Preferential α-Hydrosilylation of Terminal Alkynes by Bis-N-Heterocyclic Carbene Rhodium(III) Catalysts

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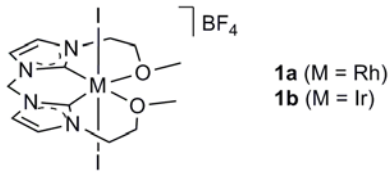
Abstract. We describe a bis-N-heterocyclic carbene Rhodium(III) complex, featuring two trifluoroacetato ligands, that affords a variety of α-vinylsilanes in good yields by hydrosilylation of terminal alkynes. Selectivities around 7:1 α/β-(E) were reached, while the β-(Z) product was only marginally obtained. This example sharply contrasts with the β-(Z)-selectivity observed for its parent diiodido complex

Vinylsilanes are valuable building blocks in organic synthesis and, therefore, new preparation methods that would pave the way to a more sustainable production of these compounds are of great interest.[1] Metal-catalyzed hydrosilylation of terminal alkynes is an efficient and atom economical route to vinylsilanes;[2] however, selectivity is a major issue for this reaction as three possible isomers may be obtained. The anti-Markovnikov syn-addition affords the □-(E)-vinylsilane, usually the major reaction product, while the anti-Markovnikov anti-addition gives the less frequent β-(Z)-vinylsilane.[3] On the other hand, Markovnikov additions to obtain selectively α-vinylsilanes are unusual.[3,4] Other noteworthy reports on the preparation of □-vinylsilanes include the hydrosilylation of terminal alkynes directed by hydroxy groups[5] or the silylcupration of terminal alkynes.[6]

Although inner-sphere mechanisms seem to explain most of the selectivities hitherto reported, we recently proposed the first ionic outer-sphere mechanism for the hydrosilylation of terminal alkynes, substantiated by DFT calculations. The solvent, namely an acetone molecule, assists the heterolytic splitting of the Si–H bond by catalysts 1a and 1b (Figure 1).[7] Subsequently, the R3Si+ moiety is transferred by means of an oxocarbenium ion ([R3Si–O(CH3)2]+) to the substrate. Finally, nucleophilic attack of the hydrido ligand over the silylation product ([R3Si–C=C–R]+) affords selectively the β-(Z)-vinylsilane as a result of the steric interactions that govern the approach of R3Si–C=C–R+ to the hydrido ligand.



1a (M = Rh)
1b (M = Ir)

Figure 1. Iodido bis-NHC Rh(III) and Ir(III) hydrosilylation catalysts.

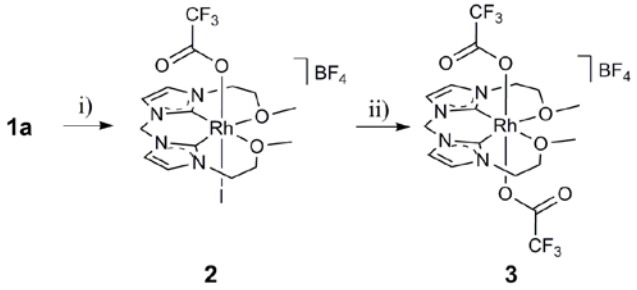
Other examples of ionic mechanisms involving hydrosilanes include substrates such as carbonyl[8] and ether[9] compounds (C–O and C=O bonds), halogenated compounds[10] (C–halide bonds) and N-heterocycles[11] (C=N bonds). In these cases the splitting of the Si–H bond takes places by interaction of a metal center with the hydrogen atom, and the substrate with the silicon atom.

Remarkably, recent work on CO2 hydrosilylation suggests that the non-coordinated oxygen atoms of a trifluoromethanesulfonato ligand aid the splitting of the Si–H bond in cooperation with an Ir(III) metal centre and, finally, transfer the R3Si+ moiety to the CO2 molecule.[12] This constitutes an unusual example of bifunctional hydrosilylation catalysis reminiscent of hydrogenation systems.[13, 14] Theoretical calculations at the DFT level on this and other systems point to the oxophilicity of the silicon atom as a key factor in the activation of the silane molecule and subsequent transfer of the R3Si+ moiety.[8e, 12]

To gain insight into the ionic activation of silanes and the selectivity trends that this scarcely explored process imposes on hydrosilylation of terminal alkynes, we have studied the effect of the inclusion of trifluoroacetato ligands. For this purpose we have chosen the [Rh(III){κ4O,C,C',O'-bis(NHC)}] scaffold. In absence of an O-donor solvent the splitting of the silane molecule could be directed by the trifluoroacetato ligand, which may force the reaction to operate by a ligand-assisted ionic mechanism.

Herein, we describe the preparation of Rh(III) complexes featuring one or two trifluoroacetato ligands that catalyze the unusual formation of a variety of α-vinylsilanes in good selectivities by non-directed hydrosilylation of terminal alkynes.

The trifluoroacetato ligand was introduced by abstraction of one of the iodides in 1a with one equivalent of silver trifluoroacetate at room temperature in acetone to give the air stable complex 2 as a bright orange solid in excellent yields. The 1H NMR spectrum of 2 closely resembles that of 1a. The most remarkable change is the AB system at δ 6.76 and 6.31 ppm (2JH-H = 13 Hz) corresponding to the diasterotopic protons of the methylene group bridging the two NHCs moieties. 19F NMR confirms the presence of both the BF4– counteranion and the CF3COO– ligand with resonances at δ 148.1 and 71.4 ppm, respectively. Treatment of 2 with an additional equivalent of AgCF3COO under the same reaction conditions affords 3 as an off-white air stable solid in 76% isolated yield. The protons of the methylene group bridging the two NHCs appear as a singlet at δ 6.63 ppm in the 1H NMR spectrum in acetone, in full agreement with the ideal C2v symmetry. The equivalent CF3COO– ligands in 3 were observed at 71.6 ppm in the 19F NMR spectrum (Scheme 1).



Scheme 1. Synthetic route for the preparation of complexes 2 and 3. Reaction conditions for (i) and (ii): 1.0 eq AgCF3COO in acetone, 1 h at room temperature.

Suitable crystals of 2 and 3 were grown by slow diffusion of diethyl ether into a saturated acetone solution.[15] The molecular structures obtained by single crystal X-ray diffraction analysis (Figure 2) confirm the coordination of the trifluoroacetato ligands in the axial positions.

The asymmetric unit of 2 contains cation [Rh(CF3COO)I(bis-NHC)]+, anion BF4–, and a CH2Cl2 molecule, whereas two crystallographically different [Rh(CF3COO)2(bis-NHC)]+ cations and their respective BF4– anions where found on that of 3. Selected bond lengths and angles are provided in the Supporting Information. Equatorial coordination of the tetratopic bis-NHC ligand in both 2 and 3 cations does not display notable geometrical differences in comparison to analogous complexes,[7,16] except for the Rh–O bond distances, which are somewhat longer in 2 due to the presence of the iodide ligand, namely, Rh–O(ether), 2.203(5) Å and 2.198(5) Å in 2, and 2.154(2) Å, 2.170(2) Å, 2.177(2) Å, and 2.176(2) Å in 3.

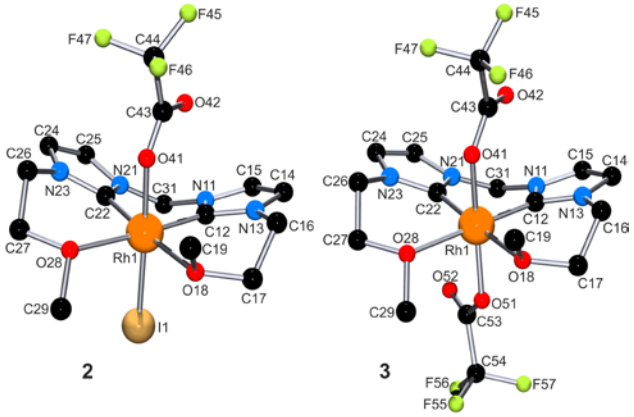
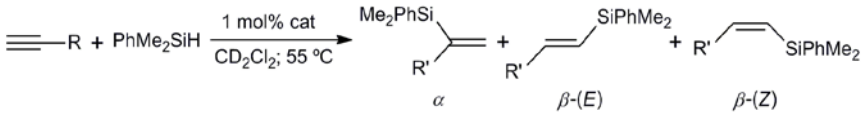


Figure 2. View of cations of 2 and one of the cations found in the asymmetric unit of 3.

Catalysis experiments on the hydrosilylation of terminal alkynes performed with complex 3, which features two trifluoroacetato ligands instead of the two iodides present in 1a, showed that good selectivities for the formation of □-vinylsilanes could be obtained for a wide range of alkynes in dichloromethane, including aromatic and aliphatic substituents with various functional groups. This sharply contrasts with the □-(Z)-selectivity obtained with the parent diiodido complex (1a). When complex 2 was tested, preferential formation of □-vinylsilanes was observed in most cases. However, the reactions are considerably less selective than those catalyzed by 3 (Tables 1 and 2). Therefore, looking at the reactivity trend that arises from the use of catalysts 1a, 2 and 3, it seems plausible that CF3COO– plays a key role in the selectivity of the reaction. Remarkably, when acetone was used as reaction solvent lower conversions were obtained. This is probably due to a competition between the hydrosilylation of the alkyne and acetone, which leads to total consumption of the silane before the alkyne is fully converted.

The reaction times required to reach total conversion span from 5 to 16 h at 55 ºC with 1.0 mol% catalyst loading (Scheme 2). Other silanes like Et3SiH or (MeO)3SiH do not improve the selectivities reported for 3, and the former gives markedly lower conversions (ca. 25% after 5h

at 55 ºC). The use of silanes more sterically demanding than PhMe2SiH, such as Ph2MeSiH leads to a drastic reduction of the α-selectivity and the activity, in fact no reaction was observed when Ph3SiH was used (see Supporting Information).



Scheme 2. Hydrosilylation of terminal alkynes.

Catalysts 2 and 3 need in general shorter reaction times and give better selectivities with aromatic than with aliphatic alkynes. Remarkably, selective conversion of tert-butylacetylene to its corresponding α-vinylsilane was also achieved in good yields despite the great steric hindrance between the two geminal substituents in the resulting molecule. The α-selectivity of the reaction is clearly improved by using the bis-trifluoroacetato complex 3. Noteworthy, catalyst 3 does not afford hydrogenation product and reduces significantly the amount of □-(Z)-vinylsilane formed during the reaction.

Table 1. Hydrosilylation of terminal alkynes with catalyst **2**.

Alkyne (R)	α (%)	β–(E) (%)	β-(Z) (%)	t (h)	Yield[c] (%)
4-CH_3O-Ph	66	18	16	5	100
4-^{t}Bu-Ph	61	29	9	16	100
4-CH_3-Ph	69	17	14	5	100
4-CF_3-Ph	76	17	7	5	100
n-Butyl	33	25	37	5	96[b]
n-Heptyl	29	13	53	16	95[b]
t-Butyl	52	31	5	16	89[b]
CH_3OCH_2–	71	19	0	16	90[b]
CH_3COO–	66	33	0	0	100

[a] General conditions: alkyne (0.15 mmol), $PhMe_2SiH$ (0.16 mmol), **2** (1.0 mol %) in 0.5 mL of CD_2Cl_2 at 55 ºC. [b] Hydrogenation product is observed. [c] Yields and selectivities were calculated by ^{1}H NMR.

Table 2. Hydrosilylation of terminal alkynes with catalyst **3**.

Alkyne (R)	α (%)	β-(E) (%)	β–(Z) (%)	t (h)	Yield[b] (%)
4-CH_3O-Ph	87	13	0	5	100
4-^{t}Bu-Ph	85	14	0	16	100
4-CH_3-Ph	85	15	0	5	100
4-CF_3-Ph	87	13	0	5	100
n-Butyl	73	16	11	5	100
n-Heptyl	72	15	13	16	100
t-Butyl	73	21	6	16	100
CH_3OCH_2–	86	14	0	16	100
CH_3COO–	81	19	0	0	100

[a)] General conditions: alkyne (0.15 mmol), $PhMe_2SiH$ (0.16 mmol), **3** (1.0 mol %) in 0.5 mL of CD_2Cl_2 at 55 ºC. [b)] Yields and selectivities were calculated by ^1H NMR.

Complex 3 represents a remarkable example of a rhodium hydrosilylation catalyst as it consistently affords α-vinylsilanes as the major reaction product in substantially better yields than those previously reported examples.[17]

In summary, we have prepared bis-NHC Rh(III) trifluoroacetate complexes (2 and 3) by substitution of the iodido ligands in the parent complex 1a, which gives rise to an outstanding selectivity change in the hydrosilylation of terminal alkynes. Complex 3 gives rise to good selectivities towards α-vinylsilanes, while 1a yields selectively β-(Z)-vinylsilanes. Assistance of the trifluoroacetato ligand is thought to play an important role in the selectivity of the reaction, perhaps as a consequence of the oxophilic nature of the oxygen atoms and their interaction with the silicon atom of the silane molecule. Mechanistic studies that aim at unveiling the operative catalytic cycle are currently in progress.

Experimental Section

General Information

All manipulations were performed using standard Schlenk techniques under an argon atmosphere, except where otherwise noted. All complexes after their formation were treated under aerobic conditions. Solvents were obtained dried from a solvent purification system from Innovative Technology Inc. Complex 1a has been prepared according to a synthetic procedure recently reported by us.[7] All other reagents were used as received. NMR spectra

were recorded on Bruker Avance 300 MHz, Bruker ARX 300 or Bruker Avance 400 MHz spectrometers. The chemical shifts are given as dimensionless δ values and are frequency referenced relative to residual solvent peaks for 1H and 13C. Coupling constants J are given in Hertz as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as “s”, “d”, or “m” for singlet, doublet, or multiplet, respectively. Mass spectra and high-resolution mass spectra were obtained on a Esquire 3000+ with ion trap detector interfaced on an Agilent 1100 HPLC analyzer, in electrospray (ES) mode unless otherwise reported. Elemental analyses C/H/N were carried out in a Perkin-Elmer 2400 CHNS/O analyzer.

Synthesis of methylenebis(N-2-methoxyethyl)imidazole-2-ylidene)(iodo)(trifluoroacetato)rhodium(III) tetrafluoroborate (2)

A solution of AgCF3COO (0.56 mmol, 0.12 g) in 10 mL of acetone was added dropwise over a solution complex 1a (0.36 g, 0.51 mmol) in acetone (10 mL) at room temperature. The reaction mixture was stirred for 1 h in the absence of light. The suspension thus obtained was filtered through a pad of celite®, evaporated under reduced pressure and the residue washed with Et2O (3 × 10 mL). The resulting yellow-orange solid was dried under vacuum to afford 0.27 g of 2 (0.38 mmol, 76% yield). 1H NMR (400 MHz, Acetone-d6): δ 7.77 (d, JH-H = 2 Hz, 2H, CHim), 7.69 (d, JH-H = 2 Hz, 2H, CHim), 6.77 (d, JH-H = 13 Hz, 1H, NCH2N), 6.32 (d, JH-H = 13 Hz, 1H, NCH2N), 4.78–4.43 (m, 8H, NCH2 y CH2O), 4.05 (s, 6H, CH3O). 13C NMR (101 MHz, Acetone-d6): δ 161.2 (q, 2JC-F = 37 Hz, CF3COO), 147.2 (d, 1JC-Rh = 46 Hz, NCimN), 125.9(CHim), 123.5 (CHim), 115.6 (q, 1JC-F = 291 Hz, CF3COO), 75.2 (OCH2), 63.6 (NCH2N), 63.5 (CH3O), 49.0 (CH2N). 19F NMR (Acetone-d6, 282 MHz): δ –148.1 (s, 4F, BF4), 71.4 (s, 3F, CF3COO). HRMS (ESI) m/z calcd for C15H20F3IN4O4Rh (M+): 606.9561, found 606.9531.

Synthesis of methylenebis(N-2-methoxyethyl)imidazole-2-ylidene)bis(trifluoroacetato)Rhodium(III) tetrafluoroborate (3)

A mixture of complex 2 (0.39 g, 5.46 mmol) with 2.2 equivalents of AgCF3COO (1.20 mmol, 0.27 g) were dissolved in acetone (20 mL) and the resulting mixture stirred for 1 h at room temperature in the absence of light. The suspension thus obtained was filtered through a pad of celite®, evaporated under reduced pressure and the residue washed with Et2O (3 × 10 mL). The resulting off-white solid was dried under vacuum to afford 0.29 g of 3 (0.42 mmol, 82% yield). 1H NMR (400 MHz, Acetone-d6): δ 7.81 (d, JH-H = 2 Hz, 2H, CHim), 7.73 (d, JH-H = 2 Hz, 2H, CHim), 6.63 (s, 2H, NCH2N), 4.63–4.73 (m, 4H, NCH2), 4.52–4.99 (m, 4H, CH2O), 4.02 (s, 6H, CH3O). 13C NMR (101 MHz, Acetone-d6): δ 162.6 (q, 2JC-F = 37.1 Hz, CF3COO), 147.2 (d, 1JC-Rh = 48 Hz, NCimN), 126.0 (CHim), 123.5 (CHim), 114.2 (q, 1JC-F = 290 Hz, CF3COO), 75.8 (OCH2), 62.8 (NCH2N), 62.4 (CH3O), 49.0 (CH2N). 19F NMR (Acetone-d6, 282 MHz): δ –148.1 (s, 4F, BF4), 71.6 (s, 6F, CF3COO). HRMS (ESI) m/z calcd for C17H20F6N4O6Rh (M+): 593.0337, found 593.0342.

Hydrosilylation of terminal alkynes

In an NMR tube complex 3 or 4 (1.5×10–3 mmol, 1.0 mol%) were dissolved in 0.5 mL of CD2Cl2. Subsequently, PhMe2SiH (26 µL, 0.16 mmol), the corresponding terminal alkyne (0.15 mmol) and 1,3,5-trimethylbenzene (0.15 mmol, 21 µL) as internal standard were added. The NMR tube was placed in an oil bath at 55 ºC for 5 to 16 h. The yields were calculated by 1H

NMR. The different isomers were unambiguously identified by means of the 3JH-H coupling constants of the vinylic protons.

Acknowledgements

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[15] Crystal data. Compound 2: [C16H22BCl2F7IN4O4Rh], triclinic, P–1, a = 8.7276(13) Å, b = 12.3476(19) Å, c = 12.838(2) Å, α = 92.591(2)º, β = 104.193(2)º, γ = 108.758(2)º, Z = 2, Mr = 778.90 g mol–1, V = 1258.4(3) Å3, Dcalcd = 2.056 g cm–3, λ(Mo Kα) = 0.71073 Å, T = 100 K, μ = 2.201 mm–1, 27137 reflections collected, 6520 observed (Rint = 0.0389), R1(Fo) = 0.0535 [I > 2σ(I)], wR2 (Fo2) = 0.1384 (all data), GOF = 1.094. CCDC 1012558. Compound 3: [C17H20BF10N4O6Rh], triclinic, P–1, a = 12.7120(10) Å, b = 13.0289(10) Å, c = 16.8111(13) Å, α = 109.7310(10)º, β = 106.7720(10)º, γ = 95.3840(10)º, Z = 4, Mr = 680.09 g mol–1, V = 2452.2(3) Å3, Dcalcd = 1.842 g cm–3, λ(Mo Kα) = 0.71073 Å, T = 100 K, μ = 0.814 mm–1, 29161 reflections collected, 11233 observed (Rint = 0.0264), R1(Fo) = 0.0415 [I > 2σ(I)], wR2 (Fo2) = 0.1403 (all data), GOF = 1.044. CCDC 1012559.

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