 8.1$ Hz, 1H), 5.25–5.18 (m, 2H), 4.95–4.83 (m, 4H), 4.62–4.57 (m, 2H), 3.5–3.4 (m, 2H), 3.1–3.0 (m, 2H), 2.42–2.28 (m, 2H), 1.98–1.93 (m, 2H), 1.73–1.53 (m, 2H), 1.07 (t, $J = 7.5$ Hz, 3H). *Minor isomer*: δ 10.04 (t, $J = 2.1$ Hz, 1H), 8.77 (dd, $J = 2.1$ and 8.1 Hz, 1H), 7.60 (d, $J = 2.1$ Hz, 1H), 7.17 (d, $J = 2.1$ Hz, 1H), 5.20–5.10 (m, 2H), 4.90–4.71 (m, 4H), 4.58–4.54 (m, 2H), 3.6–3.5 (m, 2H), 3.05–2.85 (m, 2H), 2.36–2.20 (m, 2H), 1.98–1.88 (m, 2H), 1.73–1.53 (m, 2H), 1.07 (t, $J = 7.5$ Hz, 3H). ^{13}C $\{^1H\}$ (125 MHz, $CDCl_3$): *Major isomer*: δ 182.0 (d, $J = 49$ Hz, NHC-Rh), 140.1, 128.8, 125.1, 121.8, 121.4, 120.8, 96.0 (d, $J = 4.5$ Hz), 72.7 (d, $J = 12.8$ Hz), 52.1, 31.8, 29.9, 19.9, 13.6. *Minor isomer*: δ 181.9 (d, $J = 49$ Hz, NHC-Rh), 139.7, 128.1, 122.6, 121.2, 120.3, 116.5, 95.4 (d, $J = 4.5$ Hz), 71.9 (d, $J = 12.8$ Hz), 51.6, 31.6, 29.4, 19.9, 13.6. LSIMS: 998 (M^+), 896 ($M^+ - COD$), 871($M^+ - I$), 763 ($M^+ - COD - I$), 425 ($M^+ - 2I - 2COD - Rh$).

5.5. Hydrosilylation experiments

Me_2PhSiH (0.012 g, 0.085 mmol) and the catalyst (2–3.5 mol%) were dissolved in $CDCl_3$ or benzene-d_6 (0.75 mL) in a screw-capped pressure vial. After 10 min it was combined with the alkyne (0.077 mmol), and the sealed vial was immersed in an oil bath preheated to the desired temperature. The products were characterized by NMR spectroscopy (see text).

5.6. X-ray structure determination for compound *4*

Measurements were carried out on a Bruker APEX 2 (version 1.0–22) [29] platform-CCD X-ray diffractometer system (Mo-radiation, $\lambda = 0.71073$ Å, 50 kV/40 mA power) for Rh. Data were collected at low temperature at $T = 100(2)$ K. Frames were integrated with the aid of the Bruker SAINT version 7.06A software [30] and using a narrow-frame integration algorithm.

For **4** a total of 4800 frames were collected for a hemisphere of reflections (with scan width of 0.3° in ω and ϕ angles of 0°, 90°, 180°, and 270° for every 600 frames in starting $2\theta = -30°$, and −60°, 10 s/frame exposure time). Based on an orthorhombic crystal system, the integrated frames yielded a total of 276 835 reflections at a maximum 2θ angle of 80.50° (0.55 Å resolution), of which 23 383 were independent reflections ($R_{int} = 0.0328$, $R_{sig} = 0.0169$, redundancy = 11.8, completeness = 99.9%) and 20 037 (85.7%) reflections were greater than $2\sigma(I)$. The unit cell parameters were, $a = 14.0393(2)$ Å, $b = 16.9296(2)$ Å, $c = 31.2725(4)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 7432.84(17)$ Å^3, $Z = 8$, calculated density $D_c = 1.784$ g/cm^3. Absorption corrections were applied (absorption coefficient $\mu = 2.579$ mm^{-1}; max/min transmission = 0.5481/0.3892) to the raw intensity data using the SADABS program (version 2004/1) [31].

The Bruker SHELXTL software package (version 6.14) [32] was used for phase determination and structure refinement for **4**. Direct methods of phase determination followed by subsequent Fourier cycles of refinement led to an electron density map from which most of the non-hydrogen atoms were identified. With subsequent isotropic refinement, all of the non-hydrogen atoms were identified. Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full-matrix least-squares procedure on F^2. The H-atoms were included in the refinement in calculated positions riding on the atoms to which they were attached. The largest peak/hole in the final difference map was 1.456/−0.600 e/Å^3, $R_1 = 0.0164$, $wR_2 = 0.0405$, with intensity, $I > 2\sigma(I)$.

Acknowledgment

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Appendix A. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 279032 for compound **4**. Further details on the crystal structure investigation are available free of charge at http:/www.ccdc.cam.ac.uk/ or upon request from the Director of the Cambridge Crystallographic Data centre, 12 Union Road, GB-Cambridge CB2 1EZ UK; fax: +44 1223 336 033, on quoting the full journal citation. The ^{1}H and ^{13}C NMR spectra of **4**, and the ^{1}H NMR spectrum of **1** are included. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.07.088.

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