Alcohol Synthesis by Cobalt-Catalyzed Visible-Light-Driven Reductive Hydroformylation

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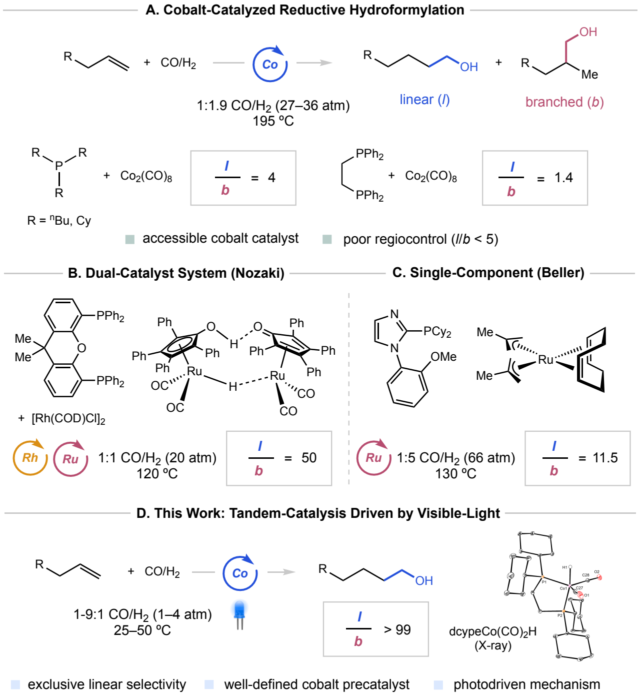
Supporting Information Placeholder

ABSTRACT: A cobalt-catalyzed reductive hydroformylation of terminal and 1,1-disubstituted alkenes is described. One-carbon homologated alcohols were synthesized directly from CO and H_2, affording anti-Markovnikov products (34–87% yield) with exclusive regiocontrol (linear/branch > 99:1) for minimally functionalized alkenes. Irradiation of the air-stable cobalt hydride, $(dcype)Co(CO)_2H$ (dcype = dicyclohexylphosphinoethane) with blue light generated the active catalyst that mediates alkene hydroformylation and subsequent aldehyde hydrogenation. Mechanistic origins of absolute regiocontrol were investigated by *in-situ* monitoring of the tandem catalytic reaction using multinuclear NMR spectroscopy with syngas mixtures.

The introduction of reactive functionality into feedstock molecules is a well-established strategy for accessing higher-value products from abundant hydrocarbons. To this end, alcohols are ideal targets for synthetic elaboration,[1] supported by an expansive methodological framework that encompasses oxidative, redox-neutral, and reductive transformations.[2] Catalytic methods that generate alcohols directly from alkenes are therefore impactful in chemical synthesis, especially where high chemo- and regioselectivity is achieved.[3]

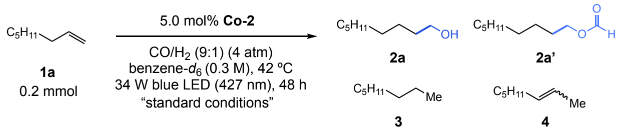
Reductive hydroformylation, a transition metal catalyzed reaction involving the addition of carbon monoxide (CO), and hydrogen (H_2) to alkenes, is an atom economical method for the direct synthesis of C_1-homologated alcohols. The tandem process involves the initial generation of aldehydes and subsequent reduction (Scheme 1A). [4,5–7] Following the discovery of Roelen's cobalt hydroformylation catalyst, $HCo(CO)_4$,[8] attempts to improve the performance of the cobalt complexes by addition phosphines ($PR_3Co(CO)_3H$; R = alkyl, aryl) modified the product distribution to include C_1-homologated alcohols arising from a more hydridic Co–H bond.[9] Poor regioselectivity and forcing conditions (>25 atm CO/H_2, >180 °C) motivated the transition to rhodium and ruthenium catalysts that exhibited improved selectivity for alcohol formation from minimally-functional alkenes.[10] While cobalt catalysis has been applied commercially for the synthesis homologated alcohols from $>C_{10}$ streams,[5] rhodium has also been used emphasizing the value of regioselectivity in the seminal reaction.

Scheme 1. A. Cobalt-Catalyzed Reductive Hydroformylation of Terminal Alkenes. B. Nozaki's Dual-Catalyst (Rh/Ru) System. C. Beller's Single-Component (Ru) Catalyst. D. Cobalt-Catalyzed Tandem Catalysis Driven by Visible Light.

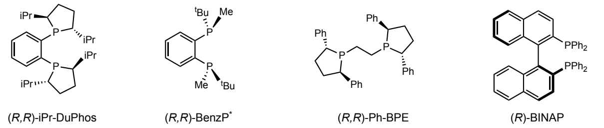


Pioneering work by Nozaki introduced a dual rhodium-ruthenium catalyst,[11] where linear alcohol synthesis was achieved with regioselectivities as high as 50:1 (*l*/*b*).[12] The combination of $[Rh(COD)Cl]_2$ and XantPhos enabled the regiocontrolled synthesis of aldehydes that were reduced in a subsequent, chemoselective hydrogenation step using Shvo's ruthenium catalyst (Scheme 1B).[13] Nozaki and Beller have since reported single-component ruthenium catalysts for the reductive hydroformylation of terminal and internal alkenes (Scheme 1C).[14] For cobalt, a catalytic method that accomplishes highly regioselective reductive hydroformylation has not yet been realized, where progress is likely inhibited by the requirement for high pressures and temperatures.[5] The paucity of Earth-abundant transition metal catalysts for the synthesis of alcohols from alkenes inspired the development of a reductive hydroformylation method, targeting synthetically-useful selectivities under mild operating conditions readily accessed in a synthetic laboratory.

Table 1. Selected Optimization Experiments for Visible-light-Driven Cobalt-Catalyzed Reductive Hydroformylation.



entry	deviation from standard conditions[a]	yield (%)[b] 2a	2a’	3	4
1	none	70	5	<1	25
2	1:1 CO/H_2	15	19	32	16
3	3:1 CO/H_2	38	3	42	16
4	25 ºC instead of 42 ºC	55	<1	<1	42
5	$Co_2(CO)_8$ + dcype (2 equiv)	25	<1	35	20
6	1 atm instead of 4 atm	19	10	13	57
7	467 nm blue LED	6	<1	3	3
8	no light	<1	<1	<1	2
9	no **Co-2**	<1	<1	<1	<1
10	(*R*,*R*)-iPr-DuPhos instead of dcype	44	9	37	8
11	(*R*,*R*)-BenzP* instead of dcype	9	<1	21	7
12	(*R*,*R*)-Ph-BPE instead of dcype	36	12	33	9
13	(*R*)-BINAP instead of dcype	15	12	<1	70



A catalytic method for selective alcohol synthesis applying the organometallic photochemistry of well-defined cobalt hydrides developed for hydroformylation was envisioned (Scheme 1D).[15] Irradiation of cobalt hydride precatalysts with visible light is known to promote ligand dissociation and has enabled chemo- and regiodivergent hydroboration and isomerization that complements reactivity under analogous thermal (dark) conditions.[16] Our group recently reported the divergent reactivity of the bis(phosphine)cobalt hydride, (*R*,*R*)-(^{iPr}DuPhos)$Co(CO)_2H$ (**Co-1**) under both thermal and photochemical conditions.[17] Hydrogen atom transfer (HAT) reactivity was operative at high temperature, whereas visible-light-irradiation of **Co-1** suppressed one-electron chemistry and enabled redox neutral catalysis leading to marked improvement in both rate and scope in hydrogenation. The possibility of a visible-light-driven reductive hydroformylation was explored with **Co-1** as the precatalyst, recognizing that photochemical CO dissociation under syngas pressure may enable alkene coordination and subsequent insertion into a relatively hydridic Co–H bond. To achieve the desired selectivity in a tandem process, CO migratory insertion from linear cobalt alkyls would follow the 1,2-insertion of an alkene into a photo-generated, 4-coordinate bis(phosphine)cobalt hydride. Acyl hydrogenolysis would then have to outcompete alkene isomerization processes that might erode regioselectivity for the aldehyde product (Scheme 2D). The observation of aldehyde release upon exposure of the well-defined cobalt acyl complex (*R*,*R*)-(^{iPr}DuPhos)$Co(CO)_2C(O)CH_2CH_2Ph$ to 4 atm of H_2,[15] suggested that the desired reaction may be accelerated by visible light.

Realizing an effective catalytic reaction with **Co-1** was complicated by the formation of [(*R*,*R*)-(^{iPr}DuPhos)$Co(CO)_2$]$_2$ in the presence of syngas (CO/H_2). Formation of the carbonyl dimer was observed as the product of photodriven H_2 release from **Co-1** and by thermal hydrogen atom abstraction (HAA) by addition of TEMPO•.[17] Suppressing dimer formation under visible light irradiation in the presence of synthesis gas was identified as a catalyst design principle to improve catalytic reductive hydroformylation performance. A selection of bis(phosphine)cobalt carbonyl hydrides including: (*R*,*R*)-(BenzP*)$Co(CO)_2H$ (**Co-3**), (*R*,*R*)-(^{Ph}BPE)$Co(CO)_2H$ (**Co-4**), and (*R*)-(BINAP)$Co(CO)_2H$ (**Co-5**)[18] was prepared using the procedure developed for **Co-2** and exhibited poor performance for the reductive hydroformylation of 1-octene with little preference for formation of 1-nonanol. Monitoring the catalytic reactions by ^{31}P NMR spectroscopy established sequestration of a significant amount of bis(phosphine)cobalt as the carbonyl-bridged dimers.[19]

Based on these observations, a bis(phosphine) ligand was targeted that would disfavor dimer formation by virtue of large alkyl substituents. Accordingly, addition of two equivalents of dicyclohexylphosphinoethane (dcype) to a toluene solution of $Co_2(CO)_8$ under 4 atm hydrogen gas at 60 °C afforded the bis(phosphine)cobalt carbonyl hydride, (dcype)$Co(CO)_2H$ (**Co-2**, $\%V_{bur} = 53.7$)[20] in 89% isolated yield. Single-crystals suitable for X-ray diffraction were obtained from a concentrated diethyl ether solution at –35 ºC (Table 2) and confirmed a five-coordinate, idealized trigonal bipyramidal structure. In benzene–d_6, a resonance was observed at δ –11.2 and assigned to the Co–H. Likewise, a diagnostic, broad ^{31}P resonance was observed at δ 102.5. Unlike **Co-1**,[15] exposure of **Co-2** to a blue Kessil lamp and 1-4 atm of syngas did not result in H_2 loss and formation of the bridging carbonyl dimer, [(dcype)$Co(CO)_2$]$_2$ suggesting that bimolecular release of dihydrogen is inhibited by the large cyclohexyl substituents.

The catalytic performance of **Co-2** was evaluated with 1-octene as a representative, minimally functionalized alkene. With 4 atm of a 1:1 CO/H_2 composition with blue Kessil lamp irradiation (34 W) for 48 hours, a 1:2.1 mixture of 1-nonanol (**2a**) and *n*-octane (**2b**) was obtained (Table 1, entry 2) with the mass balance of C_9 product made up by formate ester (**2a’**). Because bis(phosphine)cobalt hydrides are effective hydrogenation catalysts upon irradiation with visible light,[17] the relative amount of CO in the syngas mixtures was increased from 50% to 75% (3:1 CO/H_2, Table 1, entry 3), to 90% (9:1 CO/H_2, Table 1, entry 1). CO-rich syngas (9:1 CO/H_2) gave the highest selectivity for alcohol **2a** suppressing undesired alkene hydrogenation, leaving isomerization as the major competing pathway (Table 1, entry 1, "standard conditions"). Worth noting is that syngas mixtures in thermal Co- and Rh-catalyzed tandem processes typically contain excess hydrogen to prevent formation of carbonylated metal hydrides (e.g., $HCo(CO)_4$) that show poor activity toward aldehyde reduction as a result of a relatively acidic metal hydride.[5,6]

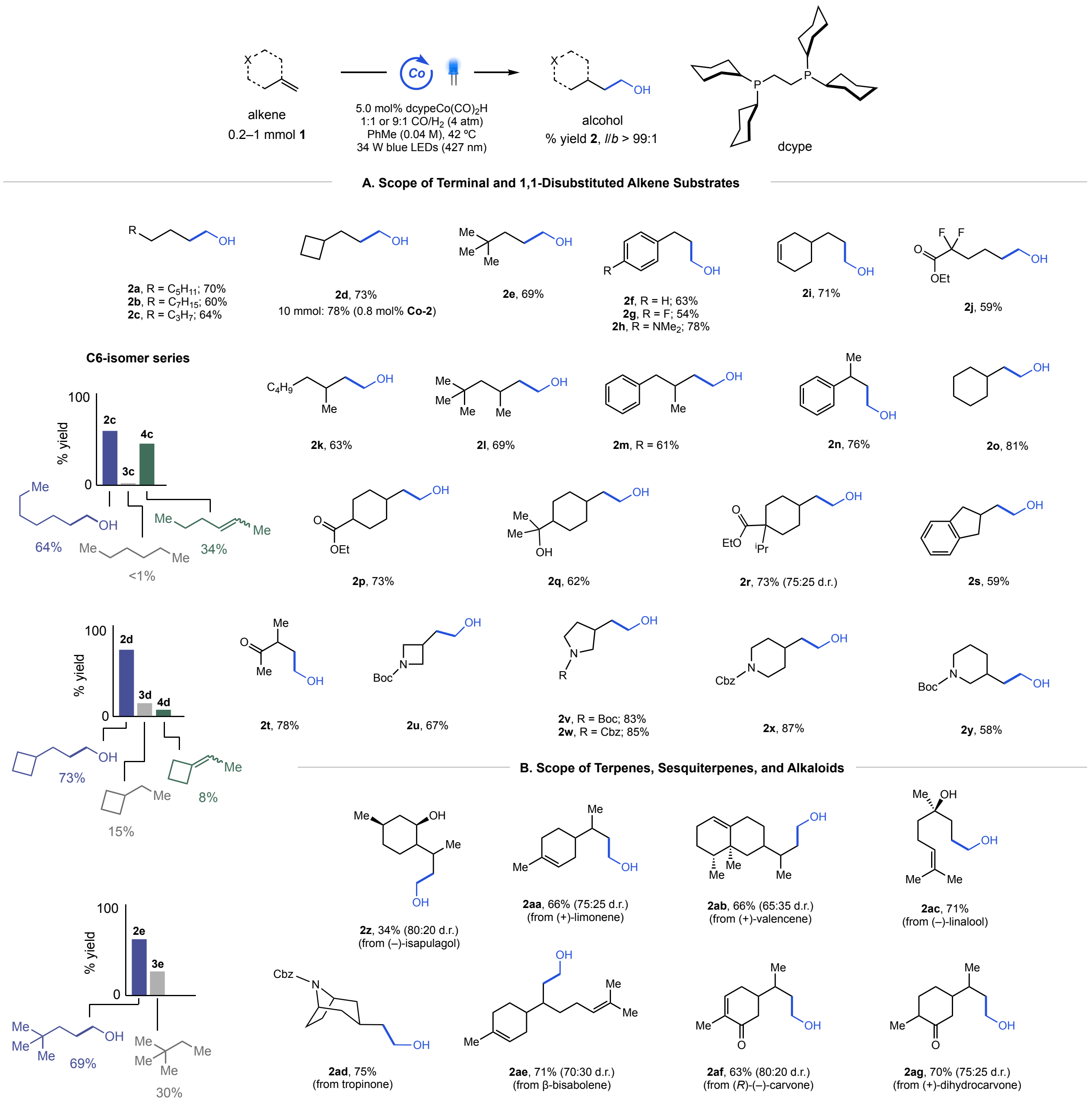
The bis(phosphine)cobalt hydride precatalyst **Co-2** was essential for the desired reactivity given that attempts to generate the catalyst *in situ* from addition of dcype to $Co_2(CO)_8$ furnished alkane **3** as the major product with comparatively low conversion of **1a** (Table 2, entry 5). Combinations of 2 equiv dcype and $Co_2(CO)_8$ in toluene generated a diethyl ether-insoluble product with a single sharp resonance at δ 107.8 in the ^{31}P NMR spectrum. An FT-IR spectrum recorded in pentane revealed a number of features resembling **Co-2** with the exception of a sharp band at 1918 cm^{-1}, assigned as the $Co(CO)_4^-$ anion.[21] Single crystals suitable for X-ray diffraction were grown from a saturated toluene solution at –35 °C, and confirmed the structure of $[(dcype)Co(CO)_3][Co(CO)_4]$. Revisiting the other cobalt hydride precatalysts using optimized conditions still gave poor conversion of starting material as a consequence of rapid dimer formation (entries 10–13). Temperature was found to affect product selectivity: at room temperature, alkene isomerization, yielding 2-octene (**4**), became the predominant competing reaction (Table 2, entry 4), whereas hydrogenation was entirely suppressed. In all cases, only the linear isomer of the C_1-homologate alcohol (**2a**) was observed. To our knowledge, this is the only example of a reductive hydroformylation process involving a minimally functionalized alkene (i.e., 1-octene) with exclusive regioselectivity in alcohol products. Competing pathways including isomerization can be suppressed by the presence of alkyl groups at the vinylic position. Stanley and coworkers recently employed a class of cationic cobalt(II) catalysts for the hydroformylation of 3,3-dimethylbutene, reporting exceptional activity and selectivity for linear aldehyde (l/b = 58).[6b,22]

Having identified conditions for regiocontrolled alcohol synthesis, a variety of feedstock alkenes was subjected to the visible-light-mediated reaction with yields ranging from 44-73%. Product distributions from a series of 6-carbon skeletal isomers including 1-hexene (**1c**), vinyl cyclobutane (**1d**), and 3,3-dimethylbutene (**1e**) illustrates a sensitivity of the cobalt catalyst towards substitution at the α-carbon of terminal alkenes (Table 2), with increased substitution suppressing alkene isomerization in favor of hydrogenation as the major competing pathway. Notably, the alcohol **2d** was synthesized on a 10 mmol-scale from vinyl cyclobutane (**1d**, 0.82 g) using a lower precatalyst loading of 0.8 mol%, though multiple additions of syngas were required to ensure full conversion. Styrenes with electron-withdrawing and donating substituents were tolerated under optimized conditions affording products (**2f**–**h**) in 63–78% yield. The ability of the catalyst to discriminate between terminal and internal alkenes in the same substrate was demonstrated in the selective reductive hydroformylation of 4-vinyl-cyclohex-1-ene, where the endocyclic alkene was retained in the product alcohol (**2i**). Alkenes bearing esters were also tolerated, providing the corresponding alcohols **2j**, **2p**, and **2r** in modest to good yield (59–73%).

The scope of cobalt-catalyzed reductive hydroformylation was extended to 1,1-disubstituted alkenes. With these substrates, 1:1 CO/H_2 syngas mixtures were effective in generating the homologated alcohols with yields typically above 60% with exclusive linear selectivity. Accordingly, substrates were cleanly converted to the corresponding alcohols with trace alkene isomerization due to steric blocking of the alkene α-methyl substituent. Increasing α-substitution (e.g., from methyl to ethyl) resulted in a significant decrease in conversion, a result of the sterically encumbered nature of the cobalt center imparted by the dcype ligand. Several naturally occurring terpenes and sesquiterpenes were identified as substrates in the photodriven tandem reaction. Under optimized conditions, the 1,1-disubstitued alkenyl fragment of (*R*)-(–)-carvone was cleanly converted to the homologated alcohol (**2aa**). Medicinally-relevant exocyclic alkenes derived from piperidine, pyrrolidine, and azetidine were all cleanly converted to their corresponding alcohols **2t**–**w** in good yields (67–87%). Exploring the generality of alcohol formation driven by visible light illustrates the remarkable chemoselectivity and regiocontrol arising from the cobalt catalyst for a variety of functionalized alkenes.

Monitoring the catalytic reaction by NMR spectroscopy was carried out to gain insight into the cobalt-catalyzed reductive hydroformylation. Notably, all spectroscopic measurements were performed in the absence of blue light irradiation. At 30-50% con

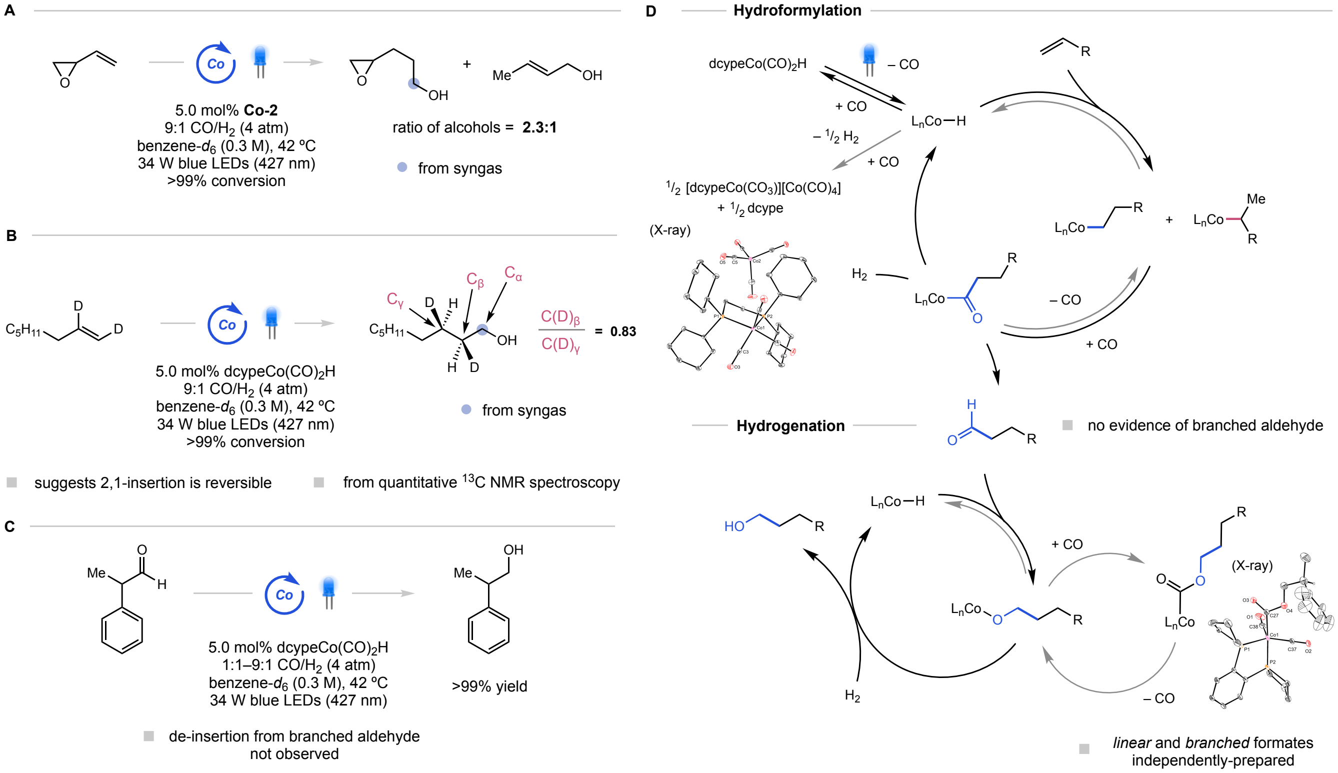
Table 2. A. Scope of Cobalt-catalyzed Visible-Light-Driven Reductive Hydroformylation with Terminal and 1,1-Disubstituted Alkenes. B. Scope of Cobalt-catalyzed Visible-Light-Driven Reductive Hydroformylation with Naturally Occurring Terpenes and Sesquiterpenes.



version of 1-octene, the benzene-d_6 ^{31}P NMR spectrum exhibited the resonance for **Co-2** (δ 102.54) along with two new peaks centered at 88.7 and 83.1 ppm, assigned as the formate complex (dcype)CoC(O)OC$_9$H$_{19}$, arising from CO migratory insertion into the putative cobalt alkoxide.[23] When the catalytic reaction reached complete (>99%) conversion, only **Co-2** was observed by ^{31}P NMR spectroscopy. To determine if both cobalt-catalyzed hydroformylation and aldehyde hydrogenation are photodriven, 3-phenylbutyraldehyde was cleanly converted to 3-phenylbutanol using 5.0 mol% **Co-2** under all mixtures of CO/H$_2$ used in this study with blue light irradiation (Scheme 2C). Notably, aldehyde reduction was not observed under thermal conditions, illustrating that visible light is required for both steps of the tandem catalytic process. Under variable H$_2$ pressures (1–4 atm), visible-light-mediated aldehyde reduction did not occur demonstrating that CO is needed in both steps of the tandem catalytic reaction.[24]

The origins of anti-Markovnikov regioselectivity in the photodriven cobalt-catalyzed reaction were investigated by subjecting both vinyl epoxide (butadiene monoxide) and *cis*-1,2-oct-1-ene-d_2 to the optimized catalytic conditions (Scheme 2A). Monitoring the progress of the reaction by ^{1}H NMR spectroscopy for the epoxide example revealed a mixture of C$_1$-homologated (linear) alcohol and 2-buten-1-ol, the result of irreversible β-oxygen elimination from the prod

Scheme 2. A. Cobalt-Catalyzed Reductive Hydroformylation of Vinyl Epoxide. B. Reductive Hydroformylation of cis-1,2-dideuteriooctene. C. Catalytic Hydrogenation of Branched Aldehyde under CO/H_2. D. Proposed Catalytic Cycle for both Hydroformylation (Above) and Hydrogenation (Below).



uct of 2,1 alkene insertion (Scheme 2B). For the labeled octene, only 1-nonanol with no detectable deuterium migration was observed. These observations support a pathway where 2,1-insertion generates a branched alkyl but does not undergo productive CO insertion en route to product formation. Notably, when an isolated 18-electron bis(phosphine)cobalt acyl complex was irradiated with visible light, CO deinsertion took place, even in the presence of syngas (*vide supra*), generating styrene following β-hydrogen elimination.[15]

In summary, a cobalt-catalyzed tandem hydroformylation/hydrogenation mediated by visible-light has been realized. The method has been applied to the synthesis of C_1-homologated alcohols from a variety of terminal and 1,1-disubstituted alkenes with exclusive linear selectivity. Preliminary mechanistic results including catalytic reactions with a deuterium labelled alkene[25] support a scenario where both 1,2- and 2,1 alkene insertion occurs under visible light, but only linear aldehydes are produced in the first of two concurrent transformations in the catalytic reaction.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website.

General considerations and experimental procedures; synthesis and characterization of cobalt precatalysts and relevant complexes; catalytic reaction procedures, including photographs of experimental setup; and spectroscopic data (PDF).

Accession Codes

CCDC **2191147–2191150**, **2203138**, and **2203139** contain the supplementary crystallographic data for this paper (CIF). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data–request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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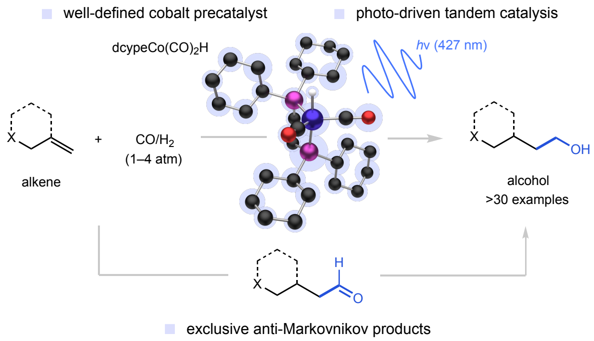
well-defined cobalt precatalyst
photo-driven tandem catalysis
dcypeCo(CO)2H
hν (427 nm)
X
alkene
+
CO/H2
(1–4 atm)
X
OH
alcohol
>30 examples
X
H
O
exclusive anti-Markovnikov products