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CpCo(III) Precatalysts for [2+2+2] Cycloadditions

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Abstract: Catalysts applied in cobalt-catalyzed cyclotrimerizations reactions in general rely on the use of Co(I) precatalysts or the in situ generation of Co(I) catalysts from Co(II) sources by reduction in the presence of steering ligands, often by addition of less noble metals. In this paper, we report the synthesis and properties of novel stable CpCo(III) complexes as precatalysts and their exemplary evaluation for application in catalytic [2+2+2] cycloadditions. The role of phosphite neutral ligands, as well as iodide and cyanide as anionic ligands, on the reactivity of the complexes was evaluated. A modified one-pot approach to the synthesis of Cp ring-functionalized Cp'Co(III) complexes was developed. The investigations demonstrated that CpCo(III) complexes can be directly applied as catalysts in catalytic cyclotrimerizations of triynes without reducing agents as additives.

Keywords: cobalt(III) complexes; complex synthesis; [2+2+2] cycloaddition reactions; cyclopentadienyl ligand; olefins; phosphites

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1. Introduction

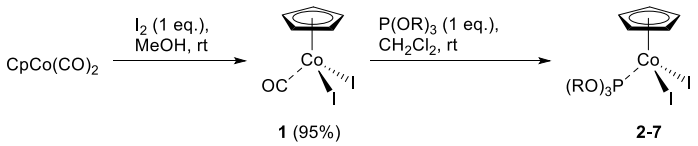
The chemistry of CpCo(III) and Cp*Co(III) complexes (Cp = cyclopentadienyl, Cp* = pentamethylcyclopentadienyl) have gained a lot of attention during the recent decade, especially also due to their role in studying C-H functionalization reactions with respect to their capability compared to the latter group 9 metals [1]. Therefore, the chemistry of the CpCo(III) fragment came into focus from the perspective of catalysis and related organometallic chemistry [2]. Novel applications of such complexes in transformations, such as transfer hydrogenations under aerobic conditions, have been studied only recently [3]. The compound $CpCo(CO)_2$ is the suitable precursor for the synthetic entry, especially due to the easy availability of air-stable CpCo(III) complexes like $CpCoI_2(CO)$ (**1**) by simple reaction with elemental iodine [4]. Since the early stages of half-sandwich complex chemistry the compound $CpCoI_2(PPh_3)$ was synthesized and further derivatization reactions were investigated [5], including the possible synthesis of cobaltacyclopentadienes by reaction with dilithiated butadienes [6]. Cationic CpCo(III) complexes, generated by abstraction of the two iodides from $CpCoI_2(PPh_3)$, have found to undergo orthometalation reaction with *trans*-azobenzene [7]. However, none of such complexes have been systematically tested as catalyst in cyclotrimerizations, neither as phosphine nor phosphite complexes [8–15]. While phosphines proved to be detrimental to the catalytic activity of the CpCo fragment, phosphites turned out to dissociate significantly easier, however, still providing sufficient stabilization of the precatalyst [16]. The presented study is concerned with the synthesis of $CpCo(III)(L)(X)_2$ complexes and the study of their reactivity as precatalysts in [2+2+2] cycloaddition reactions of triynes and diynes/nitriles.

2. Results and Discussion

2.1. Synthesis of CpCo(III) Complexes

The ligand exchange of the CO ligand in $CpCoI_2(CO)$ (**1**) for phosphite ligands is a very smooth process, which we were able to demonstrate by the ligand exchange reac-

tions shown in Scheme 1. A series of phosphites was investigated, including those with electron-donating (e.g., $P(O\textit{i}\text{-}Pr)_3$, $P(OCy)_3$) and electron-withdrawing (e.g., $P(OC_6F_5)_3$, $P(OCH(CF_3)_2)$ groups. Such substitutions on **1** have been published by Brill and Tulip et al. or Pauson et al. using $P(OMe)_3$ as the structurally simplest phosphite [17,18]. In our case, the exchange reactions occurred in general at room temperature and very good to excellent yields for **2–4**, **6** and **7** were obtained. An exception was observed for the sterically highly demanding tri(2,4-di-*tert*-butylphenyl)phosphite, which reacted very sluggishly and did not allow to isolate pure complex **5** in any useful amount. Additionally, the attempted repeated synthesis with $P(OPh)_3$ as ligand failed, which we currently cannot substantiate with an clear explanation. The products of the successful substitutions were simply isolated by filtration and washing. These complexes are air-stable compounds, soluble in polar organic solvents. It is interesting to note that the ^{31}P NMR shifts in complexes **2** (117.4 ppm) and **3** (118.0 ppm) are shifted around 50 ppm to higher field compared to the CpCo(CO)(phosphite) complexes and shifted still roughly 30 ppm to higher field in the case of CpCo(olefin)(phosphite) complexes [19]. Both classes of neutral ligands with low-lying π^* orbitals inherit ligand back-bonding capabilities for electron density from the cobalt center, thus allowing larger electron-density donation from the phosphites to the metal center compared to the iodide atoms in **2** and **3**. This trend was also observed for complex **4** containing the fluorinated phosphite $P[OCH(CF_3)_2]_3$.



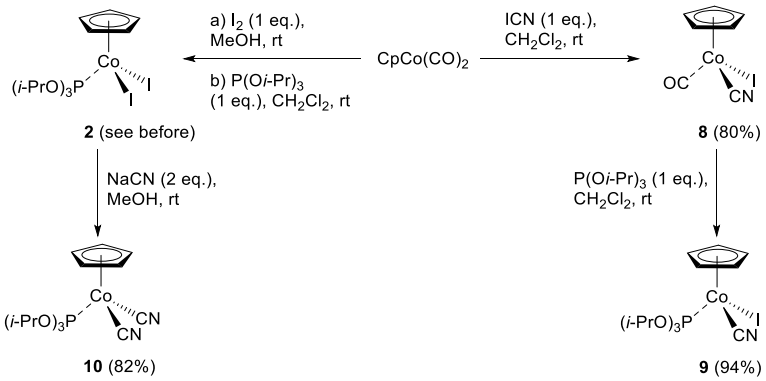
Yields for the 2. step:

$CpCoI_2[P(O\textit{i}\text{-}Pr)_3]$ (**2**): 99% yield	$CpCoI_2\{P[O\text{-}2,4\text{-}(t\text{-}Bu)_2C_6H_3]_3\}$ (**5**): no pure isolation possible
$CpCoI_2[P(OCy)_3]$ (**3**): 84% yield	$CpCoI_2[P(OC_6F_5)_3]$ (**6**): 81%
$CpCoI_2\{P[OCH(CF_3)_2]_3\}$ (**4**): 90%	$CpCoI_2[P(O\text{-}4\text{-}CF_4\text{-}C_6H_4)_3]$ (**7**): 85%

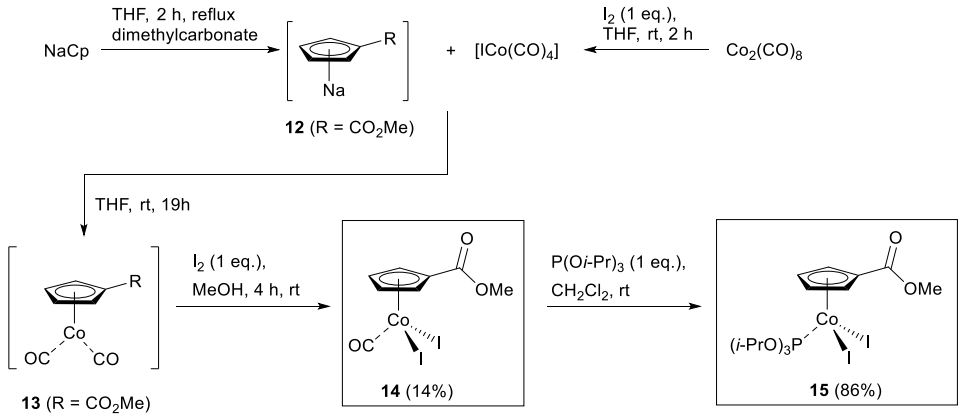
Scheme 1. Synthesis of phosphite complexes from $CpCoI_2(CO)$ (**1**) and different phosphites.

For further comparison, we also synthesized complexes containing cyano groups to elucidate the influence of this pseudo halide on complex reactivity. It is known that cyanogen iodide, ICN, reacts smoothly with $CpCo(CO)_2$, although the resulting compound has never been investigated further for catalytic purposes [20]. Again, substitution of the second CO ligand for a phosphite occurred smoothly for complex **8** as was demonstrated with $P(O\textit{i}\text{-}Pr)_3$. In addition, we realized the exchange of both iodide atoms in compound **2** in the presence of alkali metal cyanide, yielding complex **10** [21,22]. The synthesis results are displayed in Scheme 2. According to the cited reference for the synthesis [21], replacement of the iodides for cyanide groups in the presence of the CO ligand like in complex **1** is not possible, because it would lead to the formation of undesired reaction products. Therefore, the presented sequence of substitution (first CO exchange for the phosphite ligand, then substitution of the iodide for the cyanide) is mandatory.

Due to the stability of the Co(III) diiodides, we exemplarily investigated this approach for the synthesis of a functionalized $Cp'CoI_2(CO)$ complexes from the corresponding substituted cyclopentadiene and $Co_2(CO)_8$, while avoiding the work-up of intermediates like **12** or **13** (Scheme 3). The reaction started out from NaCp by acetyoxylation with dimethylcarbonate to give **12**. Cobaltation with in situ generated $[ICo(CO)_4]$ resulted in the formation of the cobalt dicarbonyl complex **13**, which was directly reacted with iodine without isolation to furnish compound **14** as pure complex with 14% yield over three steps. Subsequent ligand exchange with triisopropyl phosphite furnished complex **15** with excellent yield. Attempts to synthesize the related Cp-acetylated complex led to the formation of the expected product, however, all attempts of isolating the pure Co(III)-complexes after the methods reported for **14** and **15** were not met with success.



Scheme 2. Synthesis of CpCo(III)(phosphite) complexes from $CpCo(CO)_2$, iodine or ICN and triisopropyl phosphite.



Scheme 3. Synthesis of functionalized Cp'Co diiodides **14** and **15** in an one-pot approach.

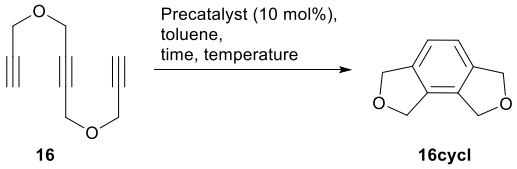
2.2. Screening on Catalytic Activity of the CpCo(III) Precatalysts

As mentioned above, we surveyed possible reducing agents in the required reduction to catalytically active CpCo(I) species. The conventional reduction protocol using zinc powder and zinc(II) iodide as additive did not work well [22]. After one hour of pretreatment of complexes **2** and **3** either in THF (50 °C) or toluene (100 °C) with 2 eq. of Zn powder and ZnI_2 each, the resulting catalyst furnished the pyridine product from 1,6-heptadiyne and benzonitrile in the test reaction with either 11% (in THF) or 6% yield (in toluene) at maximum.

We turned our attention to cyclizations with the standard testing triyne **16** and were quite surprised to see that in the initial experiment with $CpCoI_2(CO)$ without any reducing agent, the cyclization product **16cycl** was obtained with 38% yield after 19 h at reaction temperatures as low as 75 °C (Table 1, entry 1). In comparison, with $CpCo(CO)_2$ no reaction was observed under these conditions (Table 1, entry 14). Reactivity screening of complexes **2** and **3** gave yields as high as 55% with precatalyst **2** (Table 1, entry 2), while clearly the nature of the phosphite ligand does play a role, as with precatalyst **3** containing $P(OCy)_3$ a significantly lower yield of only 22% was observed (Table 1, entry 3). Investigation of other ligands containing partially or completely fluorinated groups and thus being less electron-rich like in complexes **4**, **6** and **7** gave inferior results ranging from 8% to 27% (Table 1, entries 4–6). Finally, we also investigated the complexes **8** and **9** with heteroleptic (I/CN) anionic groups beside the Cp and CO or phosphite ligand. They did not show any catalytic activity at either 75 or 100 °C (Table 1, entries 7–9). The biscyanide complex **10**, however, showed remarkably different reactivity. While no reactivity was observed at 75 °C, raising the reaction temperature to 105 °C allowed isolation of the

product **16cycl** with 84% yield (Table 1, entries 10 and 11). The difference of 30 °C in reaction temperature clearly covers the range leading to the catalyst activation, while at 75 °C the complex is completely stable and unreactive. Finally, the ester-substituted analogs **14** and **15** showed both identical results for the cyclization, although less yield of **16cycl** compared to the unsubstituted precatalyst **2** (Table 1, entries 2, 12 and 13 for comparison). Clearly, the substitution did not change the reactivity profile significantly. Interestingly, the yield obtained in this transformation for catalyst **2** is in the range of the most reactive CpCo(olefin)(phosphite) precatalysts for the reaction at 75 °C [19].

Table 1. Screening of cyclization reactions with substrate **16** using different complexes **1–4**, **6–10** and **14** and **15** as well as $CpCo(CO)_2$ for comparison.



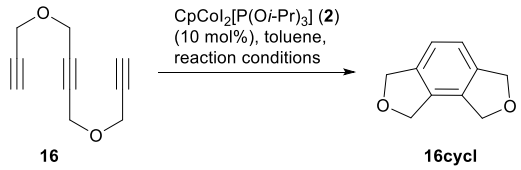
16 **16cycl**

#	Precatalyst	Time (h)	Temperature (°C)	Yield (%) [a]
Entry 1	**1**	19	75	38
Entry 2	**2**	22	75	55
Entry 3	**3**	20	75	22
Entry 4	**4**	21	75	27
Entry 5	**6**	21	75	25
Entry 6	**7**	21	75	8
Entry 7	**8**	14	75	- [b,c]
Entry 8	**9**	21	75	- [b,c]
Entry 9	**9**	23	100	- [b,c]
Entry 10	**10**	21	75	- [b,d]
Entry 11	**10**	21	105	84
Entry 12	**14**	16	75	48
Entry 13	**15**	20	75	44
Entry 14	$CpCo(CO)_2$	19	75	- [b,e]

[a] Isolated yields. [b] No reaction at all was observed. [c] **16** recovered (between 80% and 88%). [d] **16** and **10** recovered. [e] **16** was fully recovered.

We further exemplarily investigated modified reaction conditions, particularly to raise the conversion of the used testing triyne **16**. The complex $CpCo[P(O\textit{i}\text{-}Pr)_3]I_2$ (**2**) was applied as standard catalyst in these investigations (Table 2). Application of microwave reaction conditions at 100 °C shortened the reaction time but led to lower yield for **16cycl** even after 12 h reaction time compared to the reaction at 75 °C (25 and 41% vs. 55%, Table 2, entries 1 and 2). Increasing the catalyst loading to 20 mol% gave a yield of 56% (Table 2, entry 3) under microwave conditions. We also investigated the utilization of silver(I) acetate as iodide abstracting agent, often used for catalytic reactions with $Cp^*Co(CO)I_2$ [23]. In the first experiment, utilizing 20 mol% of silver(I) acetate the cyclization product **16cycl** was formed with 20% yield and the starting material was mostly reisolated (Table 2, entry 4). Repeating the experiment with only 10 mol% of silver(I) acetate under otherwise identical conditions gave with only 5% yield of **16** an even significantly lower yield (Table 2, entry 5). An experiment in which additional 10 mol% catalyst **2** were added after 12 h reaction time and the reaction run for additional 12 h was conducted but did not lead to an increase in yield (Table 2, entry 6). However, beside isolation of 43% of **16cycl** only 15% of **16** were recovered, giving a strong hint towards the occurrence of side reactions. Finally, addition of elemental zinc as reductant led to 53% product yield after 48 h at 75 °C, beside 8% of reisolated **16** (Table 2, entry 7). The missing amount of triyne not found in product or substrate again points towards side reaction with these catalysts.

Table 2. Screening of reaction conditions and additives for the cyclization of **16** using complex **2**.

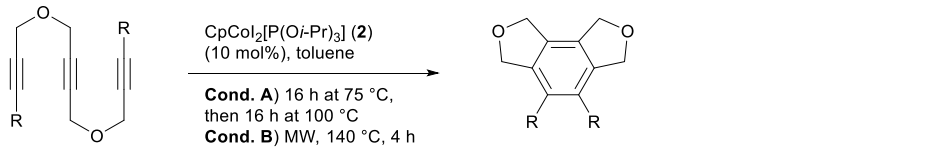


16 **16cycl**

#	2 (mol%)	Time (h)	Temperature (°C)	Yield (%) [a]
Entry 1	10	4	100 (MW) [b]	25
Entry 2	10	12	100 (MW)	41
Entry 3	20	4	100 (MW)	56
Entry 4	10	18	75	20 (58) [c,f]
Entry 5	10	18	75	5 (74) [d,f]
Entry 6	20 (2 × 10)	24 (2 × 12 h)	100	43 (15) [f]
Entry 7	10	48	75	53 (8) [e,f]

[a] Isolated yields. [b] MW = microwave. [c] Additive: AgOAc (20 mol%). [d] Additive: AgOAc (10 mol%). [e] Additive: zinc powder (10 mol%). [f] The amount of reisolated **16** is given in parentheses.

We extended our investigations to the cyclization of terminal substituted triynes, which are usually less reactive than the terminally unsubstituted triynes. The results for the substrate triynes **17** and **18** are presented in Scheme 4. In both cases using precatalyst **2**, the reaction at 75 °C did not give any progress and only unreacted triynes were observed. Due to this reason, the reaction temperature of the experiments were raised to 100 °C for additional time finally yielded cyclization products **17cycl** and **18cycl**, albeit in rather low yields. Due to the lower reactivity of the terminal substituted triynes and required higher temperatures for reaction with CpCo complexes, we investigated the reactions under microwave conditions at 140 °C. For triyne **17**, very good 75% yield of **17cycl** was obtained and isolated. However, triyne **18** gave only minor or no cyclization product **18cycl** at all. Interestingly, while under Cond. A most of triyne **18** was recovered, at the higher reaction temperatures of Cond. B only 27% of starting material was reisolated. A possible reason would be consummation of **18** by a side reaction like polymerization, as no defined further reaction products were isolated.



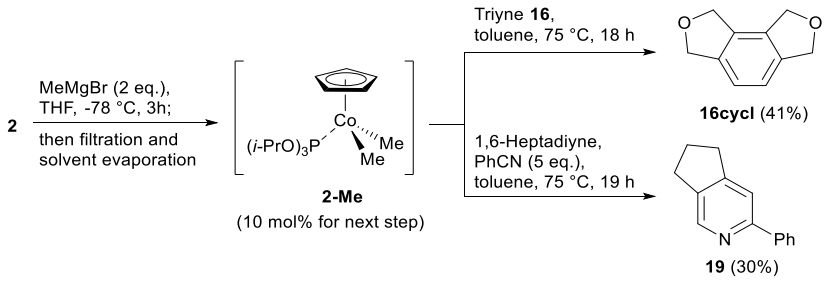
17 (R = Ph)
18 (R = Me)

Exp. 4_1: **17cycl** (R = Ph): 24% (**Cond. A**)
Exp. 4_2: **17cycl** (R = Ph): 75% (**Cond. B**)
Exp. 4_3: **18cycl** (R = Me): 5%, 76% **21** reisolated (**Cond. A**)
Exp. 4_4: **18cycl** (R = Me): 0%, 27% **21** reisolated (**Cond. B**)

Scheme 4. Conditions for cyclizations with internal triynes **17** and **18** using precatalyst **2**.

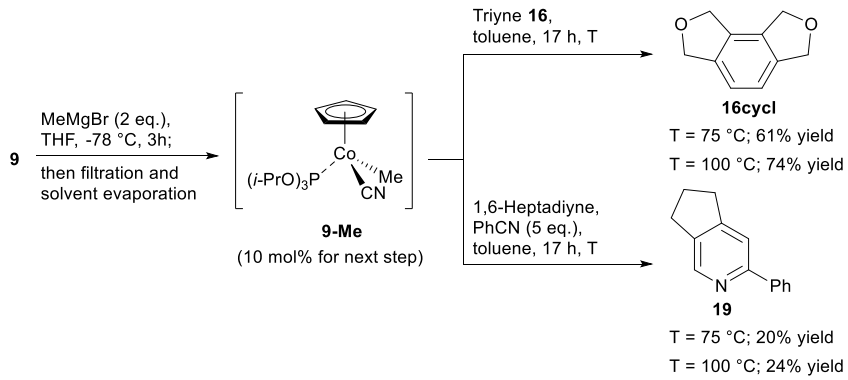
For cyclizations with CpCo complexes, the cobalt oxidation state of +1 is the common feature of the catalytically active species entering the catalytic cycle. We therefore further investigated additional methods to activate the catalyst system by facilitating intramolecular reduction from a CpCo(III) species to a CpCo(I) species by reductive elimination. For late transition metals, reductive elimination of carbon-based substituents from the metal center is a very common and important process, e.g., in C-C coupling reactions, and it has been investigated theoretically and experimentally for the reductive elimination of ethane from L_3CoMe_2I (L = PMe_3) complexes [24]. The complex $CpCo(Me)_2(PPh_3)$ has been synthesized by the reaction of $CpCoI_2(PPh_3)$ with MeMgBr and did react with alkynes afterwards under reduction and formation of cobaltacyclopentadienes [25,26]. Therefore, we attempted alkylation of the diiodide complex **2** by reaction with the Grignard reagent MeMgBr to produce the dimethylated analogue (**2-Me**) and set out to investigate

its catalytic performance (Scheme 5). ^{1}H NMR analysis confirmed the alkylation success of this reaction due to the unique shift of the resonance for the methyl group to 0 ppm, however, only partial alkylation was recognizable. Reaction control by ^{31}P NMR spectroscopy confirmed disappearance of **2** as well and emergence of two new resonances at 160 and 172 ppm. Utilization of 10 mol% (estimated for assumed complete conversion of **2**) for the catalytic cyclization of **16** furnished the expected product **16cycl**, albeit with slightly lower yield than before, not providing any significant advantage. A comparable investigation of 1,6-heptadiyne and benzonitrile as standard system for pyridine formation by co-cyclo-trimerization gave mediocre 30% yield of pyridine **19**, which is significantly lower compared to CpCo(olefin)(phosphite) precatalysts under identical conditions [19]. Replication of the experiment by treating partially fluorinated complex **4** with MeMgBr and direct subsequent reaction of the reaction product with triyne **16** gave cyclization product **16cycl** with 31% yield (44% **16** recovered).



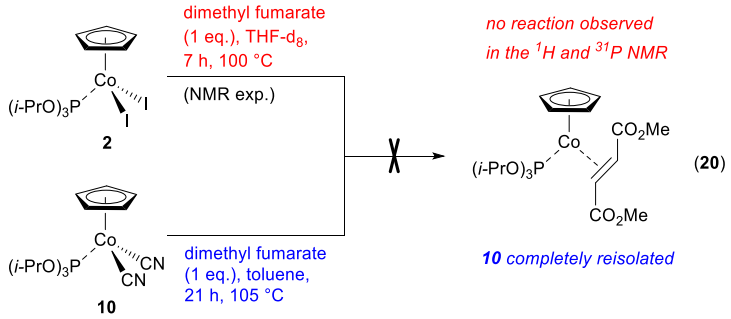
Scheme 5. Investigated cyclizations with methylated complex **2-Me**.

We repeated this procedure with the complex **9**, containing iodide and cyanide as anionic groups (Scheme 6). Reaction with one equivalent of the Grignard reagent led to conversion of **9**, being confirmed by ^{1}H and ^{31}P NMR spectroscopy reaction control, in the latter case by a shift from 126.7 ppm (**9**) to 142.4 ppm (**9-Me**). Subsequent direct use of the generated species **9-Me** as catalyst gave surprising results compared to Scheme 5. In the case of pyridine (**19**) synthesis, the yields are slightly lower, independent from the reaction temperature and no difference appeared for **9-Me** at both temperatures (compare Schemes 5 and 6, below). The picture is different for the cyclization of **16**, where the yield was basically doubled at 100 °C reaction temperature and are still significantly higher at 75 °C compared to **2-Me** (Scheme 6, top). This observation is particularly interesting, as complex **9** did not show any reactivity in the cyclization of **16** before (Table 1, entries 8, 9). Replacement of the iodide for the methyl group clearly increases the reactivity in the presence of cyanide as second anionic ligand, including reactivity already observed at 75 °C, when the biscyanide complex **10** was completely inactive (see Table 1, entry 10). A possible reason for this is the stronger bonding of the nitrile group vs. the methyl group, requiring more energy to induce the formation of a reactive species for the catalytic process.



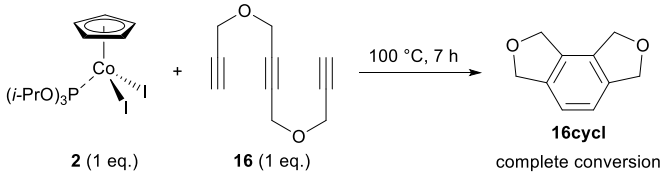
Scheme 6. Investigated cyclizations with methylated complex **9-Me**.

We assumed that the catalytic activity might arise from preceding reduction of the CpCo(III) complex to a CpCo(I) complex. There is evidence for this assumption for CpCo(III)(PPh_3)-dialkyl complexes like CpCo(Me)$_2$(PPh_3), who gave cobaltacyclopentadienes upon reaction with alkynes under thermal conditions, implying reductive elimination of the alkyl groups [25]. However, the PPh_3 ligand is detrimental for the catalytic activity of the complexes and less comparable to phosphites as ligand in this setting. Experiments with **2** under addition of elemental zinc did basically show no difference compared to catalysis with **2** without additive (compare entries Tables 1 and 2). The simplest process would thus be reductive elimination of the anionic groups. While this can be imagined with complex **9-Me** (reductive elimination of MeCN), the elimination from diiodide complex **2** or dicyanide complex **10** are significantly less likely. We investigated this possibility for the latter by scavenging experiments, as the complexes are heated in the presence of dimethyl fumarate, leading in the case of successful reductive elimination processes to CpCo[P(O*i*-Pr)$_3$](dimethyl fumarate) (**20**) and the corresponding elimination products. However, the experiments showed neither in the NMR experiment nor on preparative scale that reductive elimination occurred from the CpCo(III) complexes (Scheme 7).



Scheme 7. Attempted scavenging experiments towards reductive elimination from precatalysts **2** and **10**.

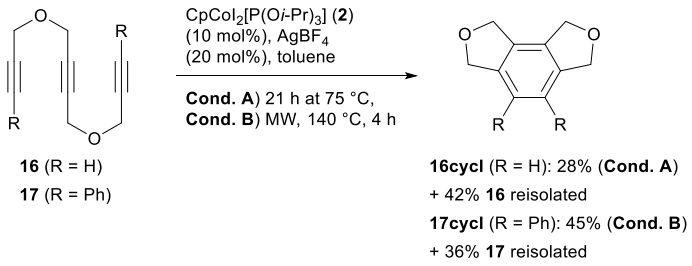
We have reacted complex **2** and triyne **16** in a 1:1 ratio to prove if complex **2** is converted during the reaction (Scheme 8). The ^{1}H and ^{31}P NMR spectra before and after heating to 100 °C showed, that complete conversion of **16** to **16cycl** has occurred. The ^{31}P NMR shows a single signal at 120 ppm before and after the reaction, corresponding to an unchanged coordination environment for the triisopropyl phosphite. However, from the spectra one cannot deduce an unchanged complex **2** after the reaction because of overlaps of signals in the ^{1}H NMR spectra and shifted or disappeared signals in the region of the Cp group. On the other hand, the spectra did not contain significant traces of byproducts or decomposition products as well and the cyclization appeared to be a rather clean process.



Scheme 8. Stoichiometric transformation of precatalyst **2** with triyne **16** for NMR investigation (in Supplementary Materials).

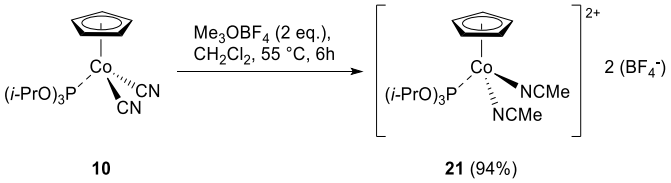
Finally, we investigated the reactivity of cationic CpCo(III) complexes in these cyclizations for comparison and to see, if they provide any cyclization activity by itself (Scheme 9). For this purpose, two eq. silver(I) tetrafluoroborate were added to the reaction mixture and a precipitate was formed. Under thermal as well as microwave conditions at higher temperatures cyclization products **16cycl** and **17cycl** were formed, however with

significantly lower yields compared to the reactions without $AgBF_4$ (compare Table 1 and Scheme 4). This result points towards a possible different reaction mechanism initiated by the cationic CpCo(III) complex compared to the commonly accepted mechanisms for CpCo complexes [27].



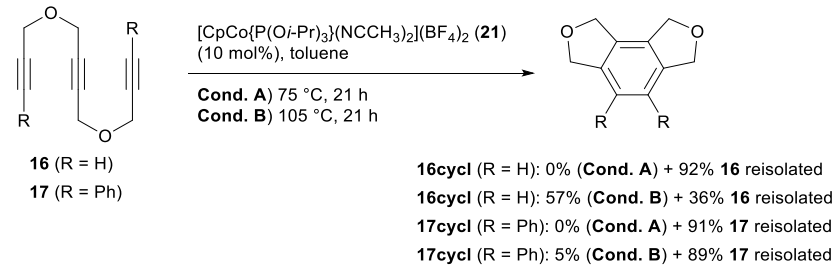
Scheme 9. Cyclizations of **16** and **17** using precatalyst **2** and $AgBF_4$ as additive.

Cationic CpCo(III) complexes can also be synthesized from the dicyano complex **10** by treatment with a strong alkylation reagent [18,21]. Reaction of **10** with trimethyloxonium tetrafluoroborate furnished the dicationic salt **21** with excellent isolated yield (Scheme 10).



Scheme 10. Transformation of complex **10** to the dicationic complex **21**.

The reactivity screening with complex **21** was again undertaken for triynes **16** and **17** (Scheme 11).



Scheme 11. Attempted cyclizations of **16** and **17** using precatalyst **21**.

The cationic precatalyst **21** did not give any reactivity at 75 °C with either triyne **16** or **17** and starting material as well as catalyst were recovered. At 105 °C terminally unsubstituted triyne **16** gave 57% yield of **16cycl** and most of unreacted **16** was recovered, pointing towards a clean conversion without by-product formation. With triyne **17** only negligible cyclization reactivity was observed, while again most of the starting material was recovered. The reactions appeared to be quite clean because no significant amount of starting material was consumed for undesired reactions, dividing this reaction from the combination of complex **2**/$AgBF_4$ (Scheme 9). Overall, the isolated complex **21** is less reactive compared to the in situ generated cationic complex, as demonstrated by the reactivity towards **16** at 75 °C reaction temperature. The complex shows no significant reactivity for the cyclization of internal triyne **17,** which is more difficult to transform compared to triyne **16**. Future investigations will be directed to the elucidation of the reactivity of such cationic CpCo(III) complexes at higher reaction temperatures and the

general differences in the mode of action in cyclizations of such CpCo(III) precatalysts compared to the common CpCo(I) precatalysts.

3. Experimental Section

3.1. Methods and Materials

All experiments were carried out under inert gas atmosphere (argon) in flame dried Schlenk tubes or glass reaction vials. The anhydrous solvents (tetrahydrofuran, toluene, dichloromethane and *n*-hexane) were dried in a solvent purification system MD-5 from Inert (former Innovative Technology, Amesbury, MA, USA). All NMR spectra were recorded on a Bruker AV 300, AV 400, AV 500 or Fourier 300 NMR spectrometer (Rheinstetten, Germany). Elemental analysis was performed at a Perkin Elmer AAS-Analyst 300 (Co) (Hamburg, Germany), Leco Microanalysator-TruSpec CHNS (C, H) (Mönchengladbach, Germany), Radiometer Analytical SAS (Titrator) Titralab 870-TIM 870 (Br) (Villeurbanne, France) and a Perkin Elmer UV/VIS-spectrometer Lambda 2 (P) (Hamburg, Germany).

3.2. Synthesis of Complexes

Attention: Due to evolution of CO gas the reactions comprising CO ligand exchange need be performed in a well-ventilated fume hood!

Synthesis of $CpCoI_2(CO)$ (**1**) [4]: $CpCo(CO)_2$ (3.0 g, 16.6 mmol) was dissolved in methanol and solid iodine (4.23 g, 16.6 mmol, 1 eq.) added in small portions, while evolution of CO gas was taking place. The color of the solution changed from red to black. The reaction mixture was stirred for additional two hours, then the methanol was removed in vacuo and the remaining black solid was dissolved in CH_2Cl_2 and filtrated over a filter frit tubing. The residual was further washed with CH_2Cl_2 and the filtrates concentrated under reduced pressure. The obtained solid product was washed three times with Et_2O and allowed to dry in air (black solid, 6.42 g, 95%). The spectroscopic data are in accordance with the literature.

General Procedure 1 (GP1), exemplified for the synthesis of $CpCoI_2[P(O\textit{i}\text{-}Pr)_3]$ (**2**): In an adoption of a reported protocol for $P(OMe)_3$ [17], $P(O\textit{i}\text{-}Pr)_3$ (520 mg, 2.5 mmol, 1 eq.) was dissolved in CH_2Cl_2 (10 mL) and added dropwise to a solution of $CpCoI_2(CO)$ (**1**, 1.0 g, 2.5 mmol) in CH_2Cl_2 (10 mL), during which the evolution of gas was observed. The reaction mixture was stirred for 16 h at 25 °C. Afterwards, the solvent was removed under reduced pressure and the residue suspended in *n*-heptane, stirred and filtrated under air. The collected black solid was dried thoroughly under reduced pressure (yield: 1.44 g, 99%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.20 (s, 5H), 4.82 (ht, *J* = 6.0 Hz, 3H), 1.37 (d, *J* = 6.0 Hz, 18H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 87.7 (d, *J* = 3.7 Hz), 73.7 (d, *J* = 9.3 Hz), 23.9 (d, *J* = 3.7 Hz) ppm. ^{31}P NMR (122 MHz, $CDCl_3$): δ = 117.4 ppm. IR: ν_{max} = 3111, 2974, 2929, 1417, 1367, 1172, 1101, 948, 879, 819, 746, 707, 542 cm^{-1}. Elemental analysis for $C_{14}H_{26}CoI_2O_3P$ (M = 586.07 g/mole): calc. C 28.69, H 4.47, Co 10.06, I 43.31, P 5.28; found C 28.53, H 4.04, Co 8.84, I 44.19, P 5.27.

Synthesis of $CpCoI_2[P(OCy)_3]$ (**3**): Following the **GP1**, $P(OCy)_3$ (810 mg, 2.5 mmol, 1 eq.) was dissolved in CH_2Cl_2 (10 mL) and added dropwise to a solution of $CpCoI_2(CO)$ (**1**, 1.0 g, 2.5 mmol) in CH_2Cl_2 (10 mL), during which the evolution of gas was observed. The reaction mixture was also stirred for 16 h at 25 °C. Afterwards, the solvent was evaporated, and the residue suspended in *n*-heptane, stirred for a short period of time and filtrated under air. The isolated blackish solid was dried thoroughly under reduced pressure (yield: 1.47 g, 84%). ^{1}H NMR (300 MHz, CDCl3): δ = 5.20 (s, 5H), 4.65–4.42 (m, 3H), 2.13–1.21 (m, 30H) ppm. ^{13}C NMR (75 MHz, CDCl3): δ = 87.7 (d, *J* = 3.7 Hz), 78.1 (d, *J* = 9.3 Hz), 33.5 (d, *J* = 3.3 Hz), 25.4, 23.7 ppm. ^{31}P NMR (122 MHz, CDCl3): δ = 118.0 ppm. IR: ν_{max} = 3106, 2930, 2855, 1447, 1369, 1260, 965, 860, 820, 762, 630, 561, 515 cm^{-1}. Elemental analysis for $C_{23}H_{38}CoI_2O_3P$ (M = 706.27 g/mole): calc. C 39.11, H 5.42, Co 8.34, I 35.94, P 4.39; found C 39.26, H 5.44, Co 7.58, I 37.50, P 4.36.

Synthesis of $CpCoI_2\{P[OCH(CF_3)_2]_3\}$ (**4**): Following the **GP1**, $P[OCH(CF_3)_2]_3$ (1.44 g, 2.71 mmol, 1 eq.) was dissolved in CH_2Cl_2 (10 mL) and added dropwise to a solution of

$CpCoI_2(CO)$ (**1**, 1.10 g, 2.71 mmol) in CH_2Cl_2 (10 mL), during which the evolution of gas was observed. The reaction mixture was stirred for additional 48 h at 25 °C. Afterwards, the solvent was evaporated, and the residue suspended in *n*-hexane, stirred for a short period of time and filtrated under argon. The isolated blackish solid was dried thoroughly under reduced pressure (yield: 2.22 g, 90%). ^{1}H NMR (300 MHz, CDCl3): δ = 5.52 (m, 3H), 5.51 (d, 5H) ppm. ^{13}C NMR (75 MHz, CDCl3): δ = 88.9 (d, *J* = 4.3 Hz), 78.1 (d, *J* = 9.3 Hz), 33.5 (d, *J* = 3.3 Hz), 25.4, 23.7 ppm. ^{31}P NMR (122 MHz, CDCl3): δ = 126.7 ppm. ^{19}F NMR (282 MHz, CDCl3): δ = −71.9 ppm.

Synthesis of $CpCoI_2[P(OC_6F_5)_3]$ (**6**): According to **GP1**, the phosphite $P(OC_6F_5)_3$ (1.43 g, 2.46 mmol, 1 eq.) was dissolved in CH_2Cl_2 (10 mL) and then added dropwise to a solution of $CpCoI_2(CO)$ (**1**, 1.0 g, 2.46 mmol) in CH_2Cl_2 (10 mL). Evolution of gas (CO) was observed during the addition. The reaction mixture was stirred for 96 h at 25 °C. The reaction work-up was performed by removal of the solvent by evaporation, suspension of the residue suspended in *n*-hexane, stirring for a short period of time and finally filtration under air. The isolated black solid was dried thoroughly under reduced pressure (yield: 1.91 g, 81%). ^{1}H NMR (300 MHz, CDCl3): δ = 5.62 (s, 2H), 5.6 (d, 3H) ppm. ^{13}C NMR (75 MHz, CDCl3): δ = 89.4, 89.01 ppm. ^{31}P NMR (122 MHz, CDCl3): δ = 121.1 ppm. ^{19}F NMR (282 MHz, CDCl3): δ = −148.0 (d, *J* = 21.8 Hz), −157.2 (t, *J* = 44.5 Hz), −161.2 (t, *J* = 42.3 Hz) ppm.

Synthesis of $CpCoI_2[P(O\text{-}4\text{-}CF_3\text{-}C_6H_4)_3]$ (**7**): Following the **GP1**, $P(O\text{-}4\text{-}CF_3\text{-}C_6H_4)_3$ (1.27 g, 2.46 mmol, 1 eq.) was dissolved in CH_2Cl_2 (10 mL) and added dropwise to a solution of $CpCoI_2(CO)$ (**1**, 1.00 g, 2.46 mmol) in CH_2Cl_2 (10 mL), during which the evolution of gas was observed. The reaction mixture was continued to be stirred for further 16 h at 25 °C. Afterwards, the solvent was evaporated and the residue suspended in *n*-hexane. After stirring for a short period of time the solid was filtered off under argon and dried thoroughly in vacuo. The product is a black solid (yield: 1.87 g, 85%). ^{1}H NMR (300 MHz, CDCl3): δ = 7.61–7.48 (m, 12H), 4.98 (m, 5H) ppm. ^{13}C NMR (75 MHz, CDCl3): δ = 153.9, 128.7, 128.2, 127.3 (m, *J* = 10.9 Hz), 122.1 (d, *J* = 4.2 Hz), 121.8, 86.6 (d, *J* = 3,8 Hz) ppm. ^{31}P NMR (122 MHz, CDCl3): δ = 128.2 ppm. ^{19}F NMR (282 MHz, CDCl3): δ = −62.2 ppm.

Synthesis of CpCoICN(CO) (**8**) [20]: $CpCo(CO)_2$ (1.177 g, 6.5 mmol) was dissolved in diethyl ether (10 mL) and a solution of cyanogen iodide (1.0 g, 6.5 mmol, 1 eq.) in diethyl ether (10 mL) was added dropwise, while evolution of CO gas was taking place. The color of the solution changed from red to brown. The reaction mixture was stirred for additional two hours and then filtrated over a tube frit, washed with diethyl ether (20 mL) and the solvent was carefully removed in vacuo and the remaining brown solid was dried on air (brown solid, 1.62 g, 80%). IR: ν_{max} = 3093, 2172, 1415, 1003, 828, 546, 432 cm^{-1}. The spectroscopic data are in accordance to the literature.

Synthesis of $CpCoICN[P(O\textit{i}\text{-}Pr)_3]$ (**9**): Following the **GP1**, $P(Oi\text{-}Pr)_3$ (341 mg, 1.64 mmol, 1 eq.) was dissolved in CH_2Cl_2 (10 mL) and added dropwise to a solution of CpCoICN(CO) (**8**, 0.5 g, 1.64 mmol) in CH_2Cl_2 (10 mL), during which the evolution of gas was observed. The reaction mixture was stirred for 20 h at 25 °C. Afterwards, the solvent was evaporated, and the residue suspended in *n*-hexane, stirred for a short period of time and filtrated under air. The blackish residue was dried under vacuo (yield: 0.745 g, 94%). ^{1}H NMR (300 MHz, CDCl3): δ = 5.22 (m, 5H), 4.81 (m, 3H), 1.27 (m, 18H) ppm. ^{13}C NMR (75 MHz, CDCl3): δ = 89.3, 73.9 (d, *J* = 9.3 Hz), 23.8 (d, *J* = 5.3 Hz) ppm. ^{31}P NMR (122 MHz, CDCl3): δ = 126.7 ppm. IR: ν_{max} = 2979, 2930, 2145, 2119, 1370, 1174, 1142, 1099, 960, 883, 844, 750, 708, 542, 426 cm^{-1}. Elemental analysis for $C_{14}H_{26}CoICNO_3P$ (M = 485.19 g/mole): calc. C 37.13, H 5.40, Co 12.15, I 26.16, P 6.38; found C 35.36, H 5.46, Co 13.78, I 25.19, P 5.86.

Synthesis of $CpCo(CN)_2[P(O\textit{i}\text{-}Pr)_3]$ (**10**) [21]: To a solution of complex **2** (228 mg, 0.39 mmol) in MeOH (10 mL) a solution of NaCN (38 mg, 0.78 mmol) in MeOH (10 mL) is added dropwise. The reaction mixture was stirred for 22 h at 25 °C during which the color changes from a dark red to reddish. Afterwards, the solvent is evaporated, the residue suspended in EtOAc and filtered over a Celite pad yielding a yellow solution. The product is isolated by column chromatography (EtOAc/*n*-heptane, 30:1 *v*/*v*) yielding

yellow crystals on evaporation of the eluent, which were dried thoroughly under reduced pressure (yield: 122 mg, 82%). ^{1}H NMR (300 MHz, CDCl3): δ = 5.33 (s, 5H), 5.04–4.85 (ht, 3H), 1.39 (d, 18H) ppm. ^{13}C NMR (300 MHz, CDCl3): δ = 90.3 (d, *J* = 2.1 Hz), 74.3 (d, *J* = 8.7 Hz), 23.9 (d, *J* = 3.8 Hz) ppm (the signals for the CN groups could not be detected). ^{31}P NMR (500 MHz, CDCl3): δ = 126.1 ppm. IR: ν_{max} = 2980, 2933, 2118, 1427, 1386, 1179, 1142, 1102, 1011, 968, 886, 846, 761, 714, 551 cm^{-1}.

Synthesis of $C_5H_4C(O)OCH_3CoI_2(CO)$ (**14**): To a solution of dicobalt octacarbonyl (6.838 g, 20 mmol) in THF (40 mL) solid iodine was added in small portions (5.076 g, 20 mmol), during which the evolution of gas was observed. The mixture was stirred for 2 h and then added dropwise a solution of freshly made sodium cyclopentadienylmethylcarboxylate (20 mmol) via a syringe during which the evolution of gas was observed. The color from the suspension changed from green to brown. It was stirred for 19 h at room temperature, before the solvent was removed under reduced pressure. The residue was dissolved in methanol (40 mL) and then solid iodine added in small portions (5.076 g, 20 mmol). The resulting brown suspension was bubbling heavily and stirred for additional 22 h. The solvent was removed under reduced pressure, the residue dissolved in dichloromethane (80 mL) and filtrated over a tube frit. The solvent was removed again and the residue filtrated over dry silica gel with THF as the eluent (yield: 1.31 g, 14%). ^{1}H NMR (300 MHz, CDCl3): δ = 5.38 (t, 2H), 5.18 (t, 2H), 3.74 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl3): δ = 165.0, 92.0, 87.5, 84.7, 52.0 ppm. IR: ν_{max} = 3088, 2848, 2027, 1963, 1697, 1474, 1358, 1271, 1192, 1137, 970, 802, 762, 614, 535 cm^{-1}.

Synthesis of $C_5H_4C(O)OCH_3CoI_2[P(O\textit{i}\text{-}Pr)_3]$ (**15**): Following the synthesis protocol for complex **2**, $P(O\textit{i}\text{-}Pr)_3$ (121 mg, 0.582 mmol, 1 eq.) was dissolved in CH_2Cl_2 (10 mL) and added dropwise to a solution of $C_5H_4C(O)OCH_3CoI_2(CO)$ (**14**, 0.27 g, 0.582 mmol) in CH_2Cl_2 (10 mL), during which the evolution of gas was observed. The reaction mixture was stirred for 20 h at 25 °C. Afterwards, the solvent was removed under reduced pressure and the residue was filtrated over dry silica gel with *n*-hexane. The collected black solid was dried thoroughly under reduced pressure (yield: 0.325 g, 88%). ^{1}H NMR (300 MHz, CDCl3): δ = 5.19 (t, 5H), 4.66 (s, 3H), 3.67 (d, *J* = 20.5 Hz, 5H), 1.19 (s, 18H) ppm. ^{13}C NMR (75 MHz, CDCl3): δ = 87.5, 85.9, 84.7, 82.6, 69.7, 24.02 (d, *J* = 3.3 Hz) ppm. ^{31}P NMR (122 MHz, CDCl3): δ = 162.2 ppm. IR: ν_{max} = 2977, 2030, 1933, 1712, 1479, 1373, 1271, 1136, 957, 878, 766, 537 cm^{-1}.

Synthesis of $\{CpCo[P(O\textit{i}\text{-}Pr)_3](NCMe)_2\}(BF_4)_2$ (**21**) [21]: Precatalyst **10** (60.1 mg, 0.16 mmol) and $(Me)_3OBF_4$ (55.0 mg, 0.31 mmol) are weighed into a Schlenk flask in an Argon filled glovebox. The compounds are dissolved in a minimum amount of DCM and refluxed at 55 °C under argon for 6 h. The solution is filtered over a Celite pad and the solvent is removed under reduced pressure yielding compound **21** as a pale-yellow powder (yield: 86.6 mg, 94%). ^{1}H NMR (500 MHz, D_2O): δ = 6.08 (s, 5H), 5.00–4.89 (ht, 3H), 3.66 (s, 6H), 1.43 (d, *J* = 6.12 Hz, 18H) ppm. ^{13}C NMR (500 MHz, D_2O): δ = 94.0, 92.4, 78.2 (d, *J* = 10.14 Hz), 31.4, 23.03 ppm). ^{31}P NMR (500 MHz, D_2O): δ = 107.8 ppm. IR: ν_{max} = 3121, 2993, 2924, 2852, 2270, 1454, 1436, 1414, 1386, 1379, 1284, 1180, 1144, 1046, 1035, 978, 874, 835, 752 cm^{-1}. Melting Point: 138 °C.

3.3. General Procedure 2 for Catalyst Screening Reactions with Triyne 16 (Table 1)

The CpCo(III) precatalyst (**1–10**, **14**, **15** or $CpCo(CO)_2$, with 10 mol% catalyst loading with regard to triyne) was added to a solution of triyne **16** (1 eq.) in toluene and was stirred at the given reaction temperature for a specific time. After cooling to room temperature, the solvent was removed and purified by column chromatography to give the product, which was identified by NMR.

Precatalyst **1** (Table 1, entry 1): Complex **1** (25 mg, 0.0616 mmol, 10 mol%) and **16** (100 mg, 0.616 mmol) were heated in toluene at 75 °C for 19 h, yielding 38 mg (38%) of **16cycl** and 32 mg (32%) of unreacted **16** was recovered.

Precatalyst **2** (Table 1, entry 2): Complex **2** (36 mg, 0.0616 mmol, 10 mol%) and **16** (100 mg, 0.616 mmol) were heated in toluene at 75 °C for 22 h, yielding 55 mg (55%) of **16cycl** and 7 mg (7%) of unreacted **16** were recovered.

Precatalyst **3** (Table 1, entry 3): Complex **3** (43 mg, 0.0616 mmol, 10 mol%) and **16** (100 mg, 0.616 mmol) were heated in toluene at 75 °C for 20 h, yielding 22 mg (22%) of **16cycl** and 27 mg (27%) of unreacted **16** was recovered.

Precatalyst **4** (Table 1, entry 4): Complex **4** (56 mg, 0.0616 mmol, 10 mol%) and **16** (100 mg, 0.616 mmol) were heated in toluene at 75 °C for 21 h, yielding 27 mg (27%) of **16cycl** and 34 mg (34%) of unreacted **16** was recovered.

Precatalyst **6** (Table 1, entry 5): Complex **5** (59 mg, 0.0616 mmol, 10 mol%) and **16** (100 mg, 0.616 mmol) were heated in toluene at 75 °C for 21 h, yielding 25 mg (25%) of **16cycl** and 60 mg (60%) of unreacted **16** was recovered.

Precatalyst **7** (Table 1, entry 6): Complex **7** (55 mg, 0.0616 mmol, 10 mol%) and **16** (100 mg, 0.616 mmol) were heated in toluene at 75 °C for 21 h, yielding 8 mg (8%) of **16cycl** and 60 mg (60%) of unreacted **16** was recovered.

Precatalyst **8** (Table 1, entry 7): Complex **8** (18.8 mg, 0.0616 mmol, 10 mol%) and **16** (100 mg, 0.616 mmol) were heated in toluene at 75 °C for 14 h; 88 mg (88%) of unreacted **16** was recovered.

Precatalyst **9** (Table 1, entry 8): Complex **9** (29.8 mg, 0.0616 mmol, 10 mol%) and **16** (100 mg, 0.616 mmol) were heated in toluene at 75 °C for 21 h; 82 mg (82%) of unreacted **16** were recovered.

Precatalyst **9** (Table 1, entry 9): Complex **9** (29.8 mg, 0.0616 mmol, 10 mol%) and **16** (100 mg, 0.616 mmol) were heated in toluene at 100 °C for 23 h; 85 mg (85%) of unreacted **16** was recovered.

Precatalyst **10** (Table 1, entry 10): Complex **10** (3.7 mg, 0.01 mmol, 10 mol%) and **16** (16.5 mg, 0.1 mmol) were heated in toluene at 75 °C for 21 h, leading to isolation of 14.8 mg (90%) of unreacted **16** and 3.5 mg of complex **10** (95%).

Precatalyst **10** (Table 1, entry 11): Complex **10** (3.8 mg, 0.01 mmol, 10 mol%) and **16** (16.5 mg, 0.1 mmol) were heated in toluene at 105 °C for 21 h, yielding 13.9 mg (84%) of **16cycl** and 2.1 mg (12%) of unreacted **16** was recovered

Precatalyst **14** (Table 1, entry 12): Complex **14** (28.6 mg, 0.0616 mmol, 10 mol%) and **16** (100 mg, 0.616 mmol) were heated in toluene at 75 °C for 16 h, yielding 48 mg (48%) of **16cycl** as well as 25 mg (25%) of unreacted **16** was recovered.

Precatalyst **15** (Table 1, entry 13): Complex **15** (40.0 mg, 0.0616 mmol, 10 mol%) and **16** (100 mg, 0.616 mmol) were heated in toluene at 75 °C for 20 h, yielding 44 mg (44%) of **16cycl** and no unreacted **16** was recovered.

Precatalyst $CpCo(CO)_2$: Reaction of $CpCo(CO)_2$ (11.1 mg, 0.0616 mmol) with triyne **16** (100 mg, 0.616 mmol) gave no conversion to **16cycl** at all.

3.4. General Procedure 3 for Microwave Reactions with Precatalyst 2 (Table 2 and Scheme 4)

CpCo(III) precatalyst **2** (with 10 or 20 mol% catalyst loading with regard to triyne) was added to a solution of triyne **16** (1 eq.) in toluene and subjected to a microwave oven and heated under stirring at the given reaction temperature for a specific time. After the reaction the solvent was removed, and the crude product purified by column chromatography over silica gel.

Table 2, entry 1: Complex **2** (36 mg, 0.0616 mmol, 10 mol%) and **16** (100 mg, 0.616 mmol) were reacted in the microwave oven in toluene at 100 °C for 4 h, yielding 25 mg (25%) of **16cycl** and 17 mg (17%) of unreacted **16** was recovered.

Table 2, entry 2: Complex **2** (36 mg, 0.0616 mmol, 10 mol%) and **16** (100 mg, 0.616 mmol) were reacted in the microwave oven in toluene at 100 °C for 12 h, yielding 41 mg (41%) of **16cycl** and 7 mg (7%) of unreacted **16** was recovered.

Table 2, entry 3: Complex **2** (72 mg, 0.1232 mmol, 20 mol%) and **16** (100 mg, 0.616 mmol) were reacted in the microwave oven in toluene at 100 °C for 4 h, yielding 56 mg (56%) of **16cycl** and 7 mg (7%) of unreacted **16** was recovered.

Table 2, entry 4: Complex **2** (36 mg, 0.0616 mmol, 10 mol%), AgOAc (21 mg, 0.123 mmol, 20 mol%) and **16** (100 mg, 0.616 mmol) were heated in toluene at 75 °C for 18 h, yielding 20 mg (20%) of **16cycl** and 58 mg (58%) of unreacted **16** was recovered.

Table 2, entry 5: Complex **2** (36 mg, 0.0616 mmol, 10 mol%), AgOAc (10.5 mg, 0.0616 mmol, 10 mol%) and **16** (100 mg, 0.616 mmol) were heated in toluene at 75 °C for 18 h, yielding 5 mg (5%) of **16cycl** and 74 mg (74%) of unreacted **16** was recovered.

Table 2, entry 6: Complex **2** (36 mg, 0.0616 mmol, 10 mol%) and **16** (100 mg, 0.616 mmol) were heated in toluene at 100 °C for 12 h after cooling to room temperature, com**plex 2** (36 mg, 0.0616 mmol, 10 mol%) was added again and heated at 100 °C for 12 h, yielding 43 mg (43%) of **16cycl** and 15 mg (15%) of unreacted **16** was recovered.

Table 2, entry 7: Complex **2** (36 mg, 0.0616 mmol, 10 mol%), zinc powder (4 mg, 0.0616 mmol, 10 mol%) and **16** (100 mg, 0.616 mmol) were heated in toluene at 75 °C for 48 h, yielding 53 mg (53%) of **16cycl** and 8 mg (8%) of unreacted **16** was recovered.

Scheme 4, Exp. 4_2: Complex **2** (19 mg, 0.0318 mmol, 10 mol%) and **17** (100 mg, 0.318 mmol) were reacted in the microwave oven in toluene at 140 °C for 4 h, yielding 75 mg (75%) of **17cycl** and 10 mg (10%) of unreacted **17** was recovered. Exp 4_1 was performed following General Procedure 2 at 75 and 100 °C, giving a yield for **17cycl** of 24% (24 mg).

3.5. Synthesis and Reactions with Methylated Complexes 2 and 9 (Schemes 5 and 6)

Reaction of $CpCoI_2[P(O\textit{i}\text{-}Pr)_3]$ with MeMgBr and subsequent cyclization (**2-Me**): Complex **2** (0.84 g, 1.43 mmol) was dissolved in 10 mL THF in a Schlenk flask. After cooling to −78 °C, MeMgBr (3M in Et_2O, 0.96 mL, 2.86 mmol, 2 eq.) was added gradually via syringe to the solution, whose color changed from violet to light brown. After additional stirring for 3 h at −78 °C, the obtained suspension was filtered, and the residue dried under vacuo to give a brown oil, which solidified. Attempted crystallization from toluene, THF, diethyl ether, dichloromethane and *n*-pentane and mixtures of solvents did not give solid **2-Me** for further characterization.

Cyclization of **16** using **2-Me** (Scheme 5): The reaction product **2-Me** obtained prior (22.3 mg, 0.0616 mmol, estimated 10 mol%) was directly reacted with triyne **16** (100 mg, 0.616 mmol) according to the General Procedure 2 by heating in toluene at 75 °C for 18 h, yielding 41 mg (41%) of **16cycl**.

Cyclization of 1,6-heptadiyne and benzonitrile using **2-Me** (Scheme 5): The reaction product **2-Me** (18 mg, 0.05 mmol, estimated 10 mol%) was directly reacted with 1,6-heptadiyne (46 mg, 0.5 mmol) and benzonitrile (257 mg, 2.5 mmol) according to the General Procedure 2 by heating in toluene at 75 °C for 20 h, yielding pyridine **19** with 30% (29 mg) yield.

Synthesis towards $CpCo(CN)Me[P(O\textit{i}\text{-}Pr)_3]$ (**9-Me**): Complex **9** (30 mg, 0.062 mmol) was dissolved in 3 mL THF in a Schlenk flask. After cooling to −78 °C, MeMgBr (3M in Et_2O, 0.02 mL, 0.062 mmol, 1 eq.) was added gradually via syringe to the solution, whose color changed from violet to light brown. After additional stirring for 3 h at −78 °C, the obtained suspension was filtered, and the residue dried under vacuo to give a brownish solid. NMR analysis (^1H, ^{13}P) confirmed conversion of **9**. The crude product was directly used in the next step.

Cyclization of **16** using complex **9-Me** (Scheme 6): The reaction product **9-Me** (23 mg, 0.0616 mmol, 10 mol%) was reacted with triyne **16** (100 mg, 0.616 mmol) according to the General Procedure 2 by heating in toluene at 75 °C for 18 h, yielding 61 mg (61%) of **16cycl**. Repeating the same procedure at 100 °C reaction temperature led to the isolation of **16cycl** with 74% (74 mg) yield.

Cyclization of 1,6-heptadiyne and benzonitrile using complex **9-Me** (Scheme 6): The reaction product **9-Me** (23 mg, 0.0616 mmol, 10 mol%) was reacted with 1,6-heptadiyne (60 mg, 0.616 mmol) and benzonitrile (317 mg, 3.08 mmol) according to the General Procedure 2 by heating in toluene at 100 °C for 24 h, yielding pyridine **19** with 24% (26 mg) yield.

3.6. Scavenger Experiment for Reductive Elimination Process (Scheme 7)

Experiment using complex **10**: In an Argon filled glovebox complex **10** (39.3 mg, 0.1 mmol) and dimethylfumarate (15.2 mg, 0.1 mmol) were weighed into a Schlenk flask and dissolved in a minimum amount of toluene resulting in a yellow solution. The reaction was heated in an oil bath to 105 °C and stirred for 21 h. Afterwards the solvent was evaporated, and column chromatography was performed (EtOAc/MeOH, 5:1 *v*/*v*) leading to quantitative reisolation of both, complex **10** and dimethylfumarate.

3.7. Reactivity of Precatalyst 2 in the Presence of $AgBF_4$ (Scheme 9)

Triyne **16** as substrate, heating with oil bath at 75 °C: According to General Procedure 2, precatalyst **2** (36 mg, 0.0616 mmol, 10 mol%), triyne **16** (100 mg, 0.616 mmol) and finally $AgBF_4$ (24 mg, 0.123 mmol, 20 mol%) were mixed in toluene and the reaction solution became turbid. The reaction suspension was heated at 75 °C for 21 h, yielding 28 mg (28%) of **16cycl** and 42 mg (42%) of unreacted **16** was recovered.

Triyne **17** as substrate, heating with microwave at 140 °C: Following General Procedure 3, precatalyst **2** (37 mg, 0.0636 mmol, 10 mol%), triyne **17** (200 mg, 0.636 mmol) and finally $AgBF_4$ (25 mg, 0.1272 mmol, 20 mol%) were mixed in toluene and the reaction solution became turbid. The reaction suspension was heated at 140 °C for 4 h in the microwave, yielding 90 mg (45%) of **17cycl** and 72 mg (36%) of unreacted **17** was recovered.

3.8. Reactivity of Isolated Precatalyst 21 (Scheme 11):

Reaction of triyne 16 at 75 °C: Complex **21** (5.8 mg, 0.01 mmol, 10 mol%) and **16** (17.1 mg, 0.10 mmol) were heated in toluene at 75 °C for 21 h, giving 15.8 mg (92%) of unreacted **16** as well as reisolated catalyst.

Reaction of triyne 16 at 105 °C: Complex **21** (5.8 mg, 0.01 mmol, 10 mol%) and **16** (17.0 mg, 0.10 mmol) were heated in toluene at 105 °C for 21 h, yielding 9.8 mg (57%) of **16cycl** and 6.1 mg (36%) of unreacted **16** was recovered.

Reaction of triyne 17 at 75 °C: Complex **21** (5.8 mg, 0.01 mmol, 10 mol%) and **17** (31.5 mg, 0.10 mmol) were heated in toluene at 75 °C for 21 h, giving 28.7 mg (91%) of unreacted **17** as well as reisolated catalyst.

Reaction of triyne 17 at 105 °C: Complex **21** (5.9 mg, 0.01 mmol, 10 mol%) and **17** (31.4 mg, 0.10 mmol) were heated in toluene at 105 °C for 21 h, yielding 1.6 mg (5%) of **17cycl** and 28.0 mg (89%) of unreacted **17** was recovered.

4. Summary

In this work, we described the synthesis and use of CpCo(III) complexes as precatalysts for cyclotrimerization reactions preferably of triynes, which usually rely on CpCo(I) precursor complexes. The reactivity behavior is interesting because cyclizations already occur at 75 °C, however, for more complete conversions higher temperatures are needed. In addition, a significant part of triyne starting material is clearly converted to byproduct(s), which were not identified and may consist of polymeric materials, which is unusual to observe with CpCo(phosphite)-based catalysts for these substrates under the reaction conditions used. All investigated $CpCoI_2$(ligand) complexes stabilized by neutral ligands like CO or phosphite showed reactivity, with CO and P(O*i*-Pr)$_3$ giving the best results, while cyano or mixed iodo/cyano complexes gave no product formation at 75 °C reaction temperature. However, at 105 °C the dicyano complex $CpCo(CN)_2$[P(O*i*-Pr)$_3$] gave excellent conversion of the triyne screening substrate.

The catalytic behavior in the present investigation therefore seems to be dominated by the anionic ligands, iodide and cyanide, corroborating the important role for the reactivity of the precatalyst. Removal of iodide (by $AgBF_4$) or cyanide (by alkylation with Meerwein salt) from the CpCo(III) compounds led to complexes with different reactivity towards alkynes at identical temperatures. On the other hand, the alkylation reaction of the iodo/cyano complex with MeMgBr led to complexes with increased reactivity for the cyclization of the terminal triyne testing substrate. finally giving the best results.

Taken together the experimental results demonstrated the ability of such CpCo(III) complexes to be suitable catalysts for cyclotrimerization reactions even without reduction. The conducted experiments also provided evidence to exclude simple reductive elimination of the anionic ligands to yield active CpCo(I) catalysts, which are known to mediate [2+2+2] cycloaddition reactions. Testing the reactions under reducing conditions in the presence of zinc at 75 °C gave only a very slightly different yield. Isolated CpCo(I) precatalysts are usually more active for the cyclization of nitriles and diynes, which was not found in our presented study, while on the other hand the yields received for cyclization of triynes are lower than those for the most active catalysts observed in the presented study [16]. Therefore, the observed discrepancy of reactivities might be indeed credited to CpCo(III) complexes as active species, and detailed studies are in progress in our laboratory to confirm the oxidation state of the active species.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/catal11050596/s1: NMR spectra (^{1}H, ^{13}C, ^{31}P, ^{19}F) for compounds **2–4**, **6–10**, **14**, **15**, **21** and cyclization products **16cycl** and **17cycl**; NMR reaction control spectra for the synthesis of compound **9-Me**; NMR reaction control spectra for the stoichiometric reaction of complex **2** and triyne **16** (Scheme 8).

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