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Bis(phosphine)cobalt Dialkyl Complexes for Directed Catalytic Alkene Hydrogenation

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Supporting Information

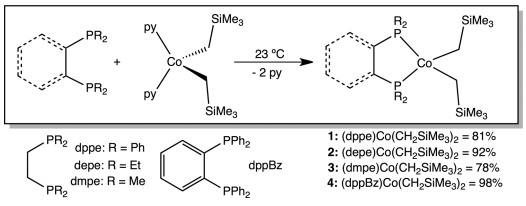
ABSTRACT: Planar, low-spin cobalt(II) dialkyl complexes bearing bidentate phosphine ligands, (P−P)Co(CH$_2$SiMe$_3$)$_2$, are active for the hydrogenation of geminal and 1,2-disubstituted alkenes. Hydrogenation of more hindered internal and endocyclic trisubstituted alkenes was achieved through hydroxyl group activation, an approach that also enables directed hydrogenations to yield contrasteric isomers of cyclic alkanes.

Homogeneous alkene hydrogenation catalysts, unlike their heterogeneous counterparts, offer the opportunity to promote site selective reactions through rational ligand design.[1] Among these, directed hydrogenations where the interaction of a functional group in the substrate with the catalyst imparts high levels of stereocontrol have found widespread application in synthesis due to the ability to access products with contrasteric selectivity.[2−4] Wilkinson's, Schrock−Osborn-type, and Crabtree's catalysts, (Ph$_3$P)$_3$RhCl, [(P−P)Rh(COD)]$^+$, and [Ir(COD)(py)(PCy$_3$)]$^+$ (COD = 1,5-cyclooctadiene, py = pyridine, Cy = cyclohexyl), respectively, have been the most widely used due to their high activity, selectivity, ease of handling, and availability. Alternative catalyst platforms that rely on base rather than precious metals not only are attractive for potential cost and environmental advantages but also offer the opportunity, by virtue of unique electronic structure properties, to access new chemical space made available by a broader substrate scope.[5]

These benefits have initiated resurgence in the study of cobalt complexes for alkene hydrogenation.[6−13] Catalysts with both redox-active[6−8] and -innocent[9] tridentate pincer ligands have proven effective for the reduction of unactivated and essentially unfunctionalized alkenes. With bis(arylimidazol-2-ylidene)pyridine ligated catalysts, activities that rival precious metal compounds have been observed and in the case with a C_1 symmetric bis(imino)pyridine ligand, high enantioselectivity was achieved.[7,8] Recently, a class of Co catalysts containing chiral bidentate bis(phosphines) was discovered expedited by high throughput experimentation.[11] Metal-phosphine combinations were identified for the hydrogenation of both unfunctionalized and acetimido-substituted alkenes establishing a broader substrate scope with this catalyst platform. These observations suggested that directed hydrogenations may also be possible using readily available achiral bidentate phosphine ligands. Here we describe the preparation, electronic structure determination, and directed hydrogenation performance of cobalt dialkyl complexes supported by common and readily available bidentate phosphines that serve as base metal alternatives to well-established Rh and Ir directed hydrogenation catalysts. These investigations uncovered an unusual activating effect of hydroxyl groups, functional groups that have typically been poisons with reduced first row metal catalysts.

The desired cobalt(II) dialkyl complexes, **1**−**4**, were prepared by displacement of pyridine from py$_2$Co(CH$_2$SiMe$_3$)$_2$[14] upon treatment with a bis(phosphine) ligand (Scheme 1). Alternatively, **1**−**4** could also be prepared via straightforward dialkylation of the corresponding bis(phosphine)cobalt dihalide with 2 equiv of LiCH$_2$SiMe$_3$.[15] Each complex was isolated as an orange solid in high yield, and magnetic measurements established an $S = 1/2$ ground state. X-band EPR spectroscopy confirmed formation of low-spin Co(II), d^7 complexes. A representative spectrum of **1** is presented in Figure 1 and exhibits a rhombic signal with large g anisotropy ($g_x = 3.58$, $g_y = 2.18$, $g_z = 1.80$), expected for planar Co(II) complexes due to

Scheme 1. Preparation of Bis(phosphine)cobalt Dialkyl Complexes, 1−4



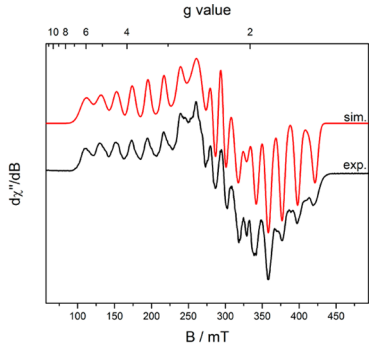


Figure 1. X-band EPR spectrum of **1** recorded at 10 K in toluene glass with microwave frequency = 9.378 GHz, power = 1.00 mW, modulation amplitude = 1 mT/100 kHz.

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strong spin−orbit coupling from a nearly degenerate set of *d* orbitals.[16,17] Coupling (A_{xx} = 1070, A_{yy} = 401, A_{zz} = 401 MHz) to the ^{59}Co (I = 7/2, 100% natural abundance) is observed but not to the ^{31}P nuclei.

The solid-state structures of **1**−**4** were determined by X-ray diffraction. Representations of two examples, **1** and **2**, are presented in Figure 2. Complexes **3** and **4** are reported in the

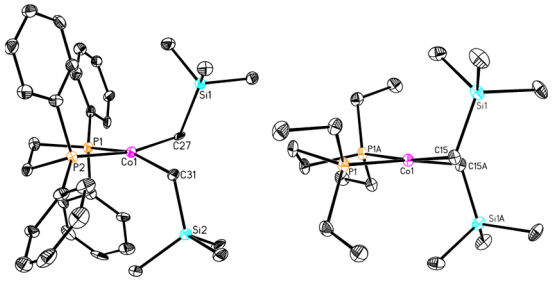
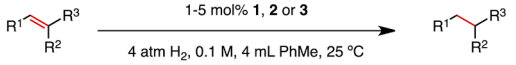


Figure 2. Representations of the molecular structures of **1** (left) and **2** (right) at 30% ellipsoid probability. H-atoms omitted for clarity.

Supporting Information (SI). In each case, idealized planar structures were observed with the large [$SiMe_3$] groups geared oppositely above and below the idealized metal−ligand plane. The observed planar geometries are in agreement with the solid-state magnetic data as well as the EPR spectra. Unrestricted DFT calculations on **1** established the d_{z^2} orbital on cobalt as the SOMO as expected for a low spin Co(II) compound in a planar ligand field (see SI for MO diagram).

The performance of the bis(phosphine) cobalt dialkyl complexes in catalytic alkene hydrogenation was evaluated. Initial studies focused on **1** and **2** as representative examples and were conducted with 0.1 M toluene solution of alkene at 25 °C with 4 atm of H_2 (Table 1). Both complexes exhibited excellent activity for the hydrogenation of 1,1-disubstituted alkenes including those with diphenyl (entry 2) and pyridine substitution (entries 3 and 4). Cyclic (entries 5 and 6) and acyclic (entry 7) disubstituted alkenes were also well tolerated and reduced over the course of hours under the standard conditions. Notably,

Table 1. Evaluation of 1 and 2 in Catalytic Alkene Hydrogenation



entry	alkene	% conversion (time)[a]	entry	alkene	% conversion (time)[a]
(1)		1% **1**: 99% (2 h) 1% **2**: 98% (2 h)	(2)		5% **1**: 99% (5 h) 5% **2**: >99% (5 h)
(3)		1% **1**: >99% (2 h) 1% **2**: 98% (4 h)	(4)		1% **1**: >99% (6 h) 1% **2**: >99% (4 h)
(5)		5% **1**: >99% (2 h) 5% **2**: 91% (2 h)	(6)		1% **1**: >99% (7 h) 1% **2**: 99% (6 h)
(7)		5% **1**: 80% (5 h) 5% **2**: 99% (20 h)	(8)		5% **1**: 57% (12 h) 5% **2**: 22% (36 h) 5% **3**: 84% (12 h)
(9)		5% **1**: <5% (16 h) 5% **2**: <5% (16 h)	(10)		1% **1**: <5% (16 h) 1% **2**: <5% (16 h)

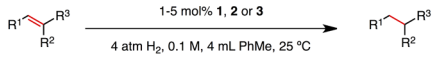
[a]Conversions determined by GC-FID by comparison to independently synthesized or commercially obtained alkane products.

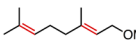
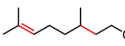
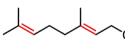
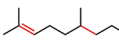
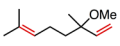
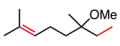
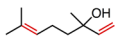
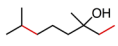
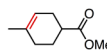
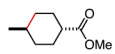
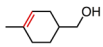
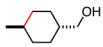
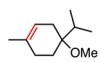
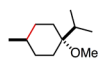
sulfolane functionality did not interfere with catalytic performance. In general, precatalyst **2** proved more active than **1**, likely a result of a reduced steric profile and the increased electron-donating ability of the alkyl rather than aryl groups on the phosphine. Further reducing the steric profile of the catalyst (**1** vs **3**) increased hydrogenation activity as *trans*-methylstilbene reached 84% conversion after 12 h under standard conditions with **3**.

Sterically hindered, unactivated tri- and tetrasubstituted alkenes proved challenging for both Co precatalysts, as only partial conversion was observed with *trans*-methylstilbene (entry 8) while no turnover was detected with methylcyclohexene (entry 9). To expand the substrate scope and overall synthetic utility of these precatalysts, hydroxylated alkenes were explored as the OH group may serve to both activate and direct the hydrogenation of the substrate. Unlike in precious metal chemistry, most base metal alkene hydrogenation catalysts are readily deactivated by acidic hydroxyl functionality.[18]

Table 2 reports the hydrogenation of various oxygenated substrates with **1** and **2** as the precatalysts. While introduction of

Table 2. Directed Hydrogenations Using 1 and 2 as Precatalysts



entry	alkene	alkane	% conversion (time)[a]
(1a)			5% **1**: <5% (18 h) 5% **2**: <5% (18 h)
(1b)			5% **1**: 99% (4 h)[b] 5% **2**: >99% (20 h)
(2a)			5% **1**: >99% (7 h) 5% **2**: >99% (2 h)
(2b)			5% **1**: 86% (13 h)[c,d] 5% **2**: 12% (7 h)[c]
(3a)			5% **1**: <5% (14 h) 5% **2**: <5% (14 h)
(3b)			5% **1**: 88% (14 h) 5% **2**: 97% (14 h)
(4a)			5% **1**: 81% (14 h) 5% **2**: 85% (14 h)
(4b)			5% **1**: >99% (14 h) 5% **2**: >99% (4 h)
(5a)			5% **1**: <5% (18 h) 5% **2**: <5% (18 h)
(5b)			5% **1**: 98% 92 : 8 dr (24 h) 5% **2**: 88% 96 : 4 dr (4 h)
(6a)			5% **1**: <5% (16 h) 5% **2**: <5% (16 h)
(6b)			1% **1**: 99% 99.8 : 0.2 dr (4 h) 1% **2**: >99% 99.9 : 0.1 dr (4 h) 1% **3**: 92% 99.8 : 0.2 dr (8 h)

[a]Conversion determined by GC or NMR. [b]24% conversion to cyclohexyl methyl ketone was observed. [c]Reactions run in diethyl ether to facilitate product isolation. [d]2% aldehyde isomer of starting material observed (NMR).

carbonyl functionality did not induce the catalytic activity of the endocyclic alkene (entry 1a), reduction of the carbonyl to the corresponding alcohol (entry 1b) enabled quantitative hydrogenation to the alkane. Again **2** proved to be more active than **1** reaching quantitative conversion with 5 mol % catalyst in 20 h. Unfortunately, the ketone functional group in entry 1a is not reduced to activate the alkene for hydrogenation.

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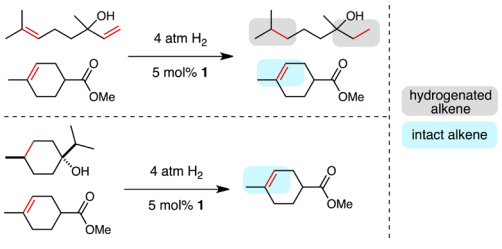
The activating effect of the hydroxyl group was further explored with various terpenoid derivatives. Prenyl alcohol (entry 2a) underwent clean conversion to *iso*-amyl alcohol with both **1** and **2** in 7 and 2 h, respectively. The hydrogenation of the tetra-substituted alkene in entry 2b was accomplished with **1** to 86% conversion in 13 h while precatalyst **2** was ineffective. This highlights the importance of hydroxyl functionality in enabling the hydrogenation of very hindered alkenes (compare Table 1, entry 10 to Table 2, entry 2b).

Exposure of the methyl ether of geraniol to 5 mol % of either **1** or **2** resulted in no detectable conversion after 14 h at 25 °C. By contrast, geraniol (entry 3b) underwent selective reduction of the alkene proximal to the hydroxyl group with both **1** and **2** with the latter reaching 97% conversion after 14 h at 25 °C. The hydrogenation of linalool (entry 4b) is also illustrative of the activating effect of the hydroxyl group, as both alkenes are reduced with 5 mol % of **1** or **2** over the course of 14 h. Methylation of the hydroxyl group again retarded hydrogenation activity, as only the terminal alkene is reduced, leaving the more hindered, trisubstituted alkene intact. Comparing the hydrogenation of geraniol and linool defines the hydroxyl effect. With the former, the activating group is six carbons removed and therefore too remote to encourage coordination and hence reduction of the trisubstituted alkene. In linalool, the four carbon tether length presumably facilitates an appropriate chelate size to encourage coordination of the hindered trisubstituted C═C bond, enabling hydrogenation.

Extension of this concept to the hydrogenation of cyclic alkenes was also explored. Reduction of substrate in entry 5b with 5 mol % of **1** reached complete conversion after 4 h at 25 °C. Notably, a dr of 92:8 was observed, highlighting the directing effect of the hydroxyl group in determining the stereochemical outcome of the reaction. Replacement of the primary alcohol group in the substrate with a methyl ester functional group again resulted in no conversion (entry 5a). With terpinen-4-ol (entry 6b) as the substrate, highly active and diastereoselective hydrogenation was observed with either **1** or **2** as catalysts. No turnover was observed with the analogous methyl ether. In both cases where a directing effect was observed (Table 2, entries 5b, 6b), the major diastereomer of the alkane was the same as that produced when using Crabtree's catalyst.[19]

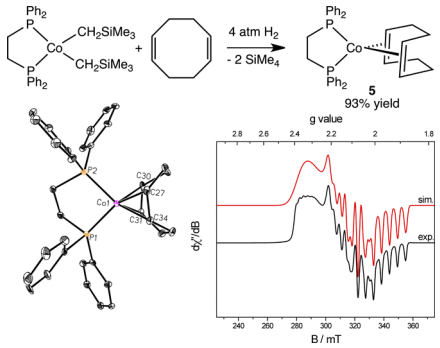
To further establish this effect as intramolecular and not a result of activation of the catalyst by specific alcohol functionality, mixing experiments between different substrates were conducted (Scheme 2). The hydrogenation of a 1:1 mixture of linalool and methyl 4-methylcyclohex-3-enecarboxylate (from Table 2, entry 5a) with 5 mol % of **1** produced clean and selective conversion of linalool to the corresponding alkane while the alkene from the more hindered substrate remained intact. A second mixing experiment involved the catalytic hydrogenation of a 1:1 mixture of methyl 4-methylcyclohex-3-enecarboxylate and 1-isopropyl-4-methylcyclohexanol (the hydrogenated alcohol of terpinen-4-ol) with 5 mol % of **1** as the catalyst precursor (Scheme 2). In this experiment, no hydrogenation of the hindered alkene was observed, establishing the necessity of intramolecular hydroxyl functionality in hydrogenating hindered alkenes.

Scheme 2. Mixing Experiments To Elucidate the Mode of Hydroxyl Group Activation in [Co]-Catalyzed Alkene Hydrogenation



Insight into the activation mode of the catalyst and mechanism of hydrogenation was provided by the hydrogenation of 1,5-cyclooctadiene (COD). In the presence of 5 mol % of **1**, only 10% conversion to a mixture of cyclooctene and cyclooctane was observed after 24 h, suggesting that the diene inhibited catalytic hydrogenation. Repeating the procedure with 5 equiv of COD followed by recrystallization from a diethyl ether−pentane mixture at −35 °C furnished dark orange crystals in 93% yield identified as (dppe)Co(COD) (**5**) (Scheme 3). A benzene-d_6 solution magnetic moment of 1.7 μB (Evans method) was measured at 293 K, establishing an $S = 1/2$ ground state, as expected for a formally Co(0), d^9 complex. Both Co(I)[20] and Co(−I)[21] COD complexes are known, but to our knowledge, Co(0) examples have not been reported. We do note however that $[(Me_3P)_3Co]_2(\mu_2,\mu_2,\eta^2,\eta^2$-NBD) (NBD = norbornadiene) has been synthesized and crystallographically characterized.[22]

Scheme 3. Preparation of (dppe)Co(COD), 5 (above); Representation of the Molecular Structure of 5 at 30% Ellipsoid Probability with H-Atoms Omitted for Clarity (bottom left); and X-Band EPR Spectrum of 5, (bottom right)



The solid-state structure was determined by X-ray diffraction, and a representation of the molecule is presented in Scheme 3. Unlike the Co(II) dialkyl complexes and well-known $[(dppe)Rh^{I}(COD)]^{+}$ which are planar,[23] (dppe)Co(COD) is significantly distorted. The geometric difference is highlighted by the orientation of the olefins relative to the metal-phosphine plane. In the Rh(I) example, the diene is perpendicular to the metal-phosphine plane, while, for the formally Co(0) compound, the alkenes are parallel to that plane. Grützmacher et al. have also prepared examples of group 9 phosphine−alkene complexes and noted distortion from tetrahedral to more planar geometries with the heavier congeners.[24] The geometry of the (dppe)Co(COD) is also evident in the toluene glass EPR spectrum recorded at 10 K. Unlike **1**, relatively small g anisotropy ($g_x = 2.32$, $g_y = 2.12$, $g_z = 1.99$) and A-values ($A_{xx} = 60$, $A_{yy} = 108$, $A_{zz} = 153$ MHz) are observed, consistent with a distortion from planarity. Because **5** was prepared from hydrogenation in the presence of COD and is paramagnetic, a degradation experiment was performed to exclude the possibility of residual H_2 coordination. Stirring a THF solution of **5** with excess *N*-chlorosuccinimide resulted in complete and rapid decomposition of the compound;

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importantly no combustible gas was collected with a Toepler pump (200 Torr expected).

The competency of (dppe)Co(COD) as a precatalyst for alkene hydrogenation was evaluated with α-methylstyrene and terpinen-4-ol as representative substrates. Complete conversion with the former was observed in 6 h under the standard conditions, while for the latter only 34% conversion was obtained after 2 h likely due to the presence of coordinating diene. Notably, a 99.1:0.9 diastereomeric ratio was observed suggesting catalyst activation similar to that for **1** (entry 6b, Table 2).

The mechanism for alkene hydrogenation by bis(phosphine)-cobalt(II) alkyl complexes involves initial hydrogenolysis of the alkyl groups to form $SiMe_4$ (observed quantitatively by NMR spectroscopy) and a thus far unobserved cobalt(II) dihydride. Fryzuk et al. have reported a related phosphine-ligated cobalt hydride, $[(^iPr_2P(CH_2)_3P^iPr_2)Co]_2(H)(\mu\text{-}H)_3$,[25] from addition of H_2 to the corresponding Co(I) allyl. Subsequent olefin insertion and reductive elimination of alkane generates a putative Co(0) species that coordinates alkene. Support for the existence of such a species is provided by the isolation and catalytic activity of (dppe)Co(COD). These observations and understanding provide a platform for future optimization of base metal alkene hydrogenation catalysts with high diastereo- and enantioselectivity.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, substrate and product characterization, and crystallographic data for **1**−**4** in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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