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Tripodal N,P Mixed-Donor Ligands and Their Cobalt Complexes: Efficient Catalysts for Acceptorless Dehydrogenation of Secondary Alcohols

Shi Xu,[†,§] Latifah M. Alhthlol,[†,∥,§] Keshav Paudel,[†,‡] Eric Reinheimer,[⊥] David L. Tyer,[†] Daniela K. Taylor,[†] Amberlynn M. Smith,[†] Jonathan Holzmann,[†] Edgar Lozano,[†] and Keying Ding*[,†,‡]

[†]Department of Chemistry and [‡]Molecular Biosciences Program, Middle Tennessee State University (MTSU), Murfreesboro, Tennessee 37132, United States

[⊥]Rigaku Americas, The Woodlands, Texas 77381, United States

[∥]King Saud bin Abdulaziz University for Health Sciences, Al Mubarraz, Alahsa 36428, Saudi Arabia

Supporting Information

ABSTRACT: A new tetradentate tripodal ligand, $^{iPr}PPPN^{H}Py^{Me}$, and the cobalt complexes were synthesized and characterized. The well-defined cobalt complexes efficiently catalyzed acceptorless dehydrogenation of secondary alcohols into ketones.

Catalytic acceptorless dehydrogenation of alcohols is an atom-economical and environmentally friendly method for the synthesis of carbonyl compounds and their derivatives without any oxidants and hydrogen acceptors. This method takes advantage of inexpensive and readily available alcohols that can be obtained from biomass resources and fermentation. Because valuable hydrogen gas is the only byproduct from alcohol dehydrogenation, alcohols can serve as important hydrogen carriers for energy-storage applications. Despite the great importance of this reaction, examples of homogeneous catalytic acceptorless dehydrogenation of alcohols are dominated by rare, expensive, and toxic precious metal catalysts including rhodium,[1] ruthenium,[2] iridium,[3] and osmium.[4] With increasing concerns on natural resource depletion and climate change, it is more desirable to replace precious metal catalysts with ones based on earth-abundant and less-toxic metals. However, because alcohol dehydrogenation is a thermodynamically uphill process, this transformation is still challenging for base-metal catalysts and such examples are rare. Zhang and Hanson reported a cobalt precatalyst supported by a bis(phosphino)amine (PNP) pincer ligand for the dehydrogenation of secondary alcohols. Further mechanistic study suggests a cobalt(I/III) cycle and metal−ligand cooperativity (MLC) is not crucial in this reaction.[5] Jones and co-workers developed highly efficient PNP pincer-ligand-stabilized iron catalysts for the reversible dehydrogenation−hydrogenation of alcohols and ketones.[6] Jones and co-workers also described a $T_P'Ni(Q^R)$ (T_p' = tris(3,5-dimethylpyrazolyl)-borate; Q = quinolinate; R = CF_3) catalyst for dehydrogenation−hydrogenation of alcohols, aldehydes, and ketones.[7] An MLC mechanism is proposed to operate in both iron and nickel catalytic systems. The Hong group reported an iron(III) acetylacetonate/1,10-phenathroline system for the dehydrogenation of secondary benzylic alcohols, despite the fact that alkyl alcohols do not work with this method.[8] Nakazawa and co-workers presented an iron catalytic system of $CpFe(CO)_2Cl_2$ (Cp = cyclopentadienyl) and a base for the dehydrogenation of 2-pyridylmethanol derivatives.[9] Dehydrogenative coupling by cobalt catalysts have recently been reported.[5a,10]

The ligand design plays a key role for such reactions mediated by base metal catalysts. In our efforts to develop first-row transition-metal catalysts, we are particularly interested in the tetradentate tripodal ligand for the following reasons: (1) It may provide extra stability to the reactive intermediates by enforcing five or six coordination on the metal center. (2) Because of the different coordination environments, metal complexes by such ligands may have catalytic reactivities very different from those of tridentate pincer ligand systems, which currently dominate the dehydrogenation of alcohols. Herein, we report an isopropyl-substituted tris(phosphino)pyridine ligand derivative (abbreviated as $^{iPr}PPPN^{H}Py^{Me}$, **1**), which is featured with an N−H linker connecting the pyridine ring and a phosphino binding moiety. Its cobalt complexes were synthesized and tested as efficient precatalysts for the acceptorless and oxidant-free dehydrogenation of secondary alcohols to afford ketones. To the best of our knowledge, it is for the first time that base transition-metal complexes supported by the tetradentate tripodal ligand are reported for the acceptorless dehydrogenation of alcohols.

The three-step ligand synthesis route from available starting materials is described in Scheme 1a. In the initial step, 1,2-dibromobenzene is activated with 1 equiv of *n*-butyllithium via lithium−halogen exchange and subsequently quenched with diisopropylchlorophosphine to give 2-(diisopropylphosphino)-phenyl bromide in 68% yield.[11] Next, 2 equiv of 2-(diisopropylphosphino)phenyl bromide reacts with 1 equiv of *n*-butyllithium, followed by the addition of phosphorus trichloride, to afford bis[2-(diisopropylphosphinophenyl)]-chlorophosphine in a yield of 52%.[12] In the final step, 2-amino-6-methylpyridine is activated with triethylamine and allowed to react with chlorophosphine to form **1** in good yield (81%). Detailed synthesis and characterization of **1** are available in the Supporting Information (SI). The $^{31}P\{^{1}H\}$ NMR spectrum of **1**

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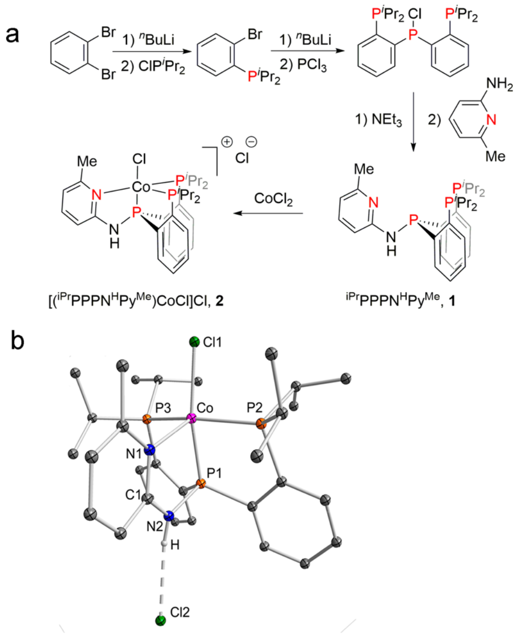
Inorg. Chem. XXXX, XXX, XXX−XXX

Scheme 1. (a) Synthesis of Ligand 1 and Complex 2 and (b) X-ray Crystal Structure of 2[a]



[a]50% probability of thermal ellipsoids; H atoms are omitted except for that of the N−H linker.

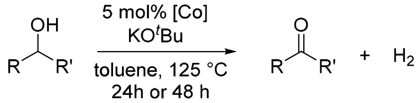
contains three sharp resonances at 298 K: a doublet of doublets at 15.0 ppm is assigned to the central phosphine, and two doublets at 3.1 ppm are assigned to the terminal phosphines in a 1:1 ratio, with a $^{31}P-^{31}P$ coupling constant of 168 Hz (Figure S2).

The treatment of **1** with $CoCl_2$ in tetrahydrofuran afforded $[(^{iPr}PPPN^{H}Py^{Me})CoCl]Cl$ (**2**) as a dark-red powder in 86% isolated yield. As expected, this species is paramagnetic, displaying broad signals in its ^{1}H NMR spectrum. The magnetic moment, determined by Evan's method in solution, was found to be 1.9 μ_B in CD_2Cl_2, consistent with a d_7 metal center with one unpaired electron with a $S = {}^{1}/_{2}$ ground state. To obtain a solid-state molecular structure, **2** was crystallized as dark-red needles by vapor diffusion of diethyl ether into a concentrated dichloromethane solution. The X-ray structure[13] revealed a distorted trigonal-bipyramidal geometry on the Co center, with the P1 and Cl1 atoms in the axial positions and the terminal phosphines (P2 and P3) and pyridine N (N1) donor in the equatorial positions. The second Cl atom (Cl2) is considered to be in the outer coordination sphere, linking with the N−H group through hydrogen bonding. A space-filling model of **2** revealed that the chloride ligand (Cl1) is nestled within a binding pocket comprised of the phosphine diisopropyl substituents and the 2-methyl substituent on the pyridine group (Figure S10).

Interestingly, the IR spectrum of **2** displays two intense N−H stretching bands with an approximate 1:1 ratio at 3570 and 3393 cm^{-1}, respectively (Figure S7). It is known that hydrogen bonding between N−H and halides will result in a decrease of the N−H stretching frequencies.[14] We postulate that **2** may have two conformers coexisting in the solid state, and the peak at 3393 cm^{-1} is tentatively assigned to the N−H stretch for the conformer with more direct N−H···Cl interaction, while 3570 cm^{-1} likely belongs to the other conformer that lacks hydrogen-bonding interaction.

Then we explored the reactivity of **2** for the dehydrogenation of secondary alcohols. After the reaction conditions were optimized (Table S2), we examined the reaction scope with a range of secondary alcohols, as shown in Table 1. Aromatic secondary alcohols with electron-donating groups such as methoxy (MeO) and methyl (Me) at the para position reacted smoothly to afford the corresponding ketones with excellent yields (entries 1 and 2). 1-Phenylethanol required a longer reaction time (48 h) to attain a comparable yield (entry 3). Substrates with electron-withdrawing groups like fluorine (F) and trifluoromethane (CF_3) at the para positions showed diminished activities (entries 4 and 5). This result is in contrast to Jones' study on the nickel-based system, where secondary alcohols bearing electron-donating groups react more slowly than those with electron-withdrawing substituents.[7] To our delight, the dehydrogenation of sterically hindered ortho-substituted 1-(2-methylphenyl)ethanol gave a 60% yield (entry 7). Cyclic alcohols 1,2,3,4-tetrahydro-1-naphthol and cycloheptanol were dehydrogenated at the same conditions, affording α-tetralone and cycloheptanone in 94% and 72% yield, respectively (entries 11 and 12). The conversion of an aliphatic alcohol 2-octanol was 43% after 24 h with 2-octanone as the only product (entry 13). Interestingly, when the reaction time was extended to 48 h, despite a higher conversion (85%), gas chromatography−mass spectrometry (GC−MS) analysis revealed mixed products of 2-octanone and 9-methylpentadecan-7-one with an approximate ratio of 1:2.5 (entry 13d). An investigation of the selectivity is currently underway. When benzyl alcohol as an example of the primary alcohol was tested, instead of benzyl aldehyde, the product was found to be exclusive benzyl benzoate, an ester that is probably generated through dehydrogenative alcohol homocouplings (entry 14).

Table 1. Dehydrogenation of Secondary Alcohols to Ketones[a]



entry	R	R′	time (h)	conv[b] (%)	yield[b] (%)
1	*p*-MeOPh	CH_3	24	94	92, 87,[c] 93[d]
2	*p*-MePh	CH_3	24	100	95
3	Ph	CH_3	48	89	84
4	*p*-FPh	CH_3	48	60	57
5	*p*-CF_3Ph	CH_3	48	43	40
6	*m*-MeOPh	CH_3	24	90	86
7	*o*-MePh	CH_3	48	64	60
8	Ph	Ph	24	75	72
9	2-Naph	CH_3	48	81	80
10	Ph	C_2H_5	48	78	75
11	1,2,3,4-tetrahydro-1-naphthol		24	100	94
12[e]	$-(CH_2)_6-$		48	73	72
13[e]	*n*-C_6H_{13}	CH_3	24	43, 85[f]	43, 12[f]
14	Ph	H	24	99	99[g]

[a]Reaction conditions: alcohol (0.25 mmol), cobalt catalyst 2 (8.2 mg, 5 mol %), KOtBu (4.2 mg, 15 mol %), toluene (1.5 mL), 125 °C. [b]Determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard. [c]Isolated yield (1 mmol scale). [d]Yield from the mercury test. [e]Determined by GC−MS. [f]The reaction ran for 48 h. [g]Benzyl benzoate was formed (in benzene).

To understand the catalyst activation process and reaction mechanism, we performed an initial mechanistic study. The

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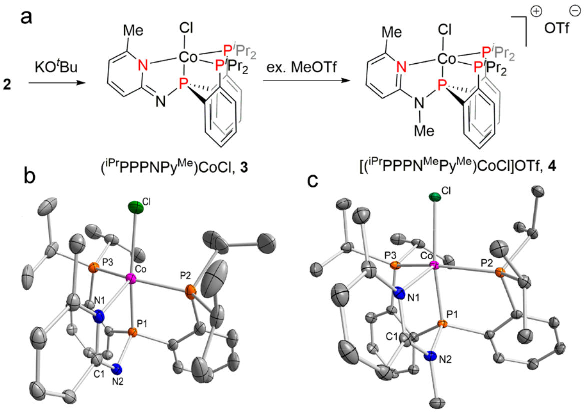
addition of **2** and 1 equiv of KOtBu in toluene at room temperature elicits an immediate white precipitation of potassium chloride, concurrent with the formation of a new cobalt complex [$(^{iPr}PPPNPy^{Me})CoCl$ (**3**)] in good yield (81%; Scheme 2a). **3** was characterized by ^1H NMR and IR spectroscopy, elemental analysis, and X-ray diffraction. The magnetic moment (1.9 μ_B) measured by Evan's method in C_6D_6 suggests a low-spin Co^{II} center. Notably, the IR spectrum of **3** shows no N−H stretching bands at ca. 3500−3300 cm^{-1}, indicating N−H deprotonation. The solid-state structure of **3**, as presented in Scheme 2b, reveals the same coordination geometry around the Co atom as that in **2**.[13] The main difference arises from the lengthening of the N1−C1 distance (Δd = 0.04 Å), concomitant with the shortening of the N2−C1 distance (Δd = 0.04 Å). This change is attributed to dearomatization of the pyridine ring in **3**. In direct contrast to those in **2**, N1−C1 is labeled as a N−C single bond, while N2−C1 is a N═C double bond in **3**. Complex **3** with 1 equiv of KOtBu demonstrates reactivity similar to that of **2** (93% yield of 4′-methoxyacetophenone; see the SI). No conversion was observed in the absence of base. These observations suggest that **3** is likely involved in the generation of the actual catalyst that may not require a base as the cocatalyst because a base is only needed for precatalyst activation via dehalogenation.[15,16]

Scheme 2. (a) Syntheses of Complexes 3 and 4, (b) Solid-State Structure of 3, and (c) Solid-State Structure of 4[a]



[a] 50% probability of thermal ellipsoids; the triflate anion in **4** and H atoms are omitted.

To investigate the possible roles of MLC originating from the N−H linker, an N−Me-substituted cobalt complex, $[(^{iPr}PPPN^{Me}Py^{Me})CoCl]OTf$ (**4**), was synthesized by reacting **3** with an excess amount of MeOTf with a good yield of 72% (Scheme 2a). The crystal structure of **4** confirmed the installation of the methyl group (Scheme 2c) on the N atom.[13] Similar to **2** and **3**, complex **4** features a Co center in a distorted trigonal-bipyramidal coordination sphere with a triflate counteranion. The catalytic activity of **4** was compared with those of **2** and **3**. The highest yield of 4′-methoxyacetophenone is 69% for **4** with various base loadings, which is not substantially lower than that of **2** or **3** (Table S3). Because the MLC pathway is inaccessible for complex **4**, our results suggest that a non-MLC pathway is catalytically viable.

It is confirmed that the byproduct is hydrogen gas (see the SI). To pinpoint whether catalysis is homogeneous or heterogeneous, we tested the catalytic reaction in the presence of mercury (100 equiv with respect to **2**) and observed no detrimental effect on the yield (Table 1, entry 1g), suggesting a homogeneous catalytic system.

In conclusion, this study describes the development of a tetradentate tripodal $^{iPr}PPPN^{H}Py^{Me}$ ligand and the cobalt complexes as precatalysts for the efficient acceptorless dehydrogenation of secondary alcohols to afford ketones. The air-stable precatalysts can be activated by a base via dehalogenation, providing a convenient way to access catalytically active species.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b00043.

Experimental details, additional figures, and other results (PDF)

Accession Codes

CCDC 1814791−1814793 contain the supplementary crystallographic data for this paper. 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.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: keying.ding@MTSU.edu.

ORCID

Keying Ding: 0000-0002-7367-129X

Author Contributions

[§] These two coauthors contributed equally to the work.

Notes

The authors declare no competing financial interest.

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(13) See Table S1 for the metrical parameters for the crystal structures of **2**−**4**.

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(15) For complex **2** with two Cl atoms, 3 equiv of KOtBu was required to achieve the optimized results (92% yield of 4′-methoxyacetophenone). Only 25% yield was recorded when 2 equiv of KOtBu was used. One possible explanation is that excess halide salt in the system may have negative effects on alcohol dehydrogenation because of the formation of inactive species. Thus, a slight excess of base is required to reactivate the catalyst. See the following example: Nguyen, D. H.; Trivelli, X.; Capet, F.; Paul, J.-F.; Dumeignil, F.; Gauvin, R. M. Manganese Pincer Complexes for the Base-Free, Acceptorless Dehydrogenative Coupling of Alcohols to Esters: Development, Scope, and Understanding. *ACS Catal.* **2017**, *7*, 2022−2032.

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