

Article

Bulky NHC–Cobalt Complex-Catalyzed Highly Markovnikov-Selective Hydrosilylation of Alkynes

Małgorzata Bolt* and Patrycja Żak 

Department of Organometallic Chemistry, Faculty of Chemistry, Adam Mickiewicz University in Poznan, Uniwersytetu Poznańskiego 8, 61-614 Poznan, Poland

* Correspondence: malgorzata.bolt@amu.edu.pl; Tel.: +48-61-829-17-31

Abstract: The hydrosilylation of alkynes is one of the most attractive and, at the same time, most challenging catalytic transformations, usually demanding the use of noble transition metals. We describe a catalytic system, based on cobalt(0) complex and bulky *N*-heterocyclic carbene (NHC) ligands, permitting the highly effective hydrosilylation of a broad scope of alkynes and silanes. The application of bulky NHC ligands allowed a decrease in the amount of cobalt necessary for an effective reaction run to 2.5 mol% and provided excellent selectivity towards challenging α -vinylsilanes. The developed method tolerates a number of substituted aryl, alkyl, and silyl acetylenes. Moreover, it is suitable for both tertiary and secondary silanes. Our findings confirm that steric hindrance around the metal center can effectively increase the activity of a catalyst and ensure better selectivity than those of analogous complexes bearing smaller ligands.

Keywords: hydrosilylation; cobalt; *N*-heterocyclic carbene; alkyne; homogeneous catalysis



Citation: Bolt, M.; Żak, P. Bulky NHC–Cobalt Complex-Catalyzed Highly Markovnikov-Selective Hydrosilylation of Alkynes. *Catalysts* **2023**, *13*, 510. <https://doi.org/10.3390/catal13030510>

Academic Editors: Victorio Cadierno and Raffaella Mancuso

Received: 7 February 2023

Revised: 24 February 2023

Accepted: 28 February 2023

Published: 2 March 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The hydrosilylation reaction of multiple carbon–carbon bonds has a special place in the contemporary world. Due to its atom economy and the numerous applications of its products, the reaction is widely used in many branches of chemistry and industry [1,2]. In particular, the hydrosilylation of alkynes can produce vinylsilanes, which are valuable compounds used in numerous applications such as building blocks for organic synthesis, reagents in cross-coupling reactions, and cross-linking agents in material science [3–6].

Apart from the many advantages of the hydrosilylation process, it still suffers from the selectivity problem. The addition of silane molecules to alkynes can produce three different isomers (α , β -(*E*), β -(*Z*)). Moreover, the reaction can be accompanied by side-processes, such as dehydrogenative silylation, the hydrogenation of olefins, or isomerization. What is more, hydrosilylation still mostly relies on noble metals, such as Pt [7–9], Rh [10], and Ir [11]. To date, platinum has been the most commonly used metal in industry due to its high activity. In particular, Karstedt’s catalyst is most widely used and, although it can provide a high conversion of products, it usually renders a mixture of regioisomers [12,13]. For economic and ecological reasons, a search for alternatives to these catalysts among Earth-abundant metals has been undertaken [14,15]. Recently, cobalt complexes have been of particular interest in terms of hydrogenation and hydroelementation reactions [16–21]. It is worth mentioning that, in recent years, the authors investigating hydrosilylation in the presence of cobalt complexes have focused on the selective preparation of α -vinylsilanes, due to the fact that the methods for the synthesis of β -(*E*) and β -(*Z*) isomers have already been well developed and described (Figure 1). The Markovnikov addition is considered to be much more demanding and reports describing selective methods of α -vinylsilanes synthesis are limited.

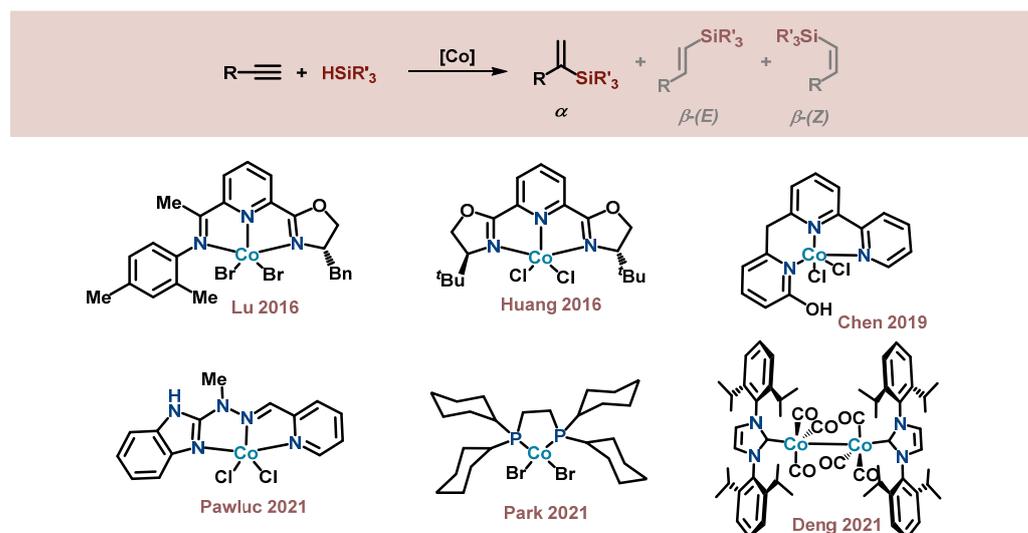


Figure 1. Selected examples of cobalt-based catalysts for α -selective hydrosilylation of alkynes [22–28].

From among the methods of synthesis of α -vinylsilanes based on cobalt catalysts, much interest is paid to those employing complexes with chelating N-donor ligands. In 2016, Lu [22] and Huang [23] independently reported the Markovnikov selective hydrosilylation of alkynes in the presence of cobalt(II) complexes with pyridinebis(oxazoline) and oxazoline iminopyridine ligands. Three years later, Chen et al. reported the synthesis of α -vinylsilanes in the presence of a cobalt complex with a 2,2'-bipyridine derivative as a ligand [24]. However, in the above-mentioned examples, the scope of substrates was limited to secondary silanes. In 2021, Pawluć et al. developed a very effective catalytic system enabling the selective hydrosilylation of alkynes with both tertiary and secondary silanes in the presence of 0.05–0.5 mol% of Schiff base cobalt(II) complex [25,26]. Except for the overall good activity of the cobalt complexes bearing tridentate (NNN) ligands, the indispensable use of an activator seems to be the major drawback of their proposal. Another recently published proposition is the synthetic protocol designed by Park et al. employing a cobalt complex with bis(dicyclohexylphosphino)ethane as a ligand [27]. This method led to the selective formation of α -vinylsilanes and α -vinylgermanes, but demanded 5 mol% of the cobalt complex and over 10 mol% of NaHBET₃ as an activator. In 2021, Deng et al. reported the synthesis of dicobalt carbonyl complex-bearing *N*-heterocyclic carbene ligand (NHC), IPr [28]. The application of this complex in hydrosilylation allowed the Markovnikov selective addition of a series of tertiary silanes to terminal acetylenes in the presence of 5 mol% of the catalyst. The octacarbonyl dicobalt(0) itself was previously used by Isobe for alkyne hydrosilylation, but this method was characterized by a moderate α/β ratio [29]. The introduction of a carbene ligand led to significant improvements in the reaction selectivity, especially in the case of sterically hindered NHCs.

Recently, bulky NHC ligands have been receiving considerable interest due to their ability to stabilize low-valent species and facilitate the reductive elimination step. Increased steric hindrance around the metal center in the complex can significantly improve the selectivity of the process or even completely change its direction [30–33]. Over recent years, our group has been exploring the application of bulky NHCs as ligands in different transition metal complexes [9,34–39]. As a consequence of interest, we decided to apply them as ligands in cobalt carbonyl complexes and check the effect of increased steric hindrance on their catalytic performance in the hydrosilylation of alkynes.

In this paper, we describe a new catalytic system based on bulky NHCs and octacarbonyl dicobalt(0), which enables the selective hydrosilylation of a broad scope of terminal and internal alkynes with both tertiary and secondary silanes.

2. Results and Discussion

2.1. Optimization of Reaction Conditions

Inspired by a recent study by Deng, we decided to synthesize a new cobalt carbonyl complex bearing bulky NHC carbene ligands used in our lab. We made attempts to isolate the corresponding cobalt(0) complex. Unfortunately, it appeared to be unstable and underwent rapid decomposition during the NMR characterization (see ESI). Since the isolated complex could not be stored for a long period of time, we decided to continue our research with the catalyst generated in situ by mixing the corresponding carbene with octacarbonyl dicobalt(0) for 30 min directly before the reaction.

At the first stage of the study, different bulky NHCs (IPr*OMe, IPr*Et, IPr*Ph) were tested to compare their reactivity and overall performance in the studied reaction with the effectiveness of smaller carbenes such as IMes or IPr. The hydrosilylation of phenyl acetylene (**1a**) with an equimolar amount of triethyl silane (**2a**) was chosen as a model reaction. We decided to start our investigation with 5 mol% of the cobalt(0) catalyst, as it was a standard catalyst concentration used in the previous report by Deng. A series of experiments aimed at the optimization of the type and amount of the catalyst was performed and the results are presented in Table 1.

Table 1. Optimization of reaction conditions—catalyst type and amount.

Reaction scheme: Phenyl acetylene (**1a**) + HSiEt₃ (**2a**) $\xrightarrow[\text{THF, 60 } ^\circ\text{C}]{2x \text{ mol\% NHC, } x \text{ mol\% Co}_2(\text{CO})_8}$ α + β (E) + β (Z)

Chemical structures of NHC ligands: IMes, IPr, IPr*OMe, IPr*Et, and IPr*Ph.

Entry	NHC	[Co] (%)	Time (h)	Conv. ¹ (%)	Selectivity ² α : β -(E): β -(Z)
1	-	5	24	76	32:68:0
2	IPr	5	5	94	95:5:0
3	IMes	5	5	90	90:10:0
4	IPr*OMe	5	3	99	99:1:0
5	IPr*Et	5	3	96	98:2:0
6	IPr*Ph	5	3	97	99:1:0
7	IPr*Ph	2.5	5	95	99:1:0
8	IPr*Ph	1	24	70	97:3:0
9	IPr*Ph	0.5	24	19	93:7:0

Reaction conditions: argon, THF, 60 °C, [1a]:[2a] = 1:1, [NHC]:[Co] = 2:1, [IPr*OMe] = 1,3-bis(2,6-bis(diphenylmethyl)-4-methoxyphenyl)imidazol-2-ylidene, [IPr*Et] = 1,3-bis(2,6-bis(diphenylmethyl)-4-ethylphenyl)imidazol-2-ylidene, [IPr*Ph] = 1,3-bis(2,4,6-tris(diphenylmethyl)phenyl)imidazol-2-ylidene; ¹ determined by GC analysis; ² determined by GC analysis and confirmed by ¹H NMR spectroscopy of the crude reaction mixture.

As presented in Table 1, the reaction without NHC ligand addition resulted in 76% of conversion with a significant excess of the anti-Markovnikov product (Entry 1). The addition of a twofold excess of IPr or IMes ligand to the cobalt(0) precursor switched the selectivity of the reaction towards the Markovnikov product and meaningfully increased the conversion of the substrates (Entry 2 and 3). The use of the IPr ligand already resulted in

very good selectivity and conversion, but only the use of bulky NHCs led to an almost fully selective reaction in the studied conditions (Entry 4–6). We did not observe significant changes between the effects of the bulky NHCs used in the reaction; thus, the study was continued using the IPr^{Ph} ligand. The amount of the catalyst based on the bulky NHC ligand could be reduced to 2.5 mol% without significant loss of the process effectiveness and at the same level of selectivity (Entry 7). Since the reduction of the cobalt(0) amount to 1 or 0.5 mol% resulted in a decrease in the substrate conversion, our study was continued using 2.5 mol% of dicobalt(0) octacarbonyl and a twofold excess of a bulky NHC ligand.

Next, we optimized the type of solvent and temperature to ensure the best conditions for the tested hydrosilylation reaction. The results are presented in Table 2.

Table 2. Optimization of reaction conditions—solvent and temperature.

$\text{1a} + \text{HSiEt}_3 \xrightarrow[\text{conditions}]{5 \text{ mol\% IPr}^{\text{Ph}}, 2.5 \text{ mol\% Co}_2(\text{CO})_8} \alpha + \beta(\text{E}) + \beta(\text{Z})$

Entry	Temp. (°C)	Solvent	Conv. ¹ (%)	Selectivity ² $\alpha:\beta(\text{E}):\beta(\text{Z})$
1	60	THF	99	99:1:0
2	40	THF	36	95:5:0
3	RT	THF	10	92:8:0
4	60	Toluene	99	99:1:0
5	60	DCM	90	97:3:0
6	60	MTBE	75	84:16:0
7	60	Acetonitrile	16	80:20:0
8	60	<i>i</i> PrOH	<5	-

Reaction conditions: argon, 5 h, [1a]:[2a] = 1:1, [Co] = 2.5 mol%, [NHC]:[Co] = 2:1; ¹ determined by GC analysis; ² determined by GC analysis and confirmed by ¹H NMR spectroscopy of the crude reaction mixture.

The results gathered in Table 2 show that the reactions performed at temperatures lower than 60 °C led to a significant decrease in the substrate conversion to 36% and 10% at 40 °C and room temperature, respectively (Entry 2 and 3). This decrease indicated the necessity of catalyst activation, which consists of the thermal dissociation of one of the carbonyl ligands. Subsequently, different organic solvents were tested at 60 °C and it was observed that besides THF, the reaction could be effectively carried out in toluene and DCM without a meaningful decrease in the selectivity (Entry 4 and 5). The application of polar aprotic solvents, such as MTBE and acetonitrile, decreased the substrate conversion (Entry 6 and 7). The reaction completely failed in protic solvents such as isopropanol, leading to only trace conversion (Entry 8).

2.2. Substrate Scope—Alkynes

Using an active and selective catalytic system based on a cobalt(0) complex and a bulky NHC ligand, a range of substrates were tested to determine the versatility of the method. At first, a broad scope of acetylenes bearing aryl moieties with both electron-withdrawing and electron-donating groups were tested, besides alkyl and silyl acetylenes, terminal diacetylenes and internal alkynes. All of the results are presented in Figure 2.

For the aryl alkynes, the excellent activity of the tested catalytic system and very good selectivity towards α -vinylsilanes were observed. The proposed system tolerates a broad scope of substituents, including methyl- (Me), *tert*-butyl- (*t*Bu), methoxy- (OMe), phenyl- (Ph), fluoro- (F), bromo- (Br), trifluoromethyl- (CF₃), dimethylamino- (NMe₂), and cyano- (CN). The reaction with alkyne-bearing thiophane moiety led to the expected product with a high selectivity (P12). On the other hand, the test with sterically demanding 1-ethynyl-naphthalene effected in a mixture of β -(E) and β -(Z) (P13), which proves that the reaction outcome is significantly dependent on the steric nature of the used reactants.

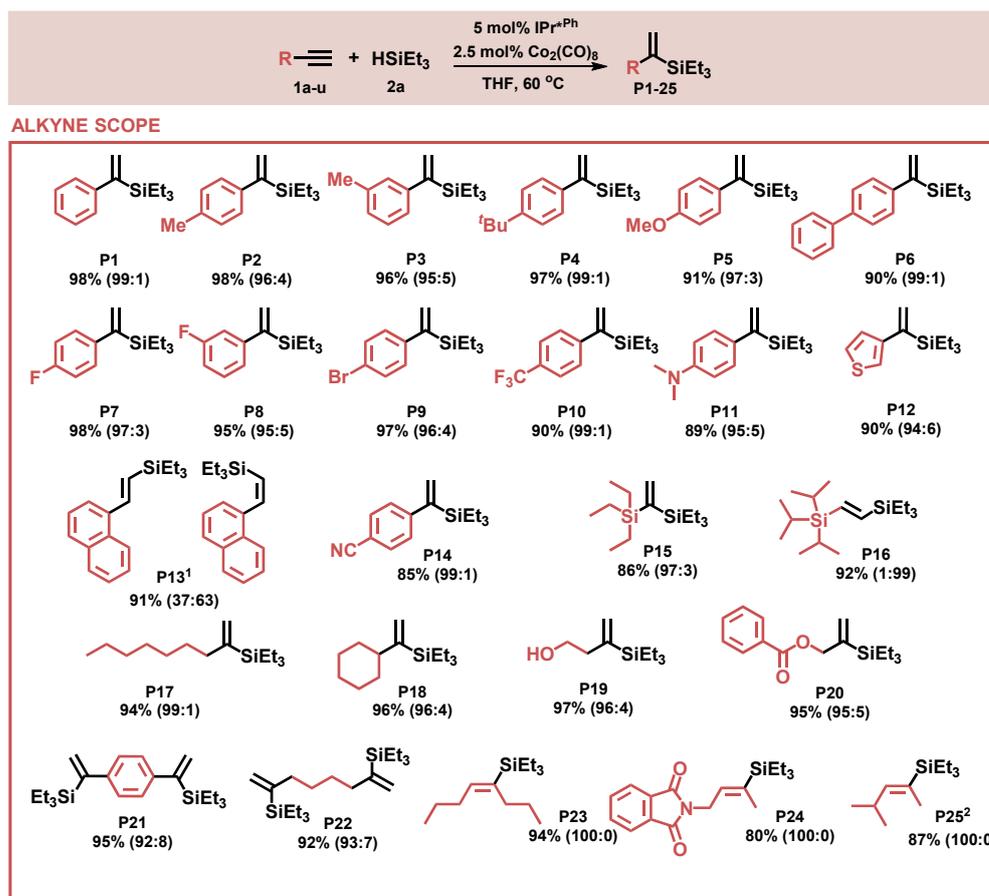


Figure 2. Substrate scope—alkynes. Reaction conditions: argon, THF, 60 °C, 5 h, [1a-u]:[2a] = 1:1, [IPr*^{Ph}] = 5 mol%, [Co] = 2.5 mol%; isolated yields are given under the product structure. Selectivity α : β -(E) is given in the parenthesis; ¹ selectivity β -(E): β -(Z) is given in the parentheses. ² Product without isolation; conversion of the substrates is given.

Encouraged by the positive results obtained for aryl alkynes, we decided to expand the scope of acetylenes. The method proposed turned out to be suitable for the hydrosilylation of silylacetylenes, although the isomer formed in the reaction strongly depended on the steric nature of the substrate. Thus, the hydrosilylation of triethylsilylacetylene led to the product of Markovnikov addition (**P15**), but the same reaction of triisopropylsilylacetylene led to the selective formation of the anti-Markovnikov product (**P16**). These results are particularly important since disilylated alkenes are extensively used as versatile reagents in organic and organosilicon synthesis [40–42].

Our protocol can also be applied in the hydrosilylation of aliphatic alkynes, such as 1-nonyne or cyclohexylacetylene (**P17** and **P18**). The newly designed catalytic system can also tolerate groups containing heteroatoms in the alkane chain, such as hydroxyl or ester groups (**P19** and **P20**). Moreover, the reactions of terminal aryl- and alkyl-diacetylenes can also be performed, leading to bis-silylated products (**P21–P22**), although their selectivity is slightly lower (up to 8% of β -E products).

Finally, we decided to test the proposed method in the hydrosilylation of internal alkynes. Recently, Deng's group has reported the selective hydrosilylation of internal alkynes in the presence of $\text{Co}_2(\text{CO})_8$ [43]. According to our results, the proposed cobalt-based catalytic system with bulky NHC ligands provides an effective means of the *syn*-addition of hydrosilanes to internal acetylenes, leading to a β -(E) product. Unfortunately, the reaction is limited to aliphatic alkynes only (**P23–P25**).

It has been established that the presence of a bulky NHC ligand provides high selectivity of the reaction towards Markovnikov products. On the other hand, the reaction

is also very sensitive to the steric nature of the alkyne substrate, which is significantly pronounced in the hydrosilylation of sterically demanding triisopropylacetylene, giving selectively β -(E)-vinylsilane **P16**. The influence of the alkyne substrates' steric nature is presented in Figure 3.

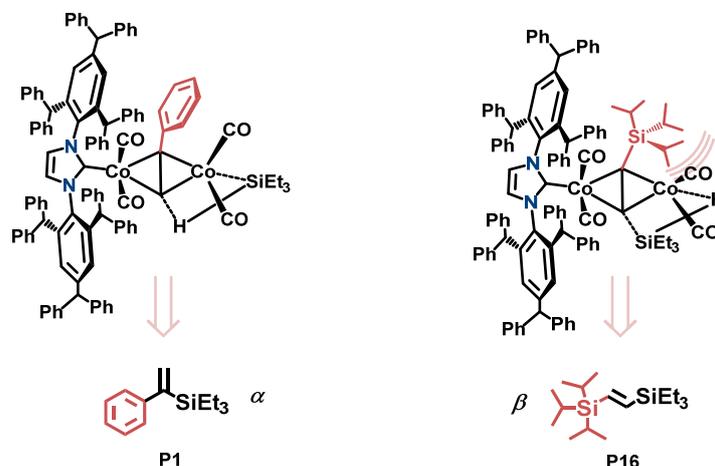


Figure 3. Influence of substrate's steric nature on reaction selectivity.

The mechanistic explanation provided by Deng et al. assumes that the active catalyst involved in the reaction is $(\text{NHC})\text{Co}_2(\text{CO})_5$. After the CO dissociation and subsequent addition of alkyne to the catalyst molecule, the dicobalt bridging alkyne complex $(\text{NHC})(\text{CO})_2\text{Co}(\mu\text{-}\eta^2\text{:}\eta^2\text{-HCCR})\text{Co}(\text{CO})_3$ is formed. In the next step, the cobalt intermediate interacts with a silane molecule to form the complex shown in Figure 3. In the case of acetylenes bearing smaller substituents (e.g., phenylacetylene), a more favorable silane complex is formed, giving α -vinylsilane as the reaction product. At the same time, using a very sterically demanding substrate (e.g., triisopropylsilylacetylene), the formation of a corresponding silyl complex is much more difficult due to the steric repulsive interactions between the alkyl substituent and hydrosilane molecule approaching the cobalt complex. Thus, in this case, the formation of Co–H is more favorable and the formation of the anti-Markovnikov product takes place.

2.3. Substrate Scope—Silanes

As the next step, a series of silanes were tested in optimized reaction conditions. The results are presented in Figure 4.

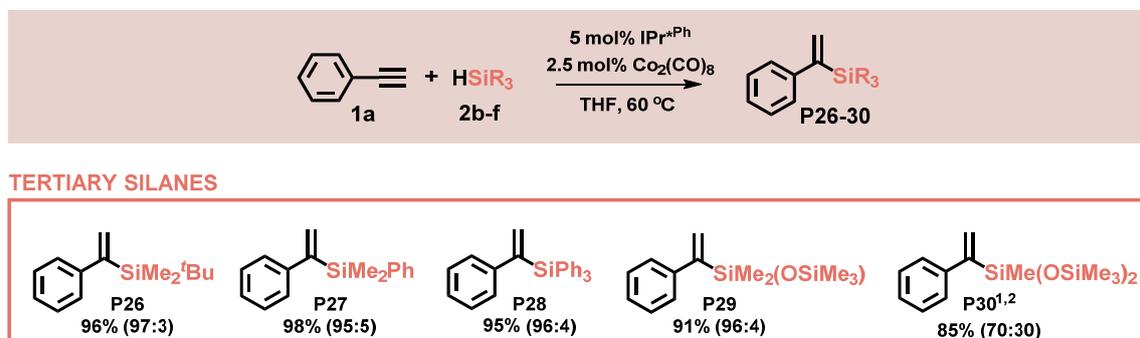


Figure 4. Substrate scope—tertiary silanes. Reaction conditions: argon, THF, 60 °C, 5 h, $[\mathbf{1a}]:[\mathbf{2b-f}] = 1:1$, $[\text{IPr}^*\text{Ph}] = 5 \text{ mol\%}$, $[\text{Co}] = 2.5 \text{ mol\%}$; isolated yields are given under the product structure. Selectivity $\alpha:\beta$ -(E) is given in the parenthesis; ¹ selectivity $\alpha:\beta$ -(E): β -(Z) is given in the parentheses; ² product without isolation, conversion of the substrates is given.

The proposed method proved to be effective for tertiary silanes containing alkyl (**P26**), aryl (**P28**), and alkyl–aryl (**P27**) substituents. Moreover, in the case of silanes containing siloxyl substituents, it was possible to effectively carry out the reaction with a high conversion of substrates (**P29**). However, in the reaction with methyl-bis(trimethylsiloxy)silane, the selectivity of the process decreased and a mixture of products also containing β -(*Z*)-vinylsilane was obtained. In this case, the ratio of the products α : β -(*E*): β -(*Z*) was 65:21:14 (**P30**).

Finally, our catalytic system was tested in the hydrosilylation of secondary silanes (Figure 5).

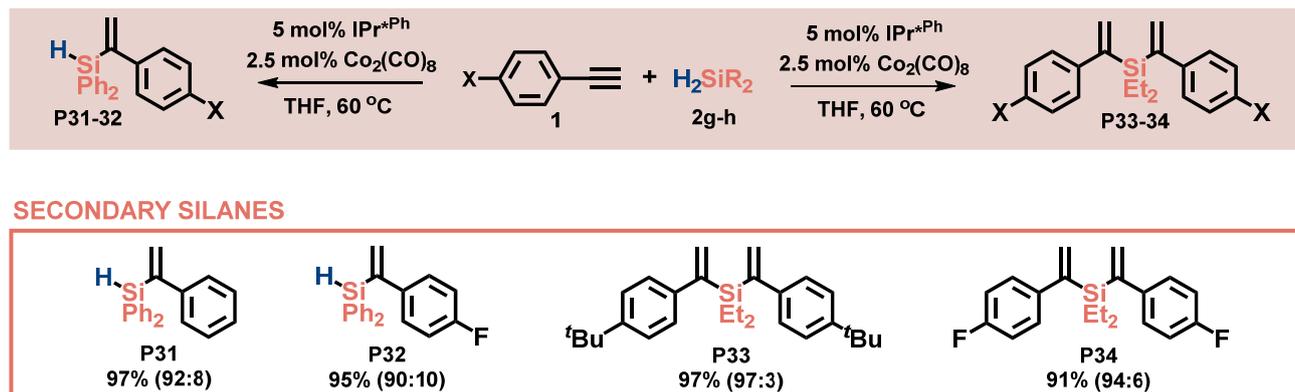


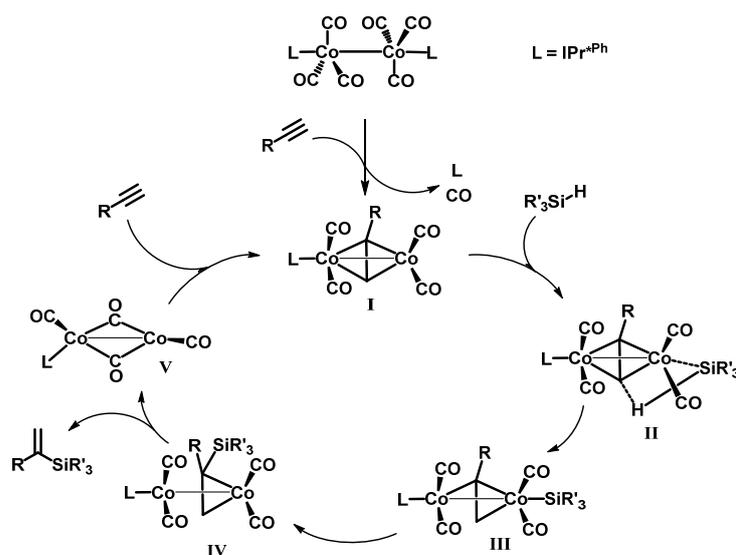
Figure 5. Substrate scope—secondary silanes. Reaction conditions: argon, THF, 60 °C, 12 h, [1a]:[2g-h] = 2:1, [IPr*Ph] = 5 mol%, [Co] = 2.5 mol%; isolated yields are given under the product structure. Selectivity α : β -(*E*) is given in the parentheses.

The catalytic methods of alkyne hydrosilylation limit the substrate scope to tertiary or secondary silanes only. This fact prompted us to perform additional tests to check the universality of the proposed method. As our aim was to obtain bis- α -vinylsilanes, a twofold excess of alkynes was added to the reaction mixture in each reaction. When diethylsilane was used as a reactant, we were able to selectively obtain products of bis-hydrosilylation (**P33** and **P34**). Surprisingly, in the same reaction conditions applied for hydrosilylation with diphenylsilane, the process led to the mono-vinylsilane product in majority (**P31** and **P32**). Additionally, traces of bis-hydrosilylation products and unreacted acetylene were observed in the post reaction mixture. In all cases, the regioselectivity towards the Markovnikov product was preserved.

2.4. Mechanistic Investigation

In order to determine whether the reaction occurs in a homogeneous manner, a mercury poisoning test was performed. The reaction of phenylacetylene (**1a**) and triethylsilane (**2a**) was performed under standard conditions. Then, after 15 min, 1000 equivalents of mercury in relation to cobalt were added to the reaction mixture. The obtained result did not indicate the inhibition of the reaction by excess mercury, and only an insignificant slow-down in the reaction rate was observed (see ESI, Figure S2). Additionally, we performed the hot filtration test for the same reaction. The obtained results confirmed that the catalytic activity of the filtrate was retained and the residue demonstrated only trace activity (see ESI, Figure S3). The selectivity of the reaction in both tests remained the same. Based on the performed tests, we assume that the reaction is occurring in a homogeneous manner.

On the basis of the available literature data and our own observations, we propose the reaction mechanism depicted in Scheme 1.



Scheme 1. Proposed mechanism.

At first, the insertion of acetylene occurs parallel to the dissociation of two ligands, leading to a dicobalt-bridging alkyne complex, which was previously confirmed by Deng. In the next step, the coordination of silane takes place. The way in which the second substrate molecule is coordinated is strongly dependent on the steric properties of both the ligand and the reagents. In most cases, the bulky NHC ligand favors the formation of the silyl complex, which subsequently leads to the formation of the Markovnikov product. After the formation of complex III, alkene complex VI is formed. In the last stage, the product molecule is eliminated, and the resulting complex can react with the next acetylene molecule. The bulky NHC ligand, due to its large steric hindrance around the metal atom, can significantly facilitate the reducing elimination step. This may explain the increased activity of the catalytic system we tested compared to those containing smaller NHC ligands. The influence of the steric hindrance of NHC ligands on the selectivity and activity of catalytic active metal species has been widely investigated. It has been proven that the introduction of a bulky NHC ligand to a metal complex can result in significantly more active and selective catalytic systems. Our observation confirmed that the bulky ligand used in these studies plays a crucial role in the highly selective and effective performance of the developed catalytic system.

3. Materials and Methods

3.1. Instruments and Reagents

All syntheses and catalytic tests were carried out under dry argon, using standard Schlenk-line and vacuum techniques. All products have been characterized using the apparatuses available at the Faculty of Chemistry, Adam Mickiewicz University in Poznań. The ^1H NMR and ^{13}C NMR spectra were recorded in CDCl_3 or C_6D_6 on a Varian 400 operating at 402.6 and 101.2 MHz, respectively. GC analyses were carried out on an Agilent 7890B instrument (column: DB-530 m ID 0.53 mm) equipped with TCD. The GC-MS analyses were performed on a Varian Saturn 2100T equipped with a DB-1 capillary column (30 m in length and 0.25 mm in internal diameter) and an ion trap detector. IR spectra were recorded on a Bruker IFS 66v/S spectrophotometer. Thin layer chromatography (TLC) was conducted on plates coated with a 250 μm thick silica gel layer and column chromatography was performed on silica gel 60 (70–230 mesh).

NHC carbene precursors were prepared according to procedures described in the literature [44–47]. All other reagents were commercially available (Merck, Acros Organics, Stanlab) and used as received. The solvents were dried over CaH_2 prior to use and stored over 4 Å molecular sieves under argon. Dichloromethane was additionally passed through

an alumina column and degassed by repeated freeze–pump–thaw cycles. The THF was dried over sodium benzophenone ketyl and freshly distilled prior to use.

3.2. Experimental Procedures

3.2.1. Catalytic Tests

The oven-dried 5 mL Schlenk vessel equipped with a magnetic stirring bar was charged with a freshly isolated NHC carbene (7.0×10^{-3} mmol) and $\text{Co}_2(\text{CO})_8$ (3.5×10^{-3} mmol) in the glove box. Then, THF (1 mL), alkyne (0.14 mmol), silane (0.14 mmol), and internal standard (decane, 15 μL) were added. The reaction mixture was stirred at the appropriate temperatures for 3–24 h (see Table 1). The conversion of the substrates and selectivity were determined by gas chromatography (GC) and confirmed by the ^1H NMR spectra of the post-reaction mixture.

3.2.2. Synthesis of Products P1–P30

The oven-dried 5 mL Schlenk vessel equipped with a magnetic stirring bar was charged with a freshly isolated NHC carbene (2.5×10^{-2} mmol) and $\text{Co}_2(\text{CO})_8$ (1.25×10^{-2} mmol) in the glove box. Then, THF (1 mL), alkyne (0.5 mmol), and silane (0.5 mmol) were added. The reaction mixture was stirred at 60 °C for 5 h. After this time, the solvent was evaporated under vacuum and the residue was purified by column chromatography (silica gel 60, *n*-hexane or *n*-hexane/DCM). Evaporation of the solvent gave the analytically pure products.

3.2.3. Synthesis of Products P31–P34

The oven-dried 5 mL Schlenk vessel equipped with a magnetic stirring bar was charged with a freshly isolated NHC carbene (5.0×10^{-2} mmol) and $\text{Co}_2(\text{CO})_8$ (2.5×10^{-2} mmol) in the glove box. Then, THF (1 mL), alkyne (1.0 mmol), and silane (0.5 mmol) were added. The reaction mixture was stirred at 60 °C for 12 h. After this time, the solvent was evaporated under vacuum and the residue was purified by column chromatography (silica gel 60, *n*-hexane/DCM). Evaporation of the solvent gave the analytically pure products.

3.2.4. Mercury Poisoning Experiment

An oven-dried 5 mL glass reactor equipped with a magnetic stirring bar was charged with a freshly isolated NHC carbene (7.0×10^{-3} mmol) and $\text{Co}_2(\text{CO})_8$ (3.5×10^{-3} mmol) in the glove box. Then, THF (1 mL), phenylacetylene **1a** (0.14 mmol), triethylsilane **2a** (0.14 mmol), and decane (15 μL) were added. The reaction was heated with stirring at 60 °C for 15 min. Then, the conversion of substrates was measured using gas chromatography, and Hg (1000 equiv. in relation to catalyst) was added. The reaction was carried out at 60 °C upon vigorous stirring for 5 h. The reaction course was monitored by gas chromatography.

3.2.5. Hot Filtration Test

A 5 mL glass reactor was charged with a freshly isolated NHC carbene (7.0×10^{-3} mmol) and $\text{Co}_2(\text{CO})_8$ (3.5×10^{-3} mmol) in the glove box. Then, THF (1 mL), phenylacetylene **1a** (0.14 mmol), triethylsilane **2a** (0.14 mmol), and decane (15 μL) were added. The reaction mixture was warmed up to 60 °C in an oil bath and carried out for 10 min. After this time, the hot solution was filtered under argon on the pad of silica gel to a new Schlenk vessel and the reaction was continued. The silica gel from filtration was transferred to a second Schlenk vessel, which was then charged with THF (1 mL), phenylacetylene **1a** (0.14 mmol), triethylsilane **2a** (0.14 mmol), and decane (15 μL). The reaction was carried out at 60 °C. The conversion of the substrates in both reactions was observed by gas chromatography.

4. Conclusions

The main conclusion from our results is that bulky NHC carbenes can effectively increase the selectivity of acetylene hydrosilylation. The synthesis with the designed catalytic system based on octacarbonyl dicobalt(0) and bulky NHC was proven to be a

universal method for the hydrosilylation of both terminal and internal alkynes using both tertiary and secondary silanes. This method ensured higher selectivity compared to that achieved using smaller NHCs and enabled the selective formation of α -alkenylsilanes under mild conditions.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal13030510/s1>: Figures S1–S65: ^1H and ^{13}C NMR spectra of isolated products and cobalt complex [9,23,25,28,41,48–53].

Author Contributions: Conceptualization, M.B. and P.Ž.; methodology, M.B.; formal analysis, M.B. and P.Ž.; investigation, M.B.; resources, P.Ž.; data curation, M.B. and P.Ž.; writing—original draft preparation, M.B.; writing—review and editing, M.B. and P.Ž.; visualization, M.B. and P.Ž.; supervision, P.Ž.; project administration, P.Ž.; funding acquisition, M.B. and P.Ž. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Ministry of Education and Science, project Diamond Grant No. DI2017 002647.

Data Availability Statement: Data are contained within the article or Supplementary Materials.

Acknowledgments: M.B. is a recipient of the Adam Mickiewicz University Foundation scholarship for the academic year 2022/2023.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Marciniak, B. (Ed.) *Hydrosilylation: A Comprehensive Review on Recent Advances*; Advances in silicon science; Springer: Berlin/Heidelberg, Germany, 2009; ISBN 978-1-4020-8171-2.
2. Nakajima, Y.; Shimada, S. Hydrosilylation Reaction of Olefins: Recent Advances and Perspectives. *RSC Adv.* **2015**, *5*, 20603–20616. [[CrossRef](#)]
3. Fleming, I.; Barbero, A.; Walter, D. Stereochemical Control in Organic Synthesis Using Silicon-Containing Compounds. *Chem. Rev.* **1997**, *97*, 2063–2192. [[CrossRef](#)]
4. Bracegirdle, S.; Anderson, E.A. Recent Advances in the Use of Temporary Silicon Tethers in Metal-Mediated Reactions. *Chem. Soc. Rev.* **2010**, *39*, 4114. [[CrossRef](#)]
5. Nakao, Y.; Hiyama, T. Silicon-Based Cross-Coupling Reaction: An Environmentally Benign Version. *Chem. Soc. Rev.* **2011**, *40*, 4893. [[CrossRef](#)]
6. Denmark, S.E.; Sweis, R.F. Organosilicon Compounds in Cross-Coupling Reactions. In *Metal-Catalyzed Cross-Coupling Reactions and More*; Wiley-VCH: Weinheim, Germany, 2014; pp. 475–532. ISBN 978-3-527-65558-8.
7. Markó, I.E.; Stérin, S.; Buisine, O.; Mignani, G.; Branlard, P.; Tinant, B.; Declercq, J.-P. Selective and Efficient Platinum(0)-Carbene Complexes as Hydrosilylation Catalysts. *Science* **2002**, *298*, 204–206. [[CrossRef](#)]
8. Berthon-Gelloz, G.; Schumers, J.-M.; De Bo, G.; Markó, I.E. Highly β -(E)-Selective Hydrosilylation of Terminal and Internal Alkynes Catalyzed by a (IPr)Pt(Diene) Complex. *J. Org. Chem.* **2008**, *73*, 4190–4197. [[CrossRef](#)]
9. Zak, P.; Bołt, M.; Kubicki, M.; Pietraszuk, C. Highly Selective Hydrosilylation of Olefins and Acetylenes by Platinum(0) Complexes Bearing Bulky N-Heterocyclic Carbene Ligands. *Dalton Trans.* **2018**, *47*, 1903–1910. [[CrossRef](#)]
10. Puerta-Oteo, R.; Munarriz, J.; Polo, V.; Jiménez, M.V.; Pérez-Torrente, J.J. Carboxylate-Assisted β -(Z) Stereoselective Hydrosilylation of Terminal Alkynes Catalyzed by a Zwitterionic Bis-NHC Rhodium(III) Complex. *ACS Catal.* **2020**, *10*, 7367–7380. [[CrossRef](#)]
11. Gao, W.; Ding, S. Progress on Iridium-Catalyzed Hydrosilylation of Alkenes and Alkynes. *Synthesis* **2020**, *52*, 3549–3563. [[CrossRef](#)]
12. Karstedt, B.D. Platinum Complexes of Unsaturated Siloxanes and Platinum Containing Organopolysiloxanes. U.S. Patent No 3,775,452, 27 November 1973.
13. Hitchcock, P.B.; Lappert, M.F.; Warhurst, N.J.W. Synthesis and Structure of Arac-Tris(Divinylsiloxy) Diplatinum(0) Complex and Its Reaction with Maleic Anhydride. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 438–440. [[CrossRef](#)]
14. Obligation, J.V.; Chirik, P.J. Earth-Abundant Transition Metal Catalysts for Alkene Hydrosilylation and Hydroboration. *Nat. Rev. Chem.* **2018**, *2*, 15–34. [[CrossRef](#)]
15. Kuciński, K.; Hreczycho, G. Hydrosilylation and Hydroboration in a Sustainable Manner: From Earth-Abundant Catalysts to Catalyst-Free Solutions. *Green Chem.* **2020**, *22*, 5210–5224. [[CrossRef](#)]
16. Guo, J.; Shen, X.; Lu, Z. Regio- and Enantioselective Cobalt-Catalyzed Sequential Hydrosilylation/Hydrogenation of Terminal Alkynes. *Angew. Chem. Int. Ed.* **2017**, *56*, 615–618. [[CrossRef](#)] [[PubMed](#)]
17. Wu, G.; Chakraborty, U.; Jacobi von Wangelin, A. Regiocontrol in the Cobalt-Catalyzed Hydrosilylation of Alkynes. *Chem. Commun.* **2018**, *54*, 12322–12325. [[CrossRef](#)]

18. Chen, J.; Shen, X.; Lu, Z. Cobalt-Catalyzed Markovnikov Selective Sequential Hydrogenation/Hydrohydrazidation of Aliphatic Terminal Alkynes. *J. Am. Chem. Soc.* **2020**, *142*, 14455–14460. [[CrossRef](#)]
19. Sun, Y.; Guo, J.; Shen, X.; Lu, Z. Ligand Relay Catalysis for Cobalt-Catalyzed Sequential Hydrosilylation and Hydrohydrazidation of Terminal Alkynes. *Nat. Commun.* **2022**, *13*, 650. [[CrossRef](#)]
20. Bera, S.S.; Szostak, M. Cobalt–N-Heterocyclic Carbene Complexes in Catalysis. *ACS Catal.* **2022**, *12*, 3111–3137. [[CrossRef](#)]
21. Park, J.-W. Cobalt-Catalyzed Alkyne Hydrosilylation as a New Frontier to Selectively Access Silyl-Hydrocarbons. *Chem. Commun.* **2022**, *58*, 491–504. [[CrossRef](#)]
22. Guo, J.; Lu, Z. Highly Chemo-, Regio-, and Stereoselective Cobalt-Catalyzed Markovnikov Hydrosilylation of Alkynes. *Angew. Chem. Int. Ed.* **2016**, *55*, 10835–10838. [[CrossRef](#)]
23. Zuo, Z.; Yang, J.; Huang, Z. Cobalt-Catalyzed Alkyne Hydrosilylation and Sequential Vinylsilane Hydroboration with Markovnikov Selectivity. *Angew. Chem. Int. Ed.* **2016**, *55*, 10839–10843. [[CrossRef](#)]
24. Kong, D.; Hu, B.; Chen, D. Highly Regio- and Stereoselective Hydrosilylation of Alkynes Catalyzed by Tridentate Cobalt Complexes. *Chem. Asian J.* **2019**, *14*, 2694–2703. [[CrossRef](#)] [[PubMed](#)]
25. Skrodzki, M.; Patroniak, V.; Pawluć, P. Schiff Base Cobalt(II) Complex-Catalyzed Highly Markovnikov-Selective Hydrosilylation of Alkynes. *Org. Lett.* **2021**, *23*, 663–667. [[CrossRef](#)] [[PubMed](#)]
26. Skrodzki, M.; Ortega Garrido, V.; Csáky, A.G.; Pawluć, P. Searching for Highly Active Cobalt Catalysts Bearing Schiff Base Ligands for Markovnikov-Selective Hydrosilylation of Alkynes with Tertiary Silanes. *J. Catal.* **2022**, *411*, 116–121. [[CrossRef](#)]
27. Sahoo, M.K.; Kim, D.; Chang, S.; Park, J.-W. Regioselective Access to α -Vinylsilanes and α -Vinylgermanes by Cobalt-Catalyzed Migratory Hydrofunctionalization of 2-Alkynes. *ACS Catal.* **2021**, *11*, 12777–12784. [[CrossRef](#)]
28. Wang, D.; Lai, Y.; Wang, P.; Leng, X.; Xiao, J.; Deng, L. Markovnikov Hydrosilylation of Alkynes with Tertiary Silanes Catalyzed by Dinuclear Cobalt Carbonyl Complexes with NHC Ligation. *J. Am. Chem. Soc.* **2021**, *143*, 12847–12856. [[CrossRef](#)] [[PubMed](#)]
29. Huang, K.-H.; Isobe, M. Highly Regioselective Hydrosilylation of Unsymmetric Alkynes Using a Phenylthio Directing Group: Highly Regioselective Hydrosilylation of Unsymmetric Alkynes. *Eur. J. Org. Chem.* **2014**, *2014*, 4733–4740. [[CrossRef](#)]
30. Clavier, H.; Nolan, S.P. Percent Buried Volume for Phosphine and N-Heterocyclic Carbene Ligands: Steric Properties in Organometallic Chemistry. *Chem. Commun.* **2010**, *46*, 841. [[CrossRef](#)]
31. Gómez-Suárez, A.; Nelson, D.J.; Nolan, S.P. Quantifying and Understanding the Steric Properties of N-Heterocyclic Carbenes. *Chem. Commun.* **2017**, *53*, 2650–2660. [[CrossRef](#)]
32. Vanden Broeck, S.M.P.; Nahra, F.; Cazin, C.S.J. Bulky-Yet-Flexible Carbene Ligands and Their Use in Palladium Cross-Coupling. *Inorganics* **2019**, *7*, 78. [[CrossRef](#)]
33. Zhao, Q.; Meng, G.; Li, G.; Flach, C.; Mendelsohn, R.; Lalancette, R.; Szostak, R.; Szostak, M. IPr#—Highly Hindered, Broadly Applicable N-Heterocyclic Carbenes. *Chem. Sci.* **2021**, *12*, 10583–10589. [[CrossRef](#)]
34. Žak, P.; Bołt, M.; Lorkowski, J.; Kubicki, M.; Pietraszuk, C. Platinum Complexes Bearing Bulky N-Heterocyclic Carbene Ligands as Efficient Catalysts for the Fully Selective Dimerization of Terminal Alkynes. *ChemCatChem* **2017**, *9*, 3627–3631. [[CrossRef](#)]
35. Žak, P.; Bołt, M.; Pietraszuk, C. Selective Synthesis of *E*-Vinylsilanes and *E, E*-Divinylsilanes via Platinum-Catalyzed Hydrosilylation of Alkynes with Secondary Silanes. *RSC Adv.* **2018**, *8*, 40016–40021. [[CrossRef](#)] [[PubMed](#)]
36. Bołt, M.; Žak, P. Application of Bulky NHC–Rhodium Complexes in Efficient S–Si and S–S Bond Forming Reactions. *Inorg. Chem.* **2021**, *60*, 17579–17585. [[CrossRef](#)]
37. Bołt, M.; Delaude, L.; Žak, P. Rhodium Catalysts with Superbulky NHC Ligands for the Selective α -Hydrothiolation of Alkynes. *Dalton Trans.* **2022**, *51*, 4429–4434. [[CrossRef](#)] [[PubMed](#)]
38. Bołt, M.; Mermela, A.; Žak, P. Influence of Bis-NHC Ligand on Platinum-Catalyzed Hydrosilylation of Internal Alkynes. *Eur. J. Inorg. Chem.* **2022**, *26*, e202200622. [[CrossRef](#)]
39. Bołt, M.; Žak, P. Solvent-Free Hydroboration of Alkynes Catalyzed by an NHC–Cobalt Complex. *RSC Adv.* **2022**, *12*, 18572–18577. [[CrossRef](#)]
40. Inoue, A.; Kondo, J.; Shinokubo, H.; Oshima, K. Facile Synthesis of Acylsilanes via Aerobic Oxidation of *g Em*-Disilylalkylcopper Compounds. *J. Am. Chem. Soc.* **2001**, *123*, 11109–11110. [[CrossRef](#)]
41. Zhang, X.; Ji, X.; Xie, X.; Ding, S. Construction of Highly Sterically Hindered 1,1-Disilylated Terminal Alkenes. *Chem. Commun.* **2018**, *54*, 12958–12961. [[CrossRef](#)]
42. Inoue, A.; Kondo, J.; Shinokubo, H.; Oshima, K. Facile Synthesis of Ketones from 1,1-Disilylethenes via Oxidation of Gem-Disilylalkanes. *Chem. Commun.* **2002**, *2*, 114–115. [[CrossRef](#)]
43. Li, H.; Yang, C.; Wang, D.; Deng, L. Cobalt-Catalyzed Regio- and Stereoselective Hydrosilylation of Alk-2-Ynes with Tertiary Silanes. *Organometallics* **2023**. [[CrossRef](#)]
44. Meiries, S.; Speck, K.; Cordes, D.B.; Slawin, A.M.Z.; Nolan, S.P. [Pd(IPr*^{OMe})(Acac)Cl]: Tuning the N-Heterocyclic Carbene in Catalytic C–N Bond Formation. *Organometallics* **2013**, *32*, 330–339. [[CrossRef](#)]
45. Saberov, V.S.H.; Evans, D.A.; Korotkikh, N.I.; Cowley, A.H.; Pekhtereva, T.M.; Popov, A.F.; Shvaika, O.P. Exceptionally Efficient Catalytic Hydrodechlorination of Persistent Organic Pollutants: Application of New Sterically Shielded Palladium Carbene Complexes. *Dalton Trans.* **2014**, *43*, 18117–18122. [[CrossRef](#)]
46. Hans, M.; Lorkowski, J.; Demonceau, A.; Delaude, L. Efficient Synthetic Protocols for the Preparation of Common N-Heterocyclic Carbene Precursors. *Beilstein J. Org. Chem.* **2015**, *11*, 2318–2325. [[CrossRef](#)]

47. Žak, P.; Bořt, M.; Dudziec, B.; Kubicki, M. Synthesis of (*E*)-1,4-Disilsesquioxylsubstituted but-1-En-3-Ynes via Platinum-Catalyzed Dimerization of Ethynylsiloxysilsesquioxanes. *Dalton Trans.* **2019**, *48*, 2657–2663. [[CrossRef](#)]
48. Rivero-Crespo, M.A.; Leyva-Pérez, A.; Corma, A.A.; Rivero-Crespo, M.A.; Leyva-Pérez, A.; Corma, A.A. A Ligand-Free Pt₃ Cluster Catalyzes the Markovnikov Hydrosilylation of Alkynes with up to 10⁶ Turnover Frequencies. *Chem. Eur. J.* **2017**, *23*, 1702–1708. [[CrossRef](#)]
49. Chauhan, B.P.S.; Sarka, A. Functionalized vinylsilanes via highly efficient and recyclable Pt-nanoparticle catalysed hydrosilylation of alkynes. *Dalton Trans.* **2017**, *46*, 8709–8715. [[CrossRef](#)]
50. Gee, J.C.; Fuller, B.A.; Lockett, H.-M.; Sedghi, G.; Robertson, C.M.; Luzyanin, K.V. Visible light accelerated hydrosilylation of alkynes using platinum–[acyclic diaminocarbene] photocatalysts. *Chem. Commun.* **2018**, *54*, 9450–9453. [[CrossRef](#)]
51. Battace, A.; Zair, T.; Doucet, H.; Santelli, M.J. Selective synthesis of (*E*)-triethyl (2-arylethenyl) silane derivatives by reaction of aryl bromides with triethyl vinylsilane catalysed by a palladium–tetrphosphine complex. *Organomet. Chem.* **2005**, *690*, 3790–3802. [[CrossRef](#)]
52. Miura, H.; Sasaki, S.; Ogawa, R.; Shishido, T. Hydrosilylation of Allenes Over Palladium–Gold Alloy Catalysts: Enhancing Activity and Switching Selectivity by the Incorporation of Palladium into Gold Nanoparticles. *Eur. J. Org. Chem.* **2018**, *2018*, 1858–1862. [[CrossRef](#)]
53. Kita, Y.; Tobisu, M.; Chatani, N. Rhodium-Catalyzed Alkenylation of Nitriles via Silicon-Assisted C-CN Bond Cleavage. *Org. Lett.* **2010**, *12*, 1864–1867. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.