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# Well-defined Low-valent Cobalt Complexes in Catalysis: An Overview.

Cassandre C. Bories\*, Alexandre Sodreau, Marion Barbazanges, Marc Petit\*

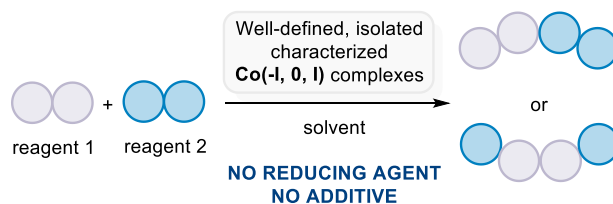
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**ABSTRACT:** For decades, transition-metal catalysts based on noble metal have proven to be highly efficient for a wide range of organic transformations. However, due to their low abundance and highly volatile price the use of such metal is now critical for the economy. Thus, the use of more sustainable alternatives is mandatory and the more abundant first-row transition metals are becoming interesting challengers. Among them low-valent 3d transition metals appeared as best candidates as they are intrinsically more reactive than high-valent ones. However, this reactivity implies that these complexes are often *in-situ* generated putting further away the aspect of atom economy and low waste. To circumvent this and to get more insight on the mechanism of reaction the concept of well-defined complexes has emerged. In this area, due to its historic development and the trouble associate with the preparation of other 3d transition metal well-defined complexes, cobalt appears as an important player. In this review, after a definition of what is a low-valent complex and the presentation of the concept of well-defined (pre)catalyst also known as the “single-component” strategy we will report the syntheses and applications in catalysis of low-valent well-defined cobalt complexes classify by their oxidation state and ligand environment.

## 1. INTRODUCTION

Catalysis can be found everywhere in modern organic chemistry. Indeed, a large majority of the commercial synthetic compounds is using a catalytic process with always the challenge of high efficiency in term of yield but also in term of selectivity. In the field of homogeneous catalysis, the transition metals have become the most attractive one. By using their d orbital, several kinds of functionalities can be activated by oxidative addition, reductive elimination or simply by coordination. Numerous examples of bond activation (H–H, C–H, Si–H...) and functionalization (C–C, C–Si, C–N, C–O...) are described in the literature using transition metals. However, in term of efficiencies, 4d and 5d noble metal are often predominant and thus their development during the last four decades was faster than the 3d ones. Transition metal catalysis is now facing news challenges since the last two decades. Indeed, to solve the main problem of noble metal resources, organic chemists must find new solutions using cheaper more abundant metals. The field of the economic direct C–H bond functionalization is the perfect example to summarize the situation: while reactions using ruthenium, rhodium, palladium and iridium have been considerably developed, it's only very recently that 3d transition metals have emerged as major challengers.<sup>1</sup> In fact, low-valent 3d transition metals appeared as better candidates as they are intrinsically more reactive compare to more stable high-valent states. However, as they are very sensitive to oxidation, the most common method to use these highly reactive low-valent 3d transition metals is to generate them *in situ*. Thus, to reach the same selectivities and efficiencies as the noble metals, a mixture of metal salt precursor, a proper ligand, a reducing reagent and additives are usually required. If the use of Group 1 and 2 metals and their organometallic reagents, or metal powders such as manganese and zinc, is simple and widely applied, the reproducibility and the formation of a huge amount of reductant-derived metal salt waste is a major drawback. Moreover, the excess of these reagents makes extremely difficult to identify the active species and the reaction mechanisms, thus hampering the

rational design and modification of the catalytic systems. In order to decipher the operative mechanism leading to potential optimized reactions, the atom economy and the waste production, the use of well-defined transition metal catalyst appears mandatory for the future. If the better candidate to replace precious metal is obviously the iron with its highest earth abundance and very low toxicity, the trouble associated with preparing low-valent well-defined iron complexes is somehow repulsive.<sup>2</sup> In the field of low-valent 3d metals catalysis cobalt appears historically as the one of most mature and promising player. Starting from the Kharash observation in the 40's for Grignard homocoupling,<sup>3</sup> through the hydroformylation,<sup>4</sup> the cycloadditions reactions with the use of  $\text{Co}_2\text{CO}_8$  (Pauson-Khand)<sup>5</sup> and the  $\text{CpCo(I)L}_2$  family ([2+2+2] reactions),<sup>6</sup> the cross-coupling reactions,<sup>7</sup> and now the radical reactions,<sup>8</sup> cobalt is omnipresent in every field. It is also interesting to point that even renowned chemist such as Richard Heck started working with cobalt before developing palladium chemistry.<sup>9</sup>



**Figure 1. Illustration of well-defined low valent cobalt catalyst catalytical activity.**

Cobalt is a  $d^9$  metal that can be found in 7 different oxidation states from -I to +V. In this review, we will focus on the evolution and the recent advances in the use of simple well-defined low-valent cobalt complexes (oxidation state from -I to +I) in catalysis. We will classify them by their oxidation state and ligand environment focusing on isolated characterized cobalt complexes that do not require any other reagent to be efficient in a

catalytic cycle (acid or base, reductant, oxidant, or any additives...). Thus, the complexes and the reactions presented in this review will be as simple as the Figure 1.

## 2. LOW-VALENT COMPLEXES

### 2.1. DEFINITION

The term of “low-valent” metal complexes is now commonly used in many articles and fairly well acknowledged although no clear definition nor reviews can be found in the literature. Indeed, this term does not refer to the valency of the metal but to its oxidation state. Joseph Chatt invoked in 1958 in his Introductory Lecture “*The stabilisation of low valent states of the transition metals*”<sup>10</sup> the connection between the valency and the oxidation state of a transition metal and gave a preliminary definition of this concept. And no better words could be employed to define it than the one from Chatt himself: “*When we speak of low valent states we mean lower than “normal” and by “normal” valent states we mean those states of the metals which are stable when they occur in aqueous solutions as salts*”. To emphasize his words, we will naturally take the cobalt as an example. The cobalt is a first-row transition metal which belongs to the group IX of the periodic table. With an atomic number  $Z=27$ , it adopts the electronic configuration  $[\text{Ar}]3d^74s^2$ . Cobalt is in the same column than rhodium and iridium and thus shares on some points the same reactivity but is far more abundant and cheaper than its congeners. Commercially and stable cobalt salts that can be found mostly concern cobalt (II). Among them we can mention the  $\text{Co}(\text{acac})_2$ ,  $\text{Co}(\text{OAc})_2$ ,  $\text{CoCl}_2$ ,  $\text{CoBr}_2$  and the  $\text{Co}(\text{NO}_3)_2$ .<sup>11</sup> Nonetheless, two stable salts of cobalt (III) can also be found, namely the  $\text{Co}(\text{acac})_3$  and the  $\text{CoF}_3$ .<sup>11</sup> So to come back to the definition of low-valent metal complexes, we can thus describe the stable oxidation state of cobalt as being Co (II) which is now well established. Concerning the other reported oxidation states, we can find cobalt (-I); (0); (I); (III) and some rare examples of cobalt (IV)<sup>12</sup> and (V).<sup>13</sup> Thus low-valent cobalt complexes concern cobalt (-I), (0) and (I). On the contrary, the other cobalt species whose oxidation state are greater than (II), will be called high-valent cobalt complexes (Figure 2).

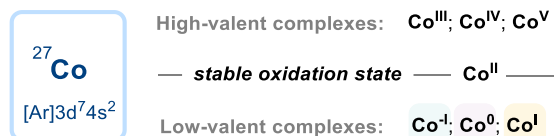
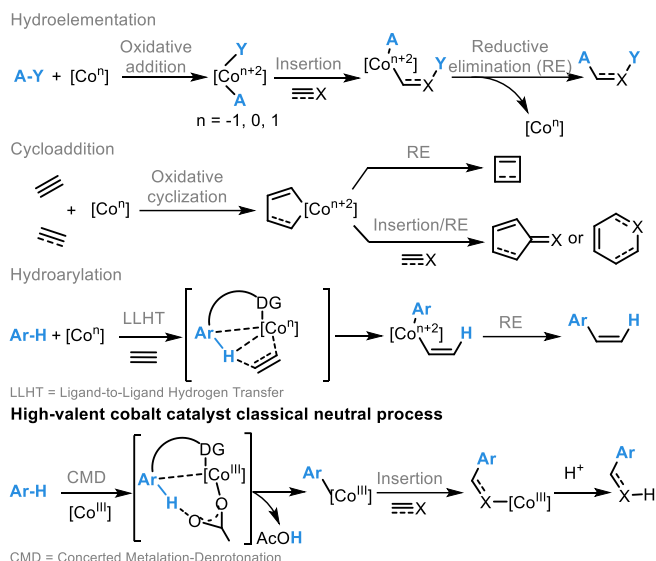


Figure 2. Classification of known cobalt oxidation states

Due to their respective  $d^{10}$ ,  $d^9$  and  $d^8$  electronic configuration the cobalt (-I); (0); (I); (III) are more prone to oxidative addition (one or two electron processes)<sup>14</sup> than the  $d^6$  high valent cobalt (III). Thus low-valent cobalt present a larger range of reactivity than the high-valent one (Scheme 1). For instance, we can find them in cycloaddition processes, hydroelementations, C-H bond activation/functionalization, coupling reactions. Some of them being versatile and are able to catalyze several types of reaction. (Scheme 1a)

### Low-valent cobalt catalysts classical 2 electrons processes

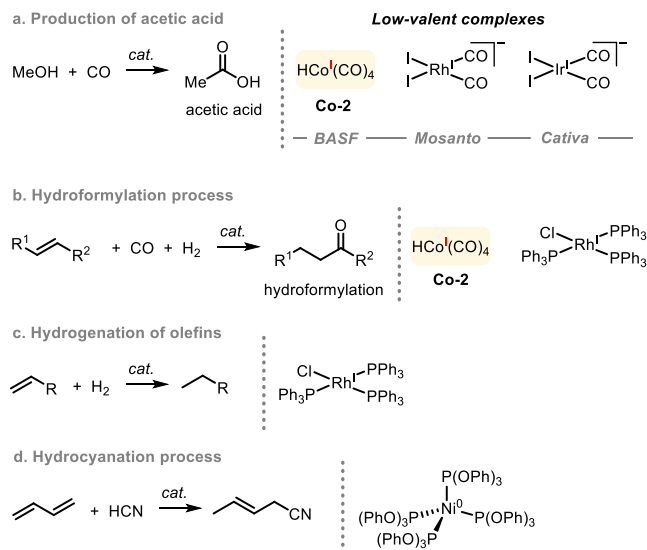


### Scheme 1. Reactivities of low-valent cobalt complexes vs high valent

Looking at well-defined cobalt (III) such as for instance the  $\text{Cp}^*\text{Co}(\text{III})$  type of complexes the application are mainly the C-H bond functionalization with often a neutral redox processes even if some Cobalt (V) intermediates are now proposed (Scheme 1b).<sup>15</sup> Some well-defined cobalt (II) and (III) porphyrin based complexes called carbene radical have unique redox properties not shown here cause not comparable to the reactivities described in this review.<sup>16</sup>

### 2.2. INDUSTRIALLY USED LOW-VALENT METAL COMPLEXES

After giving a definition of the concept of low-valent metal complexes, we will now emphasize their interest in catalysis. Indeed, mainly due to their reactivity and their ability to undergo oxidative addition, low-valent metal complexes have been widely used in many industrial processes.<sup>17</sup> The first one is the large-scale production of acetic acid which began in 1960 by BASF *via* methanol carbonylation. The  $\text{CoI}_2$  cobalt salt is used to generate the low-valent cobalt (0)  $\text{Co}_2\text{CO}_8$  **Co-1** which then reacts with water and carbon monoxide to give the low-valent hydrido cobalt (I)  $\text{HCo}(\text{CO})_4$  **Co-2** as the resting state of the catalyst.<sup>18,19</sup> The high pressure in carbon monoxide required and the poor selectivity on methanol led in 1968 to a new process using this time a rhodium catalyst. This catalytic system developed by Paulik and Roth and known as the Monsanto process is also based on a low-valent rhodium (I)  $\text{RhI}_2(\text{CO})_2^-$ .<sup>20</sup> The next improvement onto the carbonylation of methanol was the replacement of the rhodium metal center by iridium in order to overpass the rate limiting step of the oxidative addition. This process industrialized by BP Chemicals as the Cativa process relies once again on a low-valent complex, namely the iridium (I)  $\text{IrI}_2(\text{CO})_2^-$  (Scheme 2a).<sup>21</sup>



**Scheme 2. Applications of low-valent complexes in industrial processes**

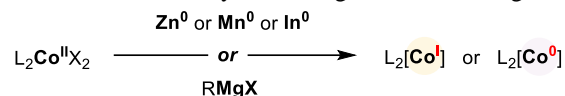
In the same spirit, the hydroformylation process, also called the oxo process, for the synthesis of aldehydes starting from olefin derivatives, was first catalysed by the low-valent cobalt (I)  $\text{HCo}(\text{CO})_4$  Co-2. This reactivity discovered by Otto Roelen was then industrialized by BASF.<sup>4</sup> Just as for the carbonylation of methanol, the cobalt catalyst was then replaced by a more efficient low-valent rhodium (I) complex (Scheme 2b), namely the Wilkinson catalyst.<sup>22</sup> The later is an important and widely used low-valent complex, that was described for the first time in 1965<sup>23</sup> for the homogeneous catalytic hydrogenation of olefins and acetylene.<sup>24</sup> Beside this reaction, this powerful catalyst is also used for numerous other organic transformations such as the catalytic hydroboration of alkenes; decarbonylation of aldehydes; [2+2+2] cycloadditions or even atom transfer radical polymerization (ATRP) of styrene and many more (Scheme 2c).<sup>25</sup> Finally, beside metals of group IX, another interesting example for the application of a low-valent complex as a catalyst relies in the hydrocyanation process developed by DuPont and using the nickel (0)  $\text{Ni}(\text{P}(\text{OPh})_3)_4$ .<sup>26</sup> Starting from the butadiene, this allows the synthesis of crotyl nitriles (Scheme 2d). As shown above, cobalt complexes were at the origin of several industrial catalytic reactions, but they have been over passed by its noble derivatives. In the perspective of reducing our dependence on noble metal feedstocks, a comeback to cobalt complexes requires an additional understanding to maintain high performances.

### 2.3. THE IN-SITU COMMON USE OF LOW-VALENT COBALT COMPLEXES

We saw the importance and the utility of low-valent complexes in industrialized processes. We also saw that low-valent cobalt complexes have been part of these industrialized catalysts for diverse reactions. In this part we want to rapidly address their usual preparation and application using the *in-situ* approach. Indeed, as said previously, low-valent cobalt complexes refer to Co (-I), Co (0), and Co (I) which are usually not the common oxidation states found for commercialized cobalt salts. Thus, as

they are sensitive and highly reactive to air, one of the most common ways to generate low-valent cobalt complexes is to generate them *in situ* starting from the commercially available high valent cobalt salts. These Co (II) and Co (III) salts have the advantages to be inexpensive and widely available. Starting from these commercialized salts, other Co (II) can be easily obtained in one step by adding L-type ligands such as phosphine or bipyridine for instance. It generally leads to  $\text{L}_2\text{CoX}_2$  type complexes where L are the added ligands and X the halogens (X = I, Br, Cl). These resulting complexes can also be used as starting pre-catalysts to form low-valent cobalt complexes.

Going from a Co (II) to a Co (I) or even lower oxidation states requires a reductant. A first simple way to proceed is the use of metal powders such as Zn or Mn. Usually applied on  $\text{L}_2\text{CoX}_2$  type complexes with X = Br, Cl, this methodology has been employed for various reactions<sup>27,28</sup> (Scheme 5a and 5b). To mention only few of them, there is the heterodimerization of acrylates or 1,3-dienes reported by Hilt and co-workers;<sup>29</sup> the hydrogenation of enamide reported by Chirik,<sup>30</sup> the vinylation of aryl halides<sup>31</sup> and other coupling reactions widely developed by Gosmini.<sup>32</sup> In the same spirit, indium powder has also been used by Dong and co-workers as a reductant starting from the iodide analogue pre-catalysts  $\text{L}_2\text{CoI}_2$  for C–H bond activation<sup>33</sup> (Scheme 5c). Another methodology which has been extensively explored is the use of alkali or alkaline earth metals and their organometallic reagents. Indeed, Grignard reagents mixed with the same  $\text{L}_2\text{CoX}_2$  type complexes or the commercialized salts  $\text{Co}(\text{acac})_{n=2,3}$  have been mostly used for C–H bond activation reactions by several groups<sup>34</sup> (Scheme 5a-b and 5d-e). Among them we can cite the group of Yoshikai who was pioneer in this field and the groups of Nakamura and Ackermann as well. The other reactivity that can be achieved with Grignard reagents is again cross-coupling reactions starting from halides substrates developed by Gosmini and Cahiez.<sup>7</sup> A completely different method to generate *in-situ* the low-valent cobalt complexes without the use of another chemical reagent is the use of electrochemistry, and particularly an iron anode.<sup>32</sup> These previous methodologies using either metal powders, organometallic reagents or electrochemistry leads to Co (I) or Co (0) species which are formed *in-situ* and most of the times not isolated nor fully characterized (Scheme 3). Some publication using this approach even mention “[Co<sup>0</sup>]” or “[Co<sup>I</sup>]” as the catalyst in the proposed catalytic cycle, without any real knowledge of the oxidation state of the catalyst or the ligands surrounding it.

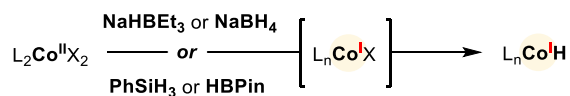


**Scheme 3. Generation of low-valent cobalt complexes from metal powders or organometallic species**

Other methods to generate low-valent cobalt complexes have also been developed. The metal hydrides  $\text{NaHBET}_3$  and the analogues  $\text{NaBH}(\text{tBu})_3$  and  $\text{LiBHEt}_3$  have been used on  $\text{L}_2\text{CoX}_2$  type complexes by the groups of Milstein and Fout for formylation and hydrogenation reactions<sup>35</sup> (Scheme 5a and 5b). Chirik and co-workers also demonstrated that it was compatible with the hydroboration of alkenes.<sup>36</sup> The sodium borohydride  $\text{NaBH}_4$  could also be used for hydrogenation reactions starting from the commercially available salts  $\text{Co}(\text{acac})_2$  or  $\text{Co}(\text{OAc})_2$  (Scheme 5e and 5f).<sup>27</sup> Aluminium reagents such as  $\text{AlMe}_3$  or  $\text{Al}(\text{tBu})_3$  are also efficient reductant to afford low-valent cobalt complexes

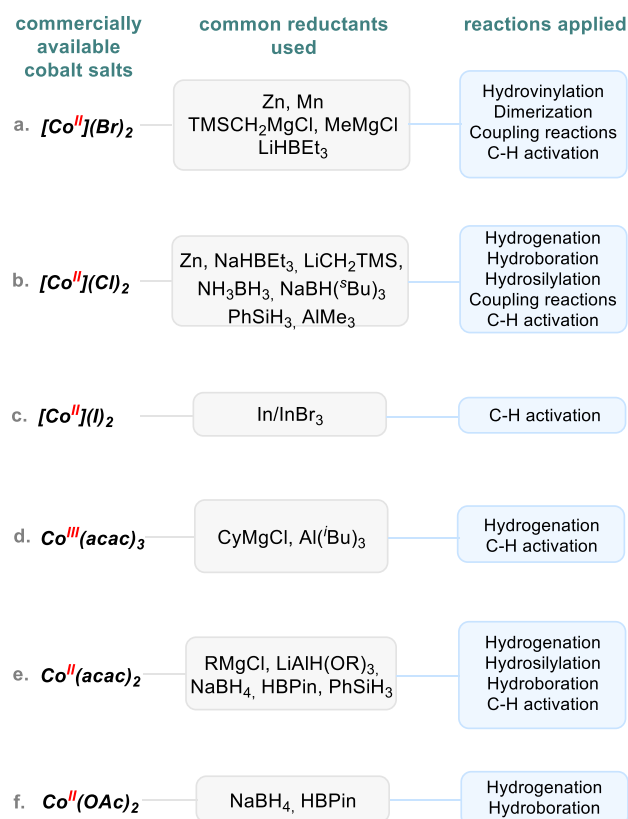


(Scheme 5b and 5d) and have been used for example by Rajanbabu for the hydrovinylation of 1,3-dienes.<sup>37</sup> Finally, more recent reports mostly from the group of Ge<sup>38</sup> but also from the group of Chirik<sup>39</sup> disclosed the use of other hydride reagents such as silanes or boranes to generate low-valent cobalt species (Scheme 5e and 5f). Starting from the Co(acac)<sub>2</sub> or Co(OAc)<sub>2</sub> salts, this methodology was used both for hydrosilylation and hydroboration reactions. In these cases, the generation of low-valent cobalt complexes from the Co (II) leads to the formation of a Co (I) which usually further reacts to generate at the end a cobalt hydride (Scheme 4).



#### Scheme 4. Generation of low-valent cobalt complexes using hydrides donor reagent

Regarding the synthesis of Co (-I) which is less described, harsher conditions are required with very strong reductant such as KC<sub>8</sub> which directly leads to the desired low-valent cobalt complex.



#### Scheme 5. Non-exhaustive usual methods to generate *in-situ* low-valent cobalt catalysts

We saw the great interest of low-valent metal complexes and particularly cobalt ones. However, as seen previously, their preparation usually requires additives which can be metals or hydrides. These types of preparations lead to *in-situ* generated

low-valent species which are not isolated. This is why we will now introduce the second concept that we will follow during all this review namely the concept of “well-defined” metal complexes.

### 3. WELL-DEFINED COMPLEXES

#### 3.1. DEFINITION

Well-defined catalysts or precatalyst (considering for instance an *in-situ* ligand release) rely on complexes prepared upstream, usually from commercially available salts, which are purified and isolated as a whole specie. As a result, these final catalysts can be fully characterized in term of structure and oxidation state. First and foremost, these complexes are then used as catalysts of the reaction with no need of additional reagent such as acid or base, reductant or oxidant to perform the catalysis (Figure 1). This concept of well-defined catalyst has also been recently designated by Don Tilley<sup>40</sup> as the “single-component” strategy which provides a straightforward path to access the active catalyst by introducing the reactants and in some cases an external stimulus. Which is not the case for *in situ* generated catalysts starting from precursors reduced or oxidized *in-situ*.

#### 3.2. ADVANTAGES OF WELL-DEFINED (PRE)CATALYSTS

Beyond the major drawback of *in situ* generated catalysts which is the formation of a great amount of reductant-derived metal salt wastes, the huge advantages of well-defined catalysts also rely on the mechanistic study and the tolerance towards functional groups. Indeed, the use of well-defined metal complexes facilitates the knowledge of the active catalyst because no additives are needed, only the catalyst and reactants co-exist in the medium. Analyses give then direct access to either catalytic intermediates or products and by-products of the reaction. The isolation of metallic intermediates is thus facilitated. Clément Mazet also summarized this point: “During optimization studies, the necessity of systematically preparing each and every catalyst might be a rather time-consuming task, but mechanistic information may be gleaned more readily by following this approach.”<sup>41</sup> The choice of the well-defined approach also gets a more realistic value of the catalyst loading. Indeed, in this case the amount of (pre)catalyst loading is usually a right reflection of the active catalyst concentration, unlike the *in-situ* generation which can lead to multiple inactive or competitive catalytic species.<sup>41</sup> At the same time, because no additives are needed, such as strong reductants or oxidants, a wider range of sensitive functional groups can be used in starting materials. Finally, another advantage of well-defined complexes is the reproducibility they offer. Indeed, this single component strategy is easier to reproduce with less uncertainties than the *in-situ* one which involves several components for the generation of the catalytic species. Therefore, we will focus exclusively on well-defined (pre)catalysts for the rest of this review.

### 4. WELL-DEFINED LOW-VALENT COBALT COMPLEXES

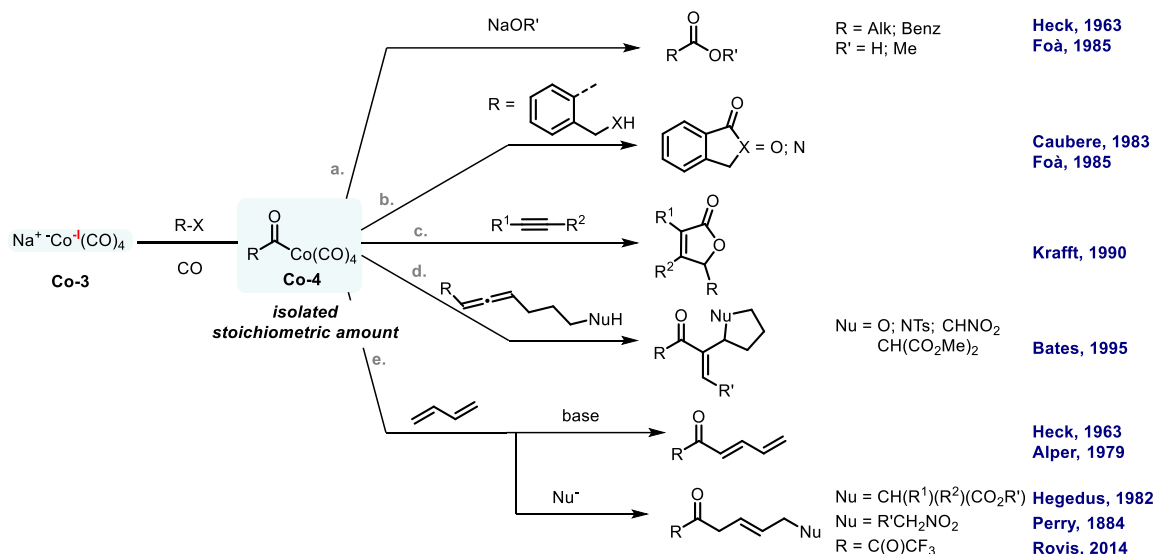
We saw the advantages of both low-valent metal complexes and well-defined catalysts. In this part we will now focus on low-valent well-defined cobalt complexes and we will report both their syntheses and their applications in catalysis. As described

before, low valent cobalt complexes refer to cobalt (-I), cobalt (0) and cobalt (I) that we will present in ascending order.

#### 4.1. COBALT (-I)

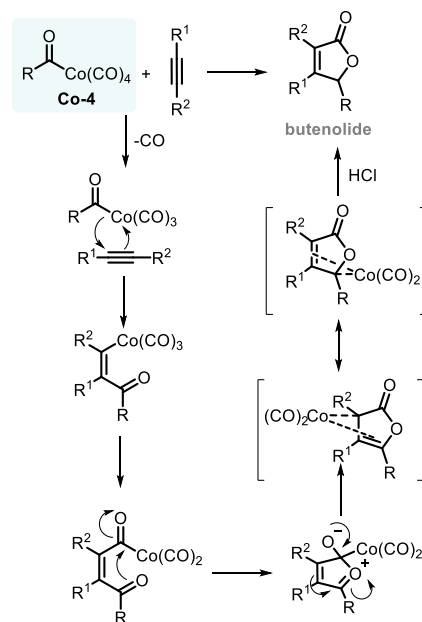
Cobalt (-I), also known as cobaltate, are the species with the lowest oxidation state known to date for cobalt. Few examples have been reported so far and even less have been applied in catalysis as well-defined catalysts. The first one has been discovered in 1952 through the reduction of  $\text{Co}_2\text{CO}_8$  **Co-1** with

sodium amalgam or sodium-ammonia to give  $\text{NaCo}(\text{CO})_4$  **Co-3**. Since, new methodologies starting from different sources of “ $\text{Co}(\text{CO})_4$ ” and other reducing agents have been developed. The potassium, lithium and thallium analogues of **Co-3** have been synthesized and characterized.<sup>42</sup> Its synthetic application was first investigated by Heck in 1963<sup>43</sup> with halogenated compounds giving the acyl cobalt species **Co-4** after insertion of a carbon monoxide (CO) (Scheme 6). These various isolated acyl cobalt tetracarbonyls **Co-4** have then been used in stoichiometric amount for various reactions (Scheme 6).<sup>42</sup>



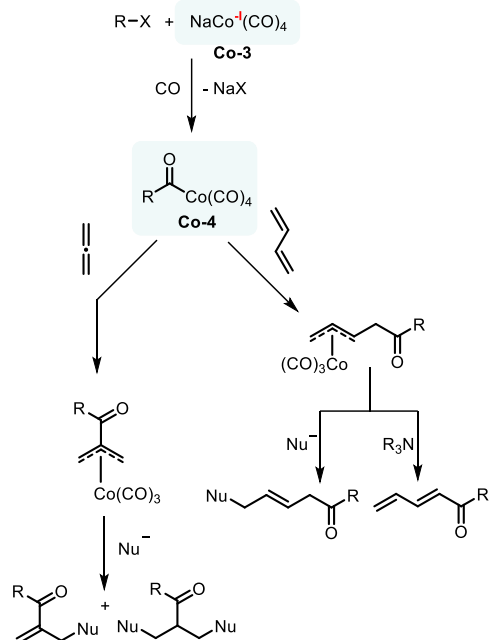
**Scheme 6. Stoichiometric reactions performed with the acyl cobalt tetracarbonyl Co-4**

Indeed, these acyl cobalt species **Co-4** can react with nucleophiles. Heck first disclosed this reactivity by using either NaOH or NaOMe which allowed to afford ester derivatives (Scheme 6a).<sup>43a</sup> The same reaction could also take place in an intramolecular manner, as reported by Caubere and Foà, leading both to lactones and lactams (Scheme 6b).<sup>43f,g</sup> On the other hand, Krafft early reported the insertion of an alkyne into the acyl cobalt tetracarbonyl species **Co-4**, leading to the corresponding vinyl cobalt (Scheme 7). After insertion of a carbon monoxide (CO) and further addition of the ketone to the acyl cobalt followed by proto-decobaltation, he could obtain butenolide derivatives (Scheme 6c and 7).<sup>43b</sup> With the same idea, very interesting reactivities have been found when using unsaturated partners such as conjugated diene or allene derivatives (Scheme 6d and 6e).<sup>43e</sup> In both cases, the acyl cobalt **Co-4** undergoes the insertion into the unsaturated system to form a  $\pi$ -allyl complex which can either react with a base to release the corresponding acylated diene (Scheme 6e) or with a nucleophile (Scheme 8).



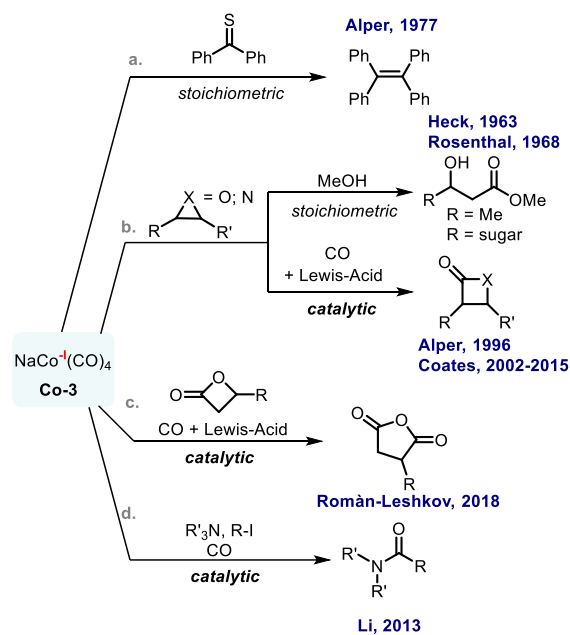
**Scheme 7. Proposed mechanism for the stoichiometric synthesis of butenolide**

Bates reported that when linking this nucleophile to the allene moiety, it could elegantly allow the intermolecular cyclization of the product (Scheme 6d).<sup>43e</sup>



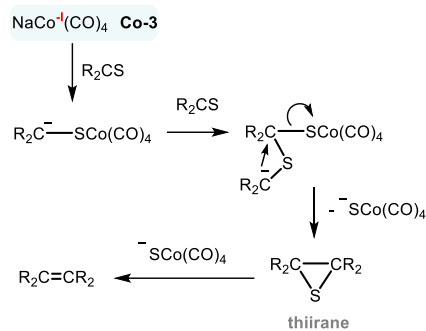
**Scheme 8. Stoichiometric reaction between Co-4 and dienes or allenes**

This strategy, even if stoichiometric, still has some interest since Rovis reported in 2014 that cobaltate **Co-3** could undergo the insertion into the trifluoroacetic acid and then provide the fluorinated acyl cobalt which further reacts with a diene, to afford fluoroacylated compounds (Scheme 6e) *via* the same mechanism presented before (Scheme 8).<sup>43d</sup>



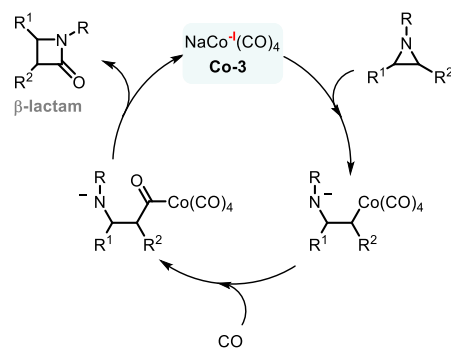
**Scheme 9. Stoichiometric and catalytic reactions performed with Co-3**

Rather than going through the acyl cobalt **Co-4** which had to be synthesized for each reaction,  $\text{NaCo}(\text{CO})_4$  **Co-3** can also be directly used as the catalyst of the reaction (Scheme 9). It was disclosed first in stoichiometric conditions with Alper who reported in 1977 a very interesting way to synthesize tetra-substituted alkenes starting from organosulfur reagents (Scheme 9a).<sup>44</sup> This McMurry-like reaction implies two primary successive thiophilic additions into the cobaltate **Co-3**. A cyclizing rearrangement then occurs to release the cobaltate  $\text{SCo}(\text{CO})_4^-$  and the thiirane, also called the episulfide, which then leads to the corresponding olefin (Scheme 10).



**Scheme 10. Stoichiometric desulfurization using Co-3**

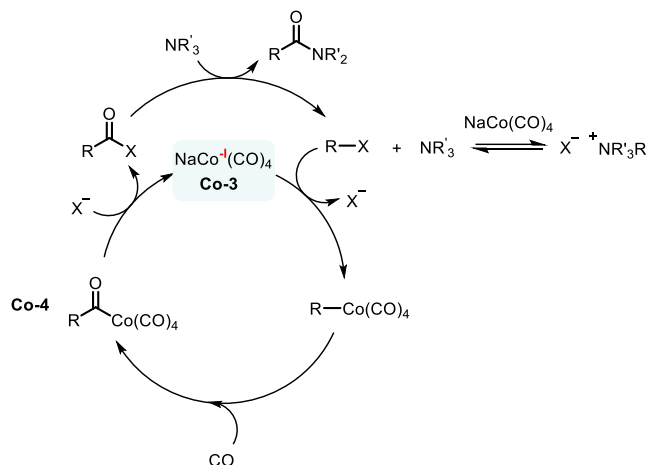
Insertion into epoxide or aziridine derivatives have also been explored (Scheme 9b), first with a stoichiometric amount of **Co-3** which undergoes the opening insertion followed by the carbon monoxide (CO) insertion. The resulting acyl cobaltate is, as seen before, trapped by methanol (MeOH) to give the ester.<sup>45</sup> Catalytic conditions have recently been developed based on the use of carbon monoxide (CO) pressure to regenerate the cobaltate complex **Co-3** after the insertion. Still using epoxides or aziridines, Alper was the first one to report the catalytic activity of **Co-3** to synthesize  $\beta$ -lactams (Scheme 9b and 11).<sup>46</sup>



**Scheme 11. Catalytic cycle for the synthesis of  $\beta$ -lactams using Co-3**

This work has since been widely extended by Coates and co-workers. By introducing the relevant Lewis-acid ( $\text{salph}(\text{thf})_2\text{Al}$ ) and other similar ones, he could play on their design and control both the regioselectivity and the enantioselectivity of this reaction (Scheme 9b).<sup>47</sup> Similarly, Román-Leshkov reported in 2018 the synthesis of anhydrides thanks to the addition of the cobaltate **Co-3** into  $\beta$ -lactones, also assisted by a Lewis-acid (Scheme 9c).<sup>48</sup> Finally, Li reported in 2013 the possibility to

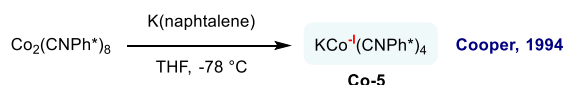
synthesize amide derivatives starting from the corresponding tertiary amines and an alkyl halide with a catalytic amount of **Co-3** (Scheme 9d).<sup>49</sup> The cobalt catalyst **Co-3** first interacts with the alkyl halide to give the alkyl cobalt which undergoes the insertion of an additional carbon monoxide (CO) molecule. The halide then promotes the release of the acyl halide from the resulting acylated cobalt **Co-4**. The tertiary amine then reacts with the acyl halide to form the desired amide (Scheme 12).



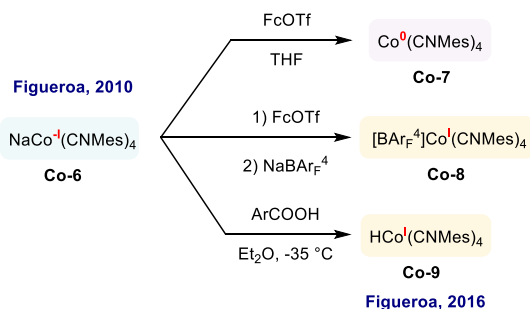
**Scheme 12.** Catalytic cycle for the synthesis of amides using **Co-3**

Taking advantage of the isoelectronicity of isocyanides compared to carbon monoxide, analogues of the cobaltate  $\text{NaCo}(\text{CO})_4$  **Co-3** have also been explored. Thanks to preliminary results reported by King in 1972<sup>50</sup> then by Stone and Green in 1977,<sup>51</sup> Cooper disclosed the synthesis of the first isocyanide cobaltate  $\text{KCo}(\text{CNPh}^*)_4$  **Co-5** in 1994 (Scheme 13a).<sup>52</sup> This class of complexes has long been unexplored until the more recent work of Figueroa who reported in 2010 that the mesityl isocyanide cobaltate  $\text{NaCo}(\text{CNMes})_4$  **Co-6** could be used to synthesize their Co (0) **Co-7** and Co (I) **Co-8** and **Co-9** analogues (Scheme 13b).<sup>53</sup>

a. Synthesis of **Co-A** as an analog of  $\text{NaCo}(\text{CO})_4$

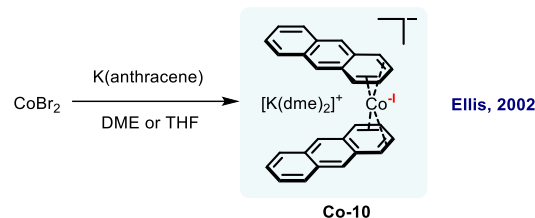


b. The use of **Co-B** as precursor of **Co-C** to **Co-E**



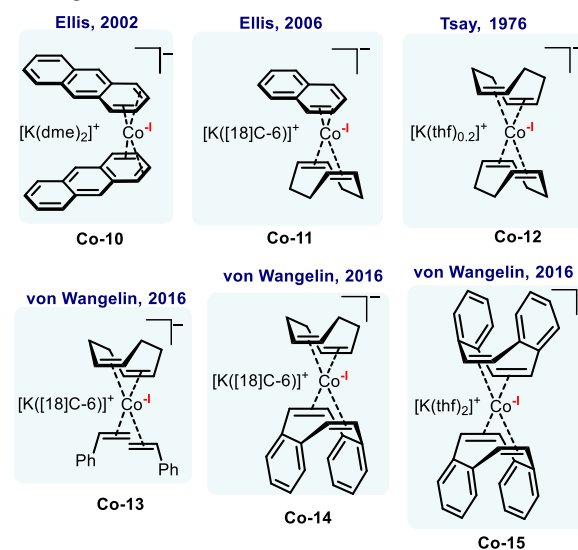
**Scheme 13.** Synthesis and use of **Co-5** to **Co-9** as analogs of  $\text{NaCo}(\text{CO})_4$  **Co-3**

Another famous category of well-defined cobalt (-I) is the cobalt-arenes. The first characterisation and isolation of cobalt-anthracene **Co-10** has been described by Ellis in 2002 (Scheme 14).<sup>54</sup>



**Scheme 14.** Example of synthesis of anthracene cobalt (-I)

Ellis, Tsay and mostly the group of Jacobi Von Wangelin then extended their syntheses to other arenes-based cobalt complexes.<sup>55,56</sup> They demonstrated that the anthracene could be replaced by naphthalene, cyclooctadiene, the analogue dibenzocyclooctadiene or even styrene as ligands to afford **Co-10-Co-15** (Figure 3).

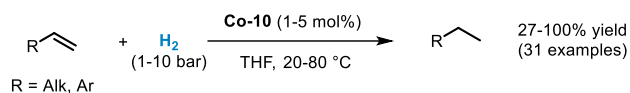


**Figure 3.** Cobalt-arenes used in catalysis

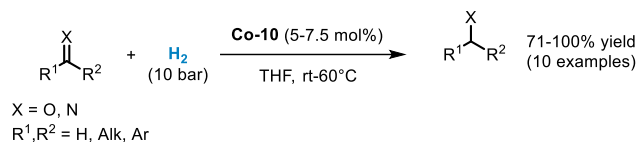
The group of Jacobi Von Wangelin demonstrated their high potential in catalysis. They indeed reported that such complexes were efficient catalysts for the hydrogenation of olefins, ketones and aldimines (Scheme 15).<sup>56</sup> Among them, aryl but also aliphatic olefins were suitable using **Co-10** as the catalyst under hydrogen pressure (Scheme 15a). Regarding polar starting materials, both aryl and aliphatic ketones but also aldimines could efficiently be reduced with the same catalyst (Scheme 15b). If the scope of substrates was made with **Co-10**, all the complexes presented above were explored as catalyst<sup>56b</sup> for the hydrogenation of styrene and 1-dodecene and the best activity was obtained for complex **Co-11**. However, regarding the reduction of imines or ketones, **Co-10** remained the best candidate. Recently, the groups of Wolf and Jacobi von Wangelin also developed a new generation of cobaltate complexes based on the bis(imino)acenaphthene (BIAN) ligand that they applied in alkene hydrogenation and other application.<sup>57</sup>



a. Hydrogenation of alkenes



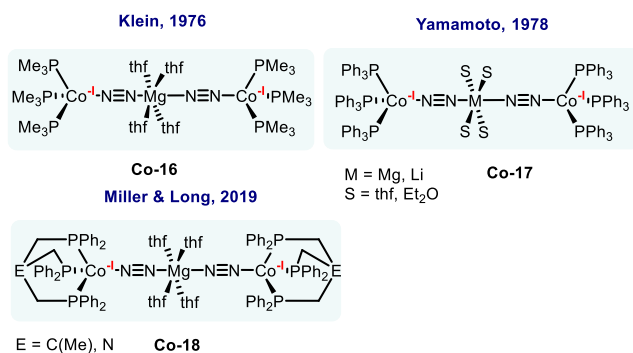
b. Hydrogenation of ketones and aldimines **Von Wangelin, 2014-2017**



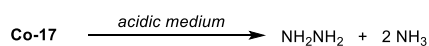
**Scheme 15. Hydrogenation of a) olefins; b) ketones and aldimines using cobalt-arenes as catalysts**

The last category of well-defined cobalt (-I) catalysts relies on dinitrogen cobalt ion complexes. In 1976 Klein reported the very first example starting from the dinitrogen trimethylphosphine cobalt hydride and diethylmagnesium.<sup>58</sup> The resulting complex **Co-16** is a dinuclear cobalt (-I) with a Co-NN-Mg-NN-Co bridging core system (Scheme 16a). Between 1978 and 1983, Yamamoto described the isolation of other analogues **Co-17** bearing PPh<sub>3</sub> or PPh<sub>2</sub>Et instead of PMe<sub>3</sub> and lithium counterion instead of magnesium.<sup>59</sup> He reported that these complexes, where N<sub>2</sub> is activated, could be converted into hydrazine and ammonia by treating the complex with an acidic medium such as hydrochloride (HCl) or sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) (Scheme 16b). These complexes appeared as very interesting molecules since Miller and Long synthesized very recently a similar new complex **Co-18** with a tridentate phosphine (Scheme 16a).<sup>60</sup> We will see that the discovery of these promising dinitrogen cobalt complexes and this preliminary reactivity result were of course followed by others for the activation of small molecules.

a. Structures of dinitrogen cobalt (-I) with Co-NN-M-NN-Co bridging core



b. Hydrogenation of N<sub>2</sub> with Co-17

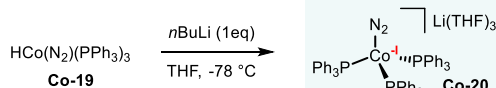


**Scheme 16. a) Structures of Co-16; Co-17 and Co-18; b) Application of Co-17 for the hydrogenation of N<sub>2</sub>**

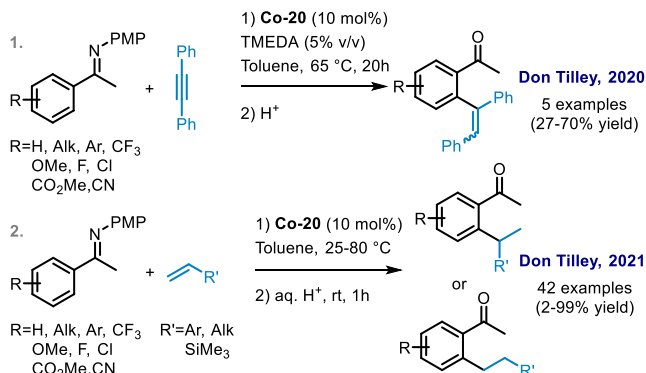
In a similar manner, the mononuclear complex **Co-18** was synthesized by Yamamoto and Kasai<sup>59</sup> using *n*-BuLi to generate it, starting from HCo(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>3</sub> **Co-19** (Scheme 17a).<sup>40</sup> This complex was then applied in catalysis by Don Tilley in 2020 and 2021.<sup>61</sup> **Co-20** was used as a well-defined catalyst for the C-H bond activation of aromatic imines with alkynes and alkenes as partners (Scheme 17b).<sup>61</sup>

a. Synthesis of Co-20

**Yamamoto & Kasai, 1983**



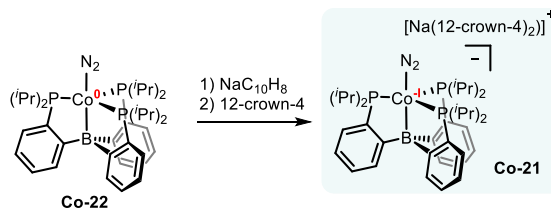
b. Application in catalysis



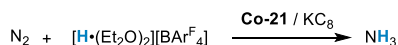
**Scheme 17. Synthesis of Co-20 and application in catalysis**

Rather than monodentate phosphines as ligands, Peters also synthesized in 2015 the Co (-I) **Co-21** bearing the tetradentate ligand *o*-(<sup>i</sup>Pr<sub>2</sub>P)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>B (TPB).<sup>62a</sup> Starting from the Co (0) **Co-22**<sup>62b</sup> in presence of NaC<sub>10</sub>H<sub>8</sub> and 12-crown-4, **Co-21** could be isolated and fully characterized including an X-Ray structure (Scheme 18a). This complex was also successfully used as a catalyst for the reduction of N<sub>2</sub> into NH<sub>3</sub> (Scheme 18b).

a. Synthesis of Co-21 starting from Co-22

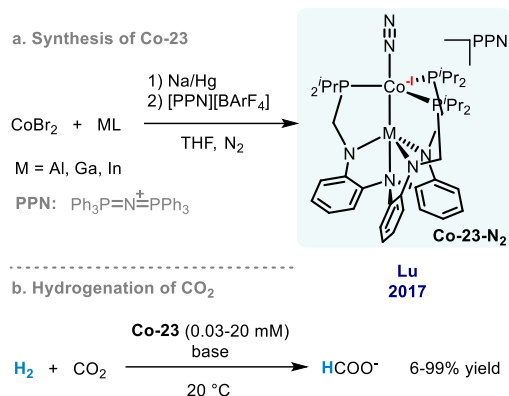


b. Reduction of N<sub>2</sub> catalyzed by Co-21



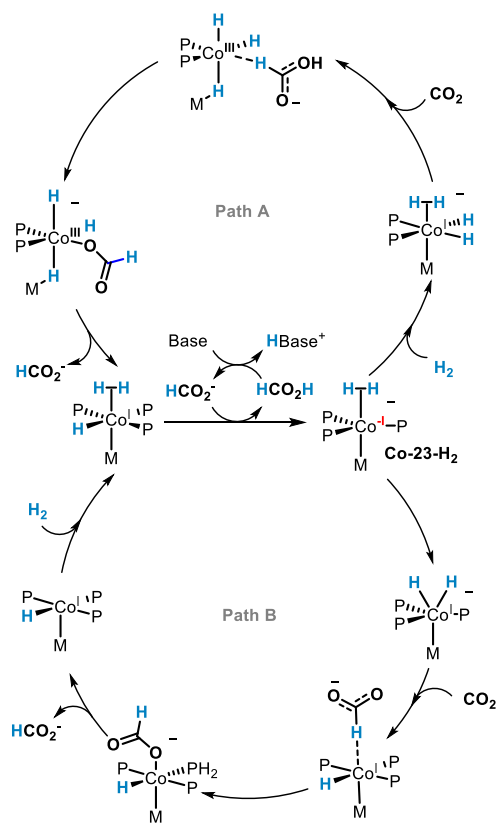
**Scheme 18. a) Synthesis of Co-21; b) Application of Co-21 for the reduction of N<sub>2</sub>**

In parallel, Lu reported in 2017 the synthesis of a new well-defined cobalt (-I) **Co-23** based on a group 13 metalloligand (M= Al, Ga, In),<sup>63</sup> starting from the commercially available salt CoBr<sub>2</sub> reduced by the sodium/mercury amalgam and further anionized with the bis(triphenylphosphine) iminium (PPN) (Scheme 19a). This innovative complex was then introduced by the same group as an efficient catalyst for the hydrogenation of CO<sub>2</sub> to formate (Scheme 19b).<sup>64</sup>



**Scheme 19. a) Synthesis of Co-23 and b) application in catalysis**

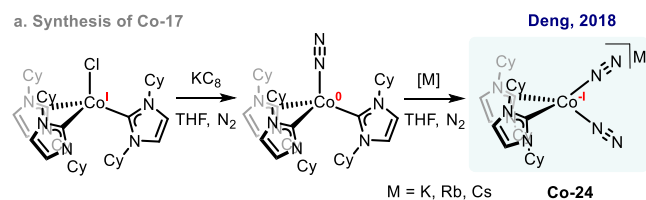
The complex **Co-23-H<sub>2</sub>** undergoes the oxidative addition of the dihydrogen (H<sub>2</sub>). The carbon dioxide is then converted into formate and further liberates the corresponding anion HCO<sub>2</sub><sup>-</sup>. The only role of the base here is thus to transform the formic acid into the formate during an off-cycle, without any interaction with the metal complex (Scheme 20).



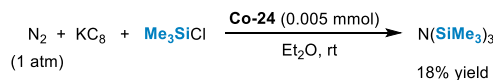
**Scheme 20. Mechanism for the hydrogenation of CO<sub>2</sub> using Co-23**

Deng reported in 2018 the synthesis of a NHC-based bis(nitrogen)cobalt (-I) **Co-24** starting from a cobalt (I) chloride which is reduced with KC<sub>8</sub> into the cobalt (0) and then in cobalt (-I) by the introduction of a metal (Scheme 21a).<sup>65</sup> Just as the complex **Co-18** developed by Miller and Long (Scheme 16a),<sup>60</sup> this complex **Co-24** was used for the catalytic silylation of nitrogen

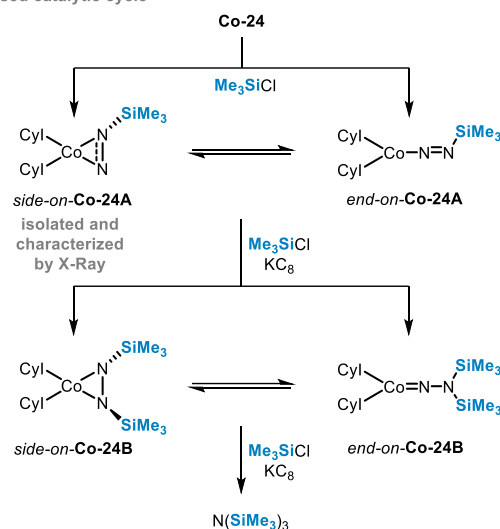
(Scheme 21b). In presence of a stoichiometric amount of Me<sub>3</sub>SiCl, the complex **Co-24A** is formed with an X-Ray structure of the *side-on* form which could be obtained. The authors suggest that a further addition of Me<sub>3</sub>SiCl and KC<sub>8</sub> promotes the generation of **Co-24B** which then releases the silylated N(SiMe<sub>3</sub>)<sub>3</sub> under the same conditions (Scheme 21c).



b. Catalytic hydrosilylation of N<sub>2</sub>



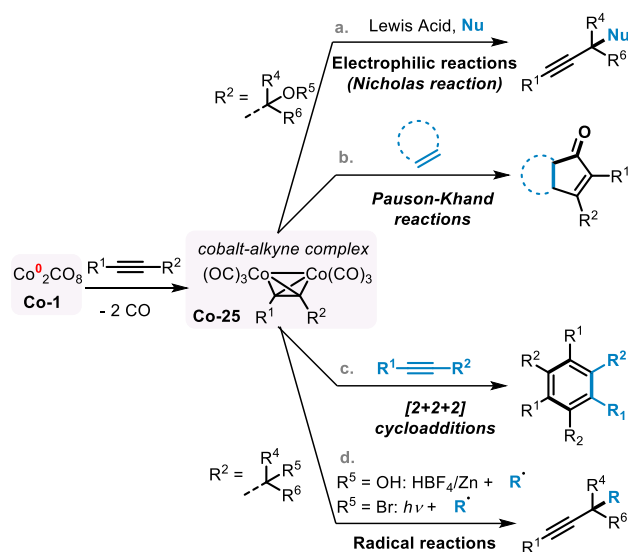
c. Proposed catalytic cycle



**Scheme 21. a) Synthesis of Co-24 and b) application in catalysis.**

## 4.2. Cobalt (0)

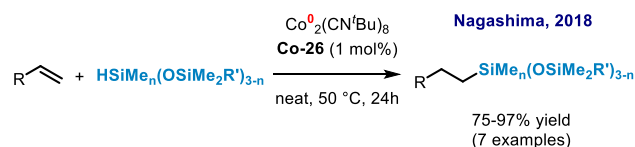
For a long time the binary Co<sub>2</sub>CO<sub>8</sub> **Co-1** was the most famous well-defined cobalt (0) complexes. Its ability to easily exchange a CO ligand for another donor one and its affinity towards alkynes made it a catalyst of choice. Despite being a source of the “Co(CO)<sub>4</sub>” moiety as we have seen in the previous paragraph (see section 4.1.), the Co<sub>2</sub>CO<sub>8</sub> **Co-1** has been famously known by Chalk and Harrod in 1965 for its reactivity towards hydrosilanes.<sup>66</sup> Further than that, in presence of a triple bond, the Co<sub>2</sub>CO<sub>8</sub> **Co-1** acts as a protecting group and leads to a cobalt-alkyne complex **Co-25** with the loss of two CO ligands (Scheme 22). This resulting cobalt-alkyne complex can then undergo different type of reactions.



**Scheme 22.** Overview of the reactivity of  $\text{Co}_2\text{CO}_8$  with alkynes.

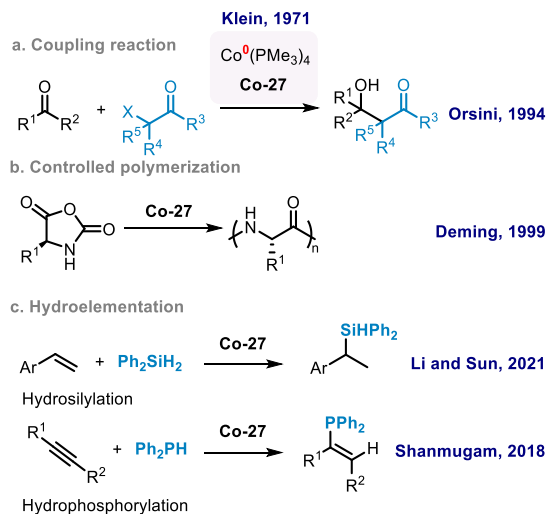
We will not compile a catalogue of all the published examples for these various reactions given the number of excellent reviews and book chapters already reported.<sup>67</sup> We will however summarize the main types of reactivity which have been reported (Scheme 22). The first type of reaction that can be mentioned is electrophilic reactions, also known as the Nicholas reaction. The cobalt-alkyne complex **Co-25** bearing an alkoxy group is activated by a Lewis-acid generating a cation which is trapped by an additional nucleophile, providing a substituted alkyne at the end (Scheme 22a). The second well-known type of reaction is the Pauson-Khand reaction which has been largely and is still used for the synthesis of  $\alpha,\beta$ -cyclopentenones (Scheme 22b). The cobalt-alkyne species **Co-25** reacts with an alkene followed by an insertion of a carbon monoxide (CO) to release the final product. The next type of reaction is the [2+2+2] cycloaddition. Indeed, the use of this catalyst is a straightforward method for the preparation of phenyl patterns starting from three alkynes moieties (Scheme 22c). Finally, the last type belongs to radical reactions. Using different methodologies depending on the substituent on the cobalt-alkyne **Co-25**, it is possible to generate a radical in alpha position of the cobalt center. The recombination with another radical species then affords the corresponding substituted alkyne (Scheme 22d).

As before (section 4.1), the analogue  $\text{Co}_2(\text{CN}^t\text{Bu})_8$  **Co-26** of  $\text{Co}_2\text{CO}_8$  **Co-1** bearing isocyanide ligands has also been synthesized by Stone and Green in 1977.<sup>51</sup> The X-Ray structure reveals a similar skeleton than **Co-1**. Its application in catalysis as a well-defined catalyst was disclosed more recently in 2018 by Nagashima for the hydrosilylation of alkenes using hydrosiloxanes (Scheme 23).<sup>68</sup>



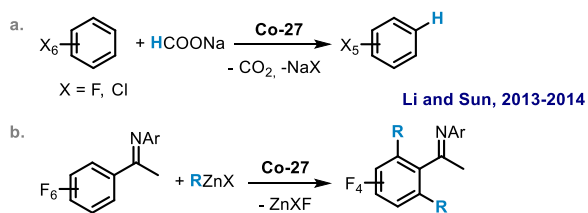
**Scheme 23.** Hydrosilylation of alkenes using **Co-26**

Beyond the  $\text{Co}_2\text{CO}_8$  **Co-1** catalyst, Klein and co-workers disclosed in 1971<sup>69</sup> the synthesis of a phosphine-based cobalt (0) complex  $\text{Co}(\text{PMe}_3)_4$  **Co-27** and its stoichiometric reactivity toward nitric oxide and azobenzene.<sup>70</sup> Since, it has been shown that this complex can undergo multiple reactions. Orsini described in 1994 an aldol-type coupling reaction between an  $\alpha$ -bromo ketone and carbonyl compound for the formation of C–C bonds (Scheme 24a).<sup>71</sup> Shortly after, Deming used the same cobalt (0) **Co-27** as an efficient initiator for the controlled polymerization of  $\alpha$ -amino acid-*N*-carboxyanhydrides (NCAs) (Scheme 24b),<sup>72</sup> a procedure that is still used by this group for their numerous works in this field of application. More recently,  $\text{Co}(\text{PMe}_3)_4$  **Co-27** has also been reported as an efficient catalyst for the reduction of alkynes and alkenes through hydrophosphorylation<sup>73</sup> and hydrosilylation<sup>74</sup> respectively (Scheme 24c).

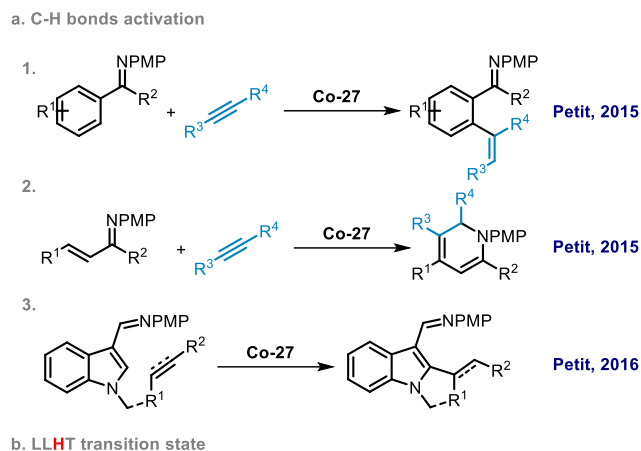


**Scheme 24.** Application of **Co-27** in catalysis

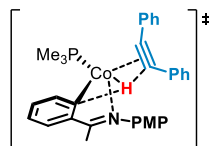
This well-defined cobalt complex also played an important role in bond activations. The halogen-bond activation started with Li and Sun in 2013 on C–F<sup>75</sup> and C–Cl<sup>76</sup> bonds. For halogenated benzenes, sodium formate is used as the source of hydrogen to promote the hydrodehalogenation (Scheme 25a). In the other case, the imine plays the role of the directing group and an organozinc reagent allows the transmetalation to afford the alkylated or arylated product (Scheme 25b).



**Scheme 25.** Application of **Co-27** in catalysis for C–X bonds activation/functionalization



b. LLHT transition state

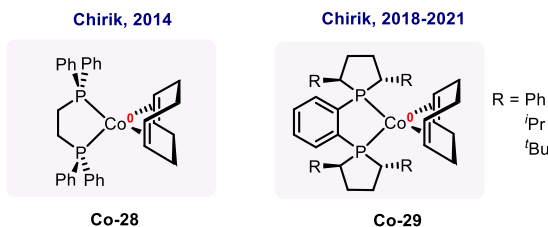


**Scheme 26. a) Application of Co-27 in catalysis for C-H bonds activation/ functionalization. b) LLHT transition state**

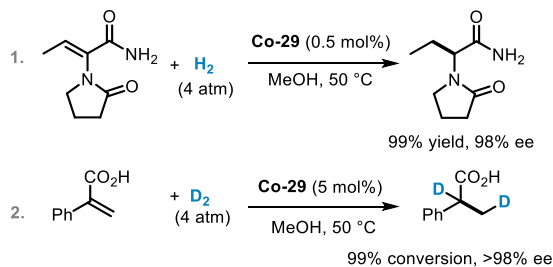
The challenging C–H bonds activation has been achieved by the Petit's group in 2015 on various substrates.<sup>77</sup> The use of the well-defined catalyst **Co-27** was a breakthrough in C–H bond activation catalyzed by low valent cobalt catalysts as it was the first one on a wide variety of substrate where the use of an additional reducing agent such as a Grignard reagent was not necessary. Alkynylation of diverse imines with different alkynes could thus be performed (Scheme 26a.1).<sup>77a</sup> When using  $\alpha,\beta$ -unsaturated imines in the same conditions, 1,2-dihydropyridines were obtained (Scheme 26a.2).<sup>77b</sup> Finally, intra- and intermolecular C–H bond activation/functionalization could also be performed on indoles bearing an imine as directing group and an alkyne or alkene group to provide polycyclic products (Scheme 26a.3).<sup>77c</sup> The simplicity of the catalyst allowed to perform detailed mechanistic studies, including deuterium-labelling experiments and DFT calculations. The group of Petit disclosed an interesting ligand-to-ligand hydrogen transfer (LLHT) mechanism was operational, a pathway not previously proposed for cobalt-catalyzed C–H functionalization. This mechanism, that could not previously be proposed due to the complex mixtures involved in generating the catalytic species, was later confirmed by Ackermann and is now well-established in the field of cobalt C–H bond activation.<sup>78</sup> In the same category of phosphine-based catalysts, Chirik described in 2014 a new class of bisphosphine and COD-based cobalt (0) **Co-28** (Scheme 27a) easily prepared from the corresponding cobalt (II) halide or the cobalt (I) halide dimer in presence of zinc and cyclooctadiene.<sup>30</sup> Others have been prepared using this time a bis-alkyl precursor in presence of hydrogen and COD. Especially some of them with chiral bisphosphines such as **Co-29** showed very good chiral induction in a high throughput evaluation for the enantioselective hydrogenation of enamides (Scheme 27b.1).<sup>79</sup> These catalysts were also used for the deuteration of  $\alpha,\beta$ -unsaturated carboxylic acids (Scheme 27b.2)<sup>80</sup> and the hydrogenation of alkenes.<sup>79a</sup> However, if they have been

reported as efficient well-defined catalysts, very few examples were reported using this methodology and the *in situ* generation was usually preferred with the addition of Zn dust for the substrate scope.

a. Structures of Co-28 and Co-29



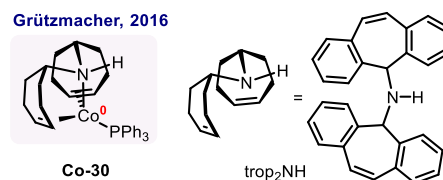
b. Catalysis



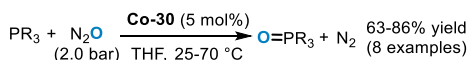
**Scheme 27. a) Structure of Co-28 and Co-29 and b) their application in catalysis**

Grützmacher developed for his part a cobalt (0) catalyst **Co-30** with a  $\text{trop}_2\text{NH}$  ligand (Scheme 28a) for the selective oxidation of phosphines including highly sensitive ones bearing a C=C, P–H or P–P bond which cannot be achieved by a classical aerobic oxidation.<sup>81</sup> The use of the greenhouse gas nitrous oxide ( $\text{N}_2\text{O}$ ) as the source of oxygen leads to clean and selective reaction under mild conditions with  $\text{N}_2$  as the sole by-product (Scheme 28b).

a. Structure of Co-30



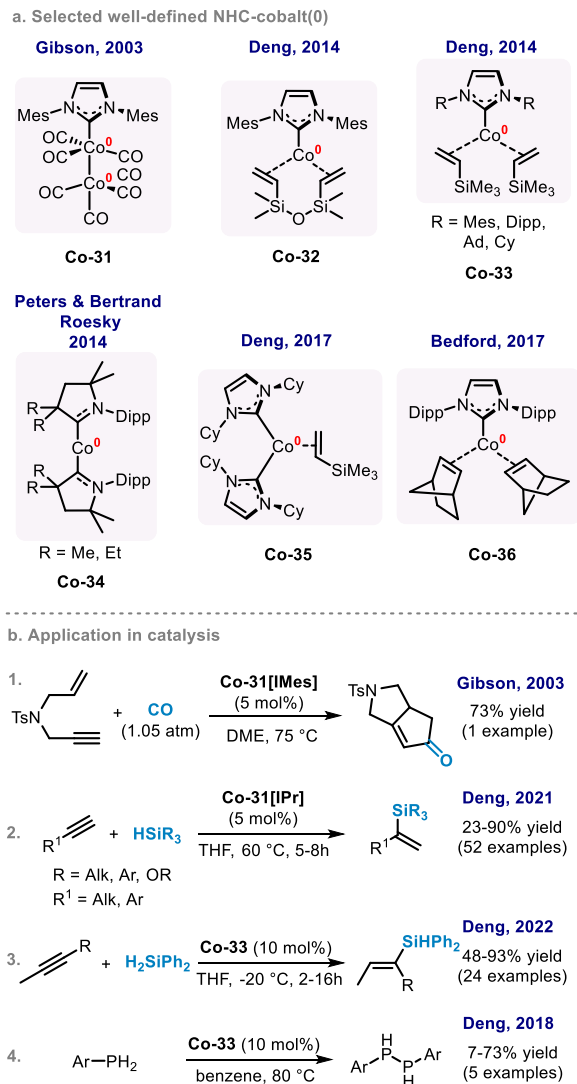
b. Application in catalysis



**Scheme 28. a) Structure of Co-30 and b) its application in catalysis**

The last class of well-defined cobalt (0) catalysts belongs to the NHC (or CAAC)-cobalt complexes,<sup>82</sup> whose first example **Co-31** was reported in 2003 by Gibson<sup>83</sup> followed in 2014 by Deng,<sup>13</sup> Peters and Bertrand,<sup>84</sup> Roesky<sup>85</sup> and others later<sup>86</sup> (Scheme 29a). They have been isolated and characterized with few of them being used in catalysis. Gibson reported the efficiency of **Co-31** for the Pauson Khand reaction (Scheme 29b.1).<sup>83</sup> Deng and co-workers then have been exploring the reactivities of low-valent NHC-cobalt (0) towards the activation

of silanes,<sup>87a</sup> including hydrosilylation of alkynes,<sup>87b,c</sup> the activation of phosphine-aryl (Scheme 29b.4)<sup>88</sup> and nitroso-aryls compounds since 2017.<sup>89</sup>



**Scheme 29. a) Selected well-defined NHC-cobalt (0) catalysts and b) selected applications in catalysis**

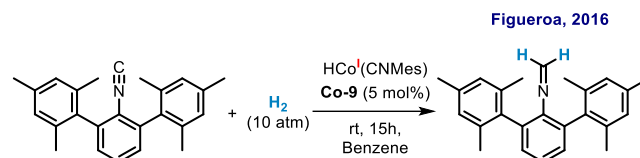
### 4.3. Cobalt (I)

Well-defined low-valent cobalt (I) species is the category where we can find the greatest number of catalysts reported. This is why we will divide them according to their ligands environment. We will first present the  $ML_nX$  class where  $L = CO, PR_3$  and  $n = 1, 2, 3$ . We will then focus on the specific case of pincer ligands, followed by the cyclopentadienyl ones. Finally, we will finish by the emerging NHC-based complexes.

#### 4.3.1. $ML_nX$ cobalt complexes ( $n=1,2,3$ )

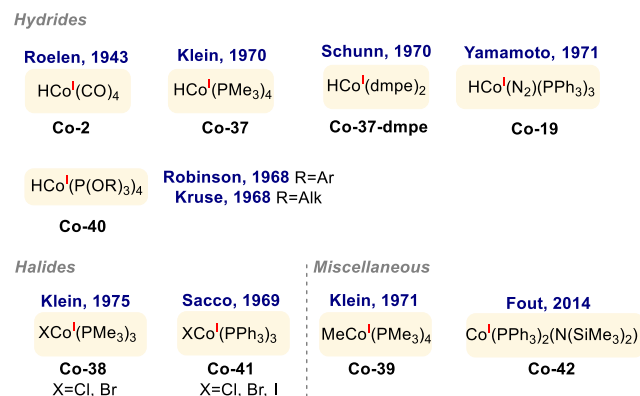
The  $ML_nX$  is one of the most abundant configuration for homogeneous cobalt complexes with the  $ML_4X$  which represents 34% of structure occurrence according to the  $MLX$  plot reported by Crabtree and Mingos.<sup>90</sup>

The first example we can mention is the well-known  $HCo(CO)_4$  **Co-2** which was used and industrialized for carbonylation of methanol and hydroformylation reactions as presented before (see section 2.2.). Once again, its cationic analog  $[PF_6]Co(CN^tBu)_6$  bearing isocyanide as ligand was synthesized first by King in 1972.<sup>50</sup> The hydrido analogue  $HCo(CNMe)_4$  **Co-9** was later synthesized by Figueroa<sup>53b</sup> as seen before (see section 4.1). This catalyst showed reactivity towards isocyanides themselves when brought back to room temperature and was applied in a catalytic hydrogenation of MesCN (Scheme 30).<sup>53b</sup> In 2021, the same group also disclosed some stoichiometric reactivity of **Co-E** toward olefins.<sup>91</sup>



**Scheme 30. Hydrogenation of CNMes using Co-9**

The synthesis of  $HCo(CO)_4$  **Co-2** was followed few years later by other phosphine-based cobalt (I) catalysts (Figure 4). Klein synthesized in the 70s the trimethylphosphine-based catalysts  $HCo(PMe_3)_4$  **Co-37**,  $XCo(PMe_3)_3$  **Co-38** (with  $X = Cl, Br$ ) and  $MeCo(PMe_3)_4$  **Co-39** bearing respectively a hydride,<sup>92a</sup> a halide<sup>92b</sup> or a methyl<sup>92c</sup> as the X ligand. An analog of the hydrido-cobalt **Co-37** was synthesized by Schunn the same year with this time the bidentate ligand 1,2-bis-dimethylphosphinoethane (dmpe).<sup>93</sup> For their part, Robinson<sup>94a</sup> and Kruse<sup>94b</sup> reported in 1968 the synthesis of the phosphite-based hydrido-cobalt complexes  $HCo(P(OR)_3)_4$  **Co-40** with aryl and alkyl phosphites respectively. Regarding the triphenylphosphine-based cobalt complexes, Yamamoto isolated the first dinitrogen-metal complex  $HCo(N_2)(PPh_3)_3$  **Co-19** in 1971<sup>95</sup> where the dinitrogen ( $N_2$ ) ligand is necessary to stabilize the hydrido complex unlike its chloride analogue  $ClCo(PPh_3)_3$  **Co-41**, first described by Sacco and Rossi in 1969,<sup>96</sup> that is stable enough on its own. Using the latter, Fout and co-workers recently reported a new variant  $Co(PPh_3)_2(N(SiMe_3)_2)$  **Co-42**.<sup>97</sup> The applications of these complexes came later and among them we can mention some examples of their use as well-defined catalysts.

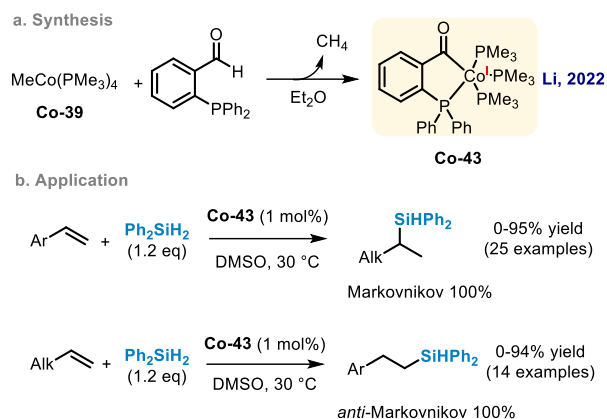


**Figure 4.  $ML_nX$  well-defined cobalt (I) complexes**

The trimethylphosphine-based complexes such as  $HCo(PMe_3)_4$  **Co-37** and  $MeCo(PMe_3)_4$  **Co-39** could also be used as efficient



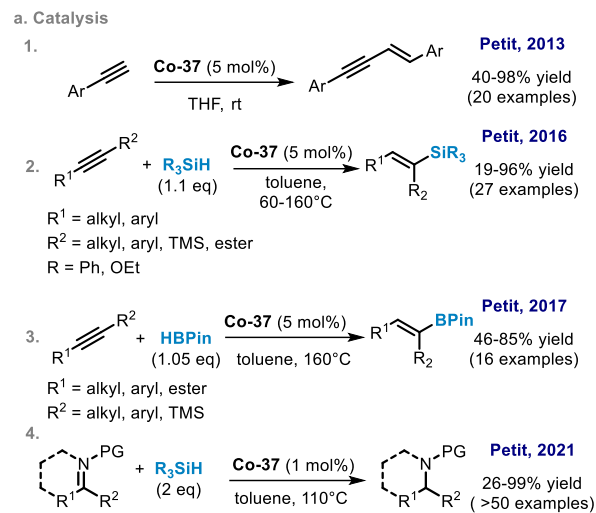
pre-catalysts to synthesize other cobalt (I) complexes due to their ability to undergo oxidative addition followed by reductive elimination of H<sub>2</sub> and methane, respectively. They were used for instance with pincer ligands to prepare pincer complexes that we will describe in detail in the next section. One example we can mention to illustrate the utility of MeCo(PMe<sub>3</sub>)<sub>4</sub> **Co-39** is the easy formation of the new (*P,C*)-chelate cobalt (I) complex **Co-43** synthesized by Li in 2022 (Scheme 31a). This catalyst is efficient for the hydrosilylation of alkenes in mild conditions and has a specific Markovnikov selectivity for styrene type compounds and an *anti*-Markovnikov one for the aliphatic alkenes (Scheme 31b).



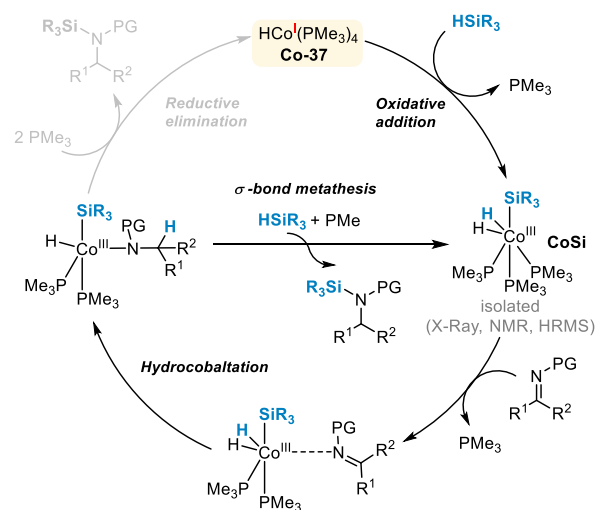
**Scheme 31. Hydrosilylation of alkenes using Co-43**

Their reactivity as stoichiometric reagents has also been widely explored since Klein described C–H activations enabled by MeCo(PMe<sub>3</sub>)<sub>4</sub>.<sup>92c</sup> Yamamoto also invoked the activation of small molecules such as nitrous oxide (N<sub>2</sub>O), carbon dioxide (CO<sub>2</sub>) or formic acid (HCOOH) using the triphenylphosphine analogue HCo(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>3</sub> **Co-19**.<sup>95</sup> Their applications in catalysis as well-defined catalysts were developed later and these cobalt hydrides were mainly found to be efficient for reduction, hydroelementation, bond activation and cycloaddition. The Petit's group was more focused on the use of HCo(PMe<sub>3</sub>)<sub>4</sub> **Co-37** and first demonstrated that it was an efficient catalyst for [2+2+2] cycloaddition of ene-diyne.<sup>98</sup> Sterically challenging [6]-helicene could also be obtained by intramolecular triyne [2+2+2] cycloaddition.<sup>99</sup> They also showed that this cobalt (I) complex was also efficient in the C–H bond activation as highlighted before with the cobalt (0) analogue. Indeed, if **Co-37** turned out to be less efficient for the previously mentioned C–H functionalization, it proved to be more efficient for the selective head-to-head dimerization of arylacetylenes (Scheme 32a).<sup>100</sup> More recently the same group focused on the hydrosilylation and the hydroboration of alkynes using HCo(PMe<sub>3</sub>)<sub>4</sub> **Co-37** (Scheme 32a).<sup>101</sup> **Co-37** revealed also efficient on the hydrosilylation of a wide range of imines (aliphatic, aryl and cyclic) to allow the formation of the corresponding amines after hydrolysis.<sup>92</sup> Thanks to the well-defined character of **Co-37** a mechanistic study was conducted. The proposed mechanism involves a first oxidative addition of the cobalt (I) **Co-37** into the Si–H bond to form **CoSi** that was characterized by X-ray diffraction. Then, after ligand exchange and hydrocobaltation, a  $\sigma$ -

bond metathesis process was proposed instead of a simple reductive elimination, based on DFT calculation, NMR experiment and kinetic studies (Scheme 32b).<sup>102</sup>

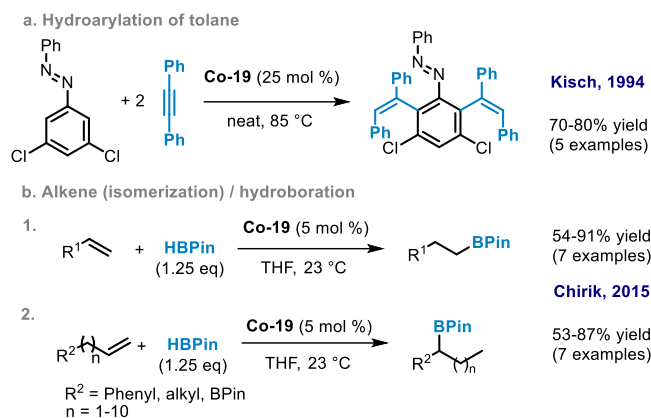


b. Mechanism



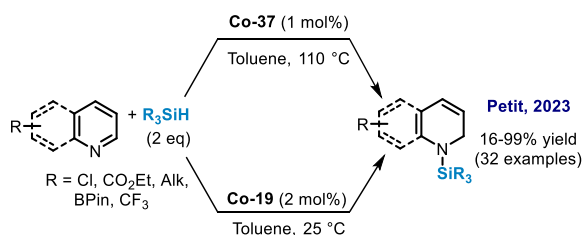
**Scheme 32. Hydro-elementations of insaturation using Co-37**

The analog **Co-37-dmpe** was also employed for the hydrogenation of CO<sub>2</sub> by Linehan.<sup>103</sup> The use of HCo(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>3</sub> **Co-19** was less developed at the beginning with applications only with a narrow scope. In 1994 the group of Kisch disclosed the first cobalt-catalyzed hydroarylation of alkynes using **Co-19** cobalt (I) complex (Scheme 33a).<sup>104</sup> Despite this considerable advance, the reaction suffered from many drawbacks: (i) high catalytic loading, (ii) narrow substrate scope, i.e. only diazobenzene and diphenylacetylene derivatives. More recently, Zhirik reported few examples of alkenes hydroboration with a Markovnikov selectivity (Scheme 33b).<sup>36</sup> He also demonstrated that the same catalyst was able to catalyze the isomerization / hydroboration of several alkenes with a good branched selectivity (Scheme 33b). In 2016, Dzik reported the hydrosilylation of dinitrogen (N<sub>2</sub>) using **Co-19** as catalyst,<sup>105</sup> however the well-defined character of the catalyst in this report was not ascertain.



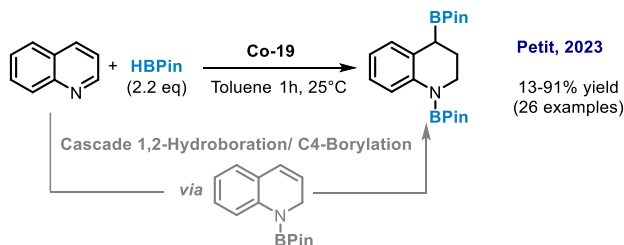
**Scheme 33. Hydroarylation of diphenylacetylene and hydroboration of alkenes using Co-19**

The Petit's group recently demonstrated that both  $HCo(PMe_3)_4$  **Co-37** and  $HCo(N_2)(PPh_3)_3$  **Co-19** were efficient for the chemo- and regioselective 1,2-silylative dearomatization of *N*-heteroarenes.<sup>106</sup> In his study he also showed that **Co-19** was efficient at room temperature thanks to the lability of the triphenylphosphine ligand compared to the trimethylphosphine. (Scheme 34)



**Scheme 34. Hydroarylation of *N*-heteroarene catalyzed by phosphine cobalt hydrides Co-19 and Co-37**

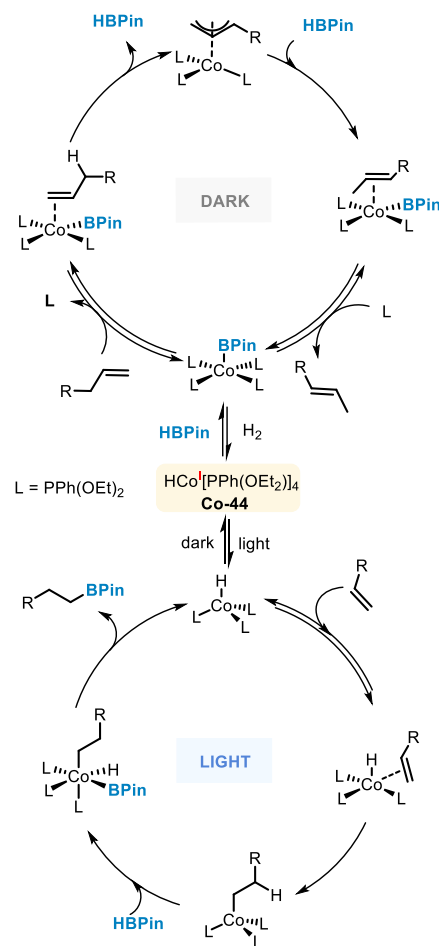
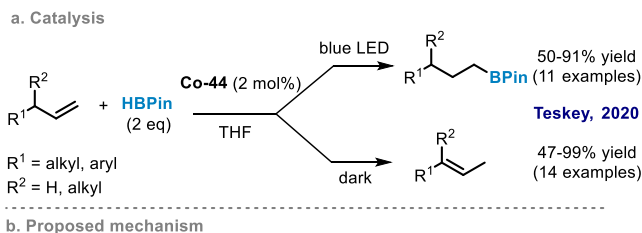
The same group recently showed that the cobalt hydride **Co-19**, in presence of HBPiPin instead of silane, was able to catalyze a selective cascade dearomatization/functionalization of quinolines. This reaction totally selective in C4 allows the synthesis of a new variety of bis-borylated quinolines in very mild conditions (Scheme 35).<sup>107</sup>



**Scheme 35. Bis-borylation of quinoline using Co-19**

The phosphite-based analogues  $HCo(P(OR)_3)_4$  **Co-40** were considered as being quite inert and less reactive species.<sup>108</sup> However, Masayoshi discovered in 1983 that using phosphinite ligands, namely a combination of phosphine and phosphite, the

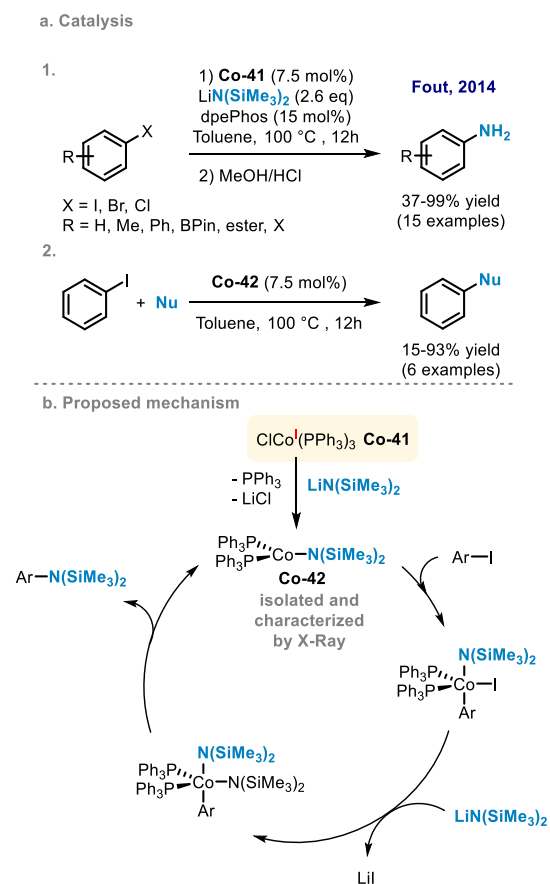
analog hydridophosphinite cobalt (I)  $HCo[PPh(OR)_2]_4$  **Co-44** could be photoactivated to promote the decooordination of a ligand and thus gain in reactivity.<sup>109</sup> Since, its potential in catalysis have recently been reported by Teskey and co-workers for the visible-light-controlled hydroboration of alkenes (Scheme 36a).<sup>110</sup>



**Scheme 36. Hydroboration/Isomerization of alkenes using Co-44**

With no photoactivation of the complex **Co-44**, no decooordination of a phosphite ligand occurs; in the presence of pinacol borane HBPiPin, an oxidative addition/reductive elimination takes place to provide the corresponding boryl cobalt (I) complex (Scheme 36b, Top). Coordination to the alkene followed by a  $\beta$ -H elimination then led to a  $\pi$ -allyl cobalt complex. The latter is able to interact with a new molecule of pinacol borane HBPiPin which promotes the isomerization of the alkene as the final product (Scheme 36b, Top). However, when the cobalt complex

**Co-44** is photoactivated under blue LEDs irradiation, a decoordination of a phosphinite is observed, leading to a different catalytic cycle (Scheme 36b, Down). This time, the coordination with the alkene induces a hydrocobaltation followed successively by an oxidative addition of the pinacol borane HBPIn and a reductive elimination of the borylated alkane (Scheme 36b, Down). The cobalt halide  $\text{ClCo}(\text{PPh}_3)_3$  **Co-41** appeared as a good catalyst for the cyclotrimerization and dimerization of alkynes and for the reduction of carbonyl compounds as well.<sup>111</sup> Fout *et al* disclosed the coupling between aryl halogenates and nucleophilic compounds in 2014 using also this catalyst (Scheme 37a.1).<sup>97</sup> The presence of  $\text{LiN}(\text{SiMe}_3)_2$  in the reaction medium generates the active catalyst of the reaction **Co-42** (Scheme 37b). However, the complex  $\text{Co}(\text{PPh}_3)_2(\text{N}(\text{SiMe}_3)_2)$  **Co-42** was also isolated, fully characterized and used as the starting catalyst of the reaction and can be therefore considered as the true well-defined catalyst of the reaction. The desired product could be obtained in a 65% yield. Moreover, the complex **Co-42** was used as the catalyst with the iodobenzene and different nucleophiles to afford the coupling products, confirming the activity of this complex as a well-defined catalyst (Scheme 37a.2) All these results together opened the doors for new opportunities using these  $\text{ML}_n\text{X}$  well-defined cobalt (I) catalysts.

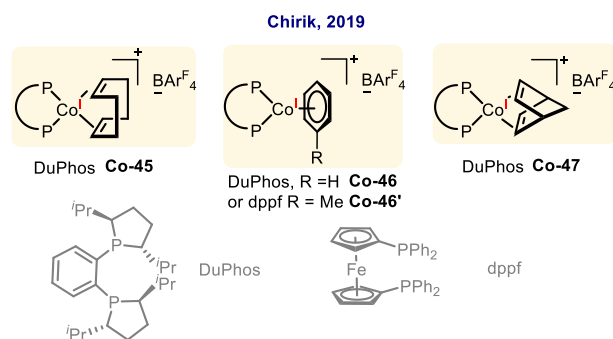


**Scheme 37. Amination of aryl halides catalysed by Co-41 or Co-42**

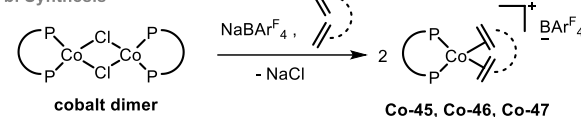
Beyond the classical monodentate phosphine complexes, well-defined cobalt (I) catalysts with bidentate ones have also been

reported. Indeed, the group of Chirik disclosed in 2019 the synthesis of cationic bisphosphine cobalt (I) complexes **Co-45-Co-47** starting from the dichloro-dicobalt dimer. Both the DuPhos and dppf can be used as the diphosphine ligand in addition of either 1,5-cyclooctadiene (COD), benzene or norbornadiene (NBD) as the labile ligands, all with the  $\text{BAR}^{\text{F}_4}$  counterion (Scheme 38).<sup>112</sup> However, for complex **Co-46'** an alternative synthesis using  $(\text{dppf})\text{Co}(\text{acac})_2$  followed by an *in-situ* oxidation with  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}][\text{BAR}^{\text{F}_4}]$  is described. The obtained  $[(\text{dppf})\text{Co}(\text{acac})_2][\text{BAR}^{\text{F}_4}]$  was then reduced with an excess of HBPIn in presence of toluene to give **Co-46'**.

a. Well-defined bisphosphine cobalt (I) complexes

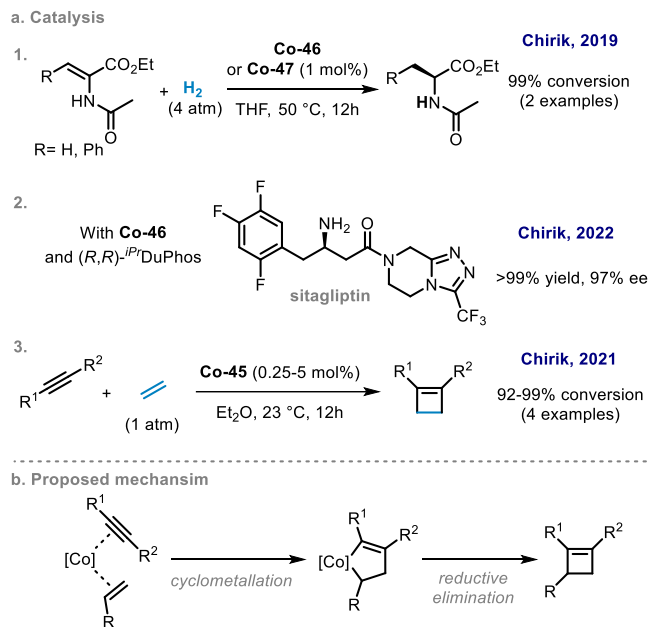


b. Synthesis



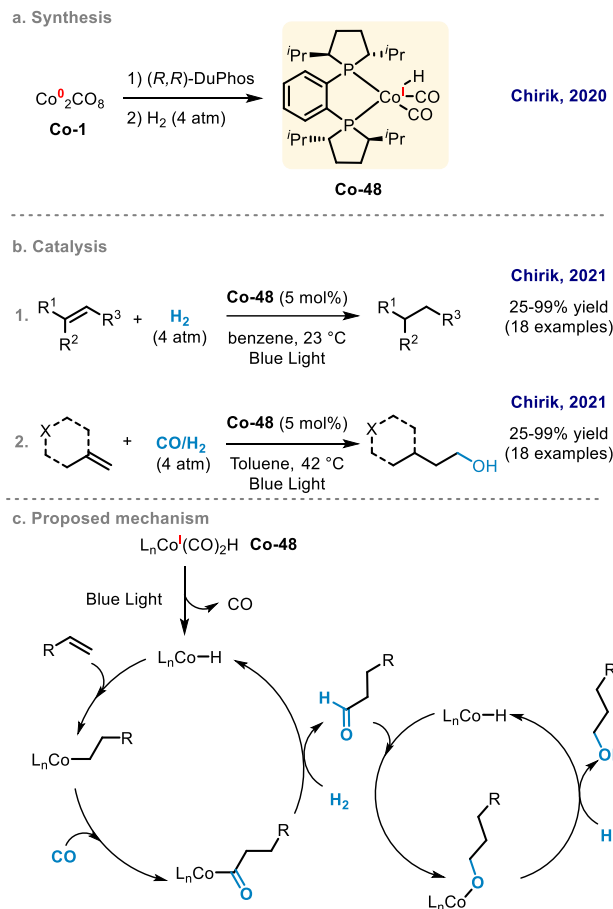
**Scheme 38. Well-defined cationic bisphosphine cobalt (I) complexes**

These complexes were found to be efficient well-defined catalysts for the hydrogenation of enamides (Scheme 39a.1) and the alkyne-alkene [2+2] cycloaddition (Scheme 39a.3). The complex **Co-46** was also used for the enantioselective gram-scale synthesis of sitagliptin used in the treatment of type 2 diabetes (Scheme 39a.2).<sup>113</sup> In this article a more versatile and scalable synthesis of cationic bis(phosphine) cobalt (I) precatalyst such as **Co-46** is also detailed. More recently the same group also described the synthesis of zavegepant with the same kind of cationic catalyst but by varying the bisphosphine ligand.<sup>114</sup> The mechanism of the cycloaddition has been studied and revealed to go through a metallacycle pathway followed by a reductive elimination (Scheme 39b).



**Scheme 39. Hydrogenation of enamides, synthesis of the Sitagliptin and [2+2] cycloaddition using Co-45-Co-47**

In 2020, the same group reported another type of well-defined bisphosphine cobalt (I) hydride complex bearing the DuPhos ligand and two carbon monoxide (CO).<sup>115</sup> The synthesis starts from the  $\text{Co}_2(\text{CO})_8$  **Co-1** with the bisphosphine ligand under a hydrogen atmosphere to afford the air-stable complex **Co-48** (Scheme 40a).

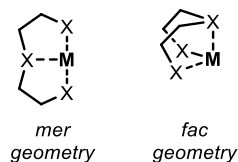


**Scheme 40. Well-defined bisphosphine cobalt (I) hydride Co-48, application in hydrogenation and hydroformylation**

It was shown that blue LED could promote the decoordination of a carbon monoxide (CO) ligand (Scheme 40c) thus enabling catalytic activity. This catalyst was successfully used for the hydrogenation of alkenes as well as the hydroformylation/reduction sequence, leading to the primary alcohol (Scheme 40b).<sup>116</sup>

#### 4.3.2. Pincer cobalt complexes

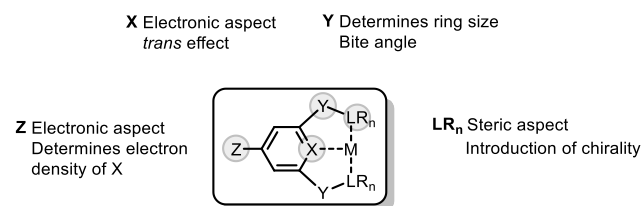
The second category of well-defined cobalt (I) catalysts is the one based on pincer ligands. The interest in pincer ligands has not stopped growing due to their diverse properties.<sup>117</sup> The term “pincer” has been introduced by Van Koten in 1989<sup>118</sup> to name a tridentate ligand which adopts preferentially a meridional (*mer*) geometry rather than a facial (*fac*) one (Figure 5).<sup>119</sup>



**Figure 5. Differentiation between *mer* and *fac* geometries**

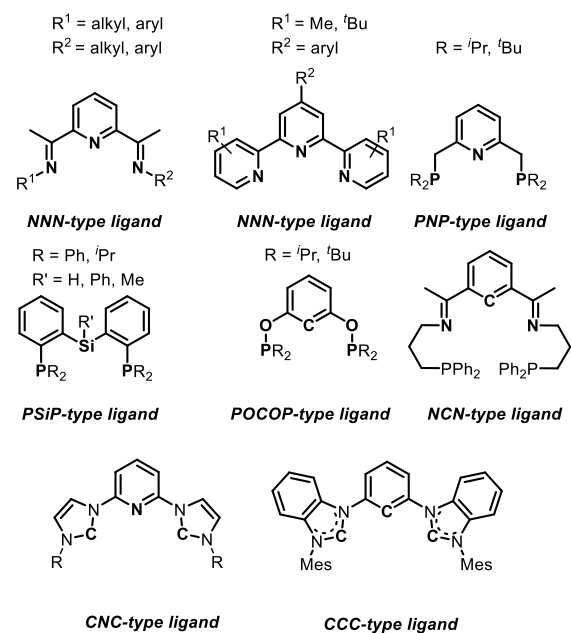
These ligands are especially used for the well-defined geometry adopted by complexes once coordinated. Pincer ligands are composed of three binding sites with a central group, often a

pyridine or a phenyl, and two side arms. The linkers between these units are most of the time rigid which explains the *mer* geometry adopted. They thus offer some rigidity, a good control towards the coordination sphere of the catalyst, and are quite stable thermodynamically which is also one of the greatest reasons for their use in homogeneous catalysis. Their application in cobalt catalysis is therefore not an exception.<sup>120</sup> The other interesting aspect in pincer ligands is the possibility to design the ligand on different points that will have an important impact on the catalyst activity (Figure 6). Among these different parameters, the first one is the central binding unit X that modulates the electronic of the catalyst with a *trans* influence, same for the substitution Z in *para* which determines the electron density of the central unit. The second aspect is the side arms Y which define the ring size and the bite angle aspect. Finally, the last parameter is localized on the two binding sites LR<sub>n</sub> which plays on the steric aspect of the ligand and is also used for the introduction of chirality.



**Figure 6.** Design of pincer ligands and influence on the catalyst activity

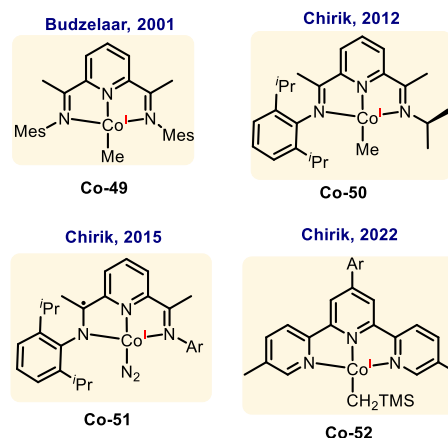
We can differentiate the pincer ligands according to their symmetry and most of them are symmetric. Pincers ligands are named and classified according to the atoms involved in the coordination and we will follow this classification below (Figure 7).



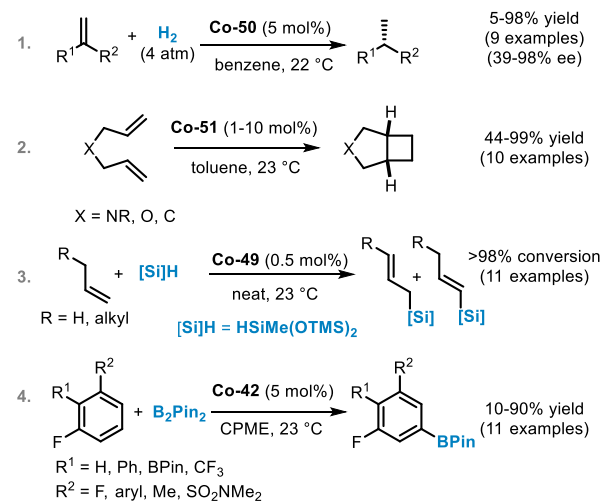
**Figure 7.** Pincer Ligands commonly found on well-defined cobalt (I) catalysts

The first class of pincer ligands that we will investigate is the *NNN*-type pincer ligands that are commonly found for well-defined cobalt (I) complexes (Scheme 41). This category includes bis-imino pyridines that have been early explored by Budzelaar in 2001 using **Co-49** for the polymerization of olefins into polyethylene, and extended to the hydrogenation of olefins in 2005.<sup>121</sup> Numerous works have then been reported by Chirik since 2012, notably for the hydrogenation of alkenes and alkynes (Scheme 41b.1) but also for [2+2] cycloadditions (Scheme 41b.2) and dehydrogenative silylation (Scheme 41b.3) using **Co-50**, **Co-51** and **Co-49** respectively.<sup>122</sup> Beyond bis-imino pyridines, the terpyridine ligands have very recently been employed by the same group using **Co-52** to catalyze the C–H borylation of arenes (Scheme 41b.4).<sup>123</sup>

a. Well-defined *NNN*-Pincer Ligand cobalt(I) catalysts



b. Application in catalysis



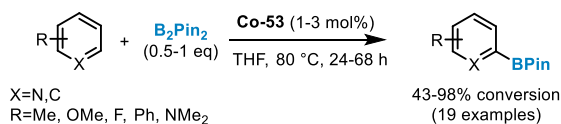
**Scheme 41.** a) *NNN*-Pincer Ligand cobalt (I) catalysts and b) their applications in catalysis

Another family of widely used pincer ligands is the *PNP*-type one, composed of two phosphines and a pyridine as the central donor unit (Scheme 42). Once again, these catalysts were mainly explored by the Chirik's group who used them for C–H

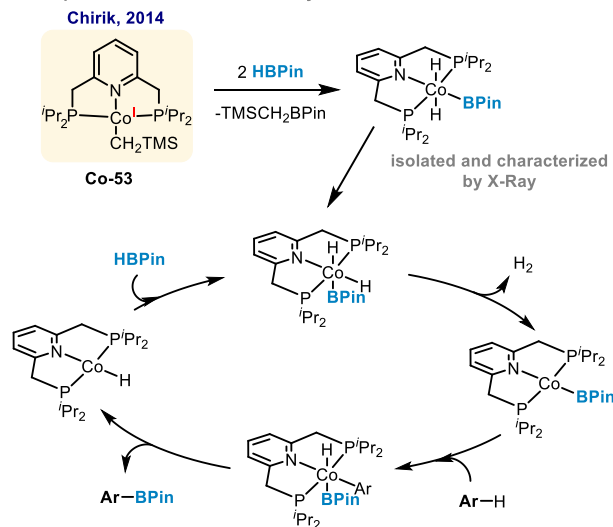


borylation as well (Scheme 42a) or even hydrosilylation of carbon dioxide (CO<sub>2</sub>).<sup>124</sup> The proposed mechanism for the C–H borylation implies a first oxidative addition of **Co-53** into HBPIn. Using a starting well-defined complex allowed the isolation and the full characterization of the boryl cobalt (III) intermediate. Then occurs a flip of the pinacol borane on the cobalt center<sup>124c</sup> followed by a reductive elimination of the dihydrogen (H<sub>2</sub>). The C–H activation of the aromatic substrate takes place on the boryl cobalt (I), leading to the corresponding cobalt (III) which undergoes the reductive elimination of the desired borylated compound (Scheme 42b). In the particular case of fluorinated arenes. The authors demonstrated later using a methylated analog that the selective *ortho* borylation of fluorinated aryl was due to a thermodynamic control of the C(sp<sup>2</sup>)-H oxidative addition to cobalt-boryl of the intermediate (Scheme 42c).<sup>125</sup>

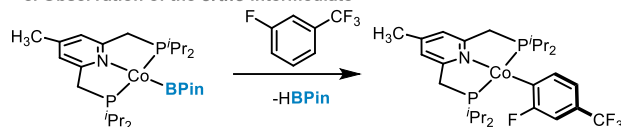
#### a. Application in catalysis



#### b. Proposed mechanism for the borylation of arenes



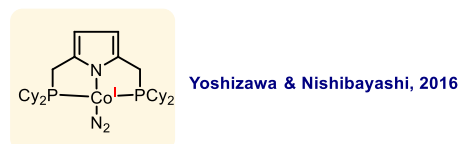
#### c. Observation of the *ortho* intermediate



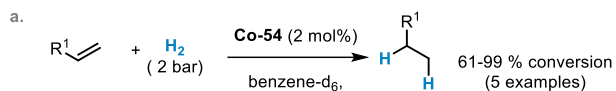
### Scheme 42. C–H borylation catalysed by the *PNP*-type complex **Co-53**

Recently the group of Tonzetich developed the chemistry of another *PNP*-type with two cyclohexylphosphines and a pyrrole moiety synthesized by the group of Yoshizawa, and Nishibayashi in 2016. They demonstrated that this well-defined low-valent cobalt (I) complex [Co(N<sub>2</sub>)(CyPNP)] **Co-54** was active in decarbonylation of aldehyde in a stoichiometric manner,<sup>126a</sup> but

also in the catalytic hydrogenation of alkenes and alkynes,<sup>126b</sup> and recently the hydrosilylation of carbonyl<sup>126c</sup> (Scheme 43a-b).

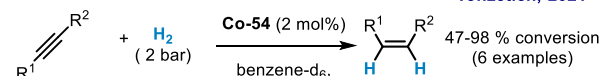


**Co-54**

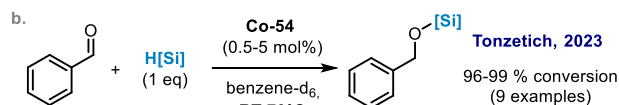


R<sup>1</sup> = alkyl or aryl

Tonzetich, 2021



Z/E = 98:2-1:3

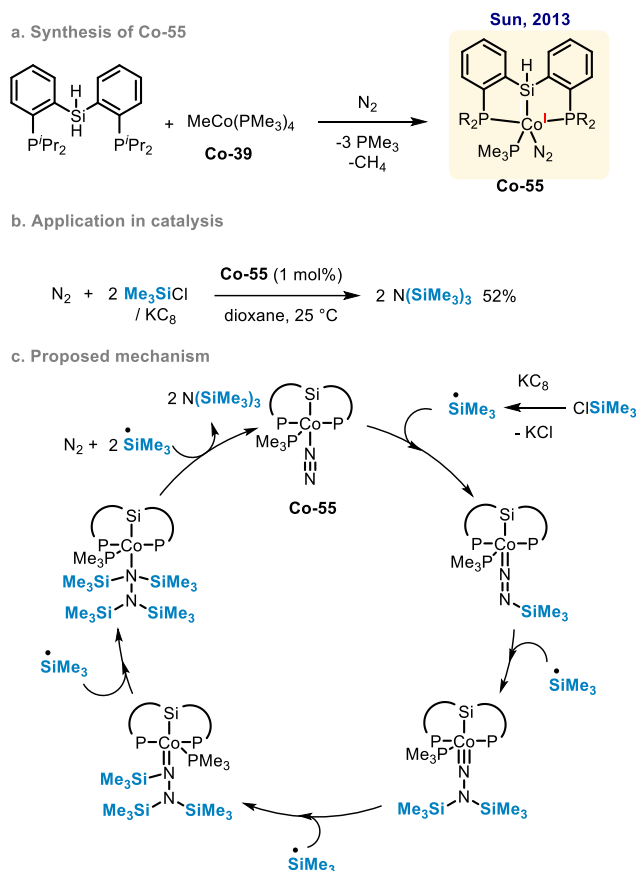


Tonzetich, 2023

[Si] = SiPh<sub>3</sub>, HSi(Ph)<sub>2</sub>, H<sub>2</sub>SiPh,  
Si(OEt)<sub>3</sub>, Si(Et)<sub>3</sub>, TMDS, PDMS,

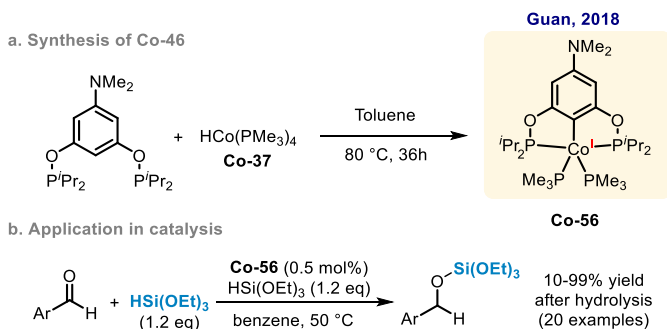
### Scheme 43. Reactivity of the *PNP*-type complex **Co-54**

Other categories of pincer ligands generated interesting reactivities on well-defined cobalt (I) catalysts. *PSiP*-types have been disclosed in 2013 by Sun.<sup>127,128</sup> They used the cobalt complex MeCo(PMe<sub>3</sub>)<sub>4</sub> **Co-39** as the precursor to synthesize the catalyst **Co-55** via an oxidative addition into the Si–H bond followed by the reductive elimination of methane (CH<sub>4</sub>) which is the driving force of the reaction (Scheme 44a). This catalyst was next applied to the hydrosilylation of dinitrogen (N<sub>2</sub>) (Scheme 44b).<sup>128</sup> Once again, the strong reducing agent KC<sub>8</sub> was required, which could be mistaken for a non-well-defined catalyst. However, the authors proposed a mechanism where the KC<sub>8</sub> does not interfere with the metal center and is only used to generate the silyl radical partner (Scheme 44c).



**Scheme 44. Hydrosilylation of N<sub>2</sub> catalysed by the PSiP-type complex Co-55**

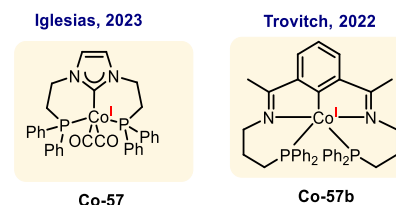
POCOP-Types have been explored by Guan for the hydrosilylation of carbonyl compounds.<sup>129</sup> They reported the use of the cobalt hydride HCo(PMe<sub>3</sub>)<sub>4</sub> **Co-37** as the precursor which, mixed to the pincer ligand in toluene at 80 °C for 36h, could afford the well-defined pincer complex **Co-56** (Scheme 45).



**Scheme 45. Hydrosilylation of carbonyl compounds catalysed by the POCOP-type complex Co-56**

The group of Iglesias recently reported the use of a pincer PCP-type **Co-57** (called NHC-phosphane) in the reductive amination of furfural and levulinic acid in presence of PhSiH<sub>3</sub> (Figure 8).<sup>130</sup> Another marginal example such as NCN-type ligands with two pyridines and an aryl moiety as the central anchor on well-defined cobalt (I) complexes **Co-57b** has also been reported by

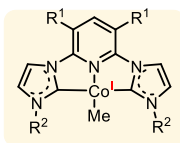
Trovitch et al. and applied to the hydrosilylation of carbonyl compounds (Figure 8).<sup>131</sup>



**Figure 8. Structure of the catalyst Co-57 and Co-57b**

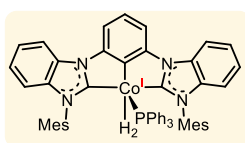
The last class of pincer we want to discuss about are the pincer based on carbenes ligands. If this type of well-defined complexes can obviously also be categorized in the last section about cobalt (I) NHC complexes (see section 4.3.4), we decided due to the importance of the third atom of the pincer to include them in this category. Chirik reported first in 2013 the use of a CNC-type pincer ligand with two carbenes in order to reach the well-defined cobalt (I) complex **Co-58** and apply it to the hydrogenation of alkenes (Scheme 46a.1).<sup>132a</sup> The use of a well-defined complex enabled the group to prove that the ligand was redox-active, thanks to extensive spectroscopic and DFT studies. The analog **Co-58'** bearing alkyl groups on the carbenes was recently used by the same group for the selective *meta* borylation of fluorinated arenes.<sup>132b</sup> This precatalyst compare to the previous NNN and PNP pincers presented above is more sterically accessible and more reactive allowing a larger scope in this reaction. The authors demonstrated also a kinetic preference for the *meta* C-H activation and showed that the aryl complex isomerize over the time allowing a control of the site-selective functionalization using two different borane donor (Scheme 46c). Finally, three years later Fout showed that a CCC-type ligands with two carbenes held by an aryl unit can also be a great pincer ligand to access the well-defined cobalt (I) catalyst **Co-59**.<sup>133</sup> This catalyst was used in alkenes hydrogenation and alkynes semi-hydrogenation by Fout (Scheme 46a.2). Regarding the latter, the pincer complex revealed efficient to reach (*E*)-selectivities due to an original pathway of a *cis* hydrogenation (Scheme 46b, Left) followed by a *trans*-isomerization (Scheme 46b, Right).

Chirik, 2013 &amp; 2023

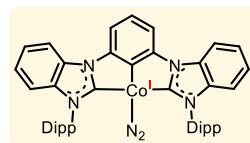


**Co-58** R<sup>1</sup> = H, R<sup>2</sup> = Dipp  
**Co-58'** R<sup>1</sup> = Me, R<sup>2</sup> = *i*Pr

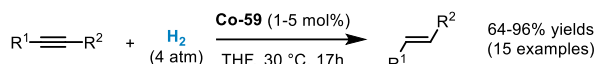
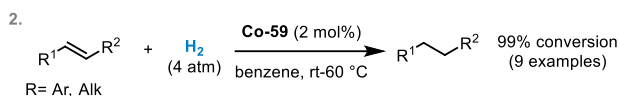
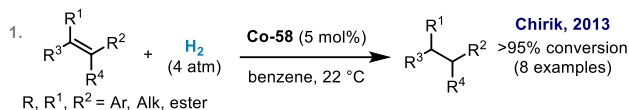
Fout, 2016

**Co-59**

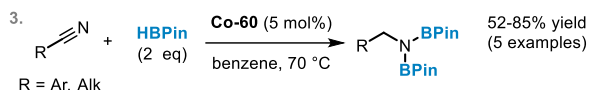
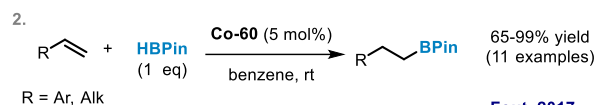
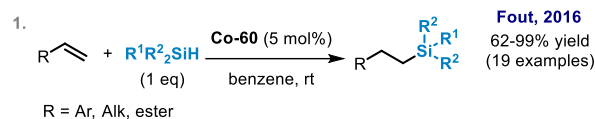
Fout, 2016

**Co-60**

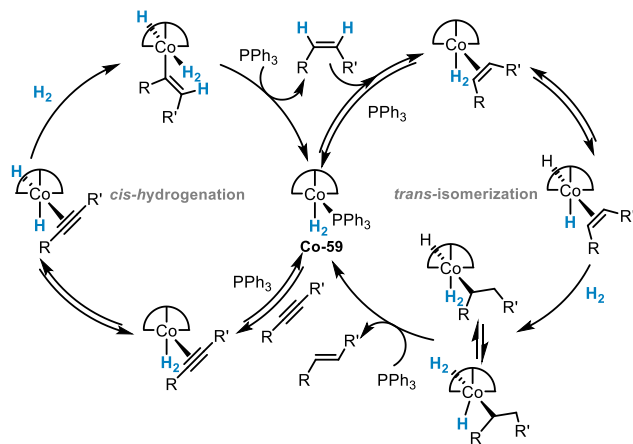
## a. Application in catalysis



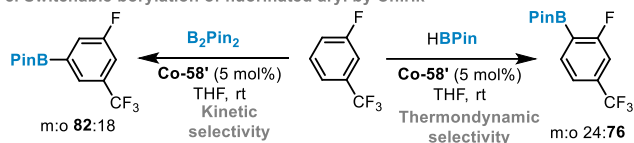
## a. Application in catalysis



## b. Proposed mechanism for the semi-hydrogenation of alkynes by Fout



## c. Switchable borylation of fluorinated aryl by Chirik



## Scheme 46. Hydrogenation of alkenes or alkynes using Co-58 and Co-59

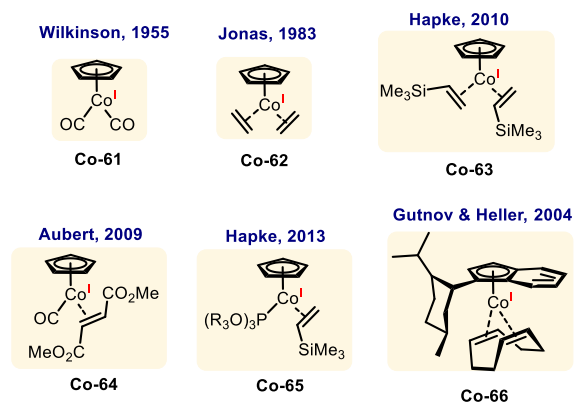
Fout also demonstrated that using this time the (DIPPCCC)CoN<sub>2</sub> complex **Co-60**, they were able to catalyze a highly chemoselective hydrosilylation of alkenes.<sup>133</sup> This report demonstrates also that tertiary silanes and alkoxy silanes can be used and that high functional group tolerance has been observed with the use of ketone, aldehyde, nitrile and also hydroxyl groups. The same complex **Co-60** was applied the next year by the same group to catalyze the hydroboration of alkene and nitrile once again with a high functional group tolerance (Scheme 47).<sup>133d</sup>

## Scheme 47. Hydroelementation of alkene and nitrile using Co-60.

Recently a parent complex of **Co-60** bearing a pyridine ligand in place of the nitrogen (MesCCC)Co-py was used for the hydrogenation of nitrile and later the deshydrogenation of ammonium borane to generate H<sub>2</sub>.<sup>133e</sup>

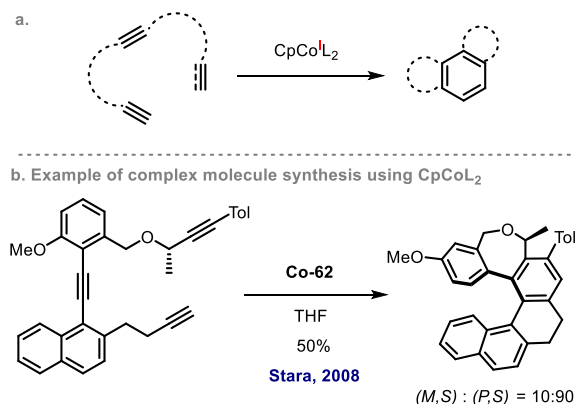
## 4.3.3. Cyclopentadienyl cobalt complexes

Well-defined cyclopentadienyl (Cp) cobalt (I) complexes are very famous catalysts for [2+2+2] cycloadditions. The subject has been extremely well reviewed several times and is not the topic of this review so we will not go deeply into details.<sup>6,67,134</sup> We will only report selected well-defined catalysts which have been pioneer for catalytic reactions development and their important evolution in the recent decades. Wilkinson and co-workers reported the synthesis and isolation of the first CpCo(CO)<sub>2</sub> **Co-61** in 1955<sup>135</sup> (Figure 9) which has been widely used, especially by the groups of Vollhardt, Malacria, Aubert, Hapke and others for numerous applications of [2+2+2] cycloadditions. In 1983, Jonas synthesized the bis ethene analogue **Co-62** which appeared much more reactive than its carbon monoxide (CO) predecessor **Co-61**, due to more labile ligands.<sup>136</sup> Many variants have been published since, based on the nature of the additional ligands (Figure 9).<sup>137</sup>



**Figure 9.** Selected well-defined Cp-cobalt (I) complexes

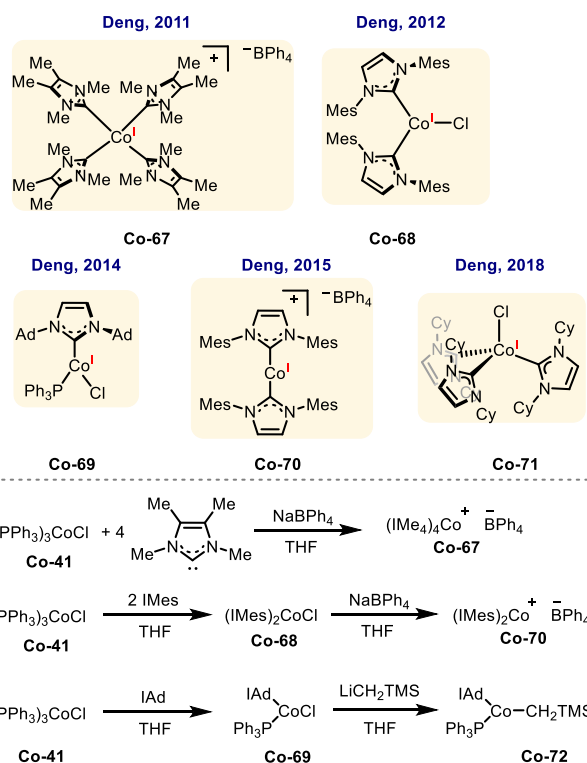
Among them, we can cite the Cp-Co containing vinylsilanes **Co-63** reported by the group of Hapke, synthesized from the cobaltocene and potassium. This complex is even more reactive than **Co-62** containing two ethene ligands. This example followed the discovery of a new Cp-Co **Co-64** bearing an electron-deficient olefin such as dialkyl fumarate which was disclosed by the group of Aubert.<sup>138</sup> This complex is air-stable with retention of reactivity since it appeared as more efficient as **Co-61** with carbon monoxide (CO) ligands on specific reactions under thermal conditions and without the need of irradiation. Hapke then reported that combining the reactivity of the vinylsilane Cp-Co catalyst **Co-63** with phosphines or phosphites could lead to a mixed complex **Co-65** bearing one vinylsilane and one phosphite. This new family of complexes thus offers a combination of stability –with the phosphite ligand– and reactivity –with the vinylsilane one.<sup>134a</sup> Substituted cyclopentadienes have also been used as ligands, notably chiral ones. Therefore, Heller and Gutnov developed **Co-66** in 2004 for the asymmetric cycloaddition of alkynes and naphthonitriles.<sup>139</sup> These well-defined catalysts were employed for the synthesis of complex molecules mostly via [2+2+2] cycloaddition.<sup>140</sup> This was extended to the access of structurally constrained helicene moieties as disclosed for example by the group of Stara with **Co-62** (Scheme 48).<sup>141</sup>



**Scheme 48.** [2+2+2] cycloaddition reactions enabled by well-defined CpCo (I) complexes

#### 4.3.4. NHC and NHSi-cobalt complexes

*N*-Heterocyclic carbene cobalt complexes have gained a lot of interest in catalysis these last 20 years due to their high reactivity.<sup>84</sup> As seen before for the other oxidation states of cobalt, a pioneer in the field of well-defined isolated ones is Deng who reported numerous examples of well-defined NHC-cobalt (I) (Scheme 49). For the cobalt (I) family, Deng showed that he is able to modulate the NHC-to-cobalt ratio in these complexes from 4 to 3 to 2 and to 1 as the NHC ligand changes from IMe<sub>4</sub> (or analogs), to ICy to IMes, and finally to IAd in correlation with the steric hindrance of the carbene. Among them we can cite the square planar tetra-NHC cobalt (I) complex **Co-67** synthesized in 2011, starting from the well-defined cobalt complex ClCo(PPh<sub>3</sub>)<sub>3</sub> **Co-41** and 4 equivalents of IMe<sub>4</sub> ligand in THF in presence of NaBPh<sub>4</sub> (Scheme 49a).<sup>142</sup> A year later the group of Deng also demonstrated that starting from the same ClCo(PPh<sub>3</sub>)<sub>3</sub> **Co-41** with this time 2 equivalents of IMes, the bis-NHC cobalt complex **Co-68** could be isolated (Scheme 49b).<sup>143</sup> The latter complex could even be further ionized using sodium borate salts such as NaBPh<sub>4</sub> or NaBAR<sup>F</sup><sub>4</sub> to lead to **Co-70** (Scheme 49b).<sup>144</sup>

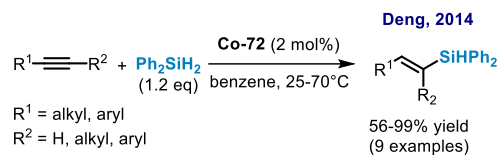


**Scheme 49.** Structures and syntheses of well-defined NHC-based cobalt (I) complexes

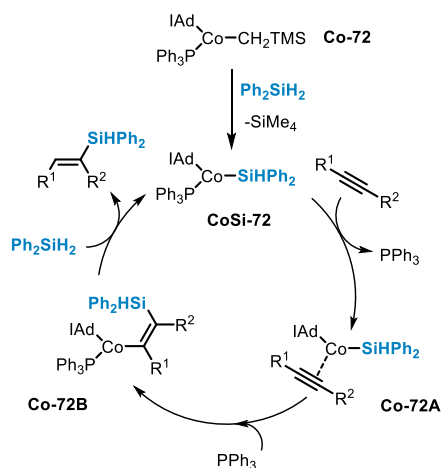
Analogues have then been synthesized with variation on the NHC ligand. Thus, **Co-69** with only one NHC ligand was synthesized in 2014 using the same methodology and 1 equivalent of IAd ligand (Scheme 49c) but also **Co-71** with three cyclohexyl NHC ligands. **Co-69** was also derivatized in the alkyl analog **Co-72** by reaction with trimethylsilylmethyl lithium. These complexes were applied in catalysis as well-defined catalysts, especially for the reduction of alkynes and alkenes moieties. The first one to be investigated was

(IAd)(PPh<sub>3</sub>)Co(CH<sub>2</sub>TMS) **Co-72** which revealed to be efficient for the hydrosilylation of alkynes (Scheme 50a).<sup>145a</sup> Deng reported a classical mechanism where the complex **Co-72** first interacts with diphenylsilane Ph<sub>2</sub>SiH<sub>2</sub> to provide the silyl cobalt (I) **CoSi-72**. This resulting complex then undergoes a ligand exchange with the alkyne followed by a sila-cobaltation. An additional molecule of silane then allows to release the desired silylated alkene and to regenerate the silyl cobalt (I) **CoSi-72** (Scheme 50b).

a. Catalysis

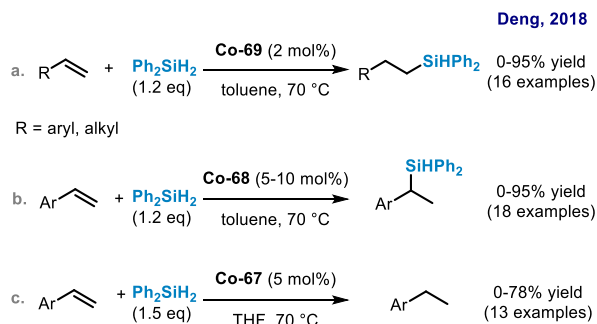


b. Proposed mechanism



### Scheme 50. Hydrosilylation of alkynes using Co-72

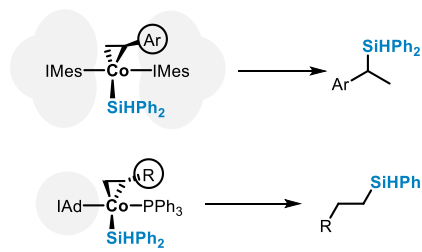
The conversions of **Co-72** into **CoSi-72** and of **Co-72B** back to **Co-72** have been hypothesized to go through an oxidative addition/reductive elimination mechanism, although no experimental evidences on this point have been proposed. In 2018, the same group reported the hydrosilylation of alkenes using this time different well-defined NHC-based cobalt (I) catalysts.<sup>145b</sup> Best results have been found with ClCo(IAd)(PPh<sub>3</sub>) **Co-69** for the selective synthesis of the linear products (Scheme 51a) whereas (IMes)<sub>2</sub>CoCl **Co-68** selectively led to the synthesis of the branched ones starting from styrene derivatives (Scheme 51b). For its part, [(IMe<sub>4</sub>)<sub>4</sub>Co][BPh<sub>4</sub>] **Co-67** led to the hydrogenated product (Scheme 51c).



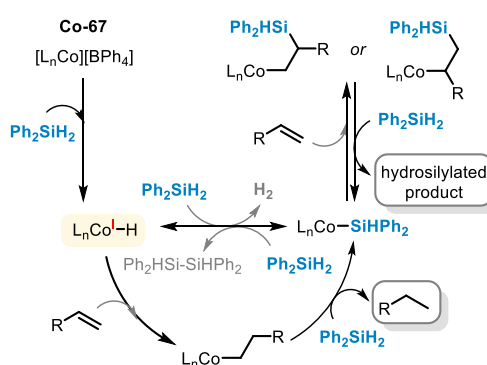
### Scheme 51. Hydrosilylation of alkenes using Co-67, Co-68, and Co-69

The authors invoked a difference of selectivity between **Co-68** and **Co-69**, based on the nature of the ligands. Indeed, in the case of IMes **Co-68**, they proposed a π-π interaction between the aryl of the styrene and the mesityl of the carbene. This interaction combined with the steric hindrance of the IMes ligand, leads to a selective Markovnikov addition whereas the IAd ligand in **Co-69**, drives to an *anti*-Markovnikov addition (Scheme 52a). Concerning the observation of the hydrogenated product, they invoked the formation of a cobalt hydride species from cationic **Co-67** and diphenylsilane Ph<sub>2</sub>SiH<sub>2</sub>, which can then undergo the insertion into the alkene leading to the hydrogenated product after addition of a molecule of silane (Scheme 52b).

a. Space filling models



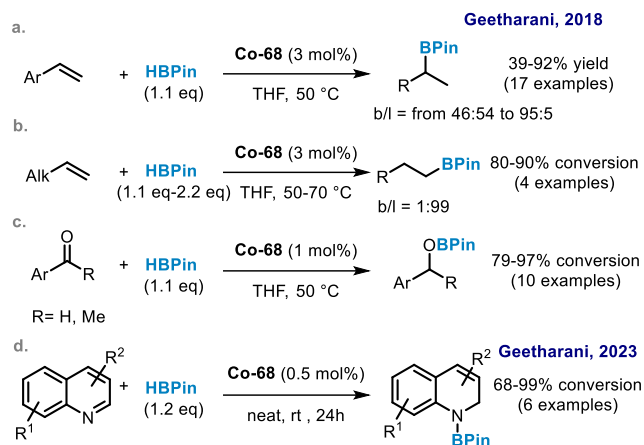
b. Proposed mechanism



### Scheme 52. Difference of selectivity for the hydrosilylation of alkenes using Co-67, Co-68 or Co-69

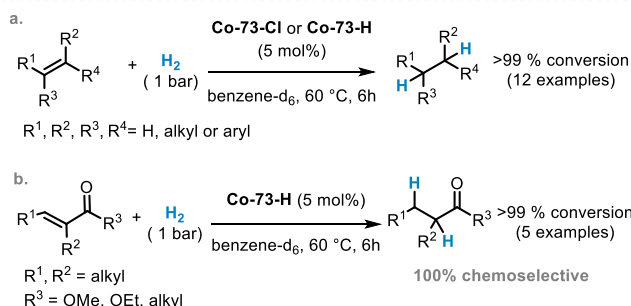
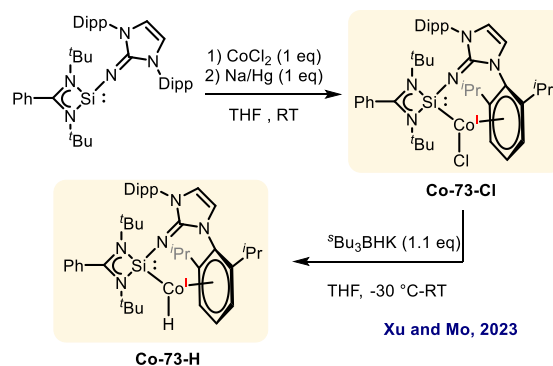
Geetharani also used the ClCo(IMes)<sub>2</sub> **Co-68** for the hydroboration of alkenes in 2018.<sup>146</sup> She observed similar results from the ones described by Deng on the hydrosilylation. Indeed, when using aryl alkenes, she obtained up to good selectivity towards the branched product, whereas when aliphatic alkenes were used, the reverse selectivity and the linear borylated alkanes were observed (Scheme 53a-b). She also showed that this methodology was suitable for the reduction of aldehydes and ketones (Scheme 53c). In 2023, the same group showed that the use of the same catalyst allows the selective 1,2-hydroboration of quinolines with only 0.5 mol% of catalyst (Scheme 53d).<sup>147</sup>





**Scheme 53. Hydroboration of alkenes, carbonyls and quinolines using Co-68**

Recently the group of Xu and Mo demonstrated that *N*-heterocyclic silylene (NHSi) can also be used as ligand on cobalt (I) complexes. Thus, starting from the corresponding easily accessible *N*-heterocyclic imino substituted silylene in presence of  $\text{CoCl}_2$  and sodium/mercury amalgam in a stoichiometric ratio they were able to isolate the low valent NHSi-Co complex **Co-73-Cl**. The latter was further converted to the hydrido analog **Co-73-H** in presence of  $^s\text{Bu}_3\text{BHK}$  (Scheme 54).<sup>148</sup>

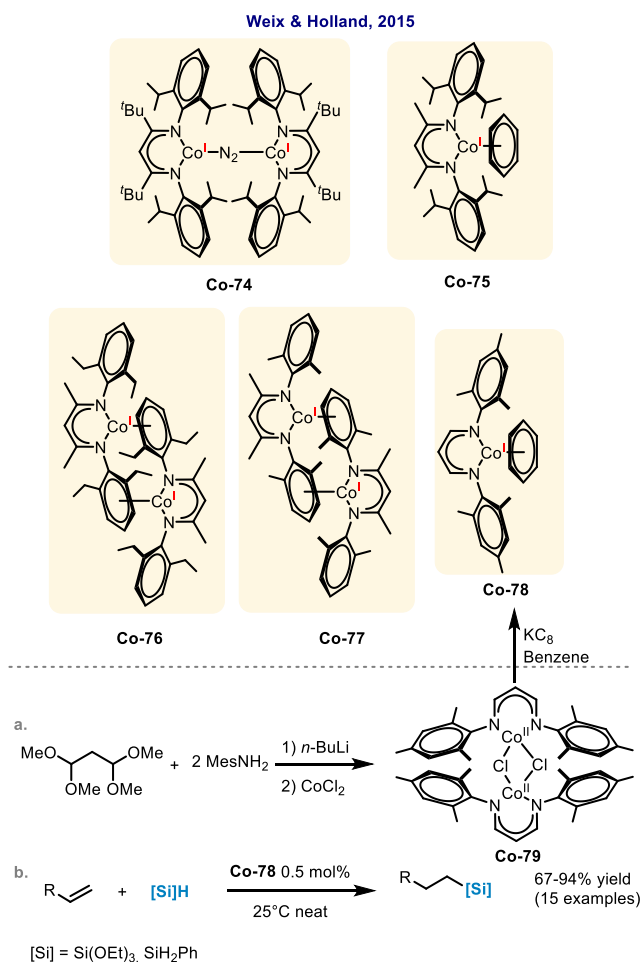


**Scheme 54. Synthesis of well-defined NHSi-Co complexes Co-73 and reactivity in hydrogenation.**

Both NHSi-Co complexes were fully characterized and engaged in the hydrogenation of olefins where the hydrido one showed better activity (Scheme 54a). It is worth mentioning that a total chemoselectivity toward the alkene was observed when using unsaturated carbonyl compound which is quite rare in cobalt chemistry (Scheme 54b).

### 4.3.5. Bidentate amino cobalt (I) arene complex

The last category of well-defined cobalt (I) complexes will focus more on complexes bearing a bidentate amino chelating ligand. Remarkable results have been obtained by the group of Holland using  $\beta$ -diketimide bidentate ligand and their application in catalysis. These complexes **Co-74-Co-78** were easily obtained from reduction of the corresponding cobalt (II) precursor in presence of Grignard or  $\text{KC}_8$ . These latter were obtained from the diketimines that were prepared on large scale from the corresponding anilines (Scheme 55a).

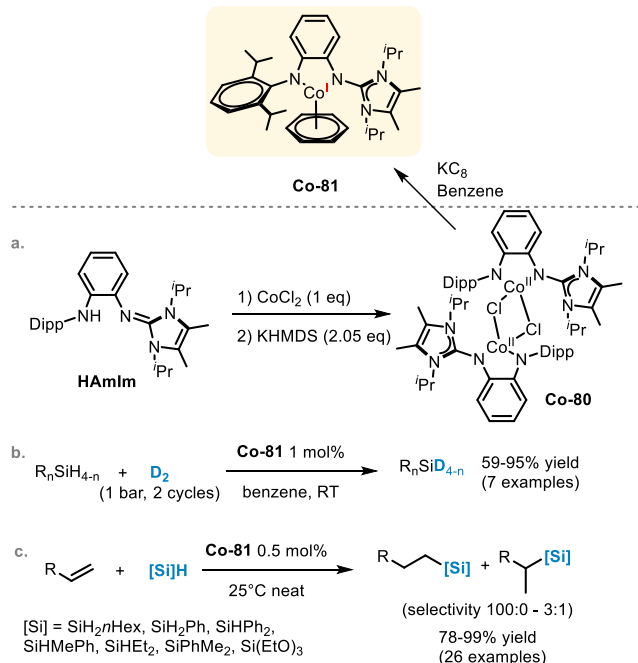


**Scheme 55. Synthesis of well-defined  $\beta$ -diketimide cobalt (I) complexes Co-78 and reactivity in hydrosilylation.**

Then Holland and Weix showed that **Co-78** was very efficient in low catalyst loading solvent free hydrosilylation of olefins with a total selectivity toward the linear alkyl silane (Scheme 55b).<sup>149</sup> It is worth mentioning that the reaction was working starting from the air stable cobalt (II) precursor **Co-79** and by generating the *in situ* the complex **Co-78** using different bases. Indeed, they proved that using 200 equivalents of  $\text{EtMgBr}$  they obtained the same linear selectivity but in lower yield. This result shows again that well-defined catalysts are more efficient with better yield and obviously less waste and higher group tolerance considering the huge excess of Grignard required. Besides the two-coordinate monoanionic  $\beta$ -diketimide ligand, the

group of Trzaskowski, Tamm and Frank used the monoanionic amido-imidazolin-2-imine ligand (AmIm) which described as a stronger  $N,N'$ - ( $\sigma$ ,  $\pi$ )-donor ligand compared to the  $\beta$ -diketimine. The synthesis of the cobalt (I) complex follows the same strategy than Holland. Thus, starting from the aminoimidazolin-2-imine ligand (HAmIm) in presence of anhydrous  $\text{CoCl}_2$  and then KHMDS the dimer **Co-80** is formed. The latter is then reduced using  $\text{KC}_8$  to generate the desired cobalt (I) complex **Co-81** which was fully characterized including X-Ray analysis (Scheme 56). The authors then evaluated its reactivity in catalysis and demonstrated that **Co-81** was an efficient catalyst to activate Si-H bonds and employed it in the H/D exchange of hydrosilanes and hydrosilylations of olefins (Scheme 56a-b).<sup>150</sup>

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**Scheme 56. Synthesis of well-defined AmIm cobalt (I) complexes Co-81 and reactivities.**

## CONCLUSION

As shown in this review, low-valent well-defined cobalt complexes are not new and some of these complexes exist for ages and have never been applied in catalysis. Many advantages can be attributed to low-valent well-defined cobalt complexes. First, due to their low oxidation states, they are highly reactive and a wide range of transformations can be achieved with competitive yields and selectivities towards noble metals. This reactivity leads most of the time to air-sensitive complexes. However, these drawbacks can be overcome through the rational design of air-stable precatalysts, whose desired function is promoted by an external stimulus such as heat or light. Another way to rule out such sensitivity problem is to start from a well-defined cobalt (II) pre-catalyst and reduce it in situ in a controlled manner. However, compared to catalyst requiring chemical additives to be active, well-defined complexes provide keys to suitably decipher catalytic mechanism. Along the review, we have seen a large variety of accessible routes for low valent cobalt complexes and even some well-established mechanisms were questioned by well-defined catalyst studies.

This work, conducted by numbers of researcher groups over 50 years, contributed to help cobalt community to better understand their catalyst behavior and thus their catalytical development. However, some of these investigations can require sophisticated ligands to obtain the appropriate complex with the right reactivity. It is worthwhile mentioning that these ligands can be complicated to synthesize or expensive. In a fundamental context, they allow us to a better understanding of 3d transition metals behavior, but economically, their complexity withdraw the advantage offer by the inexpensive price of the metal center. Indeed, a new catalyst with equal reactivity and selectivity compare to noble metal will be only interesting if the overall price, ligand plus metal is sustainable and economic.

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### Biographies



Cassandre Bories received her PhD from Sorbonne Université in 2023 under the supervision of Dr. Marc Petit focusing on low-valent and well-defined cobalt hydrides in catalysis. Since 2023 she moved to the University of Manchester for a postdoctoral position under the supervision of Pr. Igor Larrosa where she was awarded the same year a MSCA (Marie-Skłodowska Curie Actions) Individual fellowship to perform C-H bonds activations using ruthenacycles.



Alexandre Sodreau received his Ph.D degree in organometallic chemistry and nanosciences from the Université of Toulouse in 2018 under the supervision of Prof. F. Delpech and Dr. D. Madec. Following a postdoctoral fellow at Sorbonne Université with M. Petit on the topic of cobalt nanoparticles for catalytic hydrogenation (2019-2020), another postdoctoral position at Max Planck Institute for Chemical Energy Conversion (MPI-CEC) in the group of W. Leitner (2021-2022) on transition metals phosphide applied to catalysis, in 2023 he became research scientist at IFPEN. Currently, his research is focused on separation process mainly xylene isomers splitting.



Marion Barbazanges is Senior Lecturer in Organic Chemistry at Sorbonne University (Paris, France). After a PhD in method development and total synthesis (ESPCI, Paris, France) and a first post-doctoral fellowship in medicinal chemistry (Imperial College, London, UK), she specialized in organometallic chemistry at the Institut Parisien de Chimie Moléculaire (Sorbonne Université, Paris, France). Focusing on stereoselectivity in various organometallic processes, as well as on the nature of organometallic species, she also opened to helical chirality and its applications as a ligand in enantioselective processes.



Marc Petit received his PhD from Université Pierre et Marie Curie under the supervision of Prof. M. Malacria in 2002. Following a postdoctoral stay with Prof. D. Curran at the University of Pittsburgh, he secured a permanent position at CNRS in 2004 within Dr. B. Bujoli's group in Nantes. In 2010, he joined Dr. C. Aubert's group at Sorbonne Université and was promoted to Directeur de Recherche in 2018. Since 2023, he is the head of the **CASCH** team (**CA**talysis and **S**ustainable **CH**emistry). His research focuses on the use of low-valent cobalt complexes in bond activations and nanoparticle synthesis.

## Notes

The author declares no competing financial interests

## ABBREVIATIONS

Acac: acetylacetonate; Ad: adamantyl; Alk: Alkyl; Ar: Aryl; ATRP: atom transfer radical polymerization; Benz: Benzene; BPin: Pinacolatoboron; CAAC: Cyclic alkyl amino carbenes; COD: 1,5-cyclooctadiene; Cp: cyclopentadienyl; CPME: Cyclopentyl methyl ether; Cy: Tricyclohexylphosphine; DFT: Density Functional Theory; DIPP: diisopropylphenyl; Dme: Dimethylether; dmpe: 1,2-bis-dimethylphosphinoethane; DMSO: Dimethylsulfoxide; dpePhos: Bis[(2-diphenylphosphino)phenyl]ether; Dppf: 1,1'-Bis(diphenylphosphino)-ferrocene; Et: Ethyl; *fac*: facial; HAmIm: aminoimidazolin-2-imine ligand; HMDS: Bis(trimethylsilyl)amine; IAd: Bis(adamantly) NHC; <sup>i</sup>Bu: isobutyl; IMes: Bis(mesityl) NHC; <sup>i</sup>Pr: isopropyl; Me: Methyl; mer: meridional; Mes: mesitylene; NBD: norbornadiene; <sup>n</sup>Bu: normal butyl; NCAs:  $\alpha$ -amino acid-*N*-carboxyanhydrides; NHC: *N*-Heterocycle carbenes; <sup>n</sup>Hex: *n*-hexanes; NHSi: *N*-heterocyclic-silylene; OAc: acetate; Me: Methyl; PDMS: Polydimethylsiloxane; Ph: Phenyl; Ph\*: 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>; PPN: bis(triphenylphosphine)iminium; RT: room temperature; Salph: *N,N'*-Disalicylal-1,2-phenylenediamine; <sup>t</sup>Bu: *sec*-butyl; <sup>t</sup>Bu: *tert*-butyl; Thf: Tetrahydrofuran; TMDS: 1,1,3,3-Tetramethyldisiloxane; TMS: trimethylsilyl; TBP: *o*-(<sup>i</sup>Pr<sub>2</sub>P)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>B; Trop: 5H-dibenzo[a,d]cyclo-hepten-5-yl; Ts: Tosyl; VN: valence number.

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