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An Aryl Diimine Cobalt(I) Catalyst for Carbonyl Hydrosilylation

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Through the application of a redox-innocent aryl diimine chelate, the discovery and utilization of a cobalt catalyst, $(^{\mathrm{Ph_2PPr}}\mathrm{ADI})\mathrm{Co}$, that exhibits carbonyl hydrosilylation turnover frequencies of up to 330 s^{-1} is described. This activity is believed to be the highest ever reported for metal-catalyzed carbonyl hydrosilylation.

Carbonyl hydrosilylation has emerged as a facile method of alcohol synthesis[1–4] that does not require hydrogen[5] or pyrophoric inorganic hydrides.[6] Although early reports of carbonyl hydrosilylation employed precious metal catalysts,[7–10] the beginning of this century has been a golden age for sustainable alternatives that feature Earth-abundant first row metals.[11–16] Homogeneous manganese and iron catalysts have exhibited the most impressive activities for carbonyl hydrosilylation. In 2013, (3,5-^{t}Bu-Salen)MnN was found to mediate aldehyde hydrosilylation with turnover frequencies (TOFs) of up to 196 min^{-1} (0.5 mol%, 80 °C, acetonitrile).[17] More recently, 4-heptanone hydrosilylation was achieved with a TOF of 200 min^{-1} using $[(\kappa^2\text{-}P,N)\mathrm{Mn(N(SiMe_3)_2)}]$ (0.25 mol%, 25 °C, where κ^2-*P,N* is $^t\mathrm{Bu_2PN{=}C(Ph)N(2,6\text{-}^iPr_2Ph)}$).[18] Our group has focused on the utilization of Mn catalysts that feature polydentate ligands,[19] and the P-substituted bis(imino)pyridine (or pyridine diimine, PDI) chelate $^{\mathrm{Ph_2PPr}}\mathrm{PDI}$[20] allowed for the evaluation of $(^{\mathrm{Ph_2PPr}}\mathrm{PDI})\mathrm{Mn}$.[21] At 0.01 mol% loading, this complex catalyzes ketone hydrosilylation[21] with TOFs of 1,280 min^{-1} and aldehyde hydrosilylation[22] with TOFs of 4,900 min^{-1} (25 °C, **Fig. 1a-b**). Modifying the ligand to possess ethylene rather than propylene arms afforded $[(^{\mathrm{Ph_2PEt}}\mathrm{PDI})\mathrm{Mn}]_2$, which mediates aldehyde hydrosilylation with TOFs of 9,900 min^{-1} (4,950 min^{-1} per Mn) at 0.005 mol% loading.[23] Turning off chelate redox activity did not hinder carbonyl hydrosilylation, as TOFs of 2,475 min^{-1} were observed using 0.02 mol% $(^{\mathrm{PyEt}}\mathrm{PDEA})\mathrm{Mn}$ (**Fig. 1b**).[24] Iron catalysts have also been well-studied for carbonyl hydrosilylation[13] and the most effective include $(\mathrm{Cp})\mathrm{Fe}(^{\mathrm{Mes}}\mathrm{Trz}^{\mathrm{nBu}})(\mathrm{CO})\mathrm{I}$ (240 min^{-1}, 0.1 mol%, 60 °C, where Trz is η^1-triazolylidene),[25] $[(\kappa^2\text{-}P,N)\mathrm{Fe(N(SiMe_3)_2)}]$ (393 min^{-1}, 0.015 mol%, rt),[26] and activated $(^{\mathrm{H}}\mathrm{BPI}^{\mathrm{Dipp,H}})\mathrm{FeBr_2}$ (4,190 min^{-1}, 0.01 mol%, rt, where BPI is iminobipyridine).[27]

Although a significant number of cobalt catalysts have been reported to mediate carbonyl hydrosilylation,[28–41] the most act-

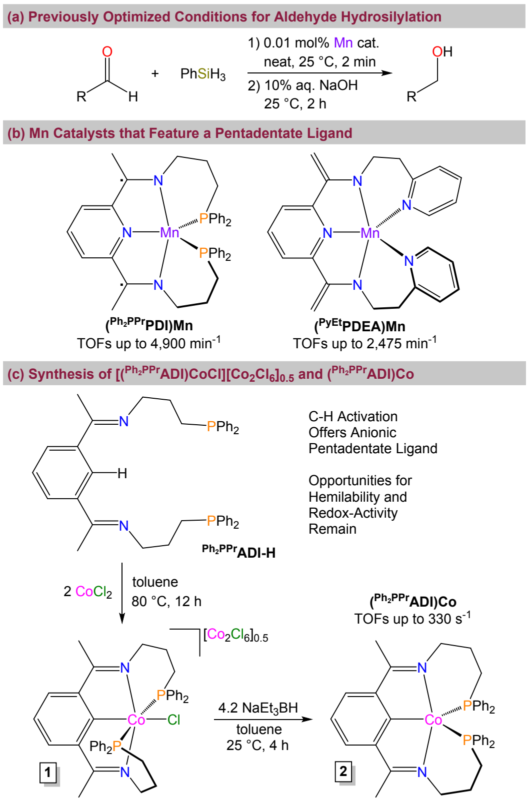

Figure 1. (a) The hydrosilylation of aldehydes to generate alcohols. (b) Efficient Mn catalysts that feature a pentadentate chelate. (c) The preparation of **1** and its reduction to **2**.

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ive by a large margin was described by Peters in 2015, (^{Ph}DPB^{Mes})Co(N$_2$) (49.5 min^{-1}, 1 mol%, rt, THF-d_8/THF, where DPB is PhB(o-^{i}Pr$_2$P-Ph)$_2$).[33,42] Since well-studied Co catalysts are two orders of magnitude less active than the most efficient Mn or Fe catalysts for this transformation, a few questions come to mind. Is cobalt simply a less effective first-row metal for carbonyl hydrosilylation? If not, is it possible to design a ligand scaffold that supports exceptional Co-based carbonyl hydrosilylation activity? Herein, the use of a pentadentate aryl diimine (ADI) chelate allows not only for the development of a highly-active Co carbonyl hydrosilylation catalyst, but also for the most efficient metal mediated trials reported to date.

Since ^{Ph_2PPr}PDI and ^{PyEt}PDEA effectively support base metal hydrosilylation catalysis,[21,24] we sought to prepare an anionic κ^5-variant that could effectively stabilize Co(I) while offering access to the metal via donor arm hemilability.[43,44] Accordingly, the Schiff-base condensation of 1,3-diacetylbenzene with 2 eq. of 3-(diphenylphosphino)-1-propanamine was performed at 80 °C, affording ^{Ph_2PPr}ADI-H (**Fig. 1c**) as an orange oil. Although this ligand features a C–H bond that must be activated to allow for κ^5-coordination, heating it to 80 °C in the presence of excess CoCl$_2$ resulted in a green, toluene-insoluble product. Interestingly, this compound was found to feature a broadened ^{1}H NMR spectrum, with resonances that are shifted slightly beyond the expected sweep width for a diamagnetic metal complex (14 to –2 ppm). Resonances for this product could not be observed by ^{13}C NMR spectroscopy, and the ^{31}P NMR spectrum exhibited a single broad resonance at 20.13 ppm, features that are consistent with paramagnetism.

To definitively identify this product, single crystals were obtained from a concentrated acetone solution at ambient temperature and X-ray diffraction analysis revealed the presence of [(^{Ph_2PPr}ADI)CoCl][Co$_2$Cl$_6$]$_{0.5}$ (**Fig. 1c**, **1,** 47% yield). The unit cell was found to possess a [CoCl$_3$]$^-$ moiety, representing one half of a [Co$_2$Cl$_6$]$^{2-}$ dianion. Interestingly, the cation of **1** features pseudo-octahedral geometry arising from chelate C–H activation, with C(10)–Co–Cl(1) and P(1)–Co(1)–P(2) angles of 177.77(8) and 170.14(3)°, respectively (**Fig. 2**, **a**). The relatively short Co(1)–C(10) bond length of 1.828(2) Å is consistent with the presence of a low-spin Co(III)[45] cation that exhibits broadened NMR resonances due to the presence of equimolar high-spin Co(II) tetrahedra. This assignment is also consistent with the magnetic susceptibility of **1**, which was determined to be 4.1 μ_B at 25 °C (i.e., one S = 3/2 Co center per molecular unit).

The addition of excess NaEt$_3$BH to **1** afforded a dark orange product identified as (^{Ph_2PPr}ADI)Co (**Fig. 1c**, **2**) in 45% yield. Diamagnetic **2** was found to exhibit a single ^{31}P NMR resonance at 33.87 ppm, indicating that the ligand phosphine functionalities are magnetically-equivalent and bound to cobalt. Single crystals of **2** were then obtained from an ether-layered toluene solution and X-ray diffraction analysis confirmed κ^5-chelate coordination (**Fig. 2, b**). Two pseudo trigonal bipyramidal molecules of **2** were located in the asymmetric unit, most easily distinguished by their P(1)–Co(1)–P(2) angles of 104.688(16)° (A) and 107.249(16)° (B). The imine distances determined for **2** [1.3220(19)–1.326(2) Å] are longer than those observed for **1** [1.303(3)–1.307(3) Å] while the backbone C–C bonds of **2** [1.428(3)–1.4398(19) Å] are contracted relative to the same distances of **1** [1.453(4)-1.461(4) Å]. These metrics suggest that **2** might possess a singly-reduced ADI chelate since PDI radical monoanions exhibit imine distances of 1.32 Å and backbone C–C distances of 1.44 Å.[46] Structures that feature κ^3-ADI coordination to transition metals, main group metals, and lanthanides have been reported;[47–50] however, ADI ligands have never been proposed to exhibit redox-activity.

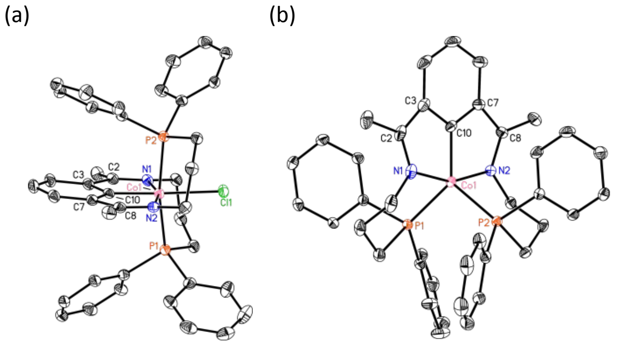


Figure 2. The solid-state structures of (a) the cationic component of **1** and (b) catalyst **2** (molecule A). Hydrogen atoms are omitted for clarity. For complete atom labeling and metrical parameters, see the Electronic Supplementary Information.

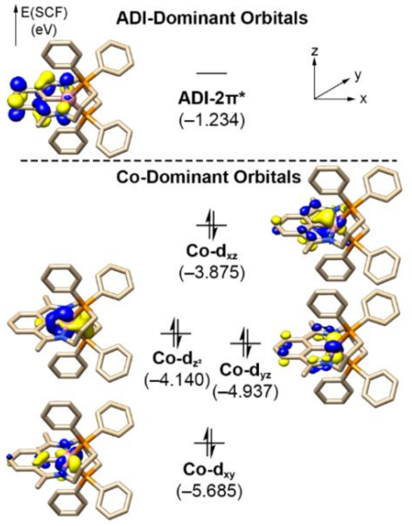


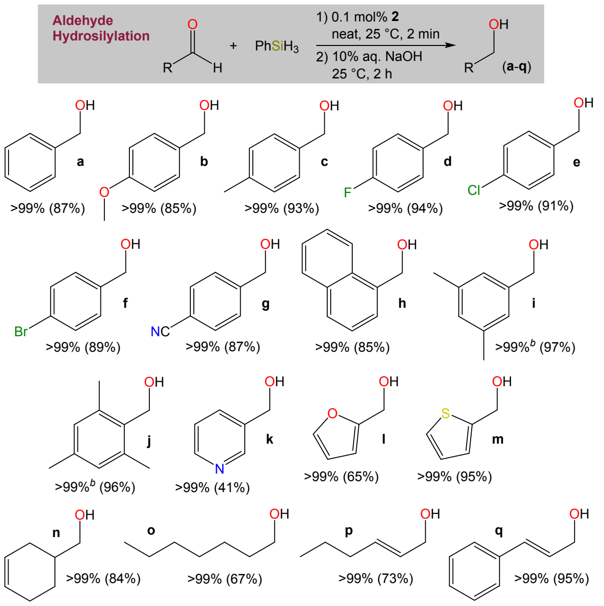
Figure 3. DFT-calculated frontier molecular orbitals of **2**. Orbital energies are given in eV. Contour isovalue of 0.05 e/Å^3 is used. Hydrogen atoms are omitted for clarity.

To gain additional insight, density functional theory (DFT) calculations were performed. The optimized structure of **2** was found to be a singlet that exhibits perfect C_2-symmetry, and the putative triplet and quintet states are 2.0 and 27.2 kcal/mol higher in energy, respectively. Notably, the imine distances of 1.322 Å are highly consistent with the experimental structure, while the backbone C–C distances of 1.447 Å are slightly elongated. The HOMO of **2** features a smaller amount of ADI-based electron density (20%, **Fig. 3**) than that from Co-d$_{xz}$ (42%, **Fig. 3**), indicating that these electrons are best assigned as metal-centered. Thus, the frontier molecular orbitals suggest that this complex has eight Co-based d-electrons and an unreduced ADI chelate. Attempts to optimize structures of **2** that have a Co(II) center with a one electron-reduced ADI chelate were unsuccessful. The anionic nature of ^{Ph_2PPr}ADI raises the frontier orbital energy, rendering this ligand far more difficult to reduce than neutral ^{Ph_2PPr}PDI.[51]

With **2** in hand, its ability to catalyze carbonyl hydrosilylation was explored. Adding an equimolar mixture of benzaldehyde and $PhSiH_3$ to 0.1 mol% **2** resulted in exotherm and complete reduction of the carbonyl within 2 min to generate a mixture of silyl ethers [this does not occur in the absence of **2**, or in the presence of AIBN,[23] Co(0), $CoCl_2$, or **1**]. Hydrolysis of the product mixture using aq. 10% NaOH solution afforded benzyl alcohol in 87% yield (**Table 1**, **a**). Greater than 99% benzaldehyde hydrosilylation was also achieved in the presence of 0.33 equiv. of $PhSiH_3$ after 2 min, indicating that all three Si-H equivalents of the reductant can be utilized. The use of other hydrosilanes provided mixed results; complete benzaldehyde hydrosilylation was observed after 2 min in the presence of Ph_2SiH_2 and 0.1 mol% **2**, while tertiary silanes proved ineffective (see Table S12).

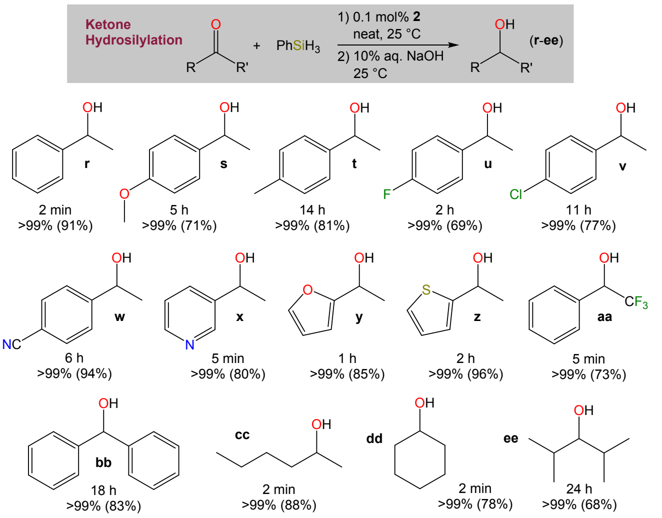
The hydrosilylation of *para*-substituted benzaldehydes proceeded seamlessly to generate the respective alcohols in high yield, and no difference in conversion was noted across a broad range of Hammett constants (**b-g**, $\sigma = -0.27$ to 0.66). Notably, **2** tolerated aryl halide and nitrile substitution without evidence for dehalogenation or nitrile hydrosilylation, respectively. This catalyst hydrosilylated 1-naphthaldehyde (**h**) within 2 min at 25 °C; however, benzaldehydes featuring two *meta*- or *ortho*-methyl groups (**i-j**) required 4 h to reach >99% conversion. Catalyst **2** was also found to reduce aldehydes in the presence of pyridine (**k**), furan (**l**), and thiophene (**m**) functionalities and it chemoselectively hydrosilylates aldehydes over alkenes (**n, p-q**). While low, our yield of pyridine-3-carbinol (**k**, 41%) is higher than observed for prior attempts to isolate this hydrosilylation product (21–27%).[22,23]

Table 1. Aldehyde hydrosilylation using 0.1 mol% **2**.[a]



[a]Substrates reach >99% conversion (based on ^{1}H NMR integration of aldehyde against silyl ether intermediates) in 2 min unless otherwise noted. Isolated yields of the alcohol provided in parenthesis. [b]Reaction conducted for 4 h.

Table 2. Ketone hydrosilylation using 0.1 mol% **2**.[a]



[a]Time required to reach >99% conversion, based on ^{1}H NMR integration of ketone against silyl ether intermediates. Isolated yields of the alcohol products are provided in parenthesis.

Similarly, conducting the equimolar hydrosilylation of acetophenone with $PhSiH_3$ and 0.1 mol% of **2** resulted in >99% conversion after 2 min and the isolation of 1-phenylethanol in 91% yield (**Table 2**, **r**). However, the inclusion of donating or withdrawing substituents significantly extended the time required to reach full conversion (from 2 h to 14 h, **s-w**). There is no apparent correlation between substituent constants and the time required to reach >99% conversion, a characteristic that was also observed for (^{Ph_2PPr}PDI)Mn.[21] As observed for aldehydes, pyridine, furan, and thiophene groups were tolerated (**x-z**). Catalyst **2** was found to reduce 2,2,2-trifluoroacetophene within 5 min (**aa**) and unhindered aliphatic ketones such as 2-hexanone (**cc**) and cyclohexanone (**dd**) within 2 min at 0.1 mol% loading.

Except for **i** and **j**, an average TOF of 495 min^{-1} was achieved for each aldehyde hydrosilylation trial in **Table 1**. Analogous TOFs were observed for **2**-based acetophenone (**r**), 2-hexanone (**cc**), and cyclohexanone hydrosilylation (**dd**). Although these activities are a full order of magnitude higher than those reported for (^{Ph}DPB^{Mes})Co(N_2) (49.5 min^{-1}),[33] efforts were made to observe even higher average TOFs by conducting reactions at a lower catalyst loading and ending them earlier. Adding equimolar benzaldehyde and phenylsilane to 0.01 mol% of **2** resulted in an exothermic reaction with >99% conversion noted after only 30 s. A TOF of 330 s^{-1} was noted for this trial, which is believed to be the highest reported for aldehyde hydrosilylation. To see if this level of activity was limited to aldehydes, the hydrosilylation of acetophenone was repeated under the same conditions, resulting in 98% conversion (TOF = 327 s^{-1}). Finally, conducting cyclohexanone hydrosilylation using 0.01 mol% of **2** allowed for complete conversion after 30 s (TOF = 330 s^{-1}), representing the highest activity ever noted for a ketone hydrosilylation trial. Maximum aldehyde and ketone hydrosilylation turnover numbers (TONs) for **2** were determined by adding 10,000 equiv. of $PhSiH_3$ and either benzaldehyde or cyclohexanone every 15 min until 40,000 equiv. of each had been added. Based on overall conversion, TONs of 19,000 and 17,600 were observed for **2**-mediated benzaldehyde and cyclohexanone hydrosilylation, respectively.

In summary, it has been found that the addition of ^{Ph_2PPr}ADI-H to $CoCl_2$ results in C–H activation and formation of the mixed-valent precursor, $[(^{Ph_2PPr}ADI)CoCl][Co_2Cl_6]_{0.5}$ (**1**). Reduction of this complex using an excess of $NaEt_3BH$ afforded the 5-coordinate complex, (^{Ph_2PPr}ADI)Co (**2**), which features a redox-innocent ADI chelate. This complex was then used to hydrosilylate 15 different aldehydes at 0.1 mol% loading in 2 min under neat conditions. The complete hydrosilylation of 14 different ketones was noted, requiring between 2 min and 24 h to reach full conversion. Lowering the catalyst loading to 0.01 mol% allowed for aldehyde and ketone hydrosilylation TOFs of up to 330 s^{-1}.

The manuscript was written and approved by all authors. A.S. and R.J.T. retain rights to **1** and **2** through U.S. Patent Application No. 63/249,151 (Sept. 2021). We thank the Institute for Basic Science (IBS-R10-A1) in Korea for financial support. This material is based upon work supported by the National Science Foundation under Grant Nos. 1651686 and 2154359.

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