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Markovnikov-selective double hydrosilylation of challenging terminal aryl alkynes under cobalt and iron catalysis†

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Geminal bis(silanes) are unique compounds with interesting properties. The most straightforward way to access them is double hydrosilylation of alkynes, which was established only recently. Previous articles about transition metal-catalysed double hydrosilylation show that terminal aryl alkynes are a challenge. We report on cobalt(II) and iron(III) complexes with the easy-to-synthesise *N,N,N*-tridentate hydrazone ligand being active precatalysts in Markovnikov-selective double hydrosilylation of terminal aryl alkynes. The influence of the hydrazone ligand structure and the potential role of the sodium triethylborohydride activator were studied. Sets of geminal bis(silanes) with two identical or different silyl groups were synthesised, showing the applicability of the reported method.

Organosilanes are valuable compounds with vast applications, including in sophisticated fundamental research,¹ organic synthesis,² materials science,³ biotechnology⁴ and medicinal chemistry.⁵ *Gem*-bis(silanes) are gaining particularly increasing attention due to their unique reactivity⁶ and structural properties.⁷ However, access to these compounds and further development of their chemistry was hampered for a long time due to the scarcity of synthetic methods for placing two silyl groups on one carbon atom.⁸ *Gem*-bis(silanes) that could be obtained with these protocols⁸ had no Si–H bonds within the bis(silyl) moiety and the lack thereof could have been holding back further developments.⁹ Currently, strenuous efforts are underway to improve the field of *gem*-bis(silane) synthesis, focusing on Si–H containing products.

Catalytic hydrosilylation stands out as a very straightforward option to access organosilanes with perfect atom-economy.^{10–12} Due to reactivity and selectivity issues with hydrosilylation of

vinylsilanes, access to *gem*-bis(silanes) through double hydrosilylation of alkynes is a challenge, and at first, such processes were observed only as side reactions.¹³ However, several research groups have recently reported successful double hydrosilylation of alkynes leading to *gem*-bis(silanes) (Scheme 1). Zhu's team utilised an iron(II) complex with a phenanthroline derived ligand that catalysed double *anti*-Markovnikov hydrosilylation of terminal aliphatic alkynes (Scheme 1a).¹⁴ Concomitantly, Lu's group published their results describing chiral cobalt(II) complexes with either imidazoline-iminopyridine or oxazoline-iminopyridine ligands that were capable of catalysing the transformation of terminal aliphatic alkynes (Scheme 1b and c).^{15,16} Notably, these chiral cobalt(II) precatalysts, when used in sequential one-pot hydrosilylation with two different silanes, led to optically pure products. Li, Cui and co-workers further expanded the scope of double hydrosilylation of alkynes by employing a lanthanum(III) bis(amido)ate complex which enabled that process on internal aryl-alkyl and silyl-alkyl alkynes (Scheme 1e).¹⁷ However, terminal aryl alkynes still remained problematic as they underwent only monohydrosilylation. Most recently, Li and team have addressed this issue by using B(C₆F₅)₃ as the catalyst allowing sequential *anti*-Markovnikov double hydrosilylation of terminal aryl alkynes, starting with tertiary silanes and followed by primary silanes (Scheme 1d).¹⁸ We would like to offer a further narrowing of the gap regarding transformation of terminal aryl alkynes into *gem*-bis(silanes) by presenting the results of our research on Markovnikov-selective cobalt- and iron-catalysed double hydrosilylation.

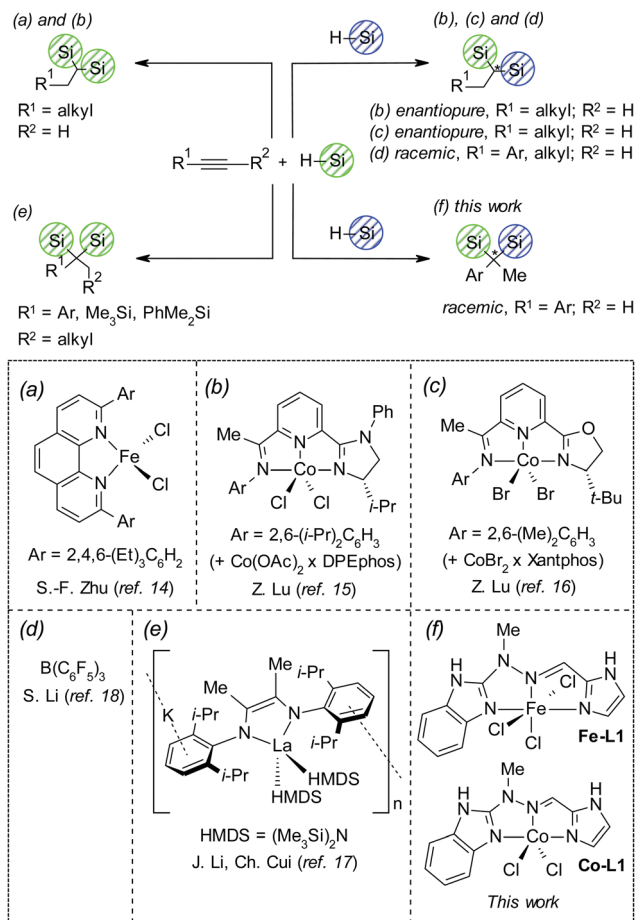
N,N,N-Tridentate hydrazone ligands, which can be easily and efficiently prepared in various structures through modular synthesis,¹⁹ served well in our studies on cobalt-catalysed hydrosilylation of alkenes²⁰ and alkynes.²¹ Thus, we also decided to utilize this system for iron complexes (Chart 1) and verify their potential catalytic activity in alkyne hydrosilylation reactions. Initial tests were conducted in THF on a range of alkynes using phenylsilane with the **Fe-L1** precatalyst and the NaHBET₃ activator. In the case of the phenylacetylene substrate we obtained an intriguing result – among a multitude of GC-MS signals from

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Scheme 1 Double hydrosilylation of alkynes without (d) or in the presence of bidentate (a, e) and tridentate (b, c, f) ligand.

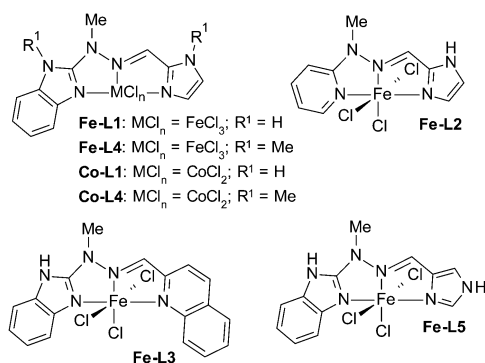


Chart 1 Cobalt and iron complexes used in this study.

different products, one stood out due to a much higher retention time and an unusually high m/z ratio of 318 for M^+ ions. We isolated the compound responsible for this signal and identified it as a product of Markovnikov-oriented double hydrosilylation of phenylacetylene (3a). This result prompted us to focus our efforts on iron-catalysed double hydrosilylation of terminal aryl alkynes, especially given the fact that phenylacetylene was repeatedly reported as a very challenging substrate in this type

Table 1 Studies on double hydrosilylation of phenylacetylene

Entry ^a	[Precat.]	Yield of 3a ^b (%)	3a : 4a : 5a : 6a : 7a : 8a ^b
1	Fe-L1	28	28 : 2 : 2 : 9 : 6 : 0
2	Fe-L2	6	6 : 2 : 3 : 10 : 1 : 4
3	Fe-L3	4	4 : 2 : 3 : 16 : 19 : 0
4	Fe-L4	2	2 : 1 : 2 : 11 : 0 : 0
5	Fe-L5	5	5 : 2 : 4 : 10 : 5 : 20
6 ^c	Fe-L1	43	43 : 1 : 3 : 7 : 2 : 0
7 ^d	Fe-L1 + Co-L1	60	60 : 3 : 8 : 1 : 0 : 0
8 ^c	Co-L1	63	63 : 1 : 4 : 1 : 0 : 0
9 ^c	Co-L4	0	0 : 1 : 1 : 4 : 0 : 0

^a Reaction conditions: **1a** (0.25 mmol), **2a** (0.50 mmol), pre-catalyst (3 mol%), NaHBET₃ (20 mol%) in THF (0.5 mL) in an argon-filled Schlenk bomb immersed in an oil bath (100 °C) for 20 h.
^b Determined by ¹H NMR using 1,1,2,2-tetrachloroethane as the internal standard.
^c 1 mol% of pre-catalyst and 7 mol% of NaHBET₃, reaction time of 12 h.
^d 1 mol% of each pre-catalyst (**Fe-L1** in two portions) and a total of 10 mol% of NaHBET₃.

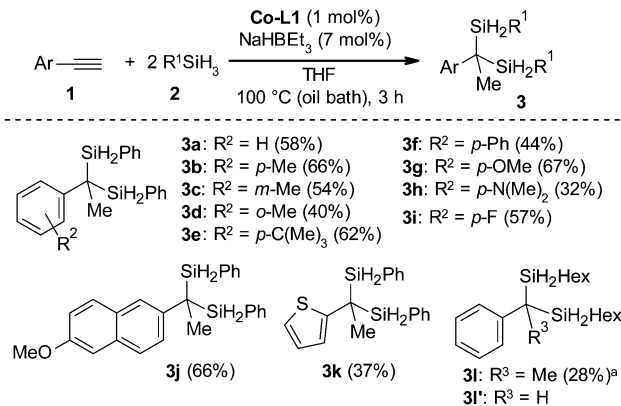
of transformation.^{14–17} Initial reaction optimisation studies focusing on solvent and activator selection allowed us to determine that THF and NaHBET₃ work the best in these regards; however, an NMR yield of only 28% was obtained (Table 1, entry 1; please see the ESI† for reaction optimisation details). Control experiments substituting **Fe-L1** for either FeCl₃ or **L1** ligand confirmed that **Fe-L1** is necessary for formation of **3a**. We then tested related iron complexes which were different from **Fe-L1** in the single aspect of the hydrazone ligand structure. First we exchanged one heterocycle on each side of **L1** for another heterocyclic structure with only one nitrogen atom (2-pyridyl or 2-quinoyl), as in the case of **Fe-L2** and **Fe-L3**. The yields of **3a** for **Fe-L2** and **Fe-L3** were similar between them (6% and 4%, respectively), but significantly lower than that for **Fe-L1** (Table 1, entries 2 and 3). Some possible explanations for such results are that the NH groups at the heterocyclic units of the ligand are somehow important in the catalytic process and that a binding geometry of a five-membered heterocycle to the iron centre serves better than a six-membered system in the catalytically active species. In order to verify these potential explanations we have synthesised **Fe-L4** with all the NH positions that are present in **Fe-L1** transformed into NMe moieties; thus the binding geometry of the ligand should stay the same as that in **Fe-L1** and the role of NH could be verified. Tests with **Fe-L4** gave a negligible yield of **3a** (Table 1, entry 4), thus confirming the practical significance of NH groups. Changing the orientation of the imidazolyl ring from 2-imidazolyl in **Fe-L1** to 4-imidazolyl in **Fe-L5** decreased the yield of **3a** to only 5% (Table 1, entry 5). Interestingly, a decrease in the loading of **Fe-L1** from 3 mol% to 1 mol% resulted in an increase of the yield of **3a** to 43%



(Table 1, entry 6), but further decrease in the **Fe-L1** loading to 0.5 mol% was not helpful (see the ESI† for details). As we anticipated that **4a** was an intermediate on the way to **3a** we decided to also employ the **Co-L1** complex in order to help in the first hydrosilylation of phenylacetylene. At first this seemed to be beneficial as the yield of **3a** improved to 60% (Table 1, entry 7). However, a control experiment using **Co-L1** without **Fe-L1** gave a 63% yield of **3a** (Table 1, entry 8). This showed that the cobalt complex is a better precatalyst than its iron analogue. Interestingly, **Co-L4** was drastically worse than **Co-L1** as **3a** was not produced when using this complex (Table 1, entry 9). Thus, a negative effect of introducing methyl groups on nitrogen atoms in heterocyclic systems of the ligand was also present in the case of cobalt complexes.

Based on our results obtained for different cobalt and iron complexes we concluded that NaHBET_3 might be involved in the modification of the ligand structure. We hypothesised that NaHBET_3 not only serves to reduce the metal centre and clear it of chlorine atoms, but also deprotonates the NH groups present in the heterocyclic units of the ligand and binds to nitrogen atoms – that is why **Fe-L1** and **Fe-L4**, as well as **Co-L1** and **Co-L4** have significantly different activities.²² In order to verify our hypothesis we conducted a series of ^1H and ^{11}B NMR experiments (see the ESI† for details). First we added NaHBET_3 to **L1** in THF- d_8 and the ^1H NMR results showed swift deprotonation of NH units. After addition of 3 eq. of NaHBET_3 to **L1** its ^{11}B NMR spectrum showed a clear singlet at -0.13 ppm which we assign to the BET_3 bonded to the nitrogen atom.²³ Further NMR experiments were carried out on **Fe-L1** and **Co-L1** complexes. Due to their paramagnetic nature their ^1H NMR spectra are illegible for the most part. However, after addition of 1 eq. of NaHBET_3 to **Fe-L1** a broad and irregular signal in the range of -3.25 ppm to -4.86 ppm appeared which we tentatively assign to Fe–H species. This signal seemed to migrate slightly as more NaHBET_3 was added. Similarly, addition of NaHBET_3 to **Co-L1** gave rise to a broad singlet at -12.05 ppm which can be a manifestation of Co–H species.²⁴ After addition of 7 eq. of NaHBET_3 to **Fe-L1** or **Co-L1**, their respective ^{11}B NMR spectra showed two signals at 1.19 ppm and -0.41 ppm which we interpret as resulting from the BET_3 units bonded to the nitrogen atoms from deprotonated NH groups in the **L1** ligand.²³

When investigating the alkyne substrate scope in the reaction with phenylsilane, we focused on **Co-L1** and started with phenylacetylene derivatives with additional substituents on the aromatic ring (Scheme 2). When compared to an unsubstituted system, the methyl group in the *meta* or *para* position essentially did not impact the yield of the *gem*-bis(silyl) product. A somewhat stronger influence was exerted by the methyl substituent in the *ortho* position as the product **3d** was isolated with a 40% yield. This is clearly due to the steric effect, which overall is not as strong as it could be expected, given the bulkiness of the quaternary centre being formed in the final product. Other substituents, like $-\text{Ph}$, $-\text{OMe}$, $-\text{N}(\text{Me})_2$ and $-\text{F}$, were also tolerated and the respective products were obtained in moderate yields. We also encountered phenylacetylene derivatives that did not yield the expected *gem*-bis(silyl) products.

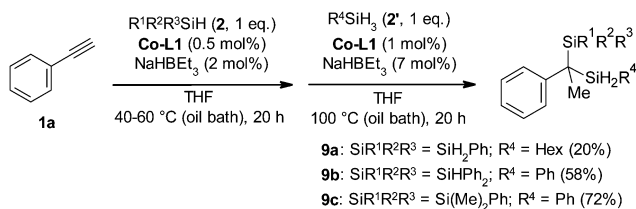


Scheme 2 Substrate scope studies on double hydrosilylation of terminal aryl alkynes. Reaction conditions: **1** (0.50 mmol), **2** (1.00 mmol), **Co-L1** (1 mol%), NaHBET_3 (7 mol%) in THF (1.0 mL) in an argon-filled Schlenk bomb flask immersed in an oil bath (100 °C) for 3 h. The reported yields are for isolated products. ^a Product **3l** contaminated with 25% of a homologue **3l'**. The reported yield accounts for this contamination.

These had substituents that have the ability to coordinate to the metal centre and/or can be the subject of hydride attack either in reduction, deprotonation or substitution processes ($-\text{CN}$, $-\text{CO}_2\text{Et}$, $-\text{NH}_2$, and $-\text{Br}$). Further studies revealed that an extended aromatic system worked well in double hydrosilylation (**3j**). We additionally tested a couple of heteroaromatic substrates. While 3-ethynylpyridine did not give the desired product, 2-ethynylthiophene gave a modest 37% yield of **3k**. Terminal alkyl alkynes did not undergo double hydrosilylation. Among internal alkynes only aryl-alkyl 1-phenyl-1-propyne yielded 18% of respective *gem*-bis(silane) (see the ESI† for details). Investigations on the silane substrate scope showed that our protocol can be applied to primary alkylsilanes, as *n*-hexylsilane also served to obtain **3l**. Interestingly, **3l** was contaminated with a homologous compound **3l'** with 14 g mol⁻¹ lower mass. Based on a set of NMR analyses (^1H - ^1H COSY, ^1H - ^{13}C HSQC and ^1H - ^{13}C HMBC; see the ESI† for details) we identified **3l'** as an analogue of **3l** devoid of the methyl group bonded to the benzylic carbon atom. Formation of **3l'** suggests the occurrence of an intriguing side reaction that is probably facilitated by the electron donating nature of alkylsilyl group(s). Secondary silanes (diethylsilane and diphenylsilane) or tertiary silanes (dimethylphenylsilane, triethylsilane and triphenylsilane) when tested on phenylacetylene did not work to obtain respective *gem*-bis(silanes).

Despite the fact that our procedure did not work for secondary and tertiary silanes we sought an intermediate solution. Knowing that **Co-L1** works well in monohydrosilylation of alkynes with secondary and even tertiary silanes^{21a} we decided to utilise this in the preparation of mixed *gem*-bis(silanes) with two different silyl groups. In order to do so, we changed the reaction conditions in such a way that in the first stage only 1 eq. of more substituted silane was used at lower temperature, while in the second stage a fresh portion of **Co-L1** and NaHBET_3 was added with the second silane at higher temperature (Scheme 3). This approach allowed us to obtain a set of racemic mixed *gem*-bis(silanes).





Scheme 3 Synthesis of mixed geminal bis(silanes). The reported yields are for isolated products. Reaction conditions: **1a** (0.50 mmol) and **2** (0.50 mmol) added to **Co-L1** (0.5 mol%) activated by NaHBET_3 (2 mol%) in THF (0.5 mL) and heated up to 40–60 °C for 20 h, followed by addition of the **Co-L1** (1 mol%) and NaHBET_3 (7 mol%) mixture in THF (0.5 mL) and **2'** (0.5 mmol).

In summary, we have developed a method for Markovnikov-selective double hydrosilylation of terminal aryl alkynes using a cobalt(II) complex with the *N,N,N*-tridentate hydrazone ligand. A similar, yet lower, activity was also found for the analogous iron complex. Studies on various cobalt(II) and iron(III) complexes with different *N,N,N*-tridentate hydrazone ligands showed that even subtle changes in the ligand structure play an important role with respect to catalytic activity. NMR experiments revealed that the NaHBET_3 activator may not only react with the metal centre of the precatalyst, but also modify the ligand and thus influence the catalytic activity of the metal centre.

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Conflicts of interest

There are no conflicts to declare.

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