JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Subscriber access provided by NEW YORK UNIV

Communication

A highly active and easy accessible cobalt catalyst for the selective hydrogenation of C=O bonds

Sina Rösler, Johannes Obenauf, and Rhett Kempe

J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/jacs.5b04349 • Publication Date (Web): 16 Jun 2015

Downloaded from http://pubs.acs.org on June 17, 2015

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

ACS Publications
High quality. High impact.

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

A highly active and easy accessible cobalt catalyst for the selective hydrogenation of C=O bonds

Sina Rösler,§ Johannes Obenauf,§ Rhett Kempe§*

§ Anorganische Chemie II - Katalysatordesign, Universität Bayreuth, 95440 Bayreuth, Germany

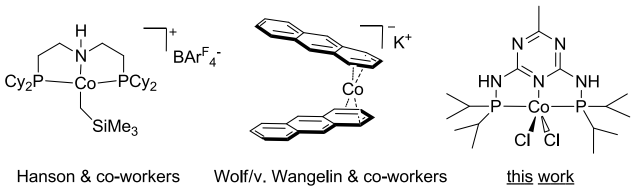
Supporting Information Placeholder

ABSTRACT: The substitution of highly priced noble metals such as Ir, Ru, Rh, Pd, and Pt by earth abundant, inexpensive metals like Co is an attractive goal in (homogenous) catalysis. Only two examples of cobalt catalysts, showing efficient C=O bond hydrogenation rates are described. Here, we report on a novel, easy to synthesize cobalt catalyst family. Catalyst activation takes place via addition of two equivalents of a metal base to the Co dichlorido pre-catalysts. 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 the Ir catalyst stabilized by the same ligand indicates the superiority of cobalt. A unique selectivity towards C=O bonds in the presence of C=C bonds has been observed. This selectivity is invers to that of existing Co catalysts and surprising because of the directing influence of a hydroxyl group in C=C bond hydrogenation.

Homogenous hydrogenation with molecular hydrogen is a key step in the industrial synthesis of fine chemicals. Typically, highly priced noble metals such as Ir, Ru, Rh, Pd and Pt play the leading role as catalytically active sites in hydrogenation catalysts.[1] The substitution of these metals by inexpensive, earth abundant metals like cobalt would give advantages in terms of costs and sustainability. Furthermore, the unique electronic structure properties of such base metals may allow observing unusual activity/selectivity profiles. Despite these and other perspectives, the development of well-defined homogenous cobalt hydrogenation catalysts has been progressed slowly especially with regard to the reduction of C=O bonds. However, with the implementation of rational ligand design, a few new cobalt catalysts for homogenous hydrogenation have been disclosed in recent years. Hydrogenation of olefins with cobalt complexes have been described by Budzelaar and coworkers[2] as well as by Chirik and coworkers.[3] A bis(phosphino)boryl cobalt catalyst (for which a boryl-metal cooperativity was observed) has been applied by Peters and coworkers in C=C bond hydrogenation.[4] Very recently, Milstein and coworkers reported on the Co complex catalyzed hydrogenation of esters.[5] To the best of our knowledge, homogenous Co catalysts for efficient C=O reduction with molecular hydrogen are only described for two examples.[6] Hanson and coworkers reported a bis[2-(dicyclohexylphosphino)ethyl]amine stabilized cobalt(II)-alkyl catalyst (Scheme 1, left) for C=C, C=N and C=O reduction.[7] The pre-catalyst is activated with one equivalent of $H[BAr^F_4]\cdot(Et_2O)_2$ (Brookhart's acid,[8] $[BAr^F_4]^-$ = tetrakis[(3,5-trifluormethyl)-phenyl]borate) and reduces C=O bonds involving 2.0 mol% catalyst loading within 1-4 bar H_2 pressure at room temperature. Notably, the dehydrogenation of alcohols has been observed with this catalyst too. [9] A heteroatom free arene-cobalt-ate catalyst for C=C, C=O and C=N hydrogenation was developed by the groups of Wolf and von Wangelin (Scheme 1, middle).[10] Carbonyl compounds are reduced in good to excellent yields with 5.0 mol% of the catalyst, 10 bar H_2 pressure at 60°C without previous activation of the catalyst.

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

Scheme 1. Known homogenous cobalt catalysts for C=O bond hydrogenation (left and middle).



We recently introduced (triazine-based) $PN_{3-5}P$-Ir complexes (an example of a cobalt complex is shown in Scheme 1, right) as highly efficient homogenous catalysts for acceptorless dehydrogenative condensation reactions.[11] Haupt and coworker introduced such PN_3P ligands[12] and Kirchner and coworker have demonstrated the broad applicability of the ligand class.[13] Reports on cobalt complexes stabilized by such ligands are rare.[13e,14,15]

Herein we report on a novel, easy to synthesize, and simply to activate homogenous cobalt C=O bond hydrogenation catalyst family (Scheme 1, right). The pre-catalysts can be synthesized quantitatively up to multi-gram scale.[16] They are air stable for a period of a few months as a crystalline material. The activation of the pre-catalysts proceeds via salt elimination by adding two equivalents of a base and is based on the ability of the used PN$_{3-5}$P ligand class to act as neutral, mono-anionic or di-anionic 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[3a] and (II) invers selectivity patterns as reported for the Hanson catalyst.[7c]

The pre-catalyst synthesis is performed by addition of an equimolar solution of the ligand to a suspension of anhydrous CoCl$_2$ in THF. The desired pre-catalysts precipitate as red crystalline solids in quantitative yields. Complexes were characterized by X-ray crystal structure analysis (XRD), elemental analysis, IR-spectroscopy and magnetic measurements. All complexes show paramagnetic behavior and an effective magnetic moment between 2.2 μ$_B$ and 2.3 μ$_B$ (studied over a temperature range of 300-2 K using a SQUID magnetometer).[17] The molecular structure of **3** is shown in Figure 1. XRD indicates an pentacoordinated cobalt(II) complex with a slightly distorted square pyramidal coordination. The neutral PN$_5$P ligand is coordinated to the cobalt 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.

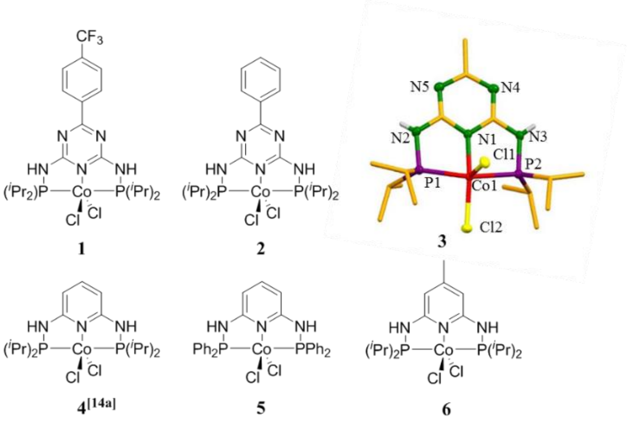
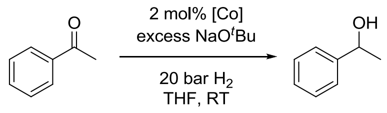


Figure 1. Synthesized PN$_{3-5}$P stabilized cobalt(II) chlorido complexes and molecular structure of **3** with 50% probability of thermal ellipsoids. Hydrogen atoms (except for the two N-H groups) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Co1–P1 2.220(1); Co1–P2 2.220(1); Co1–Cl1 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)

The catalytic activity of the complexes **1-6** (Figure 1, Table 1) and the metal precursor CoCl$_2$ was investigated in the hydrogenation of acetophenone (3.0 mmmol) using 2.0 mol% pre-catalyst in THF under 20 bar hydrogen pressure and room temperature. The pre-catalysts were initially activated with a slightly excess (4.4 mol %) of NaO^{t}Bu (^{t}Bu = tertiary-butyl). Complex **3** was identified as the most active pre-catalyst. A comparison of **3** and **6** reveals the beneficial effect of the triazine ring. Beside the altered basicity of the coordinating N-atom, an explanation can result from a stabilization of the proton shuttle chain via hydrogen bonding with the N-atoms of the triazine moiety of the PN$_5$P ligand backbone.[18]

Table 1. Hydrogenation of acetophenone with several cobalt(II) pre-catalysts (see Figure 1).[a]



Entry	Pre-catalyst	Yield[b] [%]
1	**1**	7
2	**2**	30
3	**3**	>99
4	**4**	28
5	**5**	0
6	**6**	23
6	CoCl$_2$	0

[a] Reaction conditions: Acetophenone (3.0 mmol), 2.0 mol% Co, NaO^{t}Bu (13 mg, 4.4 mol%), 2 mL THF, 20 bar H$_2$, room temperature, 24 h. [b] determined via GC with dodecane as internal standard.

To understand the role of the base in the activation process, a base loading screening was carried out (Supporting Information [SI]). Two equivalents of the metal base NaO^{t}Bu are necessary for generating a catalytically active complex. The exact structure of this complex is not fully clear yet. To gain inside, the activated species was trapped with one equivalent 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$_5$P ligand acts as a di-anionic ligand coordinating the cobalt again in the pincer like tridentate manner with an P1–Co1–P2 angle of 158.18(5)°. The oxidation state of the cobalt(II) center is not affected by the activation procedure. Complex **8** has an effective magnetic moment of 1.9 μ$_B$, expected for an 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$_5$P ligand (Figure S2, SI). Under base free conditions, the iridium catalyst shows no remarkable conversion. With a Na to Ir ratio of 1 and 2 (Figure S2, SI, green and blue graphs, respectively) a faster conversion is observed. It increases at higher base concentration and is still slower than Co (red graphs). Such activating effect of a metal base is known for other iridium C=O bond hydrogenation catalysts.[19] At very high base loadings (Na/Ir = 10, Figure S2 of the SI), the Ir catalyst is faster. NaO^{t}Bu addition higher than the two equivalent 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^{t}Bu can mediate side reactions of the educts like aldol type condensations.

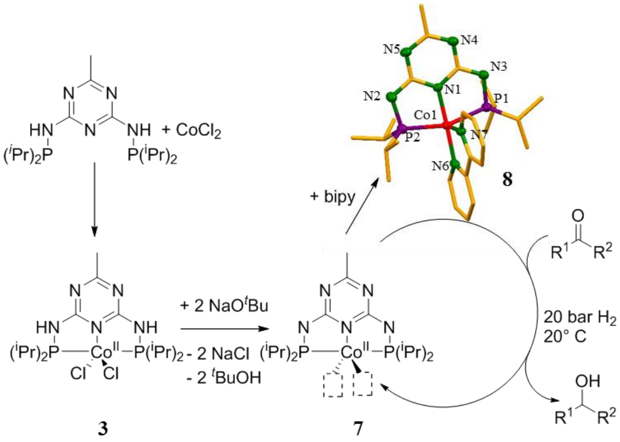
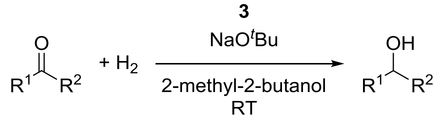


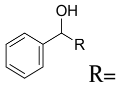
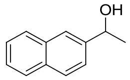
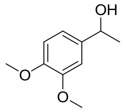
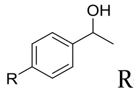
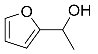
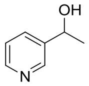
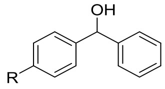
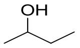
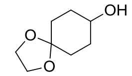
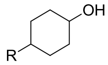
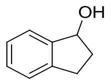
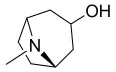
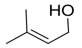
Figure 2. Synthesis and activation of **3** as well as trapping of the activated catalyst with bipyridine (**8**). The molecular structure of **8** is displayed with 50% probability of thermal ellipsoids. Hydrogens are omitted for clarity. Relevant bond lengths [Å] and angles [°]: Co1 – P1 2.214(1); 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);

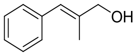
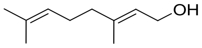
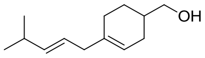
Finally, we optimized the hydrogenation reaction conditions and explored the substrate scope of our Co catalyst. For details please see the SI. To our delight, a broad product scope was observed. Aryl-alkyl ketones (Table 2, entry 1-11), diaryl ketones (Table 2, entry 12-14) as well as aliphatic ketones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

In conclusion, we reported on an easy accessible, inexpensive to activate and highly active cobalt catalyst for the homogenous hydrogenation of C=O bonds. The chosen $PN_{3\text{-}5}P$ 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 selective. Further investigations are focused towards a better understanding of the catalytically active species, the development of enantioselective $PN_{3\text{-}5}P$-Co hydrogenation catalysts, and other catalytic applications of the cobalt catalyst family described here.

Table 2. Hydrogenation of aryl-alkyl, diaryl and aliphatic carbonyl compounds[a]



Entry	Product	Cat. loading [mol%]	Yield[b] [%]
1	 R= CH_3	0.25	>99
2	R= CH_2CH_3	0.5	>99
3	R= $(CH_2)_4CH_3$	0.5	>99
4	R=H	0.5	>99
5		0.5	>99
6		0.25	>99
7	 R=F	1.0	98 (94[c])
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[c])
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[c])
19		0.5	>99
20		1.0	>99 (92[c])
21		0.5	>99

22		1.0	>99 (97[c])
23		0.5	>99
24		0.5	>99 (95[c])

[a] Reaction conditions: 3.0 mmol carbonyl compound, 2.0 mL 2-methyl-2-butanol, NaO^{t}Bu (2.0 equiv. with respect to the pre-catalyst), 20°C, 24h, 20 bar H_2, pre-catalyst **3**, [b] determined via GC with dodecane as internal standard, [c] isolated yield.

ASSOCIATED CONTENT

Supporting Information

Additional experimental procedures, spectroscopic and crystallographic data are available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: kempe@uni-bayreuth.de. Fax: +499212157.

Notes

The authors declare no competing financial interests.

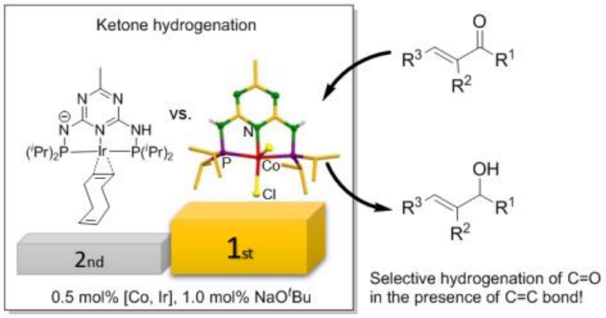
ACKNOWLEDGMENT

We thank the Deutsche Forschungsgemeinschaft, DFG, KE 756/23-2, for financial support, Charles Lochenie for the magnetic measurements, Toni Hille for synthesizing 4-methylpyridine-2,6-diamine, Detlef Heller for helping with the kinetic analysis and the reviewers for their valuable suggestions. We dedicate our work to Manfred Scheer on the occasion of his 60th birthday.

REFERENCES

(1) *The Handbook of Homogeneous Hydrogenation*; de Vries, J. G., Elsevier, C. J., Eds.; Wiley-VCH Verlag GmbH: Weinheim, 2008
(2) Knijnenburg, Q.; Horton, A. D.; Heijden, H. v. d.; Kooistra, T. M.; Hetterscheid, D. G. H.; Smits, J. M. M.; Bruin, B. d.; Budzelaar, P. H. M.; Gal, A. W. *J. Mol. Catal. A: Chem*. **2005**, *232*, 151-159.
(3) a) Friedfeld, M. R.; Margulieux, G. W.; Schaefer, B. A.; Chirik, P. J. *J. Am. Chem. Soc.* **2014**, *136*, 13178-13181; b) Yu, R. P.; Darmon, J. M.; Milsmann, C.; Margulieux, G. W.; Stieber, S. C. E.; DeBeer, S.; Chirik, P. J. *J. Am. Chem. Soc.* **2013**, *135*, 13168-13184; c) Monfette, S.; Turner, Z. R.; Semproni, S. P.; Chirik, P. J. *J. Am. Chem. Soc.* **2012**, *134*, 4561-4564.
(4) a) Lin, T.-P.; Peters, J. C. *J. Am. Chem. Soc.* **2014**, *136*, 13672-13683; b) Gunderson, W. A.; Suess, D. L. M.; Fong, H.; Wang, X.; Hoffmann, C. M.; Cutsail Iii, G. E.; Peters, J. C.; Hoffman, B. M. *J. Am. Chem. Soc.* **2014**, *136*, 14998-15009.
(5) Srimani, D.; Mukherjee, A.; Gorldberg, A. F. G.; Leitus, G.; Diskin-Posner, Y.; Shimon, L. J. W.; Ben David, Y.; Milstein, D. *Angew. Chem. Int. Ed.* **2015**, doi: 10.1002/anie.201502418.
(6) For examples of C=O bond hydrogenation catalysis based on PNP-Fe complexes see: (a) Langer, R.; Leitus, G.; Ben-David, Y.; Milstein, D. *Angew. Chem., Int. Ed.* **2011,** 50, 2120–2124; (b) Langer, R.; Diskin-Posner, Y.; Leitus, G.; Shimon, Linda J W; Ben-David, Y.; Milstein, D. *Angew. Chem., Int. Ed.* **2011,** 50, 9948–9952; (c) Ziebart, C.; Federsel, C.; Anbarasan, P.; Jackstell, R.; Baumann, W.; Spannenberg A.; Beller M. *J. Am. Chem. Soc.* **2012**, *134*, 20701-20704; (d) Werkmeister, S.; Junge, K.; Wendt, B.; Alberico, E.; Jiao, H.; Baumann, W.; Junge, H.; Gallou, F.; Beller, M. *Angew. Chem., Int. Ed.* **2014,** 53, 8722–8726; (e) Zell, T.; Ben-David, Y.; Milstein, D. *Angew. Chem., Int. Ed.***2014,** 53, 4685–4689; (f) Sonnenberg, J. F.; Lough, A. J.; Morris, R. H. *Organometallics*. **2014,** *33*, 6452–6465; (g) Gorgas, N.; Stöger, B.; Veiros, L. F.; Pittenauer, E.; Allmaier, G.; Kirchner, K. *Organometallics* **2014,** *33*, 6905–6914; (h) Lagaditis, P. O.; Sues, P. E.; Sonnenberg, J. F.; Wan, K. Y.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2014**, *136*, 1367–1380; (i) Chakraborty, S.; Lagaditis, P. O.; Förster, M.; Bielinski, E. A.; Hazari, N.; Holthausen, M. C.; Jones, W. D.; Schneider, S. *ACS Catal.* **2014**, *4*, 3994-4003; (j) Zell, T.; Ben-David, Y.; Milstein, D. *Catal. Sci. Technol.* **2015,** 5, 822–826; (k) Mazza, S.; Scopelliti, R.; Hu, X. *Organometallics*. **2015,** *34*, 1538–1545.
(7) a) Zhang, G.; Vasudevan, K. V.; Scott, B. L.; Hanson, S. K. *J. Am. Chem. Soc.* **2013**, *135*, 8668-8681; b) Zhang, G.; Hanson, S. K. *Chem. Commun.* **2013**, *49*, 10151-10153; c) Zhang, G.; Scott, B. L.; Hanson, S. K. *Angew. Chem. Int. Ed.* **2012**, *51*, 12102-12106.
(8) Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920-3922.
(9) Zhang, G.; Hanson, S. K. *Org. Lett.* **2013**, *15*, 650-653.
(10) Gaertner, D.; Welther, A.; Rad, B. R.; Wolf, R.; Wangelin, A. J. v. *Angew. Chem., Int. Ed.* **2014**, 53, 3722-3726.
(11) a) Michlik, S.; Kempe, R. *Nat. Chem.* **2013**, 5, 140-144; b) Michlik, S.; Kempe, R. *Angew. Chem. Int. Ed.* **2013**, 52, 6326-6329; c) Hille, T.; Irrgang, T.; Kempe, R. *Chem. Eur. J.* **2014**, *20*, 5569-5572; (d) Ruch, S.; Irrgang T., Kempe, R. *Chem. Eur. J.* **2014**, *20*, 13279-13285.
(12) Schirmer, W.; Flörke, U.; Haupt, H. J. *Z. Anorg. Allg. Chem.* **1987**, *545*, 83-97.
(13) a) Benito-Garagorri, D.; Puchberger, M.; Mereiter, K.; Kirchner, K. *Angew. Chem. Int. Ed.* **2008**, *47*, 9142-9145; b) Benito-Garagorri, D.; Kirchner, K. *Acc. Chem. Res.* **2008**, *41*, 201-213; c) Benito-Garagorri, D.; Wiedermann, J.; Pollak, M.; Mereiter, K.; Kirchner, K. *Organometallics* **2007**, *26*, 217-222; d) Benito-Garagorri, D.; Becker, E.; Wiedermann, J.; Lackner, W.; Pollak, M.; Mereiter, K.; Kisala, J.; Kirchner, K. *Organometallics* **2006**, 25, 1900-1913; e) Li, H.; Zheng, B.; Huang, K.-W. *Coord. Chem. Rev*. **2015**, *293-294*, 116-138.
(14) (a) Obligacion, J. V.; Semproni, S. P.; Chirik, P. J. *J. Am. Chem. Soc.* **2014**, *136*, 4133-4136; (b) Shaffer, D. W.; Johnson, S. I.; Rheingold, A. L.; Ziller, J. W.; Goddard, W. A.; Nielsen, R. J.; Yang, J. Y. *Inorg. Chem.* **2014**, 53, 13031–13041.
(15) Examples for related PNP Co catalysts/complexes in addition to Ref 3, 5 and 7 and 9: (a) Khaskin, E.; Diskin-Posner, Y.; Weiner, L.; Leitus, G.; Milstein, D. *Chem. Commun.* **2013,** *49*, 2771–2773; (b) Scheuermann, M. L.; Semproni, S. P.; Pappas, I.; Chirik, P. J. *Inorg. Chem.* **2014,** 53, 9463–9465; (c) Semproni, S. P.; Hojilla Atienza, C. C.; Chirik, P. J. *Chem. Sci.* **2014,** 5, 1956-1960; (d) Semproni, S. P.; Milsmann, C.; Chirik, P. J. *J. Am. Chem. Soc.* **2014,** *136*, 9211–9224; (e) Schaefer, B. A.; Margulieux, G. W.; Small, B. L.; Chirik, P. J. *Organometallics*. **2015,** *34*, 1307–1320. Fryzuk, M. D.; Leznoff, D. B.; Thompson, R. C.; Rettig, S. J. *J. Am. Chem. Soc.* **1998**, *120*, 10126–10135.
(16) The ligand synthesis is similarly easy. For instance, 96% isolated yield starting from commercially available educts for the PN$_5$P ligand of **3**.
(17) The spin only value for a cobalt(II) complex in a pentacoordinated ligand environment in the low spin state is 1.7 µB.
(18) Qu, S.; Dang, Y.; Song, Ch.; Wen, M.; Huang, K.W.; Wang, Z.-X. *J. Am. Chem. Soc.* **2014**, *136*, 4974-4991.
(19) a) Irrgang, T., Friedrich, D.; Kempe, R. *Angew. Chem. Int. Ed.* **2011**, 50, 2183-2186.
(20) (a) Haack, K.-J.; Hashiguchi, S.; Fujii, A.; Ikariya, T.; Noyori, R. *Angew. Chem., Int. Ed.* **1997,** *36*, 285–288; (b) Noyori, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2008–2022; (c) Clapham, S. E.; Hadzovic, A.; Morris, R. H. *Coord. Chem. Rev.* **2004,** *248*, 2201–2237; (d) Sandoval, C. A.; Ohkuma, T.; Utsumi, N.; Tsutsumi, K.; Murata, K.; Noyori, R. *Chem. Asian J.* **2006,** *1*, 102–110; (e) Casey, C. P.; Beetner, S. E.; Johnson, J. B. *J. Am. Chem. Soc.* **2008,** *130*, 2285–2295; (f) Casey, C. P.; Guan, H. *J. Am. Chem. Soc.* **2009,** *131*, 2499–2507; (g) Morris, R. H. *Chem. Soc. Rev.* **2009,** *38*, 2282–2291; (h) Morris, R. H. *Acc. Chem. Res.* **2015,** *48*, 1494–1502.

TOC


Ketone hydrogenation
N
N
N
NH
N
$(^iPr)_2P$
Ir
$P(^iPr)_2$
vs.
N
P
Co
Cl
2nd
1st
0.5 mol% [Co, Ir], 1.0 mol% NaO^tBu
O
R^3
R^1
R^2
OH
R^3
R^1
R^2
Selective hydrogenation of C=O
in the presence of C=C bond!