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Cobalt-Catalysed, Ligand-Controlled Regiodivergent Alkene Hydrosilylation

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Cobalt-Catalysed, Ligand-Controlled Regiodivergent Alkene Hydrosilylation

Jamie H. Docherty,[a] Andrew P. Dominey,[b] and Stephen P. Thomas*[a]

Abstract: Alkene hydrosilylation is amongst the largest industrial homogenous catalysis processes. Cobalt catalysis offers a sustainable alternative to commonly used platinum catalysts to achieve this transformation. Using two bisimino-pyridine cobalt(II) catalysts the regiodivergent hydrosilylation of alkenes has been developed. Variation of pre-catalyst activator and ligand substituents were investigated to enable the controlled, regiodivergent hydrosilylation of both aryl- and alkyl-substituted alkenes with phenylsilane. In contrast to other regiodivergence strategies, excellent regioselectivity for either isomer was achieved using the same ligand class but differing by a single methyl group (ethyl *vs iso*propyl).
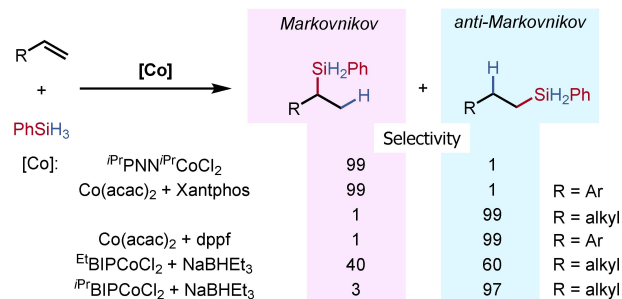
Introduction

Alkene hydrosilylation is one of the largest industrial applications of homogenous catalysis and enables fields as diverse as soft plastics and anti-foaming agents.[1,2] The most commonly used hydrosilylation catalysts remain platinum-based, with Speier's and Karstedt's complexes being key examples.[3,4] The high activity and ease of use of these platinum complexes have given these catalysts ubiquity over other transition-metal alternatives and outweighs the scarcity, volatile cost and sourcing of platinum. The dispersive nature of many hydrosilylation (end) products presents non-trivial recycling and platinum-catalysed processes contribute to the annual global consumption of approximately 27 tonnes of platinum.[5] Therefore, the development of Earth-abundant alternatives has been an area of intense research interest.
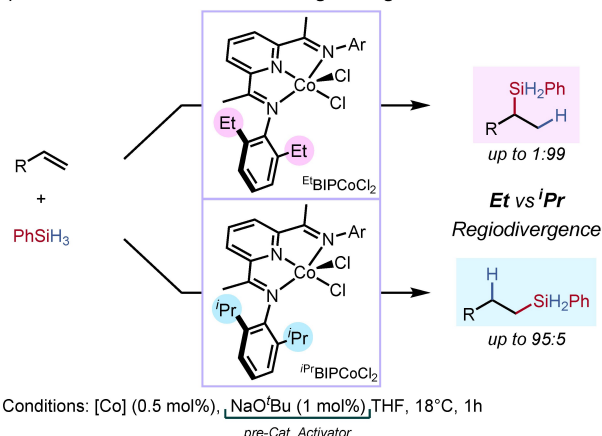
A number of hydrosilylation methodologies have been developed using first-row transition metal catalysts.[6–9] These protocols rely on the generation of a low oxidation-state metal species (eg. Fe^0 or, Co^I), typically by; a) preparation and isolation of the air- and moisture-sensitive low oxidation-state complex, b) generating the active species using an *in situ* reductant,[7,8b,9a] or c) using endogenous activation.[8c,e–f,9d] The latter approaches provide a level of operational simplicity that widens the potential user-group beyond that of the expert chemist. Given

the use of strongly reducing organometallic regents (eg. Grignard reagent or $NaHBEt_3$) for pre-catalyst activation is a well-established strategy, recent studies have questioned whether non-organometallic reagents could serve in the same capacity.[9,10] As a result, methods have been discovered and developed to illustrate that metal alkoxide salts are excellent pre-catalyst activators for a wide range of structurally unique iron(II) and cobalt(II) complexes.[11]

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a) Cobalt(II): Ligand, counterion and activation controlled hydrosilylation

[Co]:	Markovnikov	anti-Markovnikov	
	Selectivity		
$^{iPr}PNN^{iPr}CoCl_2$	99	1	
$Co(acac)_2$ + Xantphos	99	1	R = Ar
	1	99	R = alkyl
$Co(acac)_2$ + dppf	1	99	R = Ar
$^{Et}BIPCoCl_2$ + $NaBHEt_3$	40	60	R = alkyl
$^{iPr}BIPCoCl_2$ + $NaBHEt_3$	3	97	R = alkyl

b) *This Work* - Substituent directed regiodivergence

up to 1:99

Et vs ^{i}Pr
Regiodivergence

up to 95:5

Conditions: [Co] (0.5 mol%), NaO^{t}Bu (1 mol%), THF, 18°C, 1h
pre-Cat. Activator

Scheme 1. Earth-abundant-metal-catalysed alkene hydrosilylation. a) Cobalt-PNN catalyst for Markovnikov-selective alkene hydrosilylation. Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, dppf = 1,1'-bis(diphenylphosphino)ferrocene. b) Ligand-directed regiodivergent alkene hydrosilylations by only discrete modification of catalyst structure.

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The majority of alkene hydrosilylation reactions, catalysed by either precious- or Earth-abundant metals, show high levels of *anti*-Markovnikov selectivity, with Markovnikov selective examples remaining scarce until recently.[12,13] Lanthanum-based catalysts show Markovnikov selective hydrosilylation of activated alkenes such as styrene.[14] Similarly, enantiopure palladium species have been used for the enantioselective hydrosilylation of styrene.[15] For unactivated alkenes, limited examples of nickel[16] and palladium[17] catalysts have shown low- to moderate Markovnikov regioselectivity. Alkene hydrosilylation protocols with both a high Markovnikov selectivity and broad substrate scope remain rare.[12a] Notably, Huang reported a cobalt phosphine-iminopyridine catalyst that showed excellent Markovnikov selectivity in which activation of the cobalt(II) chloride pre-catalyst activation was triggered by a thermally induced hydride transfer from the silane reagent (Scheme 1a).[18] Ge reported that the combination of $Co(acac)_2$ and Xantphos gave Markovnikov-selective hydrosilylation of styrene derivatives, and that use of [1,1′-ferrocenediyl-bis(diphenylphosphine)] (dppf), in place of Xantphos, inverted the regioselectivity of hydrosilylation (Scheme 1a).[19] Of direct relevance to the current work, Rajanbabu reported the cobalt-catalysed hydrosilylation of alkyl-alkenes using bis(imino)pyridine ligands (BIP) with ^{Et}BIPCoCl$_2$ and ^{iPr}BIPCoCl$_2$ in combination with NaHBEt$_3$ as an activator (Scheme 1a).[20] The ^{Et}BIPCoCl$_2$ catalyst gave a mixture of regioisomeric alkylsilanes when using 1-octene 1a (40:60, **2a:3a**), however ^{iPr}BIPCoCl$_2$ showed good *anti*-Markovnikov selectivity (3:97 **2a:3a**).

Results and Discussion

During the course of preliminary investigations into pre-catalyst activation using alkoxide salts, and akin to the report of Rajanbabu,[20] it was discovered that cobalt complexes containing the bisiminopyridine ligand framework (BIP) would give mixtures of linear and branched alkylsilane products in alkene

hydrosilylation with improved selectivity over previous methods. Therefore, reaction parameters such as pre-catalyst activator, solvent and ligand structure were varied to ascertain if the regioselectivity could be controlled. A series of cobalt(II) BIP complexes with differing steric environments were investigated (Table 1). The least sterically encumbered cobalt(II) complex, ^{H}BIPCoCl$_2$, gave the linear alkyl silane product predominantly (17:83 **2a/3a**, Entry 2). The analogous mesityl-bearing catalyst, ^{Mes}BIPCoCl$_2$, showed a high degree of branched selectivity giving the secondary alkylsilane **2a** in excellent yield (Entry 3). Variation to the more sterically hindered, ^{Et}BIPCoCl$_2$, gave both high yield and excellent Markovnikov selectivity for the branched alkylsilane **2a** (Entry 1). The most sterically hindered complex, ^{iPr}BIPCoCl$_2$, which following the observed trend would have been expected to give improved Markovnikov selectivity, instead showed excellent selectivity for the *anti*-Markovnikov regioisomer to give the linear alkylsilane **3a** in high yield (Table 1, entry 4). Further optimisation of a number of reaction parameters including concentration, solvent and pre-catalyst activator were carried out to achieve optimal selectivity for both regioisomers (see Supporting Information). Using ethyl acetate (EtOAc) as the reaction solvent gave the hydrosilylation products **2a** and **3a** in comparable yields and regioselectivities to the same reaction conducted in THF (Table 1, entry 5), and without any reduction of the ester solvent observed. Methyl *tert*-butylether (MTBE) and dimethylcarbonate (DMC) performed similarly well, indicating the amenability of this synthetic method to a wide range of solvent systems. Previous studies using first-row transition metal pre-catalysts, particularly those using cobalt or iron, have generally necessitated the presence of an external activator for reactivity.[6a,12,21] Likewise, this manifold showed no reactivity in the absence of an activating agent (see Supporting Information). Therefore alkoxide salts were tested, all of which gave comparable results (Entries 8 and 9). However changing the pre-catalyst activator, to a more conventionally used organometallic reagent (specifically; EtMgBr, NaHBEt$_3$ and MeLi – see

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Table 1. Optimisation of reaction conditions – An overview of parameter variation. Yields determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

n-hex ⟶ [^{Et}BIPCoCl$_2$ (1 mol%) / NaO^{t}Bu (2 mol%) / PhSiH$_3$ (1.1 eq) / THF [0.16M], 1h, 18°C] ⟶ *n*-hex–SiH$_2$Ph + H Branched **2a** + *n*-hex–SiH$_2$Ph Linear **3a**

Entry	Variation From Standard Conditions	Overall Yield [%]	Regioselectivity [**2a**:**3a**]
1	*none*	>95	96:4
2	^{H}BIPCoCl$_2$	90	17:83
3	^{Mes}BIPCoCl$_2$	>95	91:9
4	^{iPr}BIPCoCl$_2$	>95	8:92
5	EtOAc instead of THF	>95	93:7
6	MTBE instead of THF	>95	95:5
7	DMC instead of THF	82	93:7
8	NaOMe instead of NaO^{t}Bu	88	96:4
9	KO^{t}Bu instead of NaO^{t}Bu	71	96:4
10	EtMgBr instead of NaO^{t}Bu	80	75:25
11	NaHBEt$_3$ instead of NaO^{t}Bu	86	40:60
12	0.5 mol% catalyst + 1 mol% NaO^{t}Bu	>95	96:4

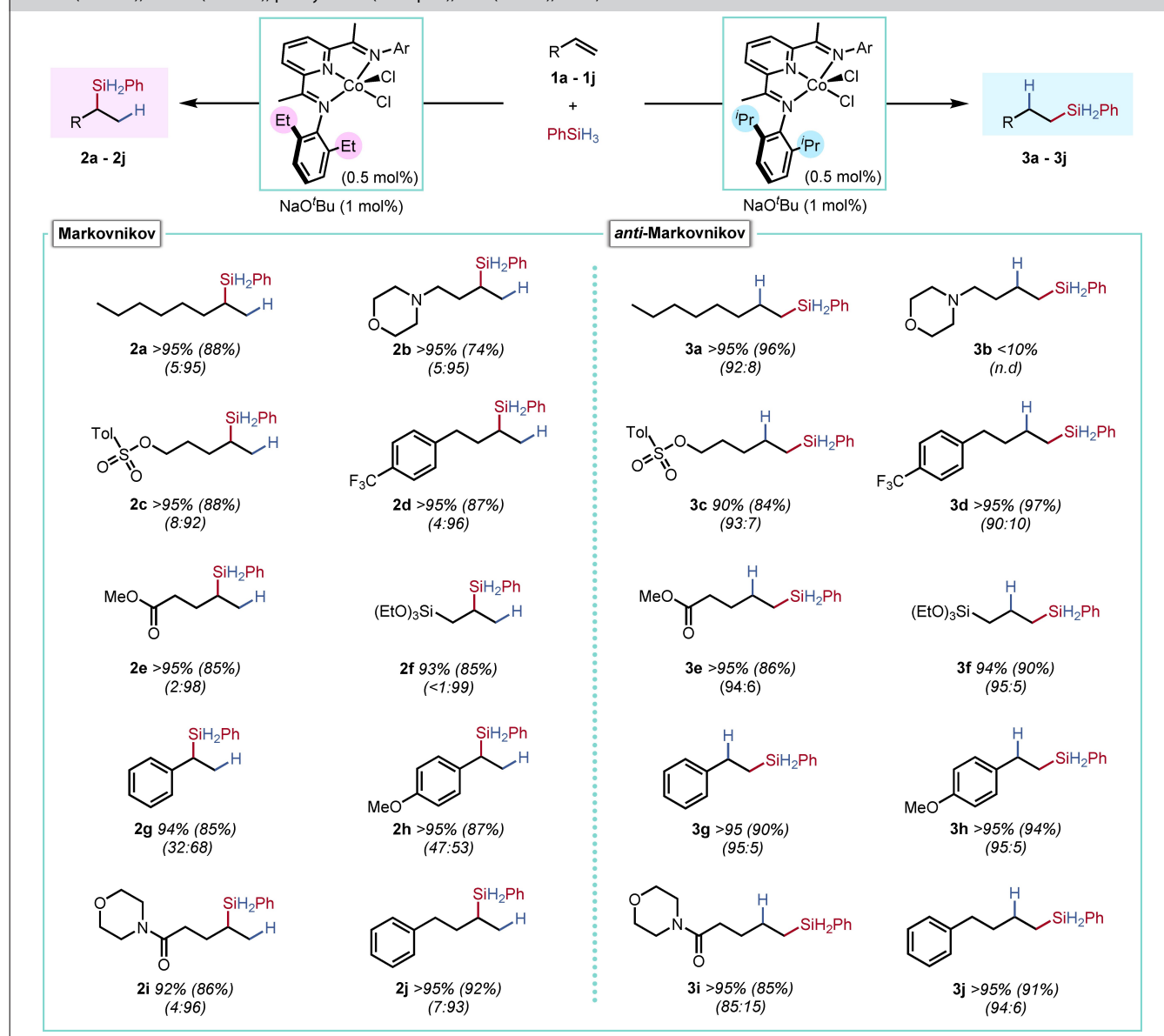**These are not the final page numbers!** ⬀⬀

Supporting Information), was detrimental to both the yield and regioselectivity of the hydrosilylation reaction (Entries 10 and 11). The regiodivergent cobalt-catalysed alkene hydrosilylation reaction was optimised to a catalyst loading of 0.5 mol%, 1 mol% NaO^{t}Bu in tetrahydrofuran at ambient temperature (Table 1, entry 12).

We assessed the generality of the regiodivergent catalysis by application to a range of alkene substrates, initially for the Markovnikov-selective hydrosilylation, using ^{Et}BIPCoCl$_2$ (Table 2, left). All of the alkyl substituted alkenes tested, **1a–1f** and **1i–1j**, underwent regioselective hydrosilylation for the secondary (branched) regioisomer. The branched alkyl silane products were obtained in high yield and with up to <1:99 regioselectivity. Styrenes **1g** and **1h** reacted with moderate selectivity to give only slight preference for the branched regioisomers **2g**

and **2h**, respectively. The reaction proved tolerant of tertiary amine **1b**, tosylate **1c**, ester **1e** and amide **1i** functionalities, each giving their respective secondary silane products **2b**, **2c**, **2e** and **2i**, showing the chemoselectivity of the reaction conditions to potentially reducible functional groups. Similarly, an allylsilane **1f** reacted under the optimised reaction conditions to give the 1,2-disilylalkane **2f** with absolute regioselectivity for the Markovnikov regioisomer.

The same substrates **1a–1j** that underwent Markovnikov-selective hydrosilylation using ^{Et}BIPCoCl$_2$ were assessed using the *anti*-Markonikov selective pre-catalyst ^{iPr}BIPCoCl$_2$ (Table 2, right). This allowed for a direct comparison of regioselectivity between both catalysts. Using ^{iPr}BIPCoCl$_2$, alkenes **1a–1j** were transformed into the primary (linear) alkylsilanes **3a–3j** in typically excellent yield and with good to excellent regioselec-

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Table 2. Scope of the regiodivergent cobalt-catalysed alkene hydrosilylation. Yields determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. Isolated yields in parenthesis and ratios refer to *anti*-Markovnikov/Markovnikov selectivity. Reaction conditions: [Co] (0.5 mol%), NaO^{t}Bu (1 mol%), alkene (1 mmol), phenylsilane (1.1 equiv.), THF (2.5 mL), 19 °C, 1 hour.

Markovnikov

2a >95% (88%) (5:95)

2b >95% (74%) (5:95)

2c >95% (88%) (8:92)

2d >95% (87%) (4:96)

2e >95% (85%) (2:98)

2f 93% (85%) (<1:99)

2g 94% (85%) (32:68)

2h >95% (87%) (47:53)

2i 92% (86%) (4:96)

2j >95% (92%) (7:93)

***anti*-Markovnikov**

3a >95% (96%) (92:8)

3b <10% (n.d)

3c 90% (84%) (93:7)

3d >95% (97%) (90:10)

3e >95% (86%) (94:6)

3f 94% (90%) (95:5)

3g >95 (90%) (95:5)

3h >95% (94%) (95:5)

3i >95% (85%) (85:15)

3j >95% (91%) (94:6)

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tivity. The only exception was a tertiary amine **1b** which underwent slow reaction to give a poor yield of the corresponding primary silane **3b**. Importantly, regioselectivity in these examples was inverted from that using ^{Et}BIPCoCl$_2$, showing clear evidence of ligand-based regiodivergent reactivity. Functional group tolerance using ^{iPr}BIPCoCl$_2$ was similar to that observed using ^{Et}BIPCoCl$_2$ as catalyst, again tolerating tosylate **1c**, ester **1e** and amide **2i** functionalities but not amine **1b**. Styrenes **1g** and **1h** gave a much greater preference for the linear alkylsilanes **3g** and **3h** when compared to reactions using Markonikov-selective ^{Et}BIPCoCl$_2$ catalyst, where decreased regioselectivity was observed.

In order to gain insight into the regiodivergence, reaction progress kinetic data were obtained for both the Markovnikov (^{iPr}BIPCoCl$_2$) and *anti*-Markovnikov (^{Et}BIPCoCl$_2$) catalysis protocols (Figure 1).[22] Using ^{Et}BIPCoCl$_2$ at varying catalyst loadings (0.5, 0.75 and 1.0 mol%) showed unique reaction progress kinetics.
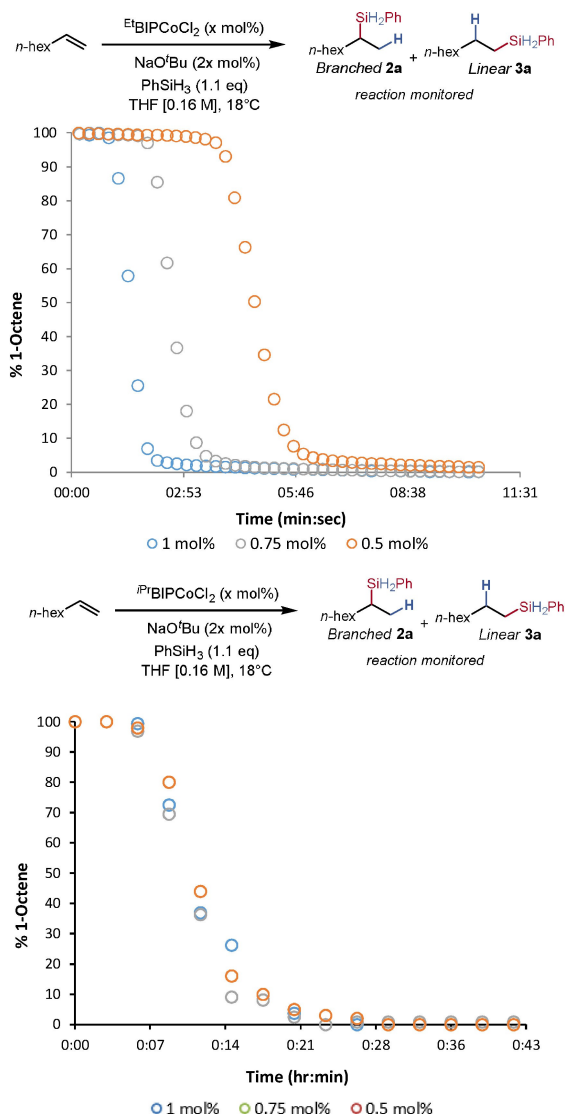
**Figure 1.** Reaction progress kinetics: Reaction of 1-octene with phenylsilane using ^{Et}BIPCoCl$_2$ (top) and ^{iPr}BIPCoCl$_2$ (bottom) with various catalyst loadings (0.5 to 1 mol%).

Each profile displayed a clear induction period, with the lowest catalyst loading resulting in a longer induction period. Using 0.5 mol% of the ^{Et}BIPCoCl$_2$ pre-catalyst, the Markovnikov selective hydrosilylation reaction was complete (> 90% yield) in less than 6 minutes. An increase in catalyst loading to 1 mol% gave a corresponding increase in the rate of reaction, with complete reaction (> 90% yield) observed in less than 2 minutes. When the NaO^{t}Bu activator was exchanged for classical organometallic activators, such as EtMgBr and NaHBEt$_3$, an induction period was not observed. This suggested a slower rate of pre-catalyst activation using the alkoxide as a cause for the observed induction period of the reaction (see Supporting Information). It should be noted that although the mechanism of pre-catalyst activation is proposed to occur by hydride transfer from the silane to the metal, an electron transfer pathway cannot be excluded.[23] In comparison, using the more sterically hindered ^{iPr}BIPCoCl$_2$ pre-catalyst for the *anti*-Markovnikov selective reaction, the rate of reaction was significantly slower. Across all catalyst loadings investigated, similar rates of reaction was observed (*ca.* 18 minutes, > 90% yield). These observations showed that the ^{Et}BIPCoCl$_2$ pre-catalyst was around three times faster than the ^{iPr}BIPCoCl$_2$-catalysed reaction at 0.5 mol% catalyst loading (6 min *vs.* 18 min). By contrast to the ^{Et}BIPCoCl$_2$ pre-catalyst, an increase in ^{iPr}BIPCoCl$_2$ catalyst loading did not result in a significant enhancement of the rate of reaction (Figure 1, lower).

Although many first-row metal catalysts have been used for hydrosilylation, mechanistic understanding for many of these systems remains elusive.[9f] Studies of cobalt-catalysed hydrosilylation reactions using cobalt-carbonyl[24] and cyclopentadienyl-cobalt complexes[25] suggested a prevalence of a modified Chalk-Harrod mechanism of alkene silyl-metallation followed by carbon-hydrogen bond forming reductive elimination.[26] However in contrast to the use of strong-field ligands in these early protocols, many emerging methods use weak-field ligands and raise the possibility of radical initiated and propagated hydrosilylation mechanisms. For example it may be possible for a weak metal-carbon bond to serve as a radical initiators by metal-carbon bond homolysis. Radical chain reactions have been used and studied for alkene hydrosilylation reactions and these mechanisms of radical initiation and propagation have been invoked in manganese-catalysed hydrosilylation reactions.[27,28]

Given the possibility of radical processes within the developed cobalt-catalysed regiodivergent system it was logical to assess whether this type of reactivity was operating. Conducting the standard regiodivergent hydrosilylation reactions with added radical traps and radical clock substrates however proved inconclusive (see Supporting Information).[29] While the use of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO, 0.5 equiv.) showed reaction inhibition using both pre-catalysts, it remains unclear if a radical process is operational or if TEMPO reacted directly with the organometallic species in solution.

Alternatively, a Chalk-Harrod, or modified variant, mechanism could be in operation in catalysis. In this scenario, cobalt silyl-, cobalt hydride- or cobalt-silane-type species would be expected to form before or during catalysis. Therefore the

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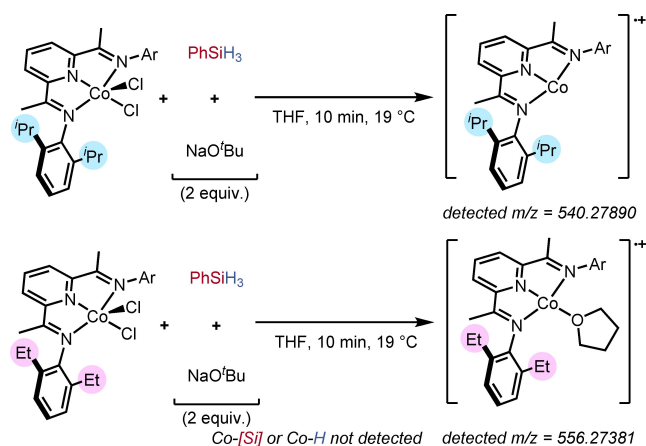
Scheme 2. Stoichiometric reactions of both ^{iPr}BIPCoCl$_2$ and ^{Et}BIPCoCl$_2$ with phenylsilane (2 equiv.) and NaO^{t}Bu (2 equiv.). The reaction mixture was directly analysed using APPI-MS (see supporting information).

Scheme 3. Mechanistic possibilities for the cobalt-catalysed hydrosilylation of alkenes. a) Radical initiated and chain reaction of silyl-radicals. b) Cobalt (I)-cobalt(III) Chalk-Harrod hydrosilylation. Alternative modified Chalk-Harrod mechanism omitted for clarity.
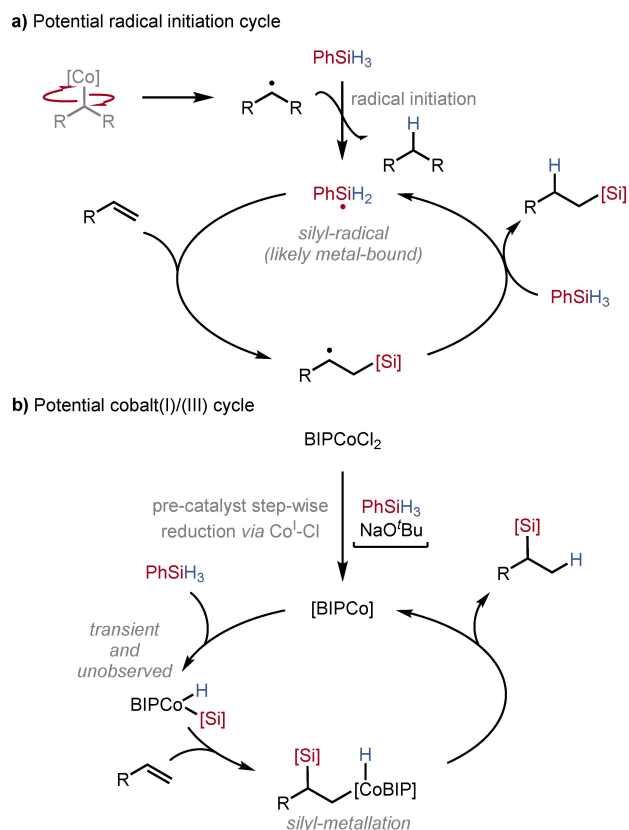
activation step and subsequently formed cobalt species were analysed by ^{1}H NMR spectroscopy and APPI-MS (Scheme 2). Addition of phenylsilane and NaO^{t}Bu to ^{Et}BIPCoCl$_2$ in THF showed immediate formation of a diamagnetic cobalt complex (see Supporting Information). The same reaction conditions applied to ^{iPr}BIPCoCl$_2$ showed formation of a comparable diamagnetic cobalt species by ^{1}H NMR spectroscopy (see Supporting Information). However, the species formed in each reaction did not correspond to previously reported diamagnetic cobalt(I) species such as a cobalt(I)-hydride or a cobalt(I)-chloride, as characterised by Budzelaar[30] or Gibson.[31]

Analysis by APPI-MS did not indicate the formation of a cobalt(I)-hydride-type species, a cobalt-silane or cobalt-silyl species (Scheme 2c). However the activation reaction of ^{iPr}BIPCoCl$_2$ showed mass identifiers consistent with the formation of an [^{iPr}BIPCo] fragment, while with ^{Et}BIPCoCl$_2$ a solvated complex [^{Et}BIPCo(THF)] was observed. This is in contrast to the work of Rajanbabu who suggested a cobalt-hydride to be operative and likely a result of the different activators used (NaHBEt$_3$ versus NaO^{t}Bu and PhSiH$_3$).[20]

These observations suggest the potential for competing mechanistic routes, although a definitive conclusion could not be drawn for either pathway operating (Scheme 3). For example, radical initiation by homolysis of a weak cobalt-carbon bond may cause hydride abstraction from phenylsilane and initiate a radical chain reaction mechanism of hydrosilylation (Scheme 3a). Alternatively, the reactions may proceed by classical Chalk-Harrod and modified variant whereby hydro-metallation and silyl-metallation are key steps in determining reactivity and regioselectivity (Scheme 3b).

Conclusion

In summary, two alkene hydrosilylation reactions have been developed using structurally similar cobalt(II) pre-catalysts. Using ^{Et}BIPCoCl$_2$ in combination with NaO^{t}Bu as an *in situ* pre-catalyst activator, a range of alkenes bearing a number of functional groups underwent chemoselective hydrosilylation using phenylsilane to give Markovnikov, secondary alkylsilanes **2a–2j**. An exchange of the ligand ethyl-substituent to an *iso*propyl-group resulted in the inversion of regioselectivity. Under otherwise identical reaction conditions, using ^{iPr}BIPCoCl$_2$ as the pre-catalyst gave the *anti*-Markovnikov, primary alkylsilane products **3a–3j**. The use of an alkoxide activator was essential for good regiocontrol, with organometallic activators giving the alkylsilane products in significantly reduced regioselectivity. Both catalysis protocols were practically straightforward to setup and proceeded quickly (<1 hr) to give the alkylsilane products in typically excellent yield and with high regioselectivity.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

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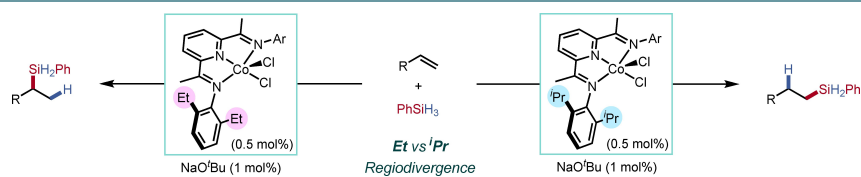
FULL PAPER

The regiodivergent hydrosilylation of alkenes is reported using two bisiminopyridine cobalt(II) catalysts. Variation of pre-catalyst activator and ligand substituents were investigated to enable the controlled, regiodivergent hydrosilylation of both aryl- and alkyl-substituted alkenes with phenylsilane. In contrast to other regiodivergence strategies, excellent regioselectivity for either isomer was achieved using the same ligand class but differing by a single methyl group (ethyl vs. *iso*propyl).

*Dr. J. H. Docherty, Dr. A. P. Dominey,
Dr. S. P. Thomas**

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Cobalt-Catalysed, Ligand-Controlled Regiodivergent Alkene Hydrosilylation