

# **CHEMISTRY** A European Journal



WILEY-VCH

Accepted Article	
<b>Fitle:</b> Additive Free Isomerization of Allylic Alcohols to Ketones with a Cobalt PNP Pincer Catalyst	
Authors: Brian Spiegelberg, Andrea Dell'Acqua, Tian Xia, Anke Spannenberg, Sergey Tin, Sandra Hinze, and Johannes Gerardus de Vries	
This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.	
To be cited as: Chem. Eur. J. 10.1002/chem.201901148	
<b>_ink to VoR:</b> http://dx.doi.org/10.1002/chem.201901148	
	e

## Additive Free Isomerization of Allylic Alcohols to Ketones with a Cobalt PNP Pincer Catalyst

Brian Spiegelberg, Andrea Dell'Acqua, Tian Xia, Anke Spannenberg, Sergey Tin, Sandra Hinze, Johannes G. de Vries\*

**Abstract:** Catalytic isomerization of allylic alcohols in ethanol as green solvent is achieved using air and moisture stable cobalt (II) complexes in the absence of any additives. Under mild conditions the cobalt PNP pincer complex substituted with phenyl groups on the phosphorus atoms appears to be the most active. High rates were obtained at 120 °C even though the addition of one equivalent of base increases the speed of the reaction drastically. Although we obtained some evidence supporting a dehydrogenation-hydrogenation mechanism, we gathered evidence that this is not the major mechanism. Instead the cobalt hydride complex formed by dehydrogenation of ethanol is capable of double bond isomerization via alkene insertion elimination.

Isomerization reactions comply with the principles of green chemistry.<sup>[1]</sup> The catalytic isomerization of allylic alcohols into the saturated carbonyl compounds is an elegant synthetic process that eliminates the more conventional two-step oxidation and reduction pathway.<sup>[2]</sup> During the last half century, many precious metal catalysts for allylic alcohol isomerization, based on Ir, Ru, Rh or Pd have been developed.<sup>[2, 3]</sup> Some of these even work well at ambient temperature.<sup>[4]</sup> Although noble metals play an indispensable role in catalysis, they are rather expensive, less abundant and generally not used in the last step of drug synthesis. Thus, catalysts based on cheap metals like iron<sup>[5]</sup> and nickel<sup>[6</sup> have been used for the isomerization of allylic alcohols recently. Nevertheless, the requirement of either activated substrates<sup>[5b]</sup> or the need for activation of the catalyst make those systems less desirable. Recently, reports have appeared on the sole use of base as catalyst for the isomerization of allylic alcohols to the corresponding ketones.<sup>[7]</sup> To the best of our knowledge, there is only one report on the use of a cobalt catalyst (HCo(CO)<sub>4</sub>) that can promote the isomerization of an allylic alcohol to an aldehyde or a ketone, but harsh conditions including the use of toxic carbon monoxide were required to achieve low conversions and selectivities towards the desired products.<sup>[8]</sup> Recently, pincer cobalt complexes have been discovered to be effective catalysts<sup>[9]</sup> for hydrogenation,<sup>[10]</sup> dehydrogenation,<sup>[10g, 11]</sup> transfer hydrogenation,<sup>[12]</sup> hydrosilylations/hydroborations,<sup>[13]</sup> alkene isomerization<sup>[14]</sup> and N<sub>2</sub>-activation<sup>[15]</sup>. Hanson and coworkers reported a cationic cobalt(II) alkyl complex, which was applied for the hydrogenation of aldehydes, ketones and imines, as well as for the isomerization of alkenes.<sup>[16]</sup> Fur-

[\*] B. Spiegelberg, A. Dell'Acqua, Dr. T. Xia, Dr. A. Spannenberg Dr. S. Tin, Dr. S. Hinze, Prof. Dr. J. G. de Vries

Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Strasse 29a, 18059 Rostock

E-mail: Johannes.deVries@catalysis.de

Homepage: https://www.catalysis.de/en/research/catalysis-withrenewable-resources/catalysis-with-renewables-platform-chemicals/

Supporting information for this article is given via a link at the end of the document.

thermore, Liu and co-workers recently reported impressive findings about pincer cobalt complexes that are suitable catalysts for regioselective olefin isomerization by using ammonia borane as activation source.<sup>[13]</sup> Although many catalytic reactions have been performed with pincer cobalt catalysts, isomerization reactions of allylic alcohols with this type of complexes are still unknown.



Figure 1. PNP-Co complexes applied to the isomerization of allylic alcohols in this work.

Herein, we report the first cobalt(II) catalyzed isomerization of allylic alcohols to ketones in ethanol as solvent. We have tested a number of cobalt PNP pincer complexes having different substituents on the phosphorus atoms. It was demonstrated, that the reaction works in the presence of a base, as well as in the absence of it or any other additives. The present work describes the successful application of (PNHP<sup>Ph</sup>)CoCl<sub>2</sub> (**Co-4**), a catalyst hitherto known for the stereospecific polymerization of 1,3-butadiene<sup>[17]</sup> and the reduction of carboxylic acid esters and nitriles.<sup>[18]</sup>

Initial studies were carried out under exploitation of different substituted cobalt pincer catalysts in diverse solvents (see ESI). The reported complexes<sup>[18, 19]</sup> are easily synthesized upon the addition of the respective ligands to THF or ethanol solutions of cobalt(II) precursors (see ESI). It was assumed that a base is required since deprotonation of the cobalt complexes results in formation of the active amido species,<sup>[11a]</sup> which should be capable of alcohol dehydrogenation. Ten different solvents were tested with various polarities and proton-donor capabilities. The alcohols turned out to be the most promising solvents, resulting in high conversions of our model substrate oct-1-en-3-ol (1) towards the desired product 3-octanone (2). Taking efficiency and environmental impact<sup>[20]</sup> into account, ethanol was selected as reaction medium for further experiments. Although different bases were examined, potassium tert-butoxide, chosen in the preliminary studies, maintains the best among the others (see ESI). However, to accommodate base-sensitive substrates and for reasons of waste reduction we also examined the possibility of base-free catalysis.

For a first screening (Figure 2) all cobalt pincer complexes (**Co-1** to **Co-6**) were tested for catalytic isomerization of oct-1en-3-ol (1) with the aid of KO<sup>t</sup>Bu. While in case of **Co-2** and

#### WILEY-VCH

#### **COMMUNICATION**



**Figure 2.** Screening of cobalt catalysts for the isomerization of oct-1-en-3-ol (1) to 3-octanone (2). Reaction conditions: 1.0 mmol substrate; 1.0 mL ethanol; 3 mol% catalyst; 3 mol% KO'Bu; 1 h. Determined by GC with *n*-dodecane as internal standard.

**Co-5** the oct-1-en-3-ol (1) stays untouched, excellent conversions were achieved by using the less sterically hindered complexes **Co-1**, **Co-3**, **Co-4** and **Co-6**. Thereupon in the second screening the most active and selective catalysts towards the formation of 3-octanone (2) were tested in the absence of base (Table 1, entries 1-3). Surprisingly, all catalysts were still capable of performing the isomerization of 1 to 2. Notably, the conversions obtained with 1 mol% of **Co-1** and **Co-6** at 120 °C dropped to 40% and 54% respectively, while in the case of **Co-4** only a slight decrease of the yield was observed (see Table 1). The selectivity related to the desired product **2** remains similar, compared to the reactions in the presence of KO'Bu. Nevertheless, **Co-4** emerges to be the best catalyst not only w.r.t. conversion of **1** but also w.r.t. 100% selective formation of 3-octanone (**2**) (Table 1, entry **3**).

Table 1. Cobalt-catalyzed isomerization of oct-1-en-3-ol (1). Optimization of the reaction conditions.  $^{[a]}$ 

	OH C <sub>5</sub> H <sub>11</sub> -	x mol% cat. ► EtOH, y °C, 1 h	C <sub>5</sub> H <sub>11</sub> 2	+C <sub>5</sub> H <sub>11</sub> 3	
Entry	Catalyst	Temperature	Conv. 1	2	3 [%] <sup>[b]</sup>
	(mol%)	[0]	[70]	[%] <sup>[b]</sup>	
1	Co-1 (1)	120	40	37	3
2	Co-6 (1)	120	54	50	4
3	Co-4 (1)	120	94	94	0
4 <sup>[c]</sup>	Co-4 (0.1)	120	100	>99	0
5	Co-4 (0.1)	120	10	10	0
6	Co-4 (1)	60	0	0	0
7	Co-4 (1)	70	32	32	0
8	Co-4 (1)	80	82	82	0
9 <sup>[d]</sup>	Co-4 (1)	120	90	90	0

[a] 1.0 mmol substrate, 1.0 mL ethanol. [b] Determined by GC with *n*-dodecane as internal standard. [c] Reaction time 8 h. [d] **Co-4** was stored 24 h under aerobic conditions before using.

Attempts to reduce the reaction temperature resulted in lower yields. The reaction did not proceed at 60 °C or lower temperatures (see ESI). Likely, the poor solubility of the cobalt complex in ethanol is the crucial factor that limits the catalytic performance. [17] However, above 70 °C the catalyst is fully soluble. On the positive side, this poor solubility allowed the easy separation of the catalyst from the reaction mixture by filtration at room temperature. It is worth to mention that, when the complex Co-4 was stored under ambient conditions before use, the catalytic activity remains and thus this catalyst precursor seems to be air and moisture stable. (Table 1, entry 9).Delighted with these results, we employed catalyst Co-4 for the isomerization of a variety of allylic alcohols, bearing aromatic or aliphatic substituents (Table 2). Noticeably, all terminal allylic alcohols could be isomerized effortlessly. Isomerization of substrates carrying internal double bonds was more problematic. However, using trifluoroethanol (TFE) as solvent, good to excellent yields of ketones could be produced with these substrates (Table 2, products 2e, 2g, 2p). Generally, fluorinated solvents display unique properties which are known to be advantageous in many catalytic processes.[21] Owing to the negative inductive effect of the fluorine substituent, the acidity of the hydroxyl group increases, hence a strong hydrogen-bond-donating character results that can be used as a promoter. We presume that chloride dissociation is promoted in this solvent leading to a higher proportion of the active catalyst (B in Figure 3). Interestingly, in marked contrast to the beneficial effect of TFE on the isomerization of internal allylic alcohols, reaction of terminal substrates in this solvent resulted in lower yields than in ethanol. Remarkably, the slope of the conversion vs time curves reveal an initial faster isomerization

Table 2. Substrate scope of cobalt-catalyzed allylic alcohol isomerization<sup>[a]</sup>



[a] 1.0 mmol substrate, 1.0 mL ethanol. Isolated yields. [b] Reaction time 8 h. cat: 0.1 mol%. 1.0 mL ethanol. [c] 1.0 mL of trifluoroethanol (TFE) instead of ethanol. [d] Reaction time 4 h. [e] Reaction time 18 h. [f] GC-yield.

of **1** to **2** in TFE which then totally stops at a conversion of 85% (see ESI). As we suspected product inhibition, different amounts of 3-octanone were added at the start of the reaction. Indeed, the addition of 2 mmol of 3-octanone in TFE resulted in complete loss of catalytic activity, confirming our suspicion.

#### WILEY-VCH





Scheme 1 Deuteration experiments.

Different aryl substituted allylic alcohols bearing an aryl, naphthyl, furanyl or thienyl group were investigated. These substrates were converted to the corresponding ketones in good to excellent isolated yields. Gratifyingly, the aliphatic products (2c-2e, 2q) were isolated almost quantitatively even at a lower catalyst loading of 0.1 mol%. To test the limitations of the catalytic performance of Co-4, homoallylic alcohols (1I, 1m) as well as a cyclic allylic alcohol (1i) were examined. While homoallylic alcohols could be still converted in moderate yields, surprisingly, the cyclic substrate *cis*-verbenol (1i) forms the ethyl ether. Presumably, due to the sterically demand of 1i alkene insertion is hindered and HCI mediated allylic substitution becomes feasible.

Isomerization of primary allylic alcohols would lead to the formation of an aldehyde.<sup>[22]</sup> Thus, cinnamyl alcohol was tested but, unfortunately, only a 13% yield of aldehyde was obtained after 18 h. This may be due to the progressive deactivation of the active catalyst caused by the abstraction of CO.<sup>[23]</sup>

To obtain insight in the mechanism, the allylic alcohol 1a was deuterated in two ways: Ph-**CD**(OH)-CHCH<sub>2</sub> and Ph-

CH(**OD**)-CHCH<sub>2</sub>) were prepared and both compounds were subjected to the isomerization reaction (Scheme 1). From these reactions the saturated ketones were obtained in which the deuterium from the CD exclusively was found in the betaposition and the deuterium from the OD in the alpha position. This labelling pattern is in agreement with both a classical alkene isomerization where the alkene inserts into the cobalt hydride bond and beta-hydride elimination takes place from the proton that is attached to the alcohol (Figure 3, left cycle). But equally it is in agreement with the dehydrogenation, 1,4reduction mechanism that we had previously calculated to be the correct mechanism for the iron-PNP-catalyzed allylic alcohol isomerization (Figure 3, right cycle).

Kinetics revealed that the reaction is first order in catalyst and in allylic alcohol (see ESI, Figure 6), which again fits with both mechanisms. However, when the reaction was stopped after 10 min (20% conversion) and 30 min (69% conversion), respectively, not a trace of  $\alpha$ , $\beta$ -unsaturated ketone was found in the crude mixture, which makes the redox mechanism less likely. In order to discriminate between the two mechanisms we performed a number of cross-over experiments (Scheme 2). First, 1-octen-3-ol was reacted in the presence of an  $\alpha$ , $\beta$ unsaturated ketone (Scheme 2, 2.1). If the reaction follows a redox mechanism one would expect that the  $\alpha$ , $\beta$ -unsaturated ketone would also be reduced to the saturated ketone. In practice this compound is hardly reduced, which would argue against the redox mechanism. However, the experiment is rather biased as the terminal double bond of 1-octen-3-one is probably 100 times more reactive than the internal double bond of benzylidene acetone. To remove this bias we examined the reaction between 3-octanol and benzylidene acetone (Scheme 2, 2.2). After overnight reaction, 30% of 3-octanone and 10% of 4-phenyl-2-butanone had formed. Although it is



Figure 3. Proposed mechanisms for the cobalt catalyzed isomerization of allylic alcohols (dehydrogenation followed by either hydrogenation or hydride addition-elimination).

#### WILEY-VCH

### COMMUNICATION

clear that this establishes the possibility of a redox mechanism it does not exclude the possibility of the double bond isomerization mechanism. To obtain more conclusive evidence, we decided to perform a cross-over experiment with a terminal α, β-unsaturated ketone (Scheme 2, 2.3). Surprisingly, in this reaction the pent-1-ene-3-ol was not reacting but instead an oxa-Michael addition of ethanol and a selfcondensation reaction presumably both mediated by the catalyst, occurred. In addition, 6% of hydrogenated product was detected caused by the slow transfer hydrogenation of ethanol. We attribute the lack of reaction of pent-1-ene-3-ol, which was rapidly converted to the ketone in 98% yield in the absence of the enone, to the insertion of the more reactive CC bond of the enone into the cobalt hydride bond. The resulting cobalt alkyl complex is stabilized by the presence of the carbonyl group and is likely to be the resting state. Given the fact that 1-phenyl-2-propen-1-ol was smoothly isomerized to butyrophenone (2a) without any trace of the oxa-Michael adduct, this experiment makes the redox mechanism highly unlikely. Thus a hydride addition-elimination mechanism would seem highly likely. To obtain further proof, allyl benzene was subjected to an alkene isomerization with Co-4. When a non-protic solvent like acetonitrile, THF or toluene was used, no isomerization product was formed (Scheme 2, 2.5) whereas using ethanol as solvent, allyl benzene was almost quantitatively isomerized to 1-phenyl-1-propene (Scheme 2, 2.6). This confirms that the cobalt hydride that is formed by dehydrogenation of ethanol is capable of alkene isomerization via alkene insertion elimination.



Figure 4. Successive dehydrogenation and condensation of ethanol by Co-4 leads to the formation of Co-4a. ORTEP representation of Co-4a (30% probability ellipsoids, hydrogen atoms are omitted for clarity).

Thus, we propose the following mechanism. The activation of the cobalt complex takes place by loss of HCI. This is accelerated by the use of base, but we assume that without base there is equilibrium between Co-4 and species B in polar solvents. In toluene the equilibrium is completely on the side of Co-4 explaining the lack of isomerization of allylbenzene in toluene. Next, either the allylic alcohol or ethanol is dehydrogenated by **B** in an outer sphere fashion to form the hydride species C. Insertion of the alkene into the cobalt hydride bond is possibly preceded by dissociation of chloride, which may bind again after the insertion of the alkene. Likewise, dissociation of the chloride is likely preceding the beta-hydride elimination, which leads to formation of the enol which tautomerizes to the ketone. Although the competing redox mechanism would seem to be much slower, it cannot be completely excluded.

Interestingly, if complex **Co-4** is stirred in ethanol overnight at 120 °C, we were able to isolate complex **Co-4a**. We assume this has formed from the dehydrogenation of ethanol to acetaldehyde, which reacts with the nitrogen of the ligand in either **Co-4** or complex **B** followed by reduction of the ensuing imine/enamine. While **Co-4** is a highly active catalyst, **Co-4a**, which has an ethyl group on the nitrogen and no N-Co bond, was a very poor catalyst in the isomerization of 3-octen-1-ol in ethanol (2.4). We assume that **Co-4a** is inactive since it can no longer form a cobalt hydride.

In summary, we tested a series of cobalt PNP-pincer complexes in the isomerization of allylic alcohols to the ketones. In particular, the versatile complex **Co-4** has been found to be the most efficient catalyst which surprisingly functions well without the addition of base. A range of allylic alcohols bearing aliphatic or aromatic groups were successfully converted. It was shown that the use of catalytic amounts of base speeds up the reaction, presumably by increasing the amount of active complex **B**.



Scheme 2. Reactions for mechanistic insight.

Allylic alcohols containing internal double bonds were converted much slower, but these reactions could be accelerated by using trifluoroethanol as solvent. We propose a mechanism in which cobalt retains its (II) oxidations state. The active catalyst is formed by dissociation of HCI followed by dehydrogenation of an alcohol to form a cobalt hydride complex, which can isomerize the allylic alcohols by a classical alkene insertion/ elimination mechanism.

#### Acknowledgements

We thank the analytical department of LIKAT for their indispensable support. We would like to thank Arend Rösel and Robert Francke for cyclic voltammetry characterization of the catalyst. We are thankful to the support of Martyna Wozniak for the graphical abstract. Tian Xia is grateful for the financial support of the Chinese Scholarship Council (CSC). This work was also supported by the state of Mecklenburg-Vorpommern

Keywords: Isomerization • Allylic alcohol • Cobalt catalyst • Pincer ligand • Ketone

## COMMUNICATION

- P. T. Anastas, J. C. Warner, Green Chemistry: Theory and Practice, Oxford University Press: New York, **1998**, p.30.
- [2] [a] D. Cahard, S. Gaillard, J.-L. Renaud, *Tetrahedron Lett.* 2015, *56*, 6159-6169;
   [b] P. Lorenzo-Luis, A. Romerosa, M. Serrano-Ruiz, *ACS Catal.* 2012, *2*, 1079–1086.
- [3] [a] H. Li, C. Mazet, Acc. Chem. Res. 2016, 49, 1232-1241; [b] N. Ahlsten, A. Bartoszewicz, B. Martin-Matute, Dalton Trans. 2012, 41, 1660-1670; [c] L. Mantilli, C. Mazet, Chem. Lett. 2011, 40, 341-344; [d] V. Cadierno, P. Crochet, J. Gimeno, Synlett 2008, 1105-1124; [e] R. Uma, C. Crévisy, R. Grée, Chem. Rev. 2003, 103, 27-52; [f] R. C. van der Drift, E. Bouwman, E. Drent, J. Organomet. Chem. 2002, 650, 1-24.
- [4] [a] N. Ahlsten, H. Lundberg, B. Martín-Matute, *Green Chem.* 2010, 12, 1628-1633; [b] S. Manzini, A. Poater, D. J. Nelson, L. Cavallo, S. P. Nolan, *Chem. Sci.* 2014, 5, 180-188.
- [5] [a] T. Xia, Z. Wei, B. Spiegelberg, H. Jiao, S. Hinze, J. G. de Vries, *Chem. Eur. J.* 2018, 24, 4043-4049; [b] D. Cahard, V. Bizet, X. Dai, S. Gaillard, J.-L. Renaud, *J. Fluorine Chem.* 2013, 155, 78-82; [c] V. Branchadell, C. Crévisy, R. Grée, *Chem. Eur. J.* 2003, 9, 2062 -2067; [d] H. Cherkaoui, M. Soufiaoui, R. Grée, *Tetrahedron* 2001, 57, 2379-2383; [e] F. G. Cowherd, J. von Rosenberg, *J. Am. Chem. Soc.* 1969, 91, 2157-2158; [f] G. Emerson, R. Pettit, *J. Am. Chem. Soc.* 1962, 84, 4591-4592.
- [6] [a] B. Corain, Gazz. Chim. Ital. 1972, 102, 687-695; [b] B. Corain, G. Puosi, J. Catal. 1973, 30, 403-408.
- [7] [a] H.-X. Zheng, C.-Z. Yao, J.-P. Qu, Y.-B. Kang, Org. Chem. Front.
  2018, 5, 1213-1216; [b] Y. Hamada, T. Kawasaki-Takasuka, T. Yamazaki, Beilstein J. Org. Chem. 2017, 13, 1507-1512; [c] S. Martinez-Erro, A. Sanz-Marco, A. Bermejo Gómez, A. Vázquez-Romero, M. S. G. Ahlquist, B. Martín-Matute, J. Am. Chem. Soc. 2016, 138, 13408-13414; [d] H.-X. Zheng, Z.-F. Xiao, C.-Z. Yao, Q.-Q. Li, X.-S. Ning, Y.-B. Kang, Y. Tang, Org. Lett. 2015, 17, 6102-6105.
- [8] R. W. Goetz, M. Orchin, J. Am. Chem. Soc. 1963, 85, 1549 -1550.
- For an overview about cobalt catalyzed reactions see: [a] W. Ai, R. Zhong, X. Liu, Q. Liu, Chem. Rev. 2019 DOI: 10.1021/acs.chemrev.8b00404; [b] K. Junge, V. Papa, M. Beller, Chem. Eur. J. 2019, 25, 122-143; [c] A. Mukherjee, D. Milstein, ACS Catal. 2018, 8, 11435–11469.
- [10] [a] K. Tokmic, B. J. Jackson, A. Salazar, T. J. Woods, A. R. Fout, J. Am. Chem. Soc. 2017, 139, 13555-13561; [b] Y. Jing, S. Chakraborty, W. W. Brennessel, W. D. Jones, ACS Catal. 2017, 7, 3735-3740; [c] K. Tokmic, C. R. Markus, L. Zhu, A. R. Fout, J. Am. Chem. Soc. 2016, 138, 11907-11913; [d] A. Z.Spentzos, C. L. Barnes, W. H. Bernskoetter, Inorg. Chem. 2016, 55, 8225-8233; [e] A. Mukherjee, D. Srimani, S. Chakraborty, Y. Ben-David, D. Milstein, J. Am. Chem. Soc. 2015, 137, 8888-8891; [f] S. Rösler, J. Obenauf, R. Kempe, J. Am. Chem. Soc. 2015, 137, 7998-8001; [g] R. Xu, S. Chakraborty, H. Yuan, W. D. Jones, ACS Catal. 2015, 5, 6350-6354; [h] S. Monfette, Z. R. Turner, S. P. Semproni, P. J. Chirik, J. Am. Chem. Soc. 2012, 134, 4561-4564.
- [11] [a] P. O. Lagaditis, B. Schluschaß, S. Demeshko, C. Würtele, S. Schneider, *Inorg. Chem.* 2016, *55*, 4529-4536; [b] G. Zhang, S. K. Hanson, *Org. Lett.* 2013, *15*, 650-653; [c] G. Zhang, K. V. Vasude-

#### WILEY-VCH

van, B. L. Scott, S. K. Hanson, J. Am. Chem. Soc. 2013, 135, 8668-8681.

- [12] [a] Z. Shao, S. Fu, M. Wei, S. Zhou, Q. Liu, Angew. Chem. Int. Ed.
  2016, 55, 14653-14657; Angew. Chem. 2016, 128, 14873-14877; [b]
  S. Fu, N.-Y. Chen, X. Liu, Z. Shao, S. P. Luo, Q. Liu, J. Am. Chem.
  Soc. 2016, 138, 8588-8594; [c] G. Zhang, Z. Yin, J. Tan, RSC Adv.
  2016, 6, 22419-22423; [d] G. Zhang, S. K. Hanson, Chem. Commun.
  2013, 49, 10151-10153.
- [13] [a] G. Zhang, J. Wu, M. Wang, H. Zeng, J. Cheng, M. C. Neary, S. Zheng, Eur. J. Org. Chem. 2017, 5814-5818; [b] J. Guo, B. Cheng, X. Shen, Z. Lu, J. Am. Chem. Soc. 2017, 139, 15316-15319; [c] A. D. Ibrahim, S. W. Entsminger, A. R. Fout, ACS Catal. 2017, 7, 3730-3734; [d] J. H. Docherty, J. Peng, A. P. Dominey, S. P. Thomas, Nat. Chem. 2017, 9, 595-600; [e] A. D. Ibrahim, S. W. Entsminger, L. Zhu, A. R. Fout, ACS Catal. 2016, 6, 3589-3593; [f] S. W. Reilly, C. E. Webster, T. K. Hollis, H. U. Valle, Dalton Trans. 2016, 45, 2823-2828; [g] A. D. Smith, A. Saini, L. M. Singer, N. Phadke, M. Findlater, Polyhedron 2016, 114, 286-291; [h] J. V. Obligacion, J. M. Neely, A. N. Yazdani, I. Pappas, P. Chirik, J. Am. Chem. Soc. 2015, 137, 5855-5858; [i] L. Zhang, Z. Zuo, X. Leng, Z. Huang, Angew. Chem. Int. Ed. 2014, 53, 2696-2700; Angew. Chem. 2014, 126, 2734-2738; [j] M. L. Scheuermann, S. P. Semproni, I. Pappas, P. Chirik, Inorg. Chem. 2014, 53, 9463-9465.
- [14] X. Liu, W. Zhang, Y. Wang, Z.-X. Zhang, L. Jiao, Q. Liu, J. Am. Chem. Soc. 2018, 140, 6873-6882.
- [15] S. Kuriyama, K. Arashiba, H. Tanaka, Y. Matsuo, K. Nakajima, K. Yoshizawa, Y. Nishibayashi, *Angew. Chem. Int. Ed.* **2016**, *55*, 14291-14295; *Angew. Chem.* **2016**, *128*, 14503-14507.
- [16] G. Zhang, B. L. Scott, S. K. Hanson, Angew. Chem., Int. Ed. 2012, 51, 12102-12106; Angew. Chem. 2012, 124, 12268-12272.
- [17] L. Chen, P. Ai, J. Gu, S. Jie, B.-G. Li, J. Organomet. Chem. 2012, 716, 55-61.
- [18] [a] J. Schneekönig, B. Tannert, H. Hornke, M. Beller, K. Junge, *Catal. Sci. Technol.* 2019 DOI: 10.1039/c9cy00225a; [b] B. Wendt, A. Cingolani, A. Spannenberg, Z. Wei, H. Jiao, M. Beller, *Chem. Eur. J.* 2018, *24*, 1046-1052.
- [19] S. Fu, N.-Y. Chen, X. Liu, Z. Shao, S.-P. Luo, Q. Liu, J. Am. Chem. Soc. 2016, 138, 8588-8594.
- [20] F. P. Byrne, S. Jin, G. Paggiola, T. H. M. Petchey, J. H. Clark, T. J. Farmer, A. J. Hunt, C. R. McElroy, J. Sherwood, *Sustainable Chem. Processes* **2016** *4:7*.
- [21] I. A. Shukov, N. V. Dubrovina, A. Börner, Synthesis 2007, 19, 2925-2943.
- [22] B. Martín-Matute, K. Bogár, M. Edin, F. B. Kaynak, J.-E. Bäckvall, *Chem. Eur. J.* 2005, *11*, 5832-5842.
- [23] [a] E. Solari, S. Gautier, R. Scopelleti, K. Severin, Organometallics
   2009, 28, 4519-4526; [b] T. Campos-Malpartida, M. Fekete, F. Joó, A. Kathó, A. Romerosa, M. Saoud, W. Wojtków, J. Organomet. Chem. 2008, 693, 468-474.

COMMUNICATION

#### WILEY-VCH

## COMMUNICATION



A powerful cobalt drive. Cobalt PNP pincer complexes were found to be efficient catalysts for the isomerization of allylic alcohols to the ketones. The catalyst with phenyl groups on the phosphorus atoms was highly active in the absence of base. A broad variety of substrates were successfully converted. The mechanism proceeds via alkene insertion in the cobalt-hydride bond followed by beta-hydride elimination.