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Highly selective silylformylation of internal and functionalised alkynes with a cationic dirhodium(II) complex catalyst

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ABSTRACT

The tetracationic complex $[Rh_2(MeCN)_2(Naft)_4](BF_4)_4$ (Naft = μ-1,8-naphthyridine) was found to be an efficient catalyst for the silylformylation of internal and functionalised alkynes to yield useful synthetic intermediates. The complex exhibits an unprecedented chemoselectivity towards alkyne silylformylation instead of simple hydrosilylation, as well as a good stereoselectivity. The catalytic efficiency of the complex is markedly superior compared to that of previously reported catalysts such as $[Rh^+C_7H_8BPh_4^-]$ or $Rh_4(CO)_{12}$; incidentally, the performance of the latter catalyst was found to vary dramatically with its shelf-life, which indicates that the catalyst evolves with ageing towards other species, most notably higher nuclearity rhodium carbonyl clusters, which are more chemoselective towards silylformylation. Preliminary results on the determination of the catalytically active species in the case of complex $[Rh_2(MeCN)_2(Naft)_4](BF_4)_4$ indicate that the complex is reduced in situ to a dirhodium(I) species which maintains the dimeric, lantern-shaped structure.

1. Introduction

Neutral dinuclear complexes of rhodium(II) are known to be catalytically active in a number of synthetically useful transformations [1]. The most thoroughly investigated reactions are metal-mediated carbene transfer reactions [2], but in the course of the last ten years the successful application of this kind of catalysts has been considerably extended to include nitrene transfer reactions [3], allylic oxidations [4], cycloadditions [5], C–C coupling reactions [6], and reactions involving silanes, such as silane alcoholysis, hydrosilylations or silylformylations [7,8].

It has been recognised that in most of these reactions the electrophilicity of the dirhodium(II) complex catalyst is a key factor in determining its activity and selectivity [2c,d,3f,5e]. This parameter has been generally modulated by varying the electron-donating character of the anionic bridging ligands in the metal complex. Recently, though, alternative approaches have been reported that allow to prepare novel dirhodium catalysts with tailored electrophilicity, namely upon oxidation of one of the rhodium atoms to the +III oxidation state [5e], introduction of an additional, substitutionally inert ligand into one of the apical positions of the complex [4d,6], or replacement of the bridging anionic ligands with neutral ones yielding a cationic complex [9].

We have an ongoing research program aimed at the preparation of different kinds of electrophilic dirhodium(II) complexes using the latter approach and at the evaluation of their catalytic performance in technologically relevant reactions [9]. Although cationic dirhodium(II) complexes in which the acetate ligands have been substituted by coordinated solvent molecules, most commonly acetonitrile, are quite well known [10], much less common are examples in which the acetate ligands are substituted by neutral bidentate ligands [9b,11,12]. The most commonly employed ligands for this purpose belong to the class of 1,8-naphthyridines [9b,11,12a,b]. In particular, we have recently prepared complex **1** (Scheme 1), a homoleptic, tetracationic dirhodium(II) complex bearing four bridging 1,8-naphthyridines as equatorial ligands and two loosely bound acetonitrile molecules as axial ligands, and we have reported preliminary results demonstrating the catalytic potency of this complex in the silylformylation of a model terminal alkyne [9b]. We now present an alternative, more efficient synthetic pathway leading to the same complex as well as the results of an evaluation of its notable catalytic activity and selectivity in the silylformylation of internal as well as functionalised alkynes.

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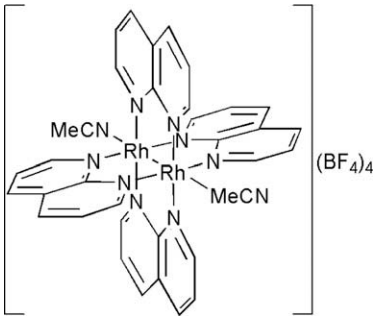


Scheme 1. Structure of complex **1**.

2. Results and discussion

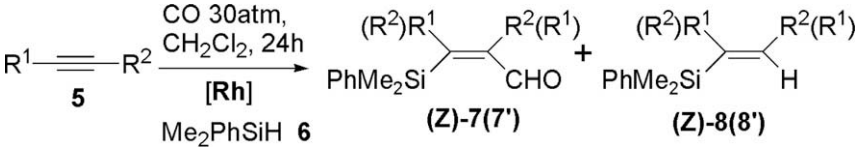
The first problem that we intended to address was the development of a more practical synthesis for complex **1**. The previously reported procedure [9b] for the synthesis of the complex involved namely at first reaction of $Rh_2(OAc)_4$ with 4 equiv. of 1,8-naphthyridine in acetic acid at reflux, with formation of a tetrakis-dirhodium(II) tetranaphthyridino complex with two acetate ligands occupying the axial coordination sites and two acetate counterions. Treatment with $NaBPh_4$ caused the substitution of the acetate counterions with two BPh_4^- anions, and subsequent reaction with Meerwein's salt triethyloxonium tetrafluoborate removed the apical acetates yielding the tetracationic complex **1**. The overall yield of this process was moderate (38%), it required extensive purification of the final product and generated a lot of waste. We have devised a cleaner and more straightforward procedure for the same synthesis which moves from the literature-known cationic complex $[Rh_2(OAc)_2(MeCN)_6](BF_4)_2$, readily obtainable in one step and high yield from commercial $Rh_2(OAc)_4$ [10a]. Reaction of this complex with 4 equiv. of 1,8-naphthyridine in acetonitrile yielded the intermediate dicationic complex $[Rh_2(OAc)_2(Naft)_4](BF_4)_2$, which was subsequently treated with triethyloxonium tetrafluoborate without further purification to remove the two apical acetates yielding complex **1**.

The catalytic performance of complex **1** had already been preliminarily evaluated [9b] in the silylformylation reaction of 1-hexyne with dimethylphenylsilane as model reagents. The complex showed both high efficiency and selectivity towards the formation of (*Z*)-2-[(dimethyl-phenyl-silyl)-methylene]-hexanal ("β-silylalkenal"). Moreover, it resulted completely unable to promote the hydrosilylation process, a common side reaction often observed under the experimental conditions of the silylformylation reaction. It seemed therefore reasonable to evaluate **1** as a general catalyst for the synthesis of β-silylalkenals, polyfunctionalised molecules that can be converted into dienes [13], dienones [14], α,β-unsaturated alcohols [15], esters and ketones [16] and can undergo fluoride promoted aryl migration [17b] thus generating 2-(arylmethyl)-aldehydes, important industrial precursors of perfumes. Consequently, we extended our investigation to internal alkynes, which are notoriously difficult to silylformylate selectively [17]. The silylformylation reactions of disubstituted alkynes (Scheme 2) were carried out under the experimental conditions already developed for terminal acetylenes, i.e. 30 atm of CO, equimolar amounts of substrates, 0.5–1 mol% of catalysts, 100 °C, 24 h (Table 1). The catalytic performance of the naphthyridine complex **1** was compared with that of three other literature-known rhodium species with different electronic and structural features: dirhodium(II) precursor $[Rh_2(OAc)_2(MeCN)_6](BF_4)_2$ (**2**), a neutral cluster species such as $Rh_4(CO)_{12}$ (**3**) and the zwitterionic rhodium(I) catalyst $[Rh^+C_7H_8BPh_4^-]$ (**4**). The last two catalysts had been already used in the silylformylation reactions of several substrates containing C=O and C–C terminal multiple bonds [17].

First of all the reactivity of phenylpropyne **5a** with Me_2PhSiH was considered, since it is well known that the presence of an aromatic ring conjugated to the triple bond has an activating effect towards the silylformylation reaction [17].

As described in Table 1, while a negligible conversion was observed running the process at room temperature (entry 1), high conversion and chemoselectivity towards the aldehydic products (93%) could be reached at 100 °C in reactions performed with a catalytic amount (0.4 mol%) of complex **1** (entry 2), the less hindered aldehydic isomer **(*Z*)-7a** being formed in more than 80% yield. On the contrary, all the other rhodium complexes afforded mainly the hydrosilylation by-products **(*Z*)-8(8′)**, even if a higher amount of catalyst was used (Table 1, entries 3–5 and 8 vs. 2). In particular, the dirhodium complex $[Rh_2(OAc)_2(MeCN)_6](BF_4)_2$ (**2**) (Table 1, entry 1) turned out to be the most active towards the hydrosilylation reaction, which result highlights the importance of the naphthyridine ligand in steering the reaction chemoselectivity.

We were surprised by the low chemoselectivity towards the silylformylation reaction recorded with $Rh_4(CO)_{12}$. Indeed, Matsuda et al. used $Rh_4(CO)_{12}$ in the silylformylation of phenylpropyne and reported a very different result (82% total selectivity for the β-silylalkenals) [17a], in spite of the fact that the reactions were performed under almost the same experimental conditions. We set out to investigate on this discrepancy in more detail and found that a sample of freshly prepared and recrystallised $Rh_4(CO)_{12}$ behaved as a poor silylformylation catalyst regardless of the amount of complex employed (Table 1, entries 4–6, catalyst indicated as $\mathbf{3_N}$), which was also unexpected since we had previously pointed out [17b] the importance of using a low quantity of $Rh_4(CO)_{12}$ in the silylformylation of sterically hindered acetylenes to improve the chemoselectivity of the process. On the other hand, when a sample of "old" $Rh_4(CO)_{12}$, i.e. kept under argon and at low temperature (3 °C) for at least 6 months (Table 1, entry 7, catalyst indicated as $\mathbf{3_O}$), was reacted with phenylpropyne and Me_2PhSiH under CO, a dramatic increase in the chemoselectivity for the silylformylation reaction was observed. An analogous trend was observed in the reactions carried out with 5-decyne (Table 1, entries 10 and 11). The obtained results indicate that freshly prepared $Rh_4(CO)_{12}$ indeed displays poor chemoselectivity towards silylformylation; on the other hand, the catalyst evolves with ageing even if properly stored towards catalytic species which are much more chemoselective. Preliminary investigations based on electrospray mass spectrometry (ESI-MS) of the two $Rh_4(CO)_{12}$ ($\mathbf{3_N}$ and $\mathbf{3_O}$) samples showed a correlation between the ageing time of the rhodium complexes and the presence of increasing amounts of $Rh_6(CO)_{16}$. We employed the method of Handerson et al. [18], who described the structural characterisation of metal carbonyl



Scheme 2. Silylformylation of 1,2-disubstituted alkynes.

Table 1
Silylformylation of internal acetylenes with dimethylphenylsilane.[a]

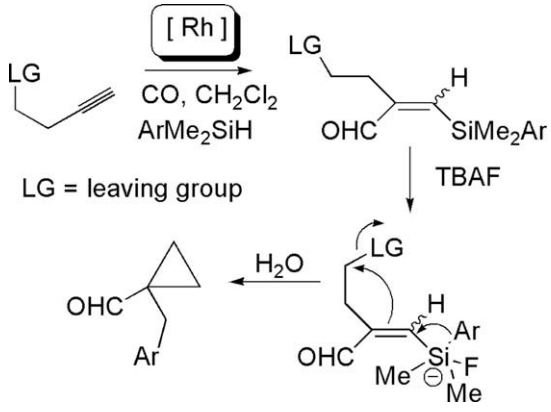
Entry	R^1	R^2	**5**	[Rh][b] (mol%)	Conv. (%)[c]	Selectivity (%)[d]	
						(*Z*)-7(7′) (7/7′)[e]	(*E*)-8(8′) (8/8′)
1[f]	Me	Ph	**a**	**1** (0.4)	7	94	6
2	Me	Ph	**a**	**1** (0.4)	100	93(83/17) [71]	7(50/50)
3	Me	Ph	**a**	**2** (0.8)	100	8(86/24)	92(68/32)
4	Me	Ph	**a**	$\mathbf{3_N}$ (0.5)	100	14(100/0)	86(75/25)
5[g]	Me	Ph	**a**	$\mathbf{3_N}$ (0.2)	100	16(100/0)	84(72/28)
6	Me	Ph	**a**	$\mathbf{3_N}$ (0.05)	100	13(100/0)	87(70/30)
7	Me	Ph	**a**	$\mathbf{3_O}$ (0.5)	86	60(82/18)	40(75/25)
8[h]	Me	Ph	**a**	**4** (1)	100	24(100/0)	76(60/40)
9	*n*Bu	*n*Bu	**b**	**1** (0.4)	98	96 [56]	4
10	*n*Bu	*n*Bu	**b**	$\mathbf{3_N}$ (0.5)	87	27	73
11	*n*Bu	*n*Bu	**b**	$\mathbf{3_O}$ (0.5)	82	50	50
12	*n*Bu	*n*Bu	**b**	**4** (1)	100	53 [41]	47
13	Me	*n*Pr	**c**	**1** (0.4)	97	82(65/35) [43]	18(52/48)
14	Me	*n*Pr	**c**	**4** (1)	100	55(73/27) [30]	45(62/38)

[a] *Reaction conditions:* 3 mmol Me_2PhSiH, 3 mmol alkyne, 3 ml CH_2Cl_2, 24 h, 30 atm P_{CO}, 100 °C.
[b] *Rhodium catalysts:* **1**: $[Rh_2(MeCN)_2(Naft)_4](BF_4)_4$ **2**: $[Rh_2(OAc)_2(MeCN)_6](BF_4)_2$, **3**: $Rh_4(CO)_{12}$; **4**: $[Rh^+C_7H_8BPh_4^-]$.
[c] Determined by GC analysis.
[d] Determined by GC and ^1H NMR analysis; the diastereomers ratio is reported in round brackets.
[e] Isolated yields (%) are reported in square brackets.
[f] Reaction performed at room temperature.
[G] Reaction performed in toluene.
[h] Reaction performed under 40 atm of CO.

compounds using ESI-MS in negative ion-mode, provided that the complexes are dissolved in methanol and treated with a drop of NaOMe in MeOH immediately before sample injection. When this alkoxide-ionization method was applied to $\mathbf{3_N}$ and $\mathbf{3_O}$, together with the expected peak at *m*/*z* 779 for $[Rh_4(CO)_{12} + MeO^-]$ another peak was observed at *m*/*z* 1097 which considerably grew on going from $\mathbf{3_N}$ to $\mathbf{3_O}$ and corresponded to the adduct $Rh_6(CO)_{16}$, a known decomposition product of the tetramer [19]. As a matter of fact, a preliminary test of silylformylation of phenylpropyne performed with a pure sample of $Rh_6(CO)_{16}$ (0.5 mol%) showed indeed at 100% conversion a good (57%) chemoselectivity towards the formation of the aldehydic products, fully comparable to the value obtained with $\mathbf{3_O}$. Consequently, our results indicate that the difference in the catalytic performance of the two rhodium samples is related to the formation of $Rh_4(CO)_{12}$ decomposition products whose exact nature and catalytic role is currently under study.

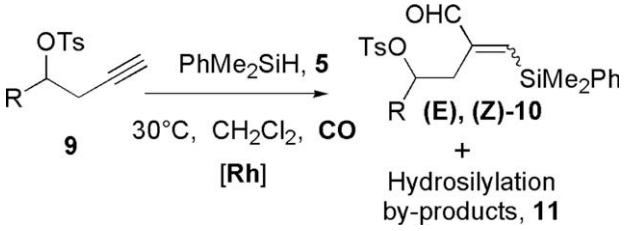
Gratifyingly, the naphthyridine complex **1** showed a reproducible behavior if stored under argon atmosphere. Most notably, it delivered a good catalytic performance also in the silylformylation reactions of internal alkynes with aliphatic substituents. Complex **1** clearly stood out as the best catalytic precursor in terms of chemoselectivity towards the β-silylalkenals **(*Z*)-7b** and **(*Z*)-7(7′)c** (Table 1, entries 9 and 13), thus allowing the extension of the silyformylation reaction to internal alkynes, regardless of the electronic and steric requirements of the groups connected to the triple bond.

The following step was to apply the naphthyridine complex **1** to the preparation of functionalised β-silylalkenals. Indeed, some of us have been studying the silyformylation reaction of ω-functionalised acetylenes for ten years [17b] and have demonstrated that the corresponding aldehydes can be obtained in high yields without involving double or triple bonds, nitrile, halogens, epoxide, hydroxyl or ester moieties present in the substrates. We were particularly interested in the silylformylation reaction of homopropargyl substituted acetylenes containing a good leaving group (Scheme 3, LG = OTs, OMs, etc.) since the corresponding β-silylalkenals can be subsequently treated with a fluoride source [17b] yielding cyclopropanecarbaldehydes (Scheme 3), important key fragments in many natural products and useful synthetic intermediates due to the ease of their ring opening [20].



Scheme 3. Rhodium catalysed synthesis of 2-(methylaryl)cyclopropanecarbaldehydes.

Therefore, a few homopropargyl tosylates **9** were prepared starting from the corresponding alcohols [21] and reacted with an equimolar amount of Me_2PhSiH under CO pressure, in the presence of a rhodium catalyst. The obtained results are reported in Scheme 4 and Table 2 and clearly indicate that both the conversion and the chemoselectivity of the process are strongly dependent on the structure of the acetylenic substrate and of the rhodium catalyst. Indeed, in the reactions performed with catalyst **3**, a dramatic reduction of the selectivity towards the aldehydic products was



Scheme 4. Silylformylation of functionalised alkynes.

Table 2
Silylformylation of homopropargyl tosylates.[a]

Entry	R	9	[Rh][b] (mol%)	P_{CO} (atm)	t (h)	Conv. (%)[c]	Selectivity (%)[c]	
							(*E*),(*Z*)-10	11[d]
1	H	**a**	**3**$_N$ (0.1)	30	24	95	100(62/38)	–
2	Et	**b**	**3**$_N$ (0.1)	30	24	100	45(89/11)	55
3	Et	**b**	**3**$_N$ (0.5)	50	24	100	42(71/29)	58
4	Et	**b**	**4** (0.5)	50	24	100	71(88/12)	29
5	Et	**b**	**1** (0.5)	50	48	72	100(79/21)	–
6	Ph	**c**	**1** (0.5)	50	48	0	–	–

[a] *Reactions conditions:* 3 mmol Me_2PhSiH, 3 mmol alkyne **9**, 3 ml CH_2Cl_2, 100 °C.
[b] *Rhodium catalysts:* **1**: $[Rh_2(MeCN)_2(Naft)_4](BF_4)_4$, **3**: $Rh_4(CO)_{12}$; **4**: $[Rh^+C_7H_8BPh_4^-]$.
[c] Determined by GC and ^1H NMR analysis; the diastereomeric ratio is reported in brackets.
[d] A mixture of the three possible isomers was detected by ^1H NMR analysis.

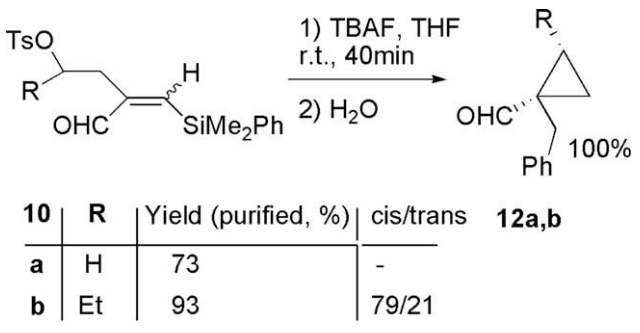
observed on going from linear to α-branched tosylates (Table 2, entries 1–3), even if both the CO pressure and the amount of the catalyst were enhanced.

The zwitterionic complex **4** showed a better selectivity with branched tosylates, but 30% of hydrosilylation by-products were still present (Table 2, entry 4). On the contrary, complex **1** yielded the desired aldehydes quantitatively (Table 2, entry 5) albeit at a lower reaction rate. Unfortunately, the steric requirements of the tosylates turned out to be still the limiting factor of the reaction, which proved unsuccessful when 4-phenyl-4-tosyl-1-butyne **9c** was reacted.

The functionalised aldehydes **(*E*),(*Z*)-10a** and (*E*),(*Z*)-**10b** were then submitted to the fluoride promoted rearrangement affording the corresponding cyclopropanecarbaldehydes **12** quantitatively and with a good stereoselectivity (Scheme 5). Indeed, according to the mechanism depicted in Scheme 3, each of the two different stereoisomers **(*E*),(*Z*)-10a** and (*E*),(*Z*)-**10b** was expected to be converted into the corresponding cyclic aldehydes **12a** and **12b** exclusively and maintaining the original diastereomeric ratio: this is precisely what was experimentally observed.

Finally we started an investigation aimed at understanding the nature of the rhodium species that gives rise to the catalytic cycle of the silylformylation process. This may well be different from complex **1**, given the relatively harsh reaction conditions employed in the silylformylation protocol, and in particular the reducing nature of the reaction mixture. Indeed, complex **1** was found to decompose in the course of the reaction ultimately yielding catalytically inactive rhodium black as the final product. On the other hand, Doyle et al. already demonstrated that the dirhodium(II) perfluorobutyrate complex that they employed as efficient silylformylation catalyst was actually reduced in situ to form monometallic rhodium(I) species [7e].

We made some preliminary attempts to evaluate the stability of complex **1** under the reaction conditions by subjecting a solution of **1** in CH_2Cl_2 to CO pressure (40 atm) and subsequently analysing the products dissolved in CH_3CN by ESI-MS (Fig. 1). Quite interestingly, the carbon monoxide atmosphere determined the complete reduction of the rhodium(II) centers to rhodium(I). Moreover, when the CO pressure was increased, all CH_3CN molecules were replaced by CO as clearly showed by the mass spectrum reported in the figure. In this case, the base peak was due to the ion $[Rh_2(Naft)_3{\cdot}2CO{\cdot}8H_2O]^{2+}$ (398 *m*/*z*) containing exclusively naphthyridines and CO ligands. The second most intense peak at 333 *m*/*z* was also demonstratedly originating from the first one and was found to be attributable to $[Rh_2(Naft)_2{\cdot}2CO{\cdot}8H_2O]^{2+}$. The presence of several molecules of water, associated to the rhodium species and presumably originally present in the employed mobile phase (i.e. acetonitrile), was confirmed by the loss of fragments of 18 Da from the precursor ion (data not shown). We are currently trying to ascertain whether the rather peculiar structure of such species may help explaining the particular reactivity exhibited by this catalytic system in the silylformylation reaction.



10	R	Yield (purified, %)	cis/trans
a	H	73	-
b	Et	93	79/21

12a,b

Scheme 5. TBAF promoted synthesis of functionalised (*cis*/*trans*) cyclopropanecarbaldehydes.

3. Conclusion

In conclusion, we have demonstrated that the tetracationic complex catalyst **1** exhibits a unique and synthetically useful chemoselectivity towards the silylformylation reaction of internal and functionalised alkynes. The stereoselectivity of the reaction is also good. On the contrary, preliminary investigations on $Rh_4(CO)_{12}$ indicate that this complex, often referred to as a typical catalyst for silylformylation reactions, is poorly chemoselective, although the catalyst was found to evolve with ageing generating other catalytically active species with enhanced chemoselectivity. We are currently further investigating on the reaction mechanism of complex **1** and on the extension of its application to the silylformylation of other functionalised alkynes yielding valuable synthetic intermediates.

4. Experimental

4.1. General procedures

The reagents (Aldrich-Chemie) were high purity products and generally used as received. 1,8-Naphthyridine (Naft) was prepared following the method of Skraup [22]. The cationic complex $[Rh_2(OAc)_2(MeCN)_6](BF_4)_2$ was prepared in almost quantitative yield from $Rh_2(OAc)_4$ according to the literature [10a]. $Rh_4(CO)_{12}$ [23] (**3**) and $[Rh^+C_7H_8BPh_4^-]$ [24] (**4**) were prepared and purified as previously reported. All rhodium species were stored refrigerated under argon. 5-Hexyn-3-ol, 1-phenyl-3-butyn-1-ol were obtained according to the procedure described by Dimitriadis and co-workers [21]. 3-Butynyl-p-toluenesulfonate (**9a**) was used as received. Me_2PhSiH (**6**), 1-phenylpropyne (**5a**), 5-octadiyne (**5b**) and 2-hexyne (**5c**) were distilled and kept under argon.

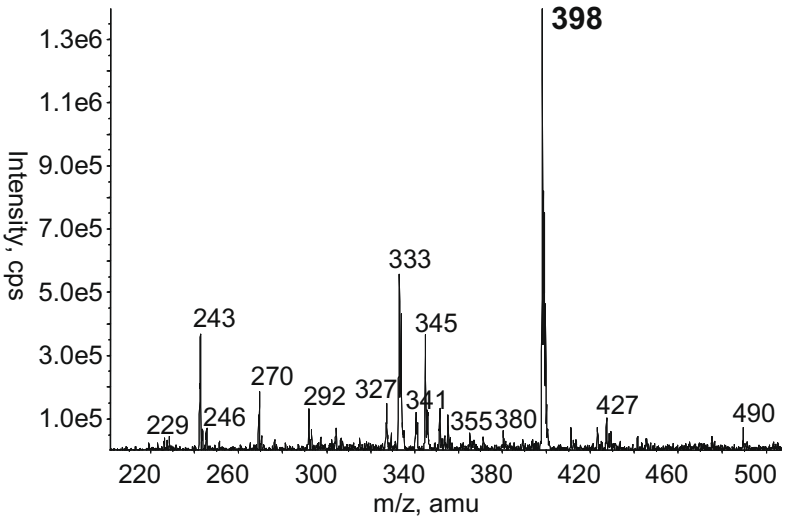


Fig. 1. ESI-MS (positive ion-mode) of complex **1** under 40 atm CO pressure.

Unless otherwise noted, solvents were dried before use and the reaction apparatus carefully deoxygenated; reactions were performed under argon and all operations were carried out under an inert atmosphere. The solution ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker Avance 300 MHz at room temperature. The chemical shifts were determined by reference to the residual solvent peaks, using tetramethylsilane as internal standard. The FT IR spectra were recorded on a Bruker Tensor27 spectrophotometer (KBr disks). GLC analyses were performed on a Perkin–Elmer 8600 Model instrument, equipped with a DB1 capillary column (30 m × 0.52 mm, 5 μm) and a flame ionization detector, with He as carrier gas. Mass spectra were obtained with an Applied Biosystems-MDS Sciex API 4000 triple quadrupole mass spectrometer (Concord, Ont., Canada), equipped with a Turbo-V ion-spray (TIS) source. The operative parameters were as follows: ion-spray voltage (IS), 5.0 kV; gas source 1(GS1), 25; gas source 2(GS2), 25; turbo temperature (TEM), 0 °C; entrance potential (EP), 10 V; declustering potential (DP), 20 V; scan range, 300–1500 *m*/*z*. MS–MS spectra were produced by collision-induced dissociation (CID) of selected precursor ions in a LINAC collision cell (Q2) and mass-analyzed in the second mass filter (Q3). Additional experimental conditions for MS–MS spectra included: collision (CAD) gas, nitrogen; CAD gas pressure, 4 mPa; collision energy (CE), ramp from 5 to 130 eV (step = 2); collision cell exit potential (CXP), 15 V. Each sample for MS (ESI) was infused by a syringe pump Harvard Mod.22 (Harvard Apparatus, Holliston, MA, USA).

4.2. Synthesis of complex *1*

150 mg (0.20 mmol) $[Rh_2(OAc)_2(MeCN)_6](BF_4)_2$ were dissolved into 30 mL acetonitrile under an inert atmosphere. 150 mg (0.80 mmol 4 equiv.) 1,8-naphthyridine (Naft) were then added, and the resulting solution was heated at reflux for 4 h. The solution was cooled to room temperature and the complex product $[Rh_2(OAc)_2(Naft)_4](BF_4)_2$ was subsequently precipitated by addition of diethylether and filtered off. The complex (115 mg, 0.113 mmol) was redissolved without further purification into 10 mL acetonitrile. 0.34 mL of a 1 M solution of $(Et_3O)(BF_4)$ in dichloromethane (0.34 mmol, 3 equiv.) were added. The reaction mixture was stirred for 24 h, then treated with diethyl ether to precipitate the product as a light brown solid, which was filtered and dried under vacuum (95 mg, 0.082 mmol, 41% overall yield from $Rh_2(OAc)_4$). Anal. Calc. for $C_{36}H_{30}N_{10}B_4F_{16}Rh_2$ (M = 1155.67): C, 37.41; H, 2.61; N, 12.11. Found: C, 37.43; H, 2.86; N, 12.01%. The characterisation data exactly matched the previously reported ones [9b].

4.3. Catalytic tests

Catalytic reactions were performed in a 25 mL stainless steel autoclave fitted with a Teflon inner crucible and a stirring bar. In a typical run, 3 mmol Me_2PhSiH, 3 mmol alkyne, 3 mL CH_2Cl_2 and a chosen amount of rhodium catalyst were put, under CO atmosphere, in a Pyrex Schlenk tube. This solution was introduced in the autoclave, previously placed under vacuum (0.1 Torr), by a steel siphon. The reactor was pressurized with carbon monoxide and the mixture was stirred for a chosen time. After removal of excess CO (fume hood), the reaction mixture was diluted with CH_2Cl_2, filtered on celite and concentrated under vacuum. The reagent conversion and the product composition were determined by GC and GC–MS analysis. Yields were confirmed by purification of the crude oil by column chromatography on silica gel 60 (230–400 mesh) using CH_2Cl_2 as eluent affording the pure aldehydes.

4.3.1. Catalytic silylformylation of internal alkynes

(Z)-2-Phenyl-3-(dimethylphenylsilyl)-2-butenal, **(*Z*)-7a** [17a]: colorless oil. ^{1}H NMR ($CDCl_3$): δ = 0.62 (s, 6H), 2.02 (s, 3H), 7.22 (m, 10H), 9.96 (s, 1H). EI-MS: *m*/*z* (relative intensity) = (265, M^+−15, 100), 203(20), 159 (10), 135(12), 115(5).

(Z)-2-Methyl-3-phenyl-3-(dimethylphenylsilyl)-propenal, **(*Z*)-7′a** [17a]: colorless oil. ^{1}H NMR ($CDCl_3$): δ = 0.37 (s, 6H), 1.68 (s, 3H), 7.20 (m, 10H), 10.03 (s, 1H). EI-MS: *m*/*z* (relative intensity) = (265, M^+−15, 100), 203(57), 174(6), 159(10), 135(20), 115(8), 91(5).

(E)-1-Phenyl-2-(dimethylphenylsilyl)-propylene, **(*E*)-8a** [25]: colorless oil. ^{1}H NMR ($CDCl_3$): δ = 0.43 (s, 6H), 2.04 (d, J = 1.8 Hz, 3H), 6.86 (q, J = 1.8 Hz, 1H), 7.35 (10H); EI-MS: *m*/*z* (relative intensity) = 252 (M^+, 38), 237 (100), 197 (10), 159 (30), 135 (21), 115 (7).

(E)-1-Phenyl-1-(dimethylphenylsilyl)-propylene, **(*E*)-8′a** [26]: colorless oil. ^{1}H NMR: 0.40 (s, 6H), 1.68 (d, J = 6.6 Hz, 3H), 6.22 (q, J = 6.6 Hz, 1H), 7.28 (m, 10H). EI-MS: *m*/*z* (relative intensity) = 252 (M^+, 47), 237 (100), 197 (16), 159 (8), 135 (35), 115 (8).

(Z)-2-Butyl-3-(dimethylphenylsilyl)-2-heptenal, **(*Z*)-7b**: colorless oil. ^{1}H NMR ($CDCl_3$): δ = 0.52 (s, 6H), 0.92 (m, 6H), 1.36 (m, 8H), 2.35 (t, J = 6.9 Hz, 2H), 2.46 (t, J = 7.2 Hz, 2H), 7.36 (m, 3H), 7.47 (m. 2H), 9.77 (s, 1H); ^{13}C NMR ($CDCl_3$): δ = 0.6 (2C), 13.7, 13.9, 23.1, 23.2, 25.6, 31.8 (2C), 33.7, 128.1, 129.2, 133.4, 139.0, 152.1,

164.2, 193.8; EI-MS: *m*/*z* (relative intensity) = 287 (M^+-15, 47), 245 (100), 195 (3), 167 (5), 135 (9), 107 (4).

(E)-5-(Dimethylphenylsilyl)-5-decene, **(*E*)-8b**: colorless oil. ^{1}H NMR ($CDCl_3$): δ = 0.35 (s, 6H), 0.83 (t, *J* = 6.9 Hz, 3H), 0.92 (t, *J* = 6.9 Hz, 3H), 1.28 (m, 8H), 2.12 (m, 4H), 5.80 (t, *J* = 7.2 Hz, 1H), 7.43 (m, 5H); EI-MS: *m*/*z* (relative intensity) = 259 (M^+-15, 20), 217 (8), 197 (26), 135 (100).

(Z)-2-Propyl-3-(dimethylphenylsilyl)-2-butenal, **(*Z*)-7c** [17a]: colorless oil. ^{1}H NMR ($CDCl_3$): δ = 0.53 (s, 6H), 0.93 (t, *J* = 7.4 Hz, 3H), 1.38 (m, 2H), 2.10 (s, 3H), 2.39 (m, 2H), 7.37 (m, 3H), 7.48 (m, 2H), 9.78 (s, 1H); ^{13}C NMR ($CDCl_3$): δ = 0.3(2C), 14.4, 22.1, 27.9, 36.7, 128.4, 129.6, 133.6, 138.7, 152.8, 162.8, 193.5.

(Z)-2-Methyl-3-(dimethylphenylsilyl)-2-hexenal, **(*Z*)-7′c** [17a]: colorless oil. ^{1}H NMR ($CDCl_3$): δ = 0.53 (s, 6 H), 0.97 (t, *J* = 7.2 Hz, 3H), 1.38 (m, 2H), 1.89 (s, 3H), 2.46 (m, 2H), 7.37 (m, 3H), 7.48 (m, 2H), 9.82 (s, 1H); ^{13}C NMR ($CDCl_3$): δ = 0.6(2C), 14.7, 22.4, 27.9, 36.7, 128.3, 129.5, 133.7, 139.0, 147.8, 164.8, 194.0.

(E)-2-(Dimethylphenylsilyl)-2-hexene, **(*E*)-8c**: colorless oil. ^{1}H NMR ($CDCl_3$): δ = 0.40 (s, 6H), 0.98 (t, *J* = 7.4 Hz, 3H), 1.49 (m, 2H), 1.72 (d, *J* = 1.8 Hz, 3H), 2.22 (m, 2H), 5.88 (tq, *J* = 1.8, 7.0 Hz, 1H), 7.29 (m, 3H), 7.65 (m, 2H). EI-MS: *m*/*z* (relative intensity) = 218 (M^+, 46), 203 (100), 175 (52), 161 (14), 135 (66), 121 (27), 105 (12).

(E)-3-(Dimethylphenylsilyl)-2-hexene, **(*E*)-8′c**: colorless oil. ^{1}H NMR ($CDCl_3$): δ = 0.42 (s, 6H), 0.90 (t, *J* = 7.2 Hz, 3H), 1.33 (m, 2H), 1.67 (d, *J* = 6.6 Hz, 3H), 2.17 (m, 2H), 6.00 (qt, *J* = 6.6, 0.9 Hz, 1H), 7.42 (m, 3H), 7.61 (m, 2H). EI-MS: *m*/*z* (relative intensity) = 218 (M^+, 30), 203 (100), 189 (10), 141 (14), 135 (24), 121 (11), 105 (5).

4.3.2. Synthesis of toluene-4-sulfonic acid 1-ethyl-but-3-ynyl ester (*9b*)

2.09 g (21.3 mmol) of 5-hexyn-3-ol [21] were added to a solution of 6.16 g (31.5 mmol) of *p*-toluensulfonyl chloride in 60 mL diethyl ether at −15 °C. 10.50 g (187 mmol) of finely powdered KOH were then added and the obtained solution was stirred for 2 h at 0 °C, quenched with ice and extracted with Et_2O (3 × 50 mL). The combined organic layers were dried over Na_2SO_4, the solvent was removed under reduced pressure yielding 4.30 g (17.0 mmol, 80%) of crude **9b** as a colorless oil that was used without any further purification. ^{1}H NMR ($CDCl_3$): δ = 0.81 (t, *J* = 7.2 Hz, 3H), 1.75 (m, 2H), 1.94 (t, *J* = 2.5 Hz, 1H), 2.43 (s, 3H), 2.50 (m, 2H), 4.50 (m, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 8.9, 21.6, 24.1, 26.3, 71.1, 78.4, 81.4, 127.7, 129.7, 133.9, 144.7.

4.3.3. Toluene-4-sulfonic acid 1-phenyl-but-3-ynyl ester (*9c*)

2.60 g (18.1 mmol) of 1-phenyl-3-butyn-1-ol [21] were added to a solution of 5.07 g (26.6 mmol) of *p*-toluensulfonyl chloride in 60 mL diethyl ether at −15 °C. 8.86 g (158 mmol) of finely powered KOH were then added and the obtained solution was stirred for 2 h at 0 °C, quenched with ice and extracted with Et_2O (3 × 50 mL). The combined organic layers were dried over Na_2SO_4, the solvent was removed under reduced pressure yielding 5.4 g (18 mmol, 99%) of crude **9c** as a white solid that was used without any further purification. ^{1}H NMR ($CDCl_3$): δ = 1.91 (t, *J* = 2.7 Hz, 1H), 2.37 (s, 3H), 2.78 (ddd, *J* = 16.8, 6.8, 2.7 Hz, 1H), 2.87 (ddd, *J* = 16,8, 6.8, 2.7 Hz, 1H), 5.50 (t, *J* = 6.8 Hz, 1H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.20 (m, 5H), 7.63 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR: ($CDCl_3$): δ = 21.5, 27.3, 71.4, 78.1, 81.3, 126.7, 127.8, 128.3, 128.8, 129.4, 133.9, 136.7, 144.5.

4.3.4. Catalytic silylformylation of homopropargyl tosylates

(E)-2-[(Dimethylphenylsilyl)-methylene]-4-p-toluensulfonyl-butanal, **(*E*)-10a**: colorless oil. ^{1}H NMR ($CDCl_3$): δ = 0.53 (s, 6H), 2.45 (s, 3H), 2.67 (t, *J* = 6.3 Hz, 2H), 3.97 (t, *J* = 6.8 Hz, 2H), 6.95 (s, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.41 (m, 3H), 7.54 (m, 2H), 7.70 (d, *J* = 8.1 Hz, 2H), 9.31 (s, 1H); ^{13}C NMR ($CDCl_3$): δ = −1.6 (2C), 21.8, 28.4, 68.1, 128.2, 128.5, 130.0 (2C), 133.1, 134.0, 136.6, 145.0, 151.3, 156.1, 195.1.

(Z)-2-[(dimethylphenylsilyl)-methylene]-4-p-toluensulfonyl-butanal, **(*Z*)-10a**: colorless oil. ^{1}H NMR ($CDCl_3$): δ = 0.52 (s, 6H), 2.45 (s, 3H), 2.67 (t, *J* = 6.3 Hz, 2H), 4.14 (t, *J* = 6.3 Hz, 2H), 7.07 (s, 1H), 7.47 (m, 9H), 9.67 (s, 1H).

(E)-2-[(dimethylphenylsilyl)-methylene]-4-p-toluensulfonyl-hexanal, **(*E*)-10b**: colorless oil. ^{1}H NMR ($CDCl_3$): δ = 0.52 (s, 3H), 0.53 (s, 3H), 0.75 (t, *J* = 7.5 Hz, 3H), 1.52 (dq, *J* = 7.5, 5.7 Hz, 2H), 2.42 (s, 3H), 2.45 (m, 2H), 4.62 (m, 1H), 6.74 (s, 1H), 7.25 (d, *J* = 7.8 Hz, 2H), 7.40 (m, 3H), 7.54 (m, 2H), 7.63 (d, *J* = 7.8 Hz, 2H), 9.09 (s, 1H); ^{13}C NMR ($CDCl_3$): δ = −1.8, −1.6, 8.7, 21.6, 28.1, 32.9, 82.2, 128.3, 128.7, 129.9(2C), 134.1, 134.4, 136.9, 144.6, 155.2, 154.9, 195.2.

(Z)-2-[(dimethylphenylsilyl)-methylene]-4-p-toluensulfonyl-hexanal, **(*Z*)-10b**: colorless oil. ^{1}H NMR ($CDCl_3$): δ = 0.56 (s, 3H), 0.58 (s, 3H), 0.84 (t, *J* = 7.8 Hz, 3H), 1.50 (m, 2H), 2.48 (s, 3H), 2.53 (m, 2H), 4.51 (m, 1H), 7.08 (s, 1H), 7.34 (m, 5H), 7.52 (m, 2H), 7.70 (d, *J* = 7.5 Hz, 2H), 9.68 (s, 1H).

4.3.5. Synthesis of 1-benzyl-cyclopropanecarbaldehyde (*12a*) [15]

0.376 g (1 mmol) (*E*),(*Z*)-2-[(dimethylphenylsilyl)-methylene]-4-*p*-toluensulfonyl-butanal, dissolved in 5 mL of THF, were added to 3 mL of tetrabutylammonium fluoride (1 M in THF) diluted with 5 mL of THF, at room temperature. The obtained solution was immediately hydrolysed with water, extracted with CH_2Cl_2 (3 × 20 mL) and the organic layers were dried over Na_2SO_4. After concentration under vacuum, the crude product was purified by column chromatography on silica gel using CH_2Cl_2 as eluent, yielding 0.108 g (0.73 mmol, 73%) of pure product as a colorless oil. ^{1}H NMR ($CDCl_3$): δ = 1.09 (m, 2H), 1.28 (m, 2H), 3.12 (s, 2H), 7.34 (m, 5H), 8.87 (m, 1H).

4.3.6. Synthesis of 1-benzyl-2-ethyl-cyclopropanecarbaldehyde (*12b*)

0.500 g (1.2 mmol) (*E*),(*Z*)-2-[(dimethylphenylsilyl)-methylene]-4-*p*-toluensulfonyl-hexanal, dissolved in 5 mL of THF, were added to 3 mL of tetrabutylammonium fluoride (1 M in THF) diluted with 5 mL of THF, at room temperature. The obtained solution was immediately hydrolysed with water, extracted with CH_2Cl_2 (3 × 20 mL) and the organic layers were dried over Na_2SO_4. After concentration under vacuum, the crude product was purified by column chromatography on silica gel using CH_2Cl_2 as eluent, yielding 0.210 g (1.11 mmol, 93%) of pure product (diastereomeric mixture: *Z*/*E* = 79/21). *Cis isomer*: ^{1}H NMR ($CDCl_3$): δ = 0.83 (t, *J* = 7.3 Hz, 3H), 1.35 (m, 5H), 2.85 (d, *J* = 15.0 Hz, 1H), 2.96 (d, *J* = 15.0 Hz, 1H), 7.14 (m, 5H), 9.18 (s, 1H); ^{13}C NMR ($CDCl_3$): δ = 14.1, 21.1, 21.7, 32.6, 36.8, 37.4, 126.2, 128.2, 129.2, 139.1, 202.2. *Trans isomer*: ^{1}H NMR ($CDCl_3$): δ = 0.96 (t, *J* = 7.2 Hz, 3H), 1.28 (m, 5H), 2.57 (d, *J* = 15.5 Hz, 1H), 3.36 (d, *J* = 15.5 Hz, 1H), 7.14 (m, 5H), 8.75 (s, 1H); ^{13}C NMR ($CDCl_3$): δ = 13.7, 19.5, 22.2, 28.7, 30.8, 37.0, 126.0, 128.3, 128.8, 139.9, 202.0.

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