

### Markovnikov Hydrosilylation

International Edition: DOI: 10.1002/anie.201601197 German Edition: DOI: 10.1002/ange.201601197

## **Base-Metal-Catalyzed Regiodivergent Alkene Hydrosilylations**

Xiaoyong Du<sup>+</sup>, Yanlu Zhang<sup>+</sup>, Dongjie Peng, and Zheng Huang<sup>\*</sup>

**Abstract:** A complementary set of base metal catalysts has been developed for regiodivergent alkene hydrosilylations: iron complexes of phosphine-iminopyridine are selective for anti-Markovnikov hydrosilylations (linear/branched up to >99:1), while the cobalt complexes bearing the same type of ligands provide an unprecedented high level of Markovnikov selectivity (branched/linear up to >99:1). Both systems exhibit high efficiency and wide functional group tolerance.

Alkene hydrosilylation is one of the largest volume reactions conducted with homogeneous catalysts.<sup>[1]</sup> Platinum-based Speier and Karstedt's complexes are the most widely used hydrosilylation catalysts because of their high activities and ease of handling.<sup>[2]</sup> However, over the last decade the low abundance, high cost, and environmental concerns associated with precious metals have spurred extensive study toward developing earth-abundant base metal alternatives.<sup>[3]</sup> To date, a few iron,<sup>[4]</sup> cobalt,<sup>[4],5]</sup> and nickel<sup>[6]</sup> catalysts have been developed for *anti*-Markovnikov alkene hydrosilylations.

While anti-Markovnikov alkene hydrosilylations are wellestablished, reactions demonstrating Markovnikov selectivity are rare. Several lanthanum metal catalysts are known for Markovnikov hydrosilylation of activated alkenes, such as styrene and acrylonitrile.<sup>[7]</sup> Markovnikov hydrosilylation of unactivated alkenes using nickel<sup>[8]</sup> and palladium<sup>[9]</sup> catalysts have been reported, but the existing systems suffer from moderate to low regioselectivities and limited substrate scope. Thus, a general method for selective Markovnikov alkene hydrosilylation requires development. Driven by our interest in developing base metal catalysts for alkene functionalizations,<sup>[4e,10]</sup> herein we report the synthesis of iron and cobalt complexes of phosphine-iminopyridine (P<sup>C</sup>NN) ligands. The iron catalysts described are highly selective for anti-Markovnikov hydrosilylations, whereas the corresponding cobalt catalysts offer the opposite regioselectivity.

During the course of our earlier studies on the phosphinite-iminopyridine ( $P^{O}NN$ ) iron catalysts for chemoselective *anti*-Markovnikov alkene hydrosilylations,<sup>[4e]</sup> we found that the  $P^{O}NN$  ligands are prone to degradation by O–P bond cleavage. To this end, we sought to prepare more robust phosphine-iminopyridine ( $P^{C}NN$ ) ligands by replacing the O-linker connecting the phosphorus atom and the pyridyl

Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201601197.



**Scheme 1.** Synthesis of phosphine-iminopyridine ( $P^cNN$ ) ligands and iron and cobalt complexes, and the ORTEP structures for **5a** and **6c**.

backbone with a methene (CH<sub>2</sub>) unit.<sup>[11]</sup> The synthesis of the P<sup>C</sup>NN ligands is outlined in Scheme 1.<sup>[12]</sup> The acetyl group of 1-(6-methylpyridin-2-yl)ethanone (**1**) was first protected with ethylene glycol. Deprotonation of the Me group at the 2-pyridyl position in **2** with LDA, followed by addition of  $tBu_2PCl$  or  $iPr_2PCl$  and subsequent deprotection of the acetyl group with HCl, generated phosphine-acetylpyridines (**3a**, **3b**). Condensations of **3a** and **3b** with arylamines bearing iPr or Me substituents at the 2,6-aryl positions gave the P<sup>C</sup>NN ligands **4a–4c** in 88–90 % yield. The Fe<sup>II</sup> and Co<sup>II</sup> dichloride complexes **5a–c** and **6a–c** were formed in high yields by reaction of **4a–c** with FeCl<sub>2</sub> or CoCl<sub>2</sub>. Single-crystal X-ray diffraction studies of complexes **5a** and **6c** revealed distorted square pyramidal geometries around the metal centers (Scheme 1).<sup>[13]</sup>

Initial studies of the catalytic activities of these new iron and cobalt complexes focused on the hydrosilylation of a simple aliphatic alkene, 1-octene, with PhSiH<sub>3</sub>. The results are summarized in Table 1. In situ activation of iron and cobalt dihalides with NaBHEt<sub>3</sub> has been reported for catalytic alkene hydrofunctionalizations.<sup>[4e, 10c, 14]</sup> Using NaBHEt<sub>3</sub> (2 mol %) as the activator, the most sterically hindered iron complex (<sup>*i*Bu</sup>P<sup>C</sup>NN<sup>*i*Pr</sup>)FeCl<sub>2</sub> (**5a**; 1 mol %) is active for *anti*-Markovnikov hydrosilylation. The reaction of 1-octene with PhSiH<sub>3</sub> in THF at 25 °C formed the linear product **8a** in 98 % yield with excellent regioselectivity (entry 1). Reducing the

 <sup>[\*]</sup> X. Du,<sup>[+]</sup> Dr. Y. Zhang,<sup>[+]</sup> Dr. D. Peng, Prof. Dr. Z. Huang State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry 345 Lingling Road, Shanghai 200032 (China) E-mail: huangzh@sioc.ac.cn

<sup>[&</sup>lt;sup>+</sup>] These authors contributed equally to this work.

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 $\textit{Table 1:}\ Iron- and cobalt-catalyzed 1-octene hydrosilylation with <math display="inline">\mathsf{PhSiH}_3^{[a]}$ 

$n-C_{6}H_{13} + PhSiH_{3} \frac{w W o NaBHEt_{3}}{THF/neat} + n-C_{6}H_{13} + n-$						SiH <sub>2</sub> Ph
Entry	Cat. [mol %]	NaBHEt₃ [mol %]	т [°С]	t [h]	Yiel <b>8a</b>	d [%] 9a
1 2 <sup>[b]</sup> 3 <sup>[c]</sup> 4 5 6 <sup>[d,e]</sup> 7 <sup>[d,f]</sup> 8 9 10	5a (1) 5b (1) 5c (1) 5a (1) 5a (0.1) 5a (0.02) 6a (1) 6b (1) 6c (1) 6c (1)	2 2 0 0.2 0.2 0.08 2 2 2 2	25 25 60 25 25 25 25 25 25 25 25	3 3 3 24 24 24 3 3 3 3	98 72 50 0 96 93 79 3 6 2	1 1 6 0 1 <1 <1 23 49 98 62
11 12 13 <sup>[d,e]</sup> 14 <sup>[g]</sup> 15 <sup>[d,e]</sup> 16	<b>6c</b> (1) <b>6c</b> (0.05) CoCl <sub>2</sub> (0.35)/ <sup>Mes</sup> PDI (1.1) <b>6c</b> (0.05)/ <b>4c</b> (0.5) CoCl <sub>2</sub> / <b>4c</b> (1)	0 0 0 0 0	25 60 60 60 60	3 12 6 6 24	< 1 <1 <1 4 <1 <1	62 98 > 99 5 78 79

[a] Conditions: 7a (0.6 mmol), PhSiH<sub>3</sub> (0.6 mmol) in THF (1 mL). The yields were determined by GC with mesitylene as an internal standard.
[b] 2% (*E*)-allylsilane was detected. [c] 7% (*E*)-allylsilane was detected.
[d] In neat conditions. [e] 3 mmol scale. [f] 10 mmol scale. [g] 7a (1.6 mmol), PhSiH<sub>3</sub> (1.6 mmol) in THF (1 mL).

steric hindrance of the P<sup>C</sup>NN ligands resulted in inferior activity and selectivity (entries 2, 3). A control experiment in the absence of NaBHEt<sub>3</sub> revealed that the activator is necessary to achieve catalytic conversion with the iron complex **5a** (entry 4). The reactions using 0.1 mol % **5a**, with or without solvent, gave **8a** in nearly quantitative yield after 24 h (entries 5, 6). In the presence of 0.02 mol % of **5a** (51 ppm iron metal), the reaction in neat conditions gave **8a** in 79% yield (TON = 3950, entry 7). The results indicate that complex (<sup>*i*Bu</sup>P<sup>C</sup>NN<sup>*i*Pr</sup>)FeCl<sub>2</sub> **5a** is significantly more active than the precatalyst (<sup>*i*Bu</sup>P<sup>O</sup>NN<sup>*i*Pr</sup>)FeCl<sub>2</sub> bearing an O-linker; the hydrosilylation reaction using the latter required 1 mol % of catalyst to attain good conversion.<sup>[4e]</sup> The selective formation of the *anti*-Markovnikov product is consistent with earlier reports using iron catalyst systems.<sup>[4]</sup>

Remarkably, regioselectivity could be reversed when cobalt analogues were employed. All cobalt complexes **6a–c** gave the Markovnikov product **9a** as the major product (entries 8–10). In particular, the least crowded precatalyst ( ${}^{PP}P^{C}NN^{Me}$ )CoCl<sub>2</sub> **6c** was very effective for Markovnikov hydrosilylation. The reaction in the presence of 1 mol % of **6c** and 2 mol % of NaBHEt<sub>3</sub> at 25 °C formed **9a** in 98 % yield after 3 h (entry 10). Surprisingly, control experiments with **6c** in the absence of NaBHEt<sub>3</sub>, afforded the branched product **9a** in 62 and 98 % yield after 3 and 12 h, respectively (entries 11, 12). These runs gave regioselectivity similar to that observed in the reaction using a combination of **6c** and NaBHEt<sub>3</sub>, albeit with a relatively slow reaction rate (entries 11 vs. 10). At elevated temperature (60 °C), in the presence of 1100 ppm of **6c** (0.05 mol %, 130 ppm cobalt metal), the reaction in neat 1-octene and PhSiH<sub>3</sub> gave 9a in quantitative yield after 6 h (TON = 2000, entry 13). Thus, an additional additive is not required for activation of the catalyst in the cobalt-catalyzed hydrosilylation reactions.<sup>[15]</sup> In a recent patent, Boyer et al. reported that a combination of bis(imino)pyridine  $(2,4,6-Me_{3}C_{6}H_{2}N=CMe)_{2}C_{5}H_{3}N$  (<sup>Mes</sup>PDI; 3 equiv) and CoCl<sub>2</sub> catalyzes Markovnikov alkene hydrosilylation with PhSiH<sub>3</sub>. It was proposed that <sup>Mes</sup>PDI acts as a promoter for catalyst activation.<sup>[16]</sup> However, using the conditions described in the patent, the reaction gave only 5% of 9a and 4% of **8a** (entry 14) in the presence of  $CoCl_2$  (0.35 mol %) and <sup>Mes</sup>PDI (1.1 mol %). To explore the role of our <sup>iPr</sup>P<sup>C</sup>NN<sup>Me</sup> ligand 4c in the hydrosilylation process, an experiment in the presence of additional ligand was conducted. The reaction with 6c (0.05 mol%) and 4c (10 equiv relative to 6c) was less effective than the reaction without 4c, implying that there is an inhibitory effect of the additional ligand on the catalysis (entries 15 vs. 13). Finally, a simple combination of 4c and CoCl<sub>2</sub> (1 mol % each) was effective for Markovnikov hydrosilvlation (entry 16), albeit with reduced catalytic efficiency in comparison with the reaction employing 6c.

Utilizing the base metal catalysts, we examined the substrate scope with respect to alkenes for regiodivergent hydrosilylations (Scheme 2). The iron catalyst mediates hydrosilylation of a diverse array of alkenes with PhSiH<sub>3</sub>, furnishing linear products in high isolated yield with excellent regioselectivities. Most reactions employed 0.5 mol % of 5a and 1 mol % NaBHEt<sub>3</sub>. Functional groups including chloride (8g), protected alcohol (8i), ether (8k), acetal (8m), and gem-disubstituted olefin (8q) were tolerated. Hydrosilylation of 1,5-hexadiene with 2 equiv of PhSiH<sub>3</sub> produced 1,6-disilylhexane (8r) in high yield. Allylarenes gave the desired products in moderate yields (8s, 60%; 8sa, 65%) with the formation of a small amount of dehydrogenative silvlation products, (E)-allylsilanes (ca. 20%). Styrene was hydrosilylated in high yield (8t). Furthermore, using the least crowded complex 5c (1 mol %) as the precatalyst, hydrosilylations of styrene with various secondary and tertiary silanes in neat conditions occurred smoothly (8ta-8te). Notably, reaction of 1-octene with (EtO)<sub>3</sub>SiH<sup>[17]</sup> or Ph<sub>2</sub>SiH<sub>2</sub> gave a mixture of the hydrosilylation (8 u or 8 v) and the dehydrogenative silylation products (allylsilane, **10u** or **10v**).<sup>[18]</sup>

A wide variety of functionalized alkenes were subjected to selective cobalt-catalyzed Markovnikov hydrosilylation (9 f-q). Most reactions were performed at 60 °C with very low catalyst loadings (0.05-0.5 mol % 6c). Reactions of substrates bearing bromide (9h, 9sc), ester (9o), amide (9p), and 1,1-disubstituted olefin (9q) functional groups proceeded in a chemo- and regioselective manner. Markovnikov additions to the two terminal double bonds in 1,5-hexadiene formed the branched disilyl product (9r). Allylbenzene and its derivatives, which bear both electron-donating and withdrawing groups, were efficiently hydrosilylated (9s-9sd). An exception was the reaction of styrene (9t), which gave the branched and linear products in an approximately 1:1 ratio. Markovnikov hydrosilylations with secondary and tertiary silanes are more difficult than that with primary silane. The catalyst generated from 6b and NaBHEt<sub>3</sub> was identified as the optimal system for Markovnikov hydro-

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### Communications





*Scheme 2.* Iron-catalyzed *anti*-Markovnikov and cobalt-catalyzed Markovnikov hydrosilylation of various alkenes. General conditions: **7** (1.2 mmol), PhSiH<sub>3</sub> (1.2 mmol) in THF (0.5–1 mL). Yield of isolated products, unless noted otherwise. Product ratios were determined by <sup>1</sup>H NMR spectroscopy. [a] With cat. (0.1 mol %). [b] With cat. (1 mol %). [c] With cat. (2 mol %). [d] 25% (*E*)-allylsilane detected. [e] 23% (*E*)-allylsilane detected. [e] 23% (*E*)-allylsilane detected. [f] With **5c** (1 mol %) and NaBHEt<sub>3</sub> (2 mol %), 1.8 mmol scale, in neat conditions. [g] With **5c** (2 mol %) and NaBHEt<sub>3</sub> (4 mol %), yield determined by NMR. [h] With **6c** (0.05 mol %). [i] Neat conditions. [j] With **6c** (2 mol %) and NaBHEt<sub>3</sub> (4 mol %). [k] Yield determined by NMR. [l] With **6b** (1 mol %) and NaBHEt<sub>3</sub> (2 mol %) in toluene (1 mL), yield determined by NMR. **10u** (18%) and **10v** (15%) detected.

silylations of 1-octene with  $Ph_2SiH_2$  (9 u, 53 %) and (EtO)<sub>3</sub>SiH (9 v, 60 %), though a small amount of allylsilanes (10 u, 18 %; 10 v, 15 %) was also detected.

Potential applications of Markovnikov hydrosilylations include the conversion of readily available  $\alpha$ -olefins into synthetically versatile secondary alcohols. Satisfactorily, treatment of various Markovnikov hydrosilylation products with HBF<sub>4</sub>:Et<sub>2</sub>O, followed by oxidation with H<sub>2</sub>O<sub>2</sub> under basic conditions, produced secondary alcohols **11** in useful yields (Supporting Information, Scheme S1).

For iron-catalyzed *anti*-Markovnikov alkene hydrosilylations, mechanistic proposals involving oxidative addition of silane, followed by olefin insertion and reductive elimination of linear alkylsilane, have previously been elucidated.<sup>[4b]</sup> Although additional experimental and theoretical studies are ongoing in an attempt to gain a full understanding of the mechanism of cobalt-catalyzed Markovnikov hydrosilylations, our preliminary experiments provide interesting results. A radical mechanism is not very likely, as the reactions of dienes **7q** and **7r** did not form any cyclized products (Scheme 2). More importantly, a diallylether (**12**) known to undergo rapid radical cyclization under conditions that allow the generation of a radical,<sup>[19]</sup> reacted with 2 equiv of PhSiH<sub>3</sub> to form a dual hydrosilylation product **13** in 86% yield; no cyclized products were detected during the catalysis [Eq. (1)]. Lastly, addition of 10 mol % of TEMPO (10 equiv relative to cobalt) as a radical trap imposed no detrimental effects, although increasing the amount of TEMPO further to 100 mol %, led to complete inhibition of catalysis (see the Supporting Information).<sup>[20]</sup>

To provide insight into the catalyst activation mode and the nature of the cobalt intermediacy, stoichiometric and deuterium-labeling experiments were conducted. Treatment of (<sup>iPr</sup>P<sup>C</sup>NN<sup>Me</sup>)CoCl<sub>2</sub> (6c) with 1 equiv of PhSiH<sub>3</sub> in [D<sub>6</sub>]benzene at 60 °C for 4 h formed a diamagnetic, putative Co<sup>I</sup> monochloride (<sup>*i*Pr</sup>P<sup>C</sup>NN<sup>Me</sup>)CoCl (14) in 49% yield, along with PhSiH<sub>2</sub>Cl in 27% yield [Eq. (2)].<sup>[21]</sup> To conclusively determine the identity of the Co<sup>I</sup> species, **14** was independently prepared using a procedure known for transforming Co<sup>II</sup> dichloride into Co<sup>I</sup> monochloride.<sup>[22]</sup> The reaction of **6c** with 1 equiv of LiMe in C<sub>6</sub>D<sub>6</sub> at room temperature gave 54% of the monochloride (14) and another diamagnetic species 15 in 10% yield. Further addition of 1.5 equiv of LiMe to the mixture resulted in the disappearance of 14 and build-up of **15**, which was identified as  $({}^{iPr}P^{C}NN^{Me})CoMe$  (71%; [Eq. (3)]). The NMR spectra of 15 display a diagnostic <sup>1</sup>H doublet at -0.62 ppm and a <sup>13</sup>C doublet at -58.1 ppm corresponding to the Co-Me moiety. Importantly, both Co<sup>I</sup> complexes 14 and 15 were active for catalytic Markovnikov hydrosilylation [Eq. (4)]. The data indicates that the Co<sup>II</sup>



dichloride can be reduced/activated with  $PhSiH_3$  to form a catalytically active  $Co^I$  species.

The reaction of 1-dodecene- $d_2$  with PhSiH<sub>3</sub> in the presence of **6c** (1 mol %) gave **9c**- $d_2$  selectively [Eq. (5)]. Additionally, the reaction of 1-octene with the deuterated silane PhSiD<sub>3</sub> yielded **9a**- $d_3$  [Eq. (6)]. No deuterium incorporation into the  $\alpha$ -carbon of the products was observed in either case. These results argue strongly against the formation of a cobalt deuteride or hydride intermediate in the catalytic cycle, because facile H/D exchange between Co-D and C<sub> $\alpha$ </sub>-H would otherwise occur through reversible olefin insertion into the Co–D bond.<sup>[10d,18]</sup>

$$\binom{{}^{Pr}P^{C}NN^{Me}}{6c}CoCl_{2} \xrightarrow{PhSiH_{3}} \binom{{}^{Pr}P^{C}NN^{Me}}{C_{6}D_{6}, 60 \ ^{\circ}C, 4 \ h} \binom{{}^{Pr}P^{C}NN^{Me}}{14, 49\%}CoCl + PhSiH_{2}Cl (2)$$

**7a** + PhSiH<sub>3</sub> 
$$\xrightarrow{3-5 \text{ mol } \% \text{ 14 or 15}}_{60 \, ^\circ\text{C}, 24 \text{ h}}$$
 **9a** 85-95%, *bll* = >99:1 (4)

$$\begin{array}{c} & & CD_2 \\ & & + & \textbf{7c-}D_2 \\ & & & \text{THF, 60 °C, 24 h} \end{array} \xrightarrow[]{H/D} = >99:1 \\ & & & \text{CHD}_2 \\ & & & \text{H}_8 \\ & & & \text{SiH}_2\text{Ph} \end{array} \xrightarrow[]{H/D} = S99:1 \\ & & & \text{SiH}_2\text{Ph} \end{array} (5)$$

On the basis of our preliminary results and reported precedent regarding cobalt-catalyzed alkene functionalization,<sup>[10d,18]</sup> we propose a silyl migration pathway involving a Co<sup>I</sup> silyl intermediate (Supporting Information, Scheme S4).<sup>[23]</sup> For apolar olefins, 1,2-insertion of the C=C double bond into the Co–Si bond prevails (presumably because of steric effects),<sup>[24]</sup> furnishing the Markovnikov product. An alternative, but less likely pathway, involves 2,1-insertion of the olefin, which leads to formation of the *anti*-Markovnikov product. For vinylarenes, 2,1-insertion may compete with the 1,2-insertion pathway because there is marked electronic discrimination between the two olefinic carbon atoms. This proposal is consistent with the data obtained from the hydrosilylation of styrene (**9t**; Scheme 2).

In summary, we have prepared a series of iron and cobalt alkene hydrosilylation catalysts bearing phosphine-iminopyridine ligands. The regioselectivity of alkene hydrosilylations can be inverted from > 99:1 to < 1:99 by changing the metal center of the catalyst from iron to cobalt. The advantages these non-precious metal catalysts offer include, high efficiency, mild conditions, and broad functional group compatibility combined with a divergent and high level of regiochemistry.

#### Acknowledgements

Financial support was provided by the National Basic Research Program of China (2015CB856600) and the National Natural Science Foundation of China (21422209, 21432011, and 21421091).

**Keywords:** alkenes · cobalt · homogeneous catalysis · hydrosilylation · iron

How to cite: Angew. Chem. Int. Ed. 2016, 55, 6671–6675 Angew. Chem. 2016, 128, 6783–6787

- [1] a) A. F. Noels in *Industrial Applications of Homogeneous Catalysis* (Ed: A. Mortreux), Kluwer, Amsterdam, **1985**, pp. 80–91; b) A. K. Roy in *Adv. Organomet. Chem.*, *Vol. 55* (Eds.: A. F. H. Robert West, J. F. Mark), Academic Press, San Diego, **2007**, pp. 1–59.
- [2] a) J. L. Speier, J. A. Webster, G. H. Barnes, J. Am. Chem. Soc. 1957, 79, 974; b) B. D. Karstedt, US patent 3,715,334, 1973.
- [3] a) R. M. Bullock, *Catalysis Without Precious Metals*, Wiley-VCH, Weinheim, **2010**, pp. 83–42; b) K. Junge, K. Schröder, M. Beller, *Chem. Commun.* **2011**, *47*, 4849; c) B. D. Sherry, A. Fürstner, *Acc. Chem. Res.* **2008**, *41*, 1500; d) I. Bauer, H.-J. Knölker, *Chem. Rev.* **2015**, *115*, 3170; e) M. D. Greenhalgh, A. S. Jones, S. P. Thomas, *ChemCatChem* **2015**, *7*, 190; f) J. Sun, L. Deng, *ACS Catal.* **2016**, *6*, 290.
- [4] For examples: a) J. C. Mitchener, M. S. Wrighton, J. Am. Chem. Soc. 1981, 103, 975; b) S. C. Bart, E. Lobkovsky, P. J. Chirik, J. Am. Chem. Soc. 2004, 126, 13794; c) A. M. Tondreau, C. C. Atienza, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. Delis, P. J. Chirik, Science 2012, 335, 567; d) C. C. Hojilla Atienza, A. M. Tondreau, K. J. Weller, K. M. Lewis, R. W. Cruse, S. A. Nye, J. L. Boyer, J. G. P. Delis, P. J. Chirik, ACS Catal. 2012, 2, 2169; e) D. Peng, Y. Zhang, X. Du, L. Zhang, X. Leng, M. D. Walter, Z. Huang, J. Am. Chem. Soc. 2013, 135, 19154; f) M. D. Greenhalgh, D. J. Frank, S. P. Thomas, Adv. Synth. Catal. 2014, 356, 584; g) J. Y. Wu, B. N. Stanzl, T. Ritter, J. Am. Chem. Soc. 2010, 132, 13214; h) R. N. Naumov, M. Itazaki, M. Kamitani, H. Nakazawa, J. Am. Chem. Soc. 2012, 134, 804; i) D. Noda, A. Tahara, Y. Sunada, H. Nagashima, J. Am. Chem. Soc. 2016, 138, 2480.
- [5] For examples: a) A. J. Chalk, J. F. Harrod, J. Am. Chem. Soc. 1965, 87, 1133; b) C. L. Reichel, M. S. Wrighton, J. Am. Chem. Soc. 1981, 103, 7180; c) M. Brookhart, B. E. Grant, J. Am. Chem. Soc. 1993, 115, 2151; d) Z. Mo, Y. Liu, L. Deng, Angew. Chem. Int. Ed. 2013, 52, 10845; Angew. Chem. 2013, 125, 11045; e) C. Chen, M. B. Hecht, A. Kavara, W. W. Brennessel, B. Q. Mercado, D. J. Weix, P. L. Holland, J. Am. Chem. Soc. 2015, 137, 13244.
- [6] I. Buslov, J. Becouse, S. Mazza, M. Montandon-Clerc, X. Hu, Angew. Chem. Int. Ed. 2015, 54, 14523; Angew. Chem. 2015, 127, 14731.
- [7] For examples: a) P.-F. Fu, L. Brard, Y. Li, T. J. Marks, J. Am. Chem. Soc. 1995, 117, 7157; b) G. A. Molander, E. D. Dowdy, B. C. Noll, Organometallics 1998, 17, 3754; c) T. I. Gountchev, T. D. Tilley, Organometallics 1999, 18, 5661; d) Y. Chen, D. Zargarian, Can. J. Chem. 2009, 87, 280.
- [8] For examples: a) M. Kumada, K. Sumitani, Y. Kiso, K. Tamao, J. Organomet. Chem. 1973, 50, 319; b) L. F. Groux, D. Zargarian,

*Organometallics* **2003**, *22*, 4759; c) Y. Chen, C. Sui-Seng, S. Boucher, D. Zargarian, *Organometallics* **2005**, *24*, 149.

- [9] a) N. Komine, M. Abe, R. Suda, M. Hirano, *Organometallics* 2015, 34, 432; b) T. Hayashi, Y. Uozumi, *Pure Appl. Chem.* 1992, 64, 1911.
- [10] a) L. Zhang, D. Peng, X. Leng, Z. Huang, Angew. Chem. Int. Ed.
  2013, 52, 3676; Angew. Chem. 2013, 125, 3764; b) L. Zhang, Z. Zuo, X. Wan, Z. Huang, J. Am. Chem. Soc. 2014, 136, 15501; c) L. Zhang, Z. Zuo, X. Leng, Z. Huang, Angew. Chem. Int. Ed.
  2014, 53, 2696; Angew. Chem. 2014, 126, 2734; d) L. Zhang, Z. Huang, J. Am. Chem. Soc. 2015, 137, 15600; e) X. Jia, Z. Huang, Nat. Chem. 2016, 8, 157.
- [11] Y. Cao, Y. Zhang, L. Zhang, D. Zhang, X. Leng, Z. Huang, Org. Chem. Front. 2014, 1, 1101.
- [12] During the preparation of this manuscript, Milstein et al. reported the synthesis of a similar P<sup>C</sup>NN ligand containing a mesitylimino group. A different procedure was used, which required five steps starting from commercially available materials, and furnished the ligand in low yield (<10%). See: B. Butschke, K. L. Fillman, T. Bendikov, L. J. W. Shimon, Y. Diskin-Posner, G. Leitus, S. I. Gorelsky, M. L. Neidig, D. Milstein, *Inorg. Chem.* **2015**, *54*, 4909.
- [13] The supplementary crystallographic data for this paper are available at CCDC 1415554 (5a) and 1415555 (6c). This data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
- [14] M. W. Bouwkamp, A. C. Bowman, E. Lobkovsky, P. J. Chirik, J. Am. Chem. Soc. 2006, 128, 13340.
- [15] Activation of Co(acac)<sub>3</sub> and Co(OAc)<sub>2</sub> without additional reagents has been reported for catalytic alkene hydrogenation, see: M. R. Friedfeld, M. Shevlin, J. M. Hoyt, S. W. Krska, M. T. Tudge, P. J. Chirik, *Science* **2013**, *342*, 1076.
- [16] J. L. Boyer, A. K. Roy, PCT Int. Appl. WO 2014/186513 A1, 2014.

- [17] Caution: HSi(OEt)<sub>3</sub> can potentially form explosive gases, and thus should be handled with the proper precautions!
- [18] C. C. H. Atienza, T. Diao, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. P. Delis, J. L. Boyer, A. K. Roy, P. J. Chirik, *J. Am. Chem. Soc.* **2014**, *136*, 12108.
- [19] a) B. Kopping, C. Chatgilialoglu, M. Zehnder, B. Giese, J. Org. Chem. 1992, 57, 3994; b) A. L. J. Beckwith, I. Blair, G. Phillipou, J. Am. Chem. Soc. 1974, 96, 1613; c) P. Burkhard, E. Roduner, J. Hochmann, H. Fischer, J. Phys. Chem. 1984, 88, 773.
- [20] Inhibition by TEMPO is not a definitive indication of a radical mechanism because TEMPO may halt catalysis by reaction with PhSiH<sub>3</sub> or the cobalt alkyl group. For example, see: A. C. Albéniz, P. Espinet, R. López-Fernández, A. Sen, J. Am. Chem. Soc. 2002, 124, 11278.
- [21] Treatment of 6c with PhSiH<sub>3</sub> (2 equiv) at 60 °C after 2 h gave 14 in 76 % yield (See the Supporting Information for a proposed pathway).
- [22] T. M. Kooistra, Q. Knijnenburg, J. M. M. Smits, A. D. Horton, P. H. M. Budzelaar, A. W. Gal, *Angew. Chem. Int. Ed.* **2001**, 40, 4719; *Angew. Chem.* **2001**, 113, 4855.
- [23] Note that Co<sup>I</sup> silyl complexes have been documented. See Ref. [18] and Z. Mo, J. Xiao, Y. Gao, L. Deng, *J. Am. Chem. Soc.* **2014**, *136*, 17414. Here the Co<sup>I</sup> monochloride **14** may react with PhSiH<sub>2</sub>Cl derived from the reaction of **6c** with PhSiH<sub>3</sub> [see Eq. (2)] to yield a Co<sup>I</sup> hydride. The Co<sup>I</sup> hydride then reacts with PhSiH<sub>3</sub> to give the Co<sup>I</sup> silyl complex (See the Supporting Information for further details).
- [24] P. Wucher, L. Caporaso, P. Roesle, F. Ragone, L. Cavallo, S. Mecking, I. Göttker-Schnetmann, *Proc. Natl. Acad. Sci. USA* 2011, 108, 8955.

Received: February 3, 2016 Revised: March 16, 2016 Published online: April 25, 2016