Cobalt Catalysts for $[2+2+2]$ Cycloaddition Reactions: Isolated Precatalysts and \textit{in situ} Generated Catalysts

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In \textit{in situ} catalyst generation, precatalysts are converted into active catalysts through various energy inputs such as heat, light, or microwave radiation. The substrates for the cycloaddition reactions include alkynes, oligoalkynes, nitriles, heterocumulenes, etc., leading to cyclization products such as benzenes, annelated benzenes, cyclohexadienes, pyridines, polymers, etc.
1. Introduction

The catalytic conversion of acetylene into valuable products by transition metal catalysis has found a large amount of (renewed) attention in recent years. The transformation into small functionalized building blocks has received industrial interest and of course also impacted synthetic organic chemistry. Even larger interest sparked the synthetic transformation of the diverse acetylene derivatives in a variety of important reactions for modern organic chemistry. Exemplary for such reactions is the Sonogashira-Hagihara reaction (in general only mentioned as Sonogashira reaction), which experienced a meteoric rise as synthetic utility for organic chemistry and material science. Foundation is the development of cross-coupling chemistry of the group 10 metals over the recent two decades, leading to applications in organic chemistry and material science. The advantage of the Sonogashira reaction is the easy introduction of alkyne moieties into many functionalized substrates and the possibility of further subsequent derivatization of the obtained alkynylated products.

The useful role of alkynes as C₂ building block has been found by systematic investigations in the 1930’s/40’s by Reppe et al., who investigated the possibilities of converting acetylene into cyclic compounds under rather mild reaction conditions using nickel catalysis (Scheme 1). The experimental work also established the decisive role of the catalyst composition on the general course of the reaction. In the presence of nickel(II) salts, cyclooctatetraene (COT) is the main product of the cyclization of acetylene. Different mechanistic proposals excluded alkyne metathesis at the metal center or insertion of acetylene in a metal-benzene complex, or proposed a binuclear metal complex as intermediate. Recent theoretical work supported the insight that the energetically most favorable pathway proceeds via mononuclear complexes like a nickelacycloheptatriene complex. While the COT is formed via an alkane insertion from the mono-ethyne nickelacycloheptatriene complex, the benzene forms in the presence of better donating neutral ligands like phosphines, which support rather reductive elimination of a [2+2+2] cycloaddition product than further acetylene insertion.

Over the following centuries the [2+2+2] cycloaddition reaction of alkynes was more a laboratory curiosity than a synthetic tool and only sporadic reports appeared. A first systematic report by Hübel et al. applied Co₅(CO)₈ (CoCa1) as catalyst for the cyclization of acetylenes. Co-alkyne-complexes of the type [Co₂(CO)₆(R)C≡C] are known since the middle of the 1950’s, but hadn’t been used for such a catalytic transformation before. Scheme 2 shows an overview of such early reactions, including the alkyne-complex intermediate. As one of the first targets hexaisopropylbenzene was synthesized from diisopropyl acetylene

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Abstract: [2 + 2 + 2] Cycloaddition reactions belong to the not even large class of reactions, which can be catalyzed or mediated by a significant number of different transition metals. Cobalt complexes belong to the catalysts that paved the way for the extensive use and profound mechanistic knowledge on this particular transformation. Beside the established role, cyclopentadienyl (Cp) cobalt complexes inherit in synthetic applications of the cyclotrimerization reaction, modification of the precatalysts opened up novel reactivities and versatility for such catalytic initiators. At the same time the development of in situ generated cobalt catalysts allowed the conversion of novel substrates as well as novel reaction modes to be realized. In this personal account recent developments will be presented and the possibilities of catalysts containing cobalt atoms in different oxidation states be discussed.

Keywords: cobalt, cyclopentadienyl complexes, [2 + 2 + 2] cycloadditions, alkynes, nitriles, oxidation states
and CoCa1 at high temperatures and long reactions times, however, with low yield.\textsuperscript{[12]}

Since these initial works the landscape of cobalt catalysts for $[2+2+2]$ cycloadditions have undergone significant improvement, based on development of novel precatalysts, insight into structure-reactivity relationships, introduction of chiral catalysts and process intensification by reaction engineering, e.g., by using photochemical or microwave reaction conditions. These developments, combined with the evolution of other molecularly defined, isolated transition metal catalysts as well as especially \textit{in situ} generated catalytic systems, have allowed the transformation of a vast variety of substrates into the corresponding cyclization products.\textsuperscript{[13,14,15]}

2. Novel CpCo-Precatalysts

The complex CpCo(PPh$_3$)$_2$ (CoCa2) has only been used in early studies on cyclotrimerization reactions, most often applied in stoichiometric reactions with alkynes. The reaction initially leads to intermediate cobaltacyclopentadienes, which were further reacted to give benzenes and heteroarenes.\textsuperscript{[17]} CpCo(I) complexes have become the workhorse in Co-based cyclotrimerization chemistry, since the introduction of CpCo(CO)$_2$ (CoCa3) as catalyst by work of Vollhardt et al. in the 1970’s.\textsuperscript{[18]} While CoCa3 is still an often applied...
catalyst, it is a rather delicate compound, requiring in general an inert reaction atmosphere. It also frequently requires high reaction temperatures and additional irradiation to provide sufficient reactivity. The further development therefore included the synthesis of CpCo(I) complexes with more labile neutral ligands compared to the rather tightly bound CO groups in CoCa3, essentially facilitating the generation of the “CpCo” fragment responsible for the initiation of the catalytic cycle by coordination to the alkyne substrates (which also includes successive exchange of the neutral ligands by the alkynes). The synthesis of the bisethylene complex CpCo(C2H4)2 (CoCa4) by Jonas et al. led to the systematic access to highly reactive classes of iron and cobalt complexes, especially the latter applicable as highly reactive cyclotrimerization catalysts.[19] The approach used cobaltocene as starting material and reductive elimination of one cyclopentadienyl group in the presence of alkali metals and olefins (ethylene, 1,5-cyclooctadiene [COD]) led to the formation of stable 18-electron CpCo(olefin)2 complexes CoCa4 and CoCa5 (Scheme 3, top).[20] The Jonas’ complex CoCa4 has found application in a number of syntheses comprising cyclotrimerization steps. Initially, Jonas et al. observed that the addition of an excess of 2-butyne to CoCa4 at −10°C results in the formation of the 20-electron complex η5-CpCo-η6-hexamethylenbenzene, which was isolated and applied as precatalyst for the [2+2+2] cyclotrimerization of acetylene, 2-butyne or acetylene in combination with a nitrile to furnish benzene, hexamethylenbenzene or the corresponding pyridine at room temperature. Since then, the capability of CoCa4 for cobalt-mediated or -catalyzed cyclizations was investigated, e.g. for the synthesis of cyclohexadienes from alkynyl pinacolylborates and alkenes (the product is isolated after oxidative demetallation from η5-CpCo-η6-cyclohexadiene) or the synthesis of triborylbenzenes in the absence of the alkene. Our group used the same general approach and investigated a number of different olefins for complexation with the CpCo fragment, however, only trimethylvinylsilane turned out to be suitable and the complex CoCa6 needs to be prepared under strictly inert conditions using elemental potassium at −78°C, yielding the complex with 80% yield (Scheme 3, below).[22] Complex CoCa6 is an excellent precursor for the assembly of other CpCo-olefin complexes, which cannot be prepared directly via the reductive methodology due, e.g. undesired side reactions and therefore difficult complex isolation. Addition of the desired olefins to CoCa6 allowed rapid ligand exchange and simple product isolation by removing the trimethylvinylsilane in vacuum. A selection of complexes synthesized from CoCa6 is shown in Scheme 4.

The reason for the smooth reaction is the high reactivity of CoCa6, as all other ligands, especially bidentate ones, deliver significantly more stable complexes. This is shown in Figure 1, where the calculated energetics of the ligand exchange process are depicted. The picture shows that even the Jonas’ complex CoCa4 is more stable than CoCa6 and that for the dienes a significant contribution by the chelate effect can be accounted, contributing to the significantly larger stability of the complexes CoCa5 and 2, 3 and 5. Indeed, complex CoCa5 is stable enough to be at least shortly handled in air, nicely correlating with the significant stabilization provided by the COD ligand.

Reactivity evaluation of CoCa6 in cyclotrimerizations of diynes (6) and nitriles (7) showed that it is exceptionally reactive and allows rapid cyclizations to pyridines (8) within minutes (Scheme 5).[21] The high reactivity comes with a price, demonstrated with the behaviour of the compound in chlorinated solvents like dichloromethane, when CoCa6 reacts with the solvent to yield [(Cp2Co)2(Cl2)] as decomposition product. In addition, it was discovered that when CoCa6 was left to stir...
in etheral solvents (Et2O, THF) or n-hexane at room temperature, a tetrannuclear cluster 9 was formed, which potentially can be imagined as a route for catalyst deactivation (Scheme 6). Evaluation in a standard cyclization demonstrated that the cluster is only to a small extent capable to mediate cyclotrimerization reactions under thermal as well as photochemical conditions, presumably by removal of single “CpCo” fragments from 9, which can act as catalysts. Therefore, an active oligonuclear cobalt species can be excluded for being responsible for the rapid cyclizations at low temperatures.

The stabilization of the CpCo fragment by introduction of electron-deficient olefins like dialkyl fumarates in CpCo(CO)2 (CoCa3) as neutral ligands was found by Aubert and Gandon et al., furnishing air-stable complexes of the type CpCo(CO)(olefin) (CoCa7) (Scheme 7). The exchange required thermal and photochemical energy supply to effect the olefin/CO exchange.

Reactivity screening of complex CpCo(CO)(trans-MeO2CH=CHCO2Me) (CoCa7Me) with triyne 10a and comparison with CoCa3 showed no large differences in refluxing toluene and additional irradiation (Scheme 8). However, under exclusive thermal conditions without irradiation, CoCa3 gave only 14% yield for 11a, while CoCa7Me...
under identical conditions performed the cyclization with excellent 85% yield. Conducting the reaction in DMF under microwave conditions (MW) at 200 °C for 10 min, the series of complexes CoCa7 gave yields between 64–75%, while 60% were accounted for CoCa3 for product 11a.

Further reactions showed, that CoCa7 can be applied to the synthesis of pyridines from diyne/nitrile and intermolecular cyclizations of alkynes under thermal and microwave conditions with mostly to very good yields.\[25\]

We have initially investigated ligand exchange reactions of CoCa6 for the introduction of different other neutral ligands aiming at modification of the catalytic reactivity.\[26\] While coordination of phosphines usually has detrimental influence on the reactivity, we investigated phosphites, which should provide a certain degree of stabilization compared to the trimethylvinylsilane ligand, without compromising the reactivity too extensively. The ligand exchange experiments surprisingly showed that only one olefin ligand in CoCa6 can be replaced easily, allowing selective access to a new class of CpCo(H,C=CHSiMe3)3[P(OR)3] complexes CoCa8 with good yields (Scheme 9). Increasing the amount of P(OR)3 even to larger than stoichiometric amounts under thermal conditions gave no selective access to the bisphosphite complexes CoCa9. However, irradiation of CoCa5 in the presence of phosphites gave selective access to the CpCo(phosphite)2 complexes CoCa9 with very good yields. Both complexes are significantly more stable than CoCa6 and are of oily consistency or even solids.

The reactivity in [2 + 2 + 2] cycloaddition reactions has been evaluated in standard test reactions, e.g. for the cyclization of 1,6-heptadiyne (6a) with benzonitrile (7a). The results for the comparison of precatalysts CoCa6, CoCa8a and CoCa9a are shown in Figure 2. The significantly different performance in the test reaction corroborates the outstanding reactivity of CoCa6 and the stabilizing properties of P(OPh)3, as phosphite, leading to largely reduced reactivity for CoCa9a, while precatalyst CoCa8a is an excellent combination of stability and reactivity.

The reactivity of complex CoCa8a was further investigated in different cyclizations and it was found that already at reaction temperatures as low as 50 °C most reactions proceed smoothly to the expected products 8 (Scheme 10). Internal diynes, when applied for the assembly of substituted analogues of pyridines like compound 8i, required longer reaction times (or higher temperatures) to deliver the product, as such alkynes in general react more sluggishly. Attempts to synthesize a pyridine containing an annellated seven-membered ring failed under these reaction conditions.

The catalyst is also reactive for the cyclization of triynes, although higher reaction temperatures are required. The completely intermolecular cyclization of alkynes and nitriles was found possible, as demonstrated for the reaction of 3-hexyne (12) and benzonitrile (7a) to yield pyridine 13 (Scheme 11).

Accordingly, we also investigated modifications on the olefin ligand to identify further influence on the precatalyst...
stability and catalytic performance. It was found possible to exchange the remaining trimethylvinylsilane ligand from CoCa8 for dimethylfumarate (dmfu) at elevated temperatures, leading to an air-stable, solid complex CoCa10a with excellent yield (Scheme 12).

Further elaboration and synthetic optimization were dedicated especially to replace CoCa6 as starting material, finally leading to the development of an efficient general route for the synthesis of a class of novel precatalysts CoCa10 starting from commercially available CpCo(CO)₂ (CoCa3) (Scheme 12 below, and see Scheme 15 for more details). The initially prepared complexes CpCo(dmfu)[P(OPh)₃] (CoCa10a) and CpCo(dmfu)[P(OEt)₃] (CoCa10b) were investigated in a variety of cyclizations to evaluate reactivity and versatility. These precatalysts were found to be useable under thermal as well as irradiation energy supply. The cyclization of diyne 14 with benzonitrile (7a) yielded the naphthylisoquinoline 15 with comparable yields for thermally and photochemically assisted reactions, however, the shortest required reaction time was found in a microwave reactor (Table 1).

Depending on the substrate, the yields are significantly higher for the reaction of diyne 16 with nitrile 7b, giving up to 96% yield for 17 within 30 minutes, while using conventional heating and irradiation also gave very good yields within significantly longer reaction times (Table 2).

The reactivity was further evaluated with a series of substrates towards the formation of the pyridine ring from functionalized nitriles and diynes and selected products (18–22) are displayed in Scheme 13.

The reactions allowed the construction of interesting structures including bidentate (or polydentate) ligands like 18 or functionalized boronates (22), with excellent yield in the latter case.
Apart from the evaluation of the effect of different modes of energy supply concerning the reactivity of CpCo(Im)(P(OEt)₃)₃ (CoCa10b) for [2 + 2 + 2] cycloadditions, the precatalyst was also directly compared to CpCo(CO)₂(CoCa3) under microwave heating (Scheme 14).

The direct comparison revealed a much higher overall reactivity of the precatalyst CoCa10b compared to the CO-containing compound CoCa3. For the synthesis of pyridine 23 from 16, CoCa3 was applicable to obtain the product in good yield, slightly better even was CoCa10b, whereas precatalyst CoCa3 failed completely for the intended synthesis of functionalized pyridine 23 from 14 and transformation of triyne 10a to 11a. In stark contrast, CoCa10b furnished pyridine 23 with at least 40%, while triaryl 11b was obtained with very good yield.

The method for the synthesis of precatalysts of the type CpCo(olefin)(phosphite) was studied further and identified to be broadly applicable. A large variety of such precatalysts has been prepared from different olefins, phosphites and phosphoramidite (Scheme 15). The general route com-

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**Table 2.** Energy supply in cyclizations with precatalyst CoCa10b and diyne 16 and nitrile 7b.

| Solvent | Energy supply | T [°C] | t [h] | Yield [%] |
|---------|---------------|--------|-------|-----------|
| Toluene | ΔT            | 100    | 22    | 82        |
| Toluene | MW            | 160    | 0.5   | 96        |
| THF     | hv            | 25     | 22    | 82        |

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**Scheme 13.** Reactivity screening for precatalyst CoCa10b with diynes and nitriles under microwave heating.

**Scheme 14.** Comparison of the activity of precatalysts CoCa3 and CoCa10b for cyclizations under microwave heating.
prises in the first step a simple exchange of CO for a phosphite ligand, favourably applying slight vacuum in the reaction vessel for complete conversion. Subsequently, the CpCo(CO)(phosphite) complexes (24) were irradiated in the presence of 1 equiv. of an olefin to furnish the complexes CoCa10.

The complexes have been investigated towards their reactivity and it turned out, that the combination of phosphite/olefine was determining the reactivity and stability of the complexes, leading in the “sweet spot” to rather stable complexes, which nevertheless are able to be activated in cyclotrimerization reactions at rather mild temperatures. A selection of such reactions catalyzed by CoCa10c is given in Scheme 16. Reactions with diyne 16 and different alkyl nitriles (7) at only 75 °C allowed the assembly of the 1-naphthylpyridines 25–27 with excellent yields in short reaction times. Also, 1-naphthyltetrahydroisoquinoline 15 was exemplarily synthesized from 14 and benzonitrile (7a) under identical conditions, although with somewhat lower yield.

The complexes CoCa10 can be activated under favourable thermal as well as mild photochemical conditions, as was demonstrated by the cyclization of triyne 10c to 11c with catalyst CoCa10c (Scheme 17).

The properties of CpCo(COD) (CoCa5) and CoCa10a have found synthetic application for several projects in our laboratories. Specifically, the synthesis of heterobiaryls has seen significant interest and as early example, we applied precatalysts CoCa5 and CoCa6 for the assembly of diastereomeric atropisomers from chiral diynes and nitriles. In another project we investigated the role of substitution of the annelated ring of the pyridine in heterobiaryls to gain information on the influence of the substitution on the configurational stability of the biaryl axis. We synthesized a series of unsymmetrically functionalized 1-naphthylidyynes (28), which were then subjected to cyclotrimerization with PhCN (7a) or MeCN. In most cases the products 29 were

Scheme 16. Reactivity screening for precatalyst CoCa10c with diynes 14 and 16 and nitriles (7) at 75 °C reaction temperature.

Scheme 17. Thermal/photochemical cyclization reaction of triyne 10c with precatalyst CoCa10c.
obtained under mild conditions using photochemically assisted cyclization with CpCo(COD) (CoCa5) with medium to good yields (Conditions A, Scheme 18). In some cases, the cyclization was achieved using CoCa10b under microwave conditions for more rapid product formation (Conditions B, Scheme 18). The obtained products were investigated by dynamic HPLC on chiral phases to estimate the barrier of rotation around the biaryl axis and the configurationally rather stable compounds showed activation barriers of ΔG° > 115 kJ mol⁻¹ depending from the substitution pattern. This is exemplified for compound 29a, which becomes configurationally unstable already at slightly elevated temperatures, while 29b–g have significantly more stable biaryl axis, especially due to the substitution of the newly formed pyridine ring pointing towards the naphthyl ring.

The stabilization concept for the CpCo fragment was applied in the approach of developing Cp’Co(II) complexes for heterogenization of the catalyst. Early attempts by Vollhardt et al. for the synthesis of heterogenized cobalt catalysts from substituted cyclopentadienes have not been met with success. We have followed up on that approach by installation of a siloxy group at the cyclopentadiene for later inclusion by sol-gel procedure or simple attachment to silica gel. The synthesis of the precatalyst for attachment to the solid phase was straight forward and is presented in Scheme 19.

The cyclopentadiene 30 was complexed using Co₂(CO)₈ (CoCa1) as cobalt(0) source and an olefin as hydrogen acceptor. The reaction runs very smooth under mild conditions with excellent yield for complex 31. The attempt to synthesize 31 from [ICO(CO)₄] and metallated 30 gave significantly lower yield beside the reaction affording much less pure product. In the next step, subsequent exchange of the CO ligands for P(OEt)₃ and dimethyl fumarate resulted in the smooth formation of CoCa11a with 38 % yield over the two substitution steps. The complex CoCa11a itself is a good precatalyst for cyclotrimerizations and is an air-stable, easy to handle solid. Heterogenization experiments finally resulted in the formation of an SiO₂-bound precatalyst CoCa11b, which was used in a test cyclization between 1,6-heptadiyne (6a) and PhCN (7a). While the cyclization was successfully promoted and the catalyst reisolated, the recycled catalysts’ activity already largely deceased in the next run unfortunately.

Most recently during experimentation with CpCo complexes we discovered to our big surprise that CpCo(III) complexes can also promote cyclotrimerizations without the addition of reductants. CpCo(III) complexes are syntheti-
ally easily accessible and air-stable compounds. The synthesis of CpCo(III) complexes containing CO and phosphite ligands, starting conveniently from CpCo(CO)₂(CoCa₃), is illustrated in Scheme 20. Oxidation of CoCa₃ with elemental iodine was followed by ligand exchange of CO for phosphite, which in all cases was managed to happen simply by stirring the reaction partners (e.g. for CoCa₁₃ and CoCa₁₅). Exchange of the anionic iodide ligands was also possible in the presence of cyanide salts like NaCN in alcoholic solution, leading to the biscyanide complex CoCa₁₄ in very good yield. In general, for these synthetically straight-forward manipulations of CpCo(III) complexes very satisfying yields have been observed.

Selected results for benchmark cyclizations of triyne 10 are presented in Scheme 21. In addition to complexes synthesized in Scheme 20, two more catalysts (CoCo₁₃Me and CpCo₁₅Me, P(OR)₃ = P(OiPr)₃) were prepared by methylation of the remaining iodide groups with Grignard reagent. All precatalysts investigated gave cyclization products already at 75°C reaction temperature and the methylated complex CoCo₁₃Me gave the best result here.

Investigation of CoCa₁₄ for the transformation of triyne 10 showed no reactivity at 75°C, but gave excellent 84% yield of product 11 at 105°C. Experimental data obtained so far could exclude the intermediacy of CpCo(I) complexes as active catalytic species, potentially caused by an unknown reduction process. However, the exact nature of the responsible species and the possible overall catalytic pathway relying on a Co(III) is currently under investigation in our group.

3. Novel isolated and in situ Generated non-Cp-Based Cobalt Catalyst Systems

Beside Co₂(CO)₈ (CoCA₈) and CpCo(I) complexes, other defined cobalt precatalysts as well as increasingly in situ generated cobalt catalyst have found significant interest over recent years. They often require much less drastic reaction conditions for the cyclization to occur and are capable to include chiral ligands for the development of asymmetric cyclizations.

Early examples of simple catalytic system have been reported by Chisuoli et al., who demonstrated the possibility of cyclizing dipropargylamines with alkynes and nitriles to corresponding carbo- and heterocycles simply using CoCl₂ and elemental manganese or zinc as reductant without requiring additional donor ligands.

Development of catalytic systems by using in situ generation from several components was initiated by work of Okamoto et al., applying bisphosphines and 2-iminopyridines as bidentate ligands as well as N-heterocyclic carbenes (NHC’s) as monodentate ligands for cobalt. Usually simple cobalt(II) chloride was used as metal source and zinc powder applied as reductant at reaction temperatures ranging from room temperature to 50°C. Further development of Co-
iminopyridine (dipimp) catalyst systems included the application of dimethyl phthalate as an additive for optimal performance, thus allowing low catalyst loadings of hydrated cobalt salt to be used without compromising the yield in the transformation of diynes (6) with alkynes (33) to highly substituted benzenes 34a–c (Scheme 22). In addition, shorter reaction times were encountered for the conversion under these modified reaction conditions.

Cheng and co-workers at the same time introduced CoI\(_2\)(dppe) as precatalyst, which under reductive conditions in the presence of elemental zinc is capable of executing inter- as well as intramolecular [2 + 2 + 2] cycloadditions towards the assembly of pyridines and benzolactones/-lactames.

Hilt et al. introduced in situ generated cobalt-based catalytic systems applying substituted diimines for the cyclization of terminal and internal alkynes. In these cases high regioselectivities for the cyclization of terminal and internal alkynes to 1,2,4-substituted vs. 1,3,5-substituted benzenes were observed. Also, sulfur-containing ligands like 1,2-(bisaryl)thio- and 1,2-bis(alkylthio)ethane were identified to be suitable for generating efficient cyclotrimerization catalysts. Interestingly, reactivity and result of the cyclotrimerization here are largely depending on the reaction solvent. A recent enhancement in terms of catalyst loading was reported by Wang and co-workers, utilizing a combination of pinacolborane (HBPin) and KO\(_t\)Bu to activate just 0.5 mol % of Co(II) iodide precatalyst to cyclotrimerize terminal alkynes with good to almost quantitative yield in the absence of additional ligands.

Since the initial development of such in situ generated catalytic systems, novel catalysts and especially applications have been reported, which all rely on the generation of the catalytically active species under reductive conditions, in general provided by the addition of elemental zinc or manganese. There are only few molecularly defined Co\(^I\) precatalysts known besides the above discussed CpCo(I) complexes, which can directly be used for cyclotrimerizations. The reason is the instability of many isolated Co\(^I\) complexes, which potentially could be used directly as molecular catalysts. We have investigated the well-known complex CoCl(PPh\(_3\)_3) (CoCa16), the cobalt analogue of the Wilkinson complex RhCl(PPh\(_3\)_3) and usually known as precursor for cobalt complex synthesis, as precatalyst for the cyclization of triynes (Scheme 23). This complex is also not stable for long periods under air, however, reasonable stable enough for easy handling and indefinite storage under inert atmosphere. The transformation of the triynes (10) into the corresponding benzene, biaryl and triaryl products (11a, 11d–j) occurred smooth and in most cases at room temperature. If the triyne substrates are bridged by malonyl units, reaction temperatures of 60–95 °C are required to yield the cyclization products in high yields.
The investigation of CoCl(PPh₃)₃ (CoCa₁₆) as suitable catalyst initiated the idea of introducing chirality into the cyclization process. For RhCl(PPh₃)₃, it was possible to use this complex as metal precursor together with chiral ligands like QUINAP to generate a chiral Rh⁺ catalyst, which can be applied in asymmetric cyclizations of triynes, however with varying success.⁴⁴ Beside using chiral ligands for the stereochemical induction, the anionic group of RhCl(PPh₃)₃ could principally also be used in terms of the asymmetric counter-anion-directed catalysis (ACDC).⁴⁵ We investigated different chiral anions, e.g. like TRIP ((R)-3,3'-bis(2,4,6-trisopropylphenyl)-1,1'-binaphthyl,2,2'-diyl hydrogen phosphate) or Δ-TRISPHAT tetrabutylammonium salt, in cyclizations of triynes with RhCl(PPh₃)₃ and other rhodium(I) salts, however, with little success as only a maximum of 11 % ee were observed. Identical experiments using CoCl(PPh₃)₃ (CoCa₁₆) as metal source with chiral anions did not yield any stereoselectivity. Interestingly, as a side effect, the cyclization reactions were significantly accelerated and furnished the cyclization products with good to very good yields.

The conception of using cobalt(II) salts and reductants in the presence of chiral, bidentate ligands on evaluation showed that traditional bidentate, chiral bisphosphines like BINAP did not allow to induce stereoselectivity. On the other side, the experiments using chiral P,N ligands like QUINAP or PINAP allowed for the first time to achieve enantioselectivity in [2+2+2] cycloadditions with cobalt catalysts. Representative results are shown in Scheme 24 for the cyclization of triynes.⁴⁶ The reaction required preactivation of the catalyst CoCa₁₇ in the presence of a reductant and ZnI₂, before the substrate 10 is added to perform the actual cyclization reaction. Cyclization reactions can be performed at temperatures as low as 0°C and the reaction appeared to be tolerant to even a full equivalent of additionally added P,N ligand without influencing its performance negatively. The utilization of malonyl-bridged triynes in the asymmetric cyclization was also possible, however, successful cyclizations required significantly higher reaction temperatures up to 95°C for successful conversion, at least giving ee values of up to 60 %.

A regio- and enantioselective synthesis of pyridines by asymmetric cobalt-catalyzed [2+2+2] cycloaddition of alkynylated malonitriles (35) and terminal alkynes was developed by Li et al.⁴⁷ The in situ catalyst system consists of a Co(II) salt as precatalyst, Ph₂SiH as the reducing agent and chiral bisoxazolinephosphine ligands NPN-1 or NPN-2 (Scheme 25). The excellent selectivity of the protocol was strongly dependent on the nature of the substituents on both, the ligand and the terminal alkyne, but also solvent effects were encountered. Hexafluorisopropanol (HFIP) or 1,2-dichloroethane (DCE) were applied as solvents for the synthesis of either 5- or 6-substituted cyanopyridines (36, 37) with up to 98% yield and stereoselectivities of up to 99 % ee. In both cases the formation of low-valent cationic catalyst species has not been excluded and the use of either ZnI₂ as Lewis acid (Scheme 24) or a cobalt source [(Co(BF₄)₂·6H₂O] containing tetrafluoroborate as weakly coordinating anion (Scheme 25) point towards the eligibility of such an assumption, although it has not been proven yet.
4. The Role of Oxidation States in Cobalt-Catalyzed Cyclotrimerizations – New Mechanistic Perceptions and Insights

The oxidations states of the active species in cobalt-catalyzed cyclotrimerization reactions is in general assumed to be Co\(^{I}\) and Co\(^{III}\), confirmed by a large number of theoretical investigations.\(^{[15c,48]}\) Such preferred oxidation states can in general be found in a large variety of transition metal-catalyzed processes, a highly prominent example being the palladium-catalyzed cross-coupling reaction, proceeding in general via Pd\(^{0}\) and Pd\(^{II}\) catalytic intermediates. Cross-coupling and C-H activation reactions are now also well known for cobalt complexes and the similarities of these and cyclotrimerization processes are quite compelling, as in both types of reaction the oxidative addition/oxidative cyclization and reductive elimination steps play most important and prominent roles.\(^{[51]}\) Generation of the active species from different cobalt precursor compounds with different oxidation states for cobalt-mediated cross-coupling reactions have been investigated, pointing towards Co\(^{I}\) as presumable catalytically active species.\(^{[50]}\) The reactivities, e.g. in C-H functionalization reactions are divided in low-valent and high-valent complexes, depending on the oxidation state of the cobalt metal center.\(^{[51]}\) Another prominent example are the different reactivities in the oxidation states of planar four-coordinated cobalt complexes, allowing a large number of different transformations.\(^{[52]}\) Recent investigations on Co\(^{I}\)-catalyzed hydrogenation reactions of saturated olefins or ketones\(^{[53]}\) or electrocatalytic oxygenations featuring Co\(^{II}/Co^{III}/Co^{IV}\) oxidation states\(^{[54]}\) illustrate the possibilities of different accessible metal oxidation states for catalytic purposes.

In the field of cyclotrimerization reactions, low-valent oxidation states have been proposed in early studies.\(^{[56]}\) Yoshikai and co-workers brought a new twist into play by furnishing pyridines (39) with good to excellent yields via application of a simple in situ catalyst system consisting of CoI\(_2\), 1,3-bis(diphenyl-phosphino)propane (dppp) and elemental zinc. A broad substrate scope is demonstrated for the [2+2+2] cyclotrimerization of internal, predominantly arylated, alkynes and nitriles, but also for the application of diynes and cyanoalkynes. Heteroaryl-substituted alkynes were also successfully applied for the synthesis of unusually substituted pyridines and represent a pinnacle of this protocol.\(^{[55]}\) Premise for this astonishing reaction pathway was the implication of a proposed low oxidation state of cobalt. Whereas Co\(^{I}\) species are well known to promote such kind of cyclizations, the activation barrier of the initial step for the oxidative coupling of two alkynes is noticeably lower for the Co\(^{0}\) complex compared to simultaneously investigated Co\(^{I}\) congener. Additionally, calculations revealed a distinct preference for the stepwise reaction pathway (Figure 3),

![Scheme 25. Regio- and enantioselective synthesis of pyridines 36 and 37 by application of chiral NPN ligands.](image)

**Figure 3.** Intermolecular synthesis of pyridines and the proposed reaction mechanism based on computational studies.
starting with the formation of cobaltacyclopentadiene (II→III) from the bisalkyne complex I, followed by the nitrile (7a) insertion (IV→V) and the subsequent reductive elimination (VI). The reaction pathway thus follows rather a Co^0/Co^II catalytic cycle than a usually assumed Co^I/Co^III cycle. The substrate scope covered different bisaryl-substituted internal alkynes (like 38 in Figure 3), including functionalities such as nitrile-esters and ether-bearing benzenes as well as thiethyl and pyridyl functionalities. The nitrile component tolerated a large manifold of functionalities, e.g. amine groups, morpholine, pyridines, alkynes or alkenes. The formation of a fused backbone was achieved by using diynes or cyanodalkynes.

Another approach to influence the oxidation state of cobalt catalysts in [2+2+2] cycloadditions is the utilization of photocatalysts to activate and control the cyclization, as initially demonstrated by Rovis and co-workers.[56] The governance of the reaction by visible light was exemplified by the cyclization of diynes with terminal alkynes to furnish benzene products under the influence of a Co-based catalytic system (Scheme 26). The catalytic cycle starts with the oxidative cyclization of the diyne with the generated Co^0 fragment and follows a similar pathway like described in Figure 4. Before insertion of the third alkyne moiety into the cobaltacyclopentadiene, the Co centre is oxidized from +II to +III by the photocatalyst, resulting in an octahedral complex intermediate to proceed in the catalytic cycle. As photocatalyst the well-known complex [Ir(dF-CF_3-ppy)_2(dtbppy)](PF_6) (PC) was applied and allowed to control the catalytic reactivity by switching the irradiation source on or off. Furthermore, this method was adapted to enable cyclotrimerization polymerizations.[57]

Extension of the methodology for the reaction shown in Scheme 26 led to the identification of a photoactive phenylethynylated Co^II precatalyst, which upon diyne coordination and irradiation at 380 nm via ligand-metal charge transfer from the anionic phenylethynyl ligand to the cobalt centre led to a Co^I species, undergoing oxidative cyclization and presumably [4+2] cycloaddition with the monoalkyne to finally furnish the cyclotrimerization product.[58] In this approach the metal catalyst has the photoactive group already "on board" and does not need an external photocatalyst.

Recent developments in combining photoredox catalysis with transition metal-based catalysts enable elaborate reaction patterns in cyclization reactions, like the successful transformation of enediynes (40, Figure 4) in cyclotrimerizations. Enediynes have formerly been very challenging substrates for cyclotrimerizations, due to the inhibiting character of the formed cyclohexadienes (41), caused by their strong metal-coordinating properties. This goal was achieved by Yamamoto and co-workers by combining an organophotocatalyst (PC2) with an in situ generated, cobalt-based catalytic system under irradiation with visible light.[59] This methodology also covers chiral applications, which allow selective formation of quaternary carbon centers. Spectroscopic observations of on-
off experiments indicate that no Co\textsuperscript{I} species is formed during the catalytic cycle shown, which could undergo the cyclization directly (Figure 4). The catalytic reaction begins with the photochemically induced reduction of Co\textsuperscript{II} to Co\textsuperscript{0}, which then undergoes the oxidative addition with the diyne 40, yielding a cobaltacyclopentadiene intermediate (I\textsubscript{a}). Subsequent photoinduced oxidation of Co\textsuperscript{II} to Co\textsuperscript{III} allows the insertion of the attached alkene fragment into the cobaltacyclopentadiene intermediate (I\textsubscript{a}). The product 41 is released by reductive elimination to form a Co\textsuperscript{I} species, which is reduced to a Co\textsuperscript{0} species, returning to the beginning of the catalytic cycle.

Following an approach to extend the product scope of cobalt-catalyzed cyclotrimerizations to unusual products, we were able to broaden the product scope to rather unusual phosphinines, the heavier congeners of pyridine, by deploying Co\textsuperscript{II} catalysts without any reductant present\textsuperscript{[60]} The reaction of phosphaalkynes (42) with (functionalized) diynes (Scheme 27) allowed the assembly of an array of aromatic phosphinines with unusual substituents. The presented method is suitable for 1,6-heptadiynes containing different bridging units and aliphatic (42a,b) and aromatic phosphaalkynes (42c). Many functional groups, e.g. like ethers (43a) or alcohols (43b) were tolerated in the backbone. Outstanding is the tolerance of one or more nitrile functionalities without the concurrent assembling of pyridines during the reaction, which selectively led to formation of phosphinines (43g–i) in good to excellent yields. The investigation of the selectivity revealed a clear preference for the pyridine formation with a lower oxidation state of the cobalt catalyst, explaining the great selectivity of the used Co\textsuperscript{II}-based catalytic system for phosphinine formation. Interestingly, investigation of CpCo(I) complexes like the Jonas complex (CoCa\textsubscript{4}) (and its indenyl analogue) towards their reaction with phosphaalkynes showed that addition of 2 equivalents of phosphaalkyne to these Co\textsuperscript{I} complexes resulted in the substitution of the ethylene ligands and the formation of the 18-electron complex (η\textsuperscript{2}-Cp or η\textsuperscript{2}-indenyl)Co(η\textsuperscript{4}-1,3-di phosphacyclobutadiene)\textsuperscript{[61]}

Computational studies of the reaction pathway (Figure 5) revealed a variation of classical cyclotrimerization mechanisms elucidating a cationic complex as the catalytically active species. The sequence is initiated with the coordination of the diyne (I\textsubscript{a}), followed by oxidative cyclization leading to the formation of a cobaltacyclopentadiene (II\textsubscript{a}). Subsequently, the phosphaalkyne is coordinating terminally by the phosphorus lone pair to the cobalt centre (III\textsubscript{a}), before via a formal [2+2] cycloaddition intermediate (IV\textsubscript{a}) the final insertion into the cobalt-carbon bond takes place, resulting in the formation of a seven-membered cobaltaphosphacycloheptatriene (V\textsubscript{a}). Reductive elimination furnished the complex containing the coordinated phosphine (VI\textsubscript{a}), from which the free phosphinine is finally released to return the catalyst species to the cycle. In contrast to the previously described catalytic pathway of Yoshikai et al., in this case each intermediate appears to be cationic.

The selected examples presented in this section show the possibilities of unusual oxidation states for cyclization reactions off the beaten track and future development in photo- as well
as electrocatalysis might open novel venues for exciting reactions with novel substrates.

5. Summary and Outlook

The recent two decades saw the further development of catalysts based on the CpCo fragment as well as the introduction of novel in situ generated catalytic systems, the latter taking advantage from the variety of available different ligands, especially bidentate P,P-, P,N- or N,N-based ligands, allowing chemo-, regio- and stereoselective reactions to be executed. For the CpCo complexes, neutral ligand combinations of olefins and phosphites provide novel, interesting features to the precatalyst, including possible activation under thermal as well as irradiation conditions at rather mild temperatures. Some in situ generated catalyst systems also rely on photoredox catalysis to generate the catalytically active species. The substrate scope for cobalt-catalyzed reactions is very broad, allowing the synthesis of unsaturated and aromatic carbocycles and heterocycles from alkynes, olefins, olefins, nitriles and heterocumulenes. Novel substrates for such cyclizations are constantly explored to broaden the application scope. As an example, very recently the assembling of phosphinines from a 1:1 mixture of diyne/phosphaalkyne using a cobalt-bispiphinole complex was reported. The development of novel reaction methodology including photoredox catalysis, electrocatalysis and development of ligand/precatalyst architectures can be expected to open excited new possibilities in cyclotrimerization chemistry and possibly other related transformations. While the field of asymmetric [2 + 2 + 2] cycloadditions is dominated by chiral rhodium catalysts, the development and application of chiral cobalt catalysts in this direction still has significant potential for constructing chiral scaffolds.

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