Primary Alcohols via Nickel Pentacarboxycyclopentadienyl Diamide-Catalyzed Hydrosilylation of Terminal Epoxides.

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ABSTRACT: The efficient and regioselective hydrosilylation of epoxides co-catalyzed by a pentacarboxycyclopentadienyl (PCCP) diamide nickel complex and Lewis acid is reported. This method allows for the reductive opening of terminal, monosubstituted epoxides to form unbranched, primary alcohols. A screen of diamide PCCP ligands revealed a correlation of steric demand and regioselectivity, with smaller ligands being optimal, while the addition of Lewis acid enabled efficient reactions at room temperature. A range of substrates including both terminal and non-terminal epoxides are shown to work, and a mechanistic rationale is provided. This work represents the first use of a PCCP derivative as a ligand for transition metal catalysis.

Epoxide-opening reactions offer a versatile means to access a variety of functional group patterns. Among the myriad possibilities, one simple yet underdeveloped transformation is the conversion of epoxides to alcohols via catalytic reductive epoxide opening.¹ Although epoxide-opening reactions offer versatile access to a variety of functional group patterns, one simple yet underdeveloped transformation is the conversion of epoxides to alcohols through catalytic reductive epoxide opening.² A major challenge in this arena has been the catalytic reductive opening of terminal epoxides **1** to form primary alcohols **2** (Figure 1a).³ Coupled with epoxidation,⁴ such a reaction could serve as an attractive alternative to the traditional hydroboration/oxidation approach for the anti-Markovnikov hydration of alkenes **3**.⁵ Unfortunately, catalytic reductive epoxide opening has proven to be very difficult, particularly in regard to the regioselective reaction of terminal epoxides. Hydrogenolysis has been successfully applied to epoxide reduction, but these methods generally suffer from limited scope, are selective towards the Markovnikov product, and require forcing conditions.⁶ Recently, Norton reported the generation of anti-Markovnikov alcohols via radical-based reduction of epoxides,⁷ although the method did not extend to terminal, mono-substituted epoxides. During the preparation of this manuscript, Beller reported a major advance in this area with an iron-catalyzed hydrogenation of terminal epoxides with anti-Markovnikov selectivity.⁸ Although the yields were generally high, this reaction required high pressure and elevated temperatures. Thus, the development of regioselective epoxide reductions that occur at ambient temperature and pressure remains an unmet challenge.⁹

In this regard, a number of reports have focused on catalytic hydrosilylation¹⁰ as a milder approach to epoxide

reduction, but none have achieved the regioselective reduction of terminal, monosubstituted epoxides.¹¹ To address this problem, we reasoned that increasing the Lewis acidity of a metal complex through new ligand development might be beneficial for both reactivity and regioselectivity.

Figure 1. (a) Conversion of terminal alkenes to primary alcohols. (b) PCCP **4** and PCCP-diamide **5** metal complexes.

One class of ligands that has a long and eminent history is the cyclopentadienyl (CP) anions, which participate in a variety of binding modes, most famously the η^5 -mode canonically found in ferrocene.¹² In addition to the parent compound, substituted-CP ligands continue to offer useful new tools for reaction design.¹³ On the other hand, one distinct category of CP ligands that has not been exploited for catalysis is the pentacarboxycyclopentadienes (PCCPs) **4**, despite their established ability to ligate metals via a variety of different binding modes (Figure 1b).¹⁴ Our group has exploited the highly electron-deficient nature, synthetic accessibility, and broad structural diversity¹⁵ of PCCPs in the development of a novel class of Brønsted acid catalysts.¹⁶ Furthermore, the multiple Lewis basic sites on the PCCP framework offer the possibility of cooperative activation via interaction with Lewis acidic additives, which we speculated might be particularly useful for reactions with epoxide substrates.¹⁷ Here, we show that derivatives of these intriguing materials, PCCP diamides **5**, can also be useful as ligands for transition metal catalysis by offering a solution to the

long-standing problem of catalytic, regioselective hydrosilylation of terminal epoxides.

Table 1. Optimization for Ni-PCCP catalyzed hydrosilylative opening of 1-decene oxide.^a

L1

L2

L3

entry	ligand	solvent	temp (°C)	additive	conv(%)	selectivity (7:8)
1	L1	MeCN	80	—	0	—
2	L2	MeCN	80	—	36	39:61
3	L2	MeCN	60	—	30	48:52
4	L2	MeCN	40	—	23	84:16
5	L2	MeCN	rt	—	11	85:15
6	L2	PhMe	rt	—	7	62:40
7	L2	CH ₂ Cl ₂	rt	—	8	80:20
8	L2	MeCN	rt	5% BF ₃ •OEt ₂	67	76:24
9	L2	MeCN	rt	10% BF ₃ •OEt ₂	100 ^b	75:25
10	L2	MeCN	rt	15% BF ₃ •OEt ₂	100 ^c	78:22
11	—	MeCN	rt	15% BF ₃ •OEt ₂	0 ^d	—
12	L3	MeCN	rt	15% BF ₃ •OEt ₂	100	85:15

^a Reaction Conditions: 5 mol% Ni(OAc)₂, 5 mol% PCCP ligand, 10 mol% KO-*t*-Bu, 1.1 eq silane at room temperature for 16 h. Conversion was determined by ¹H NMR against mesitylene internal standard. ^b 43% conversion after 4 h. ^c 65% conversion after 4 h. ^d Reaction was performed without Ni(OAc)₂ or KO-*t*-Bu.

For this work, we first examined the reaction of 1-decene oxide **6** (Table 1). Reactions were conducted by mixing 5 mol% Ni(OAc)₂, 5 mol% ligand, 10 mol% KO-*t*-Bu, and 1.1 equiv Ph₂SiH₂, followed by addition of the epoxide. Our initial attempt to use pentacarbomethoxycyclopentadiene **L1** as ligand was unproductive (entry 1). On the other hand, the use of PCCP diamide ligands led to appreciable product formation. Aniline-derived ligand **L2** enabled 36% conversion over 16 h at 80 °C (entry 2), albeit with a 1:2 regioselectivity in favor of the secondary product **8**. Interestingly, reducing the temperature led to a reversal of selectivity (entries 2–5); at room temperature, the ratio of products **7**:**8** was 85:15 (entry 5). Unfortunately, modifications to the phenyl substituents of **L2** were universally detrimental (see SI for full ligand screen). Meanwhile, of the solvents screened, acetonitrile proved optimal for both reactivity and selectivity (entries 5–7). To increase reactivity, we found that the addition of up to 15 mol% BF₃•OEt₂ dramatically increased the reaction rate, albeit with a small decrease in regioselectivity (entries 8–10).¹⁷ Importantly, the BF₃•OEt₂ on its own did not result in conversion of the epoxide (entry 11).¹⁸ Finally, we found that ligand **L3** provided higher levels of selectivity than **L2** while still retaining high reactivity (entry 12).

We next examined the scope of this method (Table 2). In addition to 1-decanol (**9**, entry 1), 1-hexanol was also formed in good yield (**10**, entry 2). Branching near the epoxide was tolerated (entries 3 and 4), although a small drop in regioselectivity was observed when the branch point was next to the site of reduction (entry 4). 3-Phenylpropene oxide gave rise to 3-phenylpropanol (**13**) with good yield and selectivity (entry 5). In terms of functional group compatibility, we found that halogens and ethers

were tolerated (entries 6–8), with minimal effect on regioselectivity. Strongly electron-withdrawing phenylsulfonyl and phosphine oxide groups led to a single regioisomer of product (**17** and **18**, entries 9 and 10). Notably, alkenyl and alkynyl substrates furnished products **19** and **20** with no hydrosilylation across the π-bonds (entries 11 and 12). However, in the case of substrate **21**, in which the alkene was in closer proximity to the epoxide, hydrosilylation across the alkene was observed.¹⁹ Additionally, we note that reactions with substrates bearing sensitive (e.g. **22**) or significantly Lewis basic (**23–26**) functionality were not viable substrates for this catalyst system.

Table 2. Scope studies for hydrosilylation of mono-substituted terminal epoxides.^a

L3

entry	substrate	product	yield (%)	selectivity
(1)	1-decene oxide	1-decanol (9)	65%	85:15
(2)	1-hexene oxide	1-hexanol (10)	66%	84:16
(3)	3-methyl-1-pentene oxide	3-methyl-1-pentanol (11)	71%	83:17
(4)	2-methyl-2-butene oxide	2-methyl-2-butanol (12)	73%	78:22
(5)	3-phenylpropene oxide	3-phenylpropanol (13)	72%	81:19
(6)	1-chloro-2-methoxyethane oxide	1-chloro-2-methoxyethanol (14)	70%	82:18
(7)	1-bromo-2-methoxyethane oxide	1-bromo-2-methoxyethanol (15)	71%	79:21
(8)	1-ethoxy-2-methoxyethane oxide	1-ethoxy-2-methoxyethanol (16)	61%	79:21
(9)	1-phenylsulfonyl-2-methoxyethane oxide	1-phenylsulfonyl-2-methoxyethanol (17)	64%	single regioisomer
(10)	1-(diphenylphosphino)ethane oxide	1-(diphenylphosphino)ethanol (18)	76%	single regioisomer
(11)	1-octene oxide	1-octanol (19)	58%	87:13
(12)	1-octyne oxide	1-octanol (20)	68%	80:20

Unsuccessful Substrates

21

22

23

24

25

26

^a Reaction Conditions: 5 mol% Ni(OAc)₂, 5 mol% **L3** ligand, 10 mol% KO-*t*-Bu, 1.1 eq silane at room temperature for 16 h. Yields determined on purified products of major isomer. Selectivity determined by ¹H NMR of crude reaction mixture. Hydrolysis Conditions: 15% NaOH (aq) and MeOH at room temperature for 8 h. ^b Yields determined by ¹H NMR versus mesitylene as an internal standard.

We also examined the ability of this catalyst system to reduce other types of epoxides (Table 3). In these cases, the more synthetically accessible ligand **L2** was suitable. As shown a variety of 1,1-disubstituted (entries 1 and 2), cyclic disubstituted (entries 3–5), trisubstituted (entry 6), and tetrasubstituted (entry 7) epoxides reacted with high efficiency and complete regioselectivity. Styrenyl epoxides led to the anti-Markovnikov products **34–36** exclusively in each case (entries 8–10). Finally,

both ester and amide functionality were compatible with this chemistry (entries 11 and 12), albeit with lower efficiencies.

Table 3. Scope studies for hydrosilylation of non-terminal and 1,1-disubstituted epoxides.^a

^a Reaction Conditions: 5 mol% Ni(OAc)₂, 5 mol% **L2** ligand, 10 mol% KO-*t*-Bu, 15 mol% BF₃•OEt₂, 1.1 eq silane at room temperature for 16 h. Yields determined on purified products. In all cases, a single regioisomer was detected by ¹H NMR on crude reaction mixtures. Hydrolysis Conditions: 15% NaOH (aq) and MeOH at room temperature for 8 h. ^bYield determined by ¹H NMR versus mesitylene internal standard. ^cTBAF deprotection used for desilylation.

Our mechanistic rationale involves initial reaction of the PCCP ligand (**L2** or **L3**), Ni(OAc)₂, two equivalents of KO-*t*-Bu, and an equivalent of silane to generate the active nickel hydride intermediate **41** (Figure 2).²⁰ Coordination of **41** to the epoxide **1** (cf. **42**) followed by hydride insertion leads to the nickel alkoxide **43**, which then engages another equivalent of silane to furnish product **44** and regenerate the complex **41**. We speculate that BF₃•OEt₂ increases the Lewis acidity of the complex by coordinating to the PCCP ligand, which helps to weaken the internal C–O bond of the epoxide and thereby improve both the reaction rate and the regioselectivity.

In addition to the in situ generation of the catalyst, the presumed nickel-alkoxide species **40b** was also isolated to assess its reactivity directly. Ligand complexation of Ni(OAc)₂ and **L2** followed by reaction with KO-*t*-Bu resulted in the precipitation of KOAc and a paramagnetic solid, presumed to be **40b**. A comparison of the infrared spectra of **39b** and **40b** revealed a new stretch at 1006 cm⁻¹, consistent with the C–O stretching frequency of previously reported nickel alkoxide species.²¹ In addition, **40b** was found to be active for the reduction of 1-decene oxide under the standard conditions (97% conversion after 16 h to furnish a 77:23 mixture of 1-decanol and 2-decanol). Because the Ni-PCCP complex was found to be viable after removal of the KOAc byproduct, this result rules out the possibility that the role of BF₃•OEt₂ is to sequester the acetate byproduct of ligation.

Figure 2. Mechanistic rationale for Ni-PCCP diamide / BF₃•OEt₂ catalyzed hydrosilylation of epoxides.

Alternatively, we considered that the product might also arise by way of Meinwald rearrangement (cf. **45**→**46**) followed by carbonyl hydrosilylation (Figure 2b),²² although we viewed this possibility as less likely since catalytic BF₃•OEt₂ itself did not effect such a rearrangement (eq. 1), a fact which has been reported previously.^{18,23} In further evidence against this mechanism, when the reactions of terminal epoxide **49** was conducted with Ph₂SiD₂ (Figure 2c), the only observed product was 2-*d*-**18**. The absence of the regioisomeric product 1-*d*-**18** rules out this mechanism but is consistent with the pathway shown in Figure 2a.

In conclusion, we have developed a method for the regioselective reduction of terminal, monosubstituted epoxides. This effort was enabled by the use of PCCP-diamides as a new class of ligand, which in conjunction with a co-catalytic Lewis acid allowed for the generation of a highly active nickel complex.

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