

# A Highly Active and Easily Accessible Cobalt Catalyst for Selective Hydrogenation of C=O Bonds

Sina Rösler, Johannes Obenauf, and Rhett Kempe\*

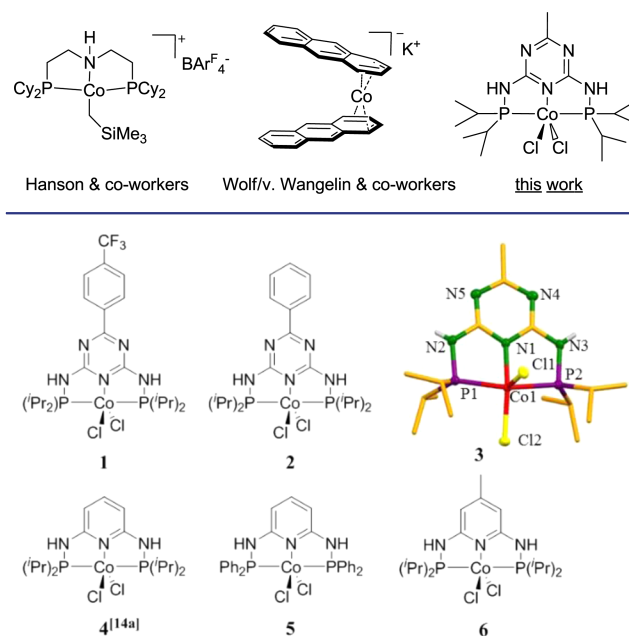
Anorganische Chemie II—Katalysatordesign, Universität Bayreuth, 95440 Bayreuth, Germany

**S** Supporting Information

**ABSTRACT:** The substitution of high-price noble metals such as Ir, Ru, Rh, Pd, and Pt by earth-abundant, inexpensive metals like Co is an attractive goal in (homogeneous) catalysis. Only two examples of Co catalysts, showing efficient C=O bond hydrogenation rates, are described. Here, we report on a novel, easy-to-synthesize Co catalyst family. Catalyst activation takes place via addition of 2 equiv of a metal base to the cobalt dichlorido precatalysts. Aldehydes and ketones of different types (dialkyl, aryl-alkyl, diaryl) are hydrogenated quantitatively under mild conditions partially with catalyst loadings as low as 0.25 mol%. A comparison of the most active Co catalyst with an Ir catalyst stabilized by the same ligand indicates the superiority of Co. Unique selectivity toward C=O bonds in the presence of C=C bonds has been observed. This selectivity is opposite to that of existing Co catalysts and surprising because of the directing influence of a hydroxyl group in C=C bond hydrogenation.

Homogeneous hydrogenation with molecular hydrogen is a key step in the industrial synthesis of fine chemicals. Typically, high-price noble metals such as Ir, Ru, Rh, Pd, and Pt play the leading role as catalytically active sites in hydrogenation catalysts.<sup>1</sup> Substitution of these metals by inexpensive, earth-abundant metals like Co would give advantages in terms of costs and sustainability. Furthermore, the unique electronic structural properties of such base metals may allow the observation of unusual activity/selectivity profiles. Despite these and other perspectives, the development of well-defined homogeneous Co hydrogenation catalysts has progressed slowly, especially with regard to the reduction of C=O bonds. However, with the implementation of rational ligand design, a few new Co catalysts for homogeneous hydrogenation have been disclosed in recent years. Hydrogenation of olefins with Co complexes has been described by Budzelaar and co-workers<sup>2</sup> as well as by Chirik and co-workers.<sup>3</sup> A bis-(phosphino)borylcobalt catalyst (for which a boryl–metal cooperativity was observed) has been applied by Peters and co-workers in C=C bond hydrogenation.<sup>4</sup> Very recently, Milstein and co-workers reported on the Co-complex-catalyzed hydrogenation of esters.<sup>5</sup> To the best of our knowledge, homogeneous Co catalysts for efficient C=O reduction with molecular hydrogen are only described for two examples.<sup>6</sup> Hanson and co-workers reported a bis[2-(dicyclohexylphosphino)ethyl]amine-stabilized cobalt(II)–alkyl catalyst

## Scheme 1. Known Homogenous Cobalt Catalysts for C=O Bond Hydrogenation (Left and Middle)



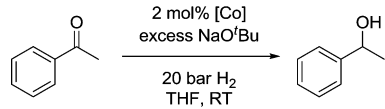
**Figure 1.** Synthesized PN<sub>3-5</sub>P-stabilized Co(II) chlorido complexes and molecular structure of 3 with 50% probability of thermal ellipsoids. H-atoms (except for the two N–H groups) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Co1–P1 2.220(1); Co1–P2 2.220(1); Co1–Cl1 2.437(1); Co1–Cl2 2.238(1); Co1–N1 1.925(4); P1–Co1–P2 167.04(6); N1–Co1–Cl1 93.0(1); N1–Co1–Cl2 160.3(1); N2–P1–Co1 98.8(2); N3–P2–Co1 99.1(2); C1–N2–P2 119.4(4); C3–N3–P2 118.6(4).

(Scheme 1, left) for C=C, C=N, and C=O reduction.<sup>7</sup> The precatalyst is activated with 1 equiv of H[BAR<sup>F</sup><sub>4</sub>](Et<sub>2</sub>O)<sub>2</sub> (Brookhart's acid,<sup>8</sup> [BAR<sup>F</sup><sub>4</sub>]<sup>−</sup> = tetrakis[(3,5-trifluoromethyl)phenyl]borate) and reduces C=O bonds involving 2.0 mol% catalyst loading within 1–4 bar H<sub>2</sub> pressure at room temperature. Notably, dehydrogenation of alcohols has been observed with this catalyst, too.<sup>9</sup> A heteroatom-free arene-cobalt-ate catalyst for C=C, C=O, and C=N hydrogenation was developed by the group of Wolf and von Wangelin (Scheme 1, middle).<sup>10</sup> Carbonyl compounds are reduced in good to excellent yields with 5.0 mol% of the catalyst, 10 bar H<sub>2</sub> pressure at 60 °C, without previous activation of the catalyst.

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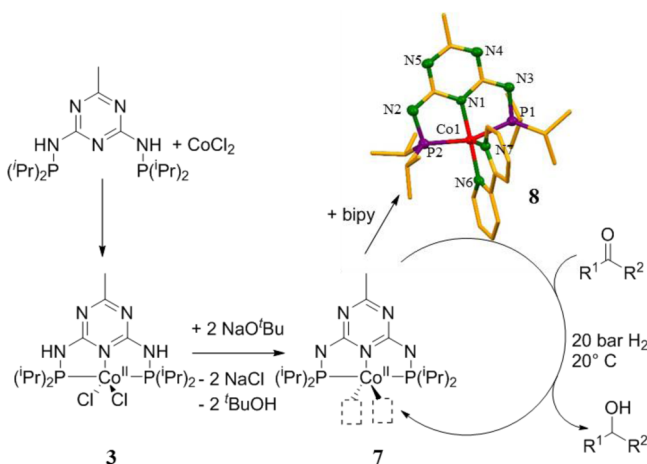
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**Table 1. Hydrogenation of Acetophenone with Several Cobalt(II) Precatalysts (See Figure 1)<sup>a</sup>**



entry	precatalyst	yield <sup>b</sup> [%]
1	1	7
2	2	30
3	3	>99
4	4	28
5	5	0
6	6	23
6	CoCl <sub>2</sub>	0

<sup>a</sup>Reaction conditions: acetophenone (3.0 mmol), 2.0 mol% Co, NaO<sup>t</sup>Bu (13 mg, 4.4 mol%), 2 mL of THF, 20 bar H<sub>2</sub>, room temperature, 24 h. <sup>b</sup>Determined via GC with dodecane as internal standard.



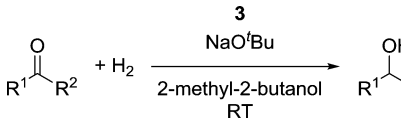
**Figure 2.** Synthesis and activation of **3** as well as trapping of the activated catalyst with bipyridine (**8**). The molecular structure of **8** is displayed with 50% probability of thermal ellipsoids. H-atoms are omitted for clarity. Relevant bond lengths [Å] and angles [°]: Co1–P1 2.214(1); Co1–P2 2.223(1); Co1–N1 1.915(3); Co1–N6 1.930(3); Co1–N7 2.016(3); P1–Co1–P2 158.18(5); N1–Co1–N6 178.0(1); N1–Co1–N7 97.7(1); N2–P2–Co1 102.3(1); N3–P1–Co1 105.1(1); P1–N3–C3 112.0(3); P2–N2–C1 113.3(3).

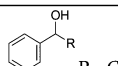
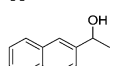
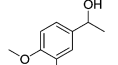
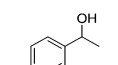
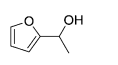
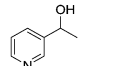
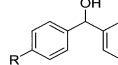
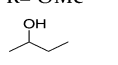
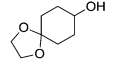
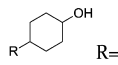
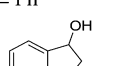
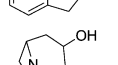
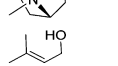
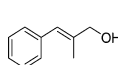
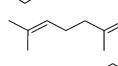
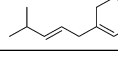
The above-mentioned Co catalysts, able to mediate C=O bond hydrogenation (Scheme 1), represent impressive progress in hydrogenation chemistry. Unfortunately, they also suffer from disadvantages like labile ligand coordination, expensive activation agents, and restricted capabilities for ligand modifications.

We recently introduced (triazine-based) PN<sub>3–5</sub>P-Ir complexes (an example of a Co complex is shown in Scheme 1, right) as highly efficient homogeneous catalysts for acceptorless dehydrogenative condensation reactions.<sup>11</sup> Haupt and co-workers introduced such PN<sub>3</sub>P ligands,<sup>12</sup> and Kirchner and co-workers demonstrated the broad applicability of the ligand class.<sup>13</sup> Reports on Co complexes stabilized by such ligands are rare.<sup>13e,14,15</sup>

Herein we report on a novel, easy-to-synthesize, and simple-to-activate homogeneous cobalt C=O bond hydrogenation catalyst family (Scheme 1, right). The precatalysts can be synthesized quantitatively up to multigram scale.<sup>16</sup> They are air stable for a period of a few months as a crystalline material.

**Table 2. Hydrogenation of Aryl-alkyl, Diaryl, and Aliphatic Carbonyl Compounds<sup>a</sup>**



Entry	Product	Cat. loading [mol%]	Yield <sup>[b]</sup> [%]
1	 R = CH <sub>3</sub>	0.25	>99
2	R = CH <sub>2</sub> CH <sub>3</sub>	0.5	>99
3	R = (CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>	0.5	>99
4	R = H	0.5	>99
5		0.5	>99
6		0.25	>99
7	 R = F	1.0	98 (94 <sup>[c]</sup> )
8	R = Cl	1.0	>99
9	R = Br	2.0	64
10		3.0	91
11		3.0	95
12	 R = H	0.25	>99
13	R = Me	0.5	>99 (97 <sup>[c]</sup> )
14	R = OMe	0.5	97
15		0.5	98
16		0.5	>99
17	 R = H	0.25	>99
18	R = Ph	0.5	>99 (93 <sup>[c]</sup> )
19		0.5	>99
20		1.0	>99 (92 <sup>[c]</sup> )
21		0.5	>99
22		1.0	>99 (97 <sup>[c]</sup> )
23		0.5	>99
24		0.5	>99 (95 <sup>[c]</sup> )

<sup>a</sup>Reaction conditions: 3.0 mmol of carbonyl compound, 2.0 mL of 2-methyl-2-butanol, NaO<sup>t</sup>Bu (2.0 equiv with respect to the precatalyst), 20 °C, 24 h, 20 bar H<sub>2</sub>, precatalyst **3**. <sup>b</sup>Determined via GC with dodecane as internal standard. <sup>c</sup>Isolated yield.

Activation of the precatalysts proceeds via salt elimination by adding 2 equiv of a base and is based on the ability of the used PN<sub>3–5</sub>P ligand class to act as neutral, monoanionic, or dianionic

ligand. The modularly assembled structure of the chosen ligands allows the employment of catalyst libraries for activity screenings. Selective hydrogenation of C=O bonds in the presence of C=C bonds was observed despite (i) the directing influence of a hydroxyl group in olefin hydrogenation for Co catalysts<sup>3a</sup> and (ii) inverse selectivity patterns as reported for the Hanson catalyst.<sup>7c</sup>

The precatalyst synthesis is performed by addition of an equimolar solution of the ligand to a suspension of anhydrous CoCl<sub>2</sub> in THF. The desired precatalysts precipitate as red crystalline solids in quantitative yields. Complexes were characterized by X-ray diffraction (XRD) analysis, elemental analysis, IR spectroscopy, and magnetic measurements. All complexes show paramagnetic behavior and an effective magnetic moment between 2.2 and 2.3  $\mu_B$  (studied over a temperature range from 300 to 50 K using a SQUID magnetometer).<sup>17</sup> The molecular structure of **3** is shown in Figure 1. XRD indicates an pentacoordinated Co(II) complex with a slightly distorted square pyramidal coordination. The neutral PN<sub>3</sub>P ligand is coordinated to the Co center in the typical tridentate mode, with a P1–Co1–P2 angle of 167.04(6)°. Both N–H hydrogen atoms could be located in the difference electron density map. Selected bond distances and angles are given in the caption of Figure 1.

The catalytic activity of complexes **1–6** (Figure 1, Table 1) and the metal precursor CoCl<sub>2</sub> was investigated in the hydrogenation of acetophenone (3.0 mmol) using 2.0 mol% precatalyst in THF under 20 bar hydrogen pressure and room temperature. The precatalysts were initially activated with a slight excess (4.4 mol%) of NaO<sup>t</sup>Bu (<sup>t</sup>Bu = *tert*-butyl). Complex **3** was identified as the most active precatalyst. Comparison of **3** and **6** reveals the beneficial effect of the triazine ring. Besides the altered basicity of the coordinating N-atom, an explanation can be the stabilization of the proton shuttle chain via hydrogen-bonding with the N-atoms of the triazine moiety of the PN<sub>3</sub>P ligand backbone.<sup>18</sup>

To understand the role of the base in the activation process, a base-loading screening was carried out (Supporting Information [SI]). A 2 equiv amount of the metal base NaO<sup>t</sup>Bu is necessary to generate a catalytically active complex. The exact structure of this complex is not fully clear yet. To gain insight, the activated species was trapped with 1 equiv of bipyridine. The resulting red-orange complex (**8**, Figure 2) was analyzed by XRD. Both chlorido ligands as well as both N–H protons were salt-eliminated by the base. The PN<sub>3</sub>P ligand acts as a dianionic ligand, coordinating the Co again in the pincer-like tridentate manner with a P1–Co1–P2 angle of 158.18(5)°. The oxidation state of the Co(II) center is not affected by the activation procedure. Complex **8** has an effective magnetic moment of 1.9  $\mu_B$ , expected for a Co(II) low-spin complex in a pentacoordinated environment.

Next, we became interested in comparing the activity of the catalyst based on **3** with an Ir complex stabilized by the same PN<sub>3</sub>P ligand (Figure S2, SI). Under base-free conditions, the iridium catalyst shows no remarkable conversion. With Na-to-Ir ratios of 1 and 2 (Figure S2, green and blue graphs, respectively), a faster conversion is observed. It increases at higher base concentration and is still slower than that with Co (red graphs). Such an activating effect of a metal base is known for other iridium C=O bond hydrogenation catalysts.<sup>19</sup> At very high base loadings (Na/Ir = 10, Figure S2), the Ir catalyst is faster. NaO<sup>t</sup>Bu addition beyond the 2 equiv needed for its activation is not beneficial for **3**. The comparison indicates that

different mechanistic pathways seem relevant and the Co catalyst is superior under base free-conditions or at low base concentrations including identical conditions. Base-free conditions are advantageous since metal bases like NaO<sup>t</sup>Bu can mediate side reactions of the educts, like aldol-type condensations.

Finally, we optimized the hydrogenation reaction conditions and explored the substrate scope of our Co catalyst. For details, please see the SI. To our delight, a broad product scope was observed. Aryl-alkyl ketones (Table 2, entries 1–11), diaryl ketones (Table 2, entries 12–14), and aliphatic ketones (Table 2, entries 15–20) were reduced to the corresponding alcohols in quantitative yields (except entry 9), tolerating diverse functional groups. In most cases, the catalyst loading amount was 0.25 or 0.5 mol%. In the case of unsaturated carbonyl compounds (Table 2, entries 21–24), a distinct selectivity toward the C=O bond was observed. No directing effect of a (generated) hydroxyl group, as described by Chirik and co-workers,<sup>3a</sup> is noticed. The selectivity we observe is inverse to that of the Hanson catalyst, for which selective hydrogenation of the C=C bond in 2-methyl-5-(prop-1-en-2-yl)cyclohexanone was reported<sup>7c</sup> and for which a bifunctional mechanism has been proposed.<sup>7a,20</sup>

In conclusion, we report on an easily accessible, inexpensive to activate, and highly active Co catalyst for the homogeneous hydrogenation of C=O bonds. The chosen PN<sub>3–5</sub>P ligand family allows an easy fine-tuning or optimizing of the catalyst performance, and its flexibility with regard to the protonation or charge allows an efficient generation of the catalytically active species. The best catalyst operates under mild conditions and addresses a broad substrate scope covering dialkyl, diaryl, and aryl-alkyl ketones. The hydrogenation of C=O bonds in the presence of C=C bonds can proceed highly selectively. Further investigations are focused on better understanding the catalytically active species, the development of enantioselective PN<sub>3–5</sub>P–Co hydrogenation catalysts, and other catalytic applications of the Co catalyst family described here.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Additional experimental procedures; spectroscopic and crystallographic data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b04349.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*kempe@uni-bayreuth.de

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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