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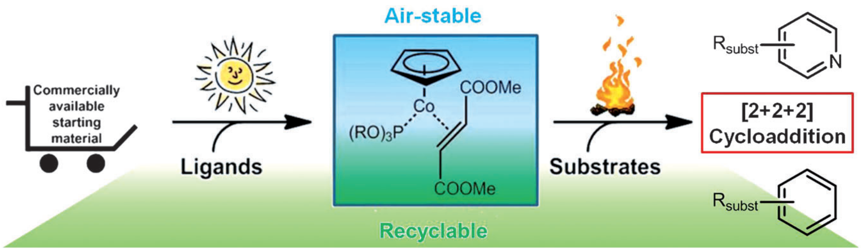

An open-air ligand concerto: Air-stable and recyclable CpCo^I-complexes, which are active in the [2+2+2] cycloaddition reaction, are synthesized. The application of heteroleptic complexes with one electron-poor olefin and one phosphite ligand proved to be the superior catalysts to other ligand combinations with regard to activity and stability.

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Synthesis of Air-Stable and Recyclable CpCo^I-Complexes

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Synthesis of Air-Stable and Recyclable CpCo^{I}-Complexes

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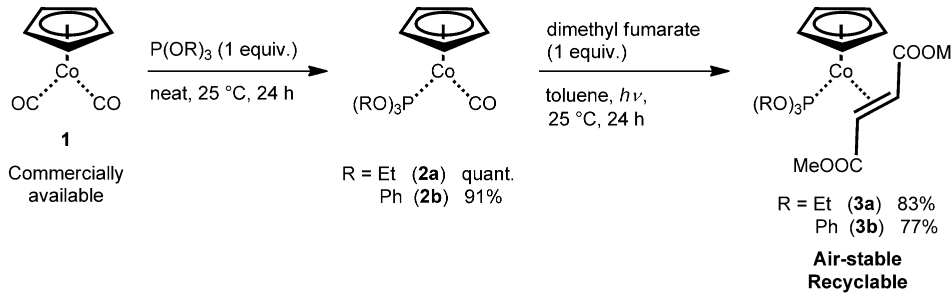
The advances in transition metal-catalysed [2+2+2] cycloaddition reactions of alkynes and heterocumulenes have demonstrated that a vast number of transition metals are able to catalyse this atom-economic cyclotrimerisation reaction.[1] Nevertheless, group 9 transition metals, and especially cobalt, are of particular importance and interest owing to their long-standing history and versatility in this area.[1u] The most commonly used cobalt-based complexes such as $[CpCo(CO)_2]$ (**1**) or [CpCo(cod)] (cod = 1,5-cyclooctadiene) require high temperatures, irradiation with light, or both to be activated. Only a few examples such as the Jonas reagent, $[CpCo(H_2C{=}CH_2)_2]$ or our recently developed catalyst $[CpCo(H_2C{=}CHSiMe_3)_2]$[2] are already active at or below room temperature and have found application. However, one disadvantage of all these CpCo^{I} systems is their sensitivity towards air, requiring inert handling and reaction conditions. Up to now, only Gandon et al. reported on the preparation and application of air-stable complexes of the type [CpCo(CO)(dialkyl fumarate)].[3]



Scheme 1. Synthesis of [CpCo(CO)(phosphite)] and [CpCo(dimethyl fumarate)(phosphite)] complexes.

We recently developed CpCo^{I} systems with two different ligands, namely an olefin and a phosphite ligand, representing a novel class of catalysts that are both reactive and stable complexes.[4] These systematic studies corroborated the advantages heteroleptic ligand combinations can provide for the properties of transition metal precatalysts.[5] The phosphite–olefin combination proved especially advantageous because it principally allowed the variation of the electronic σ donor/π acceptor abilities and steric demands of each type of ligand. To further expand the library of these [CpCo(olefin)(phosphite)] compounds and to unearth novel interesting properties, we set out to synthesise complexes with different olefin–phosphite combinations. Especially electron-poor olefins, displaying improved π acceptor abilities, should provide a higher stability for the precatalyst owing to tighter bonding to the metal centre.[6] Initial experiments starting from $[CpCo(H_2C{=}CHSiMe_3)_2]$ and replacement of the first trimethylvinylsilane ligand for a phosphite $P(OR)_3$ followed by the substitution of the second one for dimethyl fumarate as an electron-deficient olefin at elevated temperatures proceeded only in the case of triphenylphosphite and dimethyl fumarate in excellent yield (98%). As we intend to establish convenient and efficient synthetic routes for the new complexes, we set forth to pursue a different approach and developed a synthetic strategy starting from the commercially available $[CpCo(CO)_2]$ (**1**) and two successive ligand replacements (Scheme 1). The first CO ligand is easily exchanged for a phosphite ligand by simply stirring the two liquids at room temperature for 24 h.[7] Removal of the second CO ligand also takes place at room temperature but only under radiation with light.[8] The synthetic approach starting from **1** was exemplarily performed for $P(OPh)_3$ as well as for $P(OEt)_3$ as a more electron-rich phosphite and both steps can be achieved in excellent yields (Scheme 1). While complexes **2a**-**b** are air-sensitive as most CpCo^{I}-complexes, **3a**-**b** are air-stable solids and can be stored on the bench for months.

Interestingly, the sequential substitution has to be in the order 1) phosphite, then 2) olefin to yield the clean compounds **3a**–**b** in excellent yields. If dimethyl fumarate is reacted with **1** the mixed [CpCo(CO)(dimethyl fumarate)] complex (**4**) is formed in very good yields.[3a] Addition of one equivalent of triethylphosphite and irradiation of the reaction mixture with light, only yields 40% of **3a**. The reaction mixture contains additional **2a** (32%), $[CpCo\{P(OEt)_3\}_2]$ (20%) and free dimethyl fumarate (8%). This suggests that the phosphite can substitute both the CO as well as the olefin ligand in **4**, leading to both monosubstituted phosphite complexes as well as the bisphosphite complex through a second substitution reaction. It can therefore be assumed that under these conditions the phosphite ligand coordinates more strongly to the cobalt than the dimethyl fumarate. We were able to obtain crystals of **3a** and **b** suitable for X-ray analysis from pentane solutions at 4°C (see the Supporting Information).[9] The characteristic data for **3a** and **b** as the bond length for the coordinated double bond

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of the olefin are in agreement with those described for Gandon's complex [CpCo(CO)($MeO_2C\mathbf{C}H{=}\mathbf{C}HCO_2Me$)] (**4**) (see Figure 1).

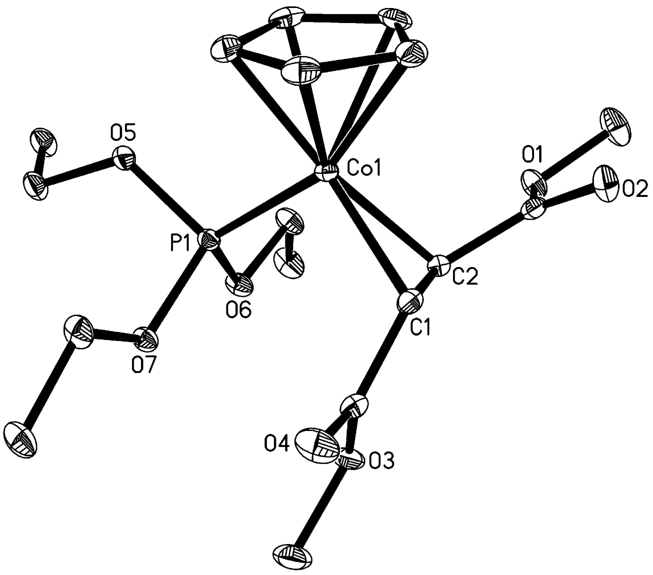
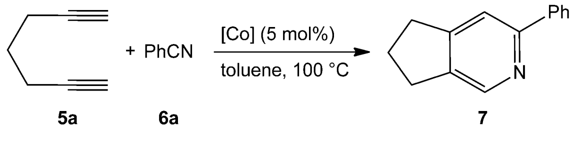


Figure 1. ORTEP drawing of the molecular structure of **3a**. Ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] for CpCo–olefin–phosphite complex **3a**: C1–C2 1.422(4), Co1–C1 2.011(3), Co1–C2 2.002(2); **3b**: C1–C2 1.4274(17), Co1–C1 2.0122(13), Co1–C2 2.0191(13). For comparison, C–C olefin bond distance for **4**: [CpCo(CO)($MeO_2C\mathbf{C}H{=}\mathbf{C}HCO_2Me$)] 1.438.[3a]

Having found these new air-stable compounds we set out to synthesise analogues with other olefin ligands, to verify the general synthetic approach described before. In the case of cyclooctene (coe) the exchange reaction proceeded only smoothly when reacted with **2a** to yield [CpCo(coe){$P(OEt)_3$}] (**3c**) in 70% yield. If **2b** was used only 41% yield of the desired complex [CpCo(coe){$P(OPh)_3$}] (**3d**) could be obtained with the major product with 45% being [CpCo{$P(OPh)_3$}$_2$]. Irradiation of a solution of **2b** in the presence of an excess of trimethylvinylsilane for only 4 h led to [CpCo($H_2C{=}CHSiMe_3$){$P(OPh)_3$}] (**3e**) in excellent 92% yield.[10] The use of other olefins, including norbornene or a fluorinated olefin such as (*E*)-5*H*,6*H*-perfluoro dec-5-ene, however, did not lead to any product at all and the starting compound could be reisolated.[11]

The catalytic activity of the new mixed complexes CpCo–CO–phosphites **2a–b** and CpCo–olefin–phosphites **3a–c**, which were obtained through sequential substitution of the CO ligands from **1**, has been assessed in the test reaction between 1,6-heptadiyne (**5a**) and benzonitrile (**6a**) (Scheme 2). In Figure 2, it is shown clearly that a ligand combination of olefin and phosphite is superior to a combination of CO and phosphite with regard to catalytic activity. Complexes **2a** and **b** need reaction times as long as 24 h to reach yields between 50 and 70%, whereas complexes **3a–c** reach full conversions after 3–5 h at 100°C.[12]



Scheme 2. Evaluation of reactivity in a [2+2+2] cycloaddition test reaction.

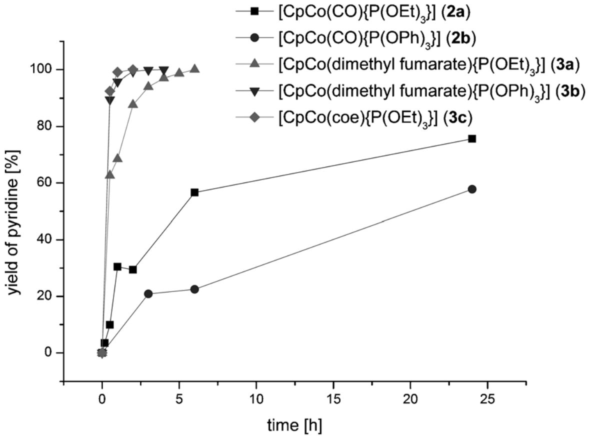


Figure 2. Catalytic activity of CpCo-complexes **2a–b** and **3a–c** in the cycloaddition test reaction (Scheme 2).

We were also interested in the recyclability of our precatalysts after the cycloaddition reaction. Therefore, recycling experiments were conducted exemplarily for **3a**.[13] The complex could be reisolated quantitatively after at least three successive cycles by column chromatography, with no decrease in the yield of the cyclotrimerisation product observed.[14] As surprising as this "boomerang effect" and the re-coordination of one $P(OEt)_3$ and one dimethyl fumarate ligand to the $CpCo^{I}$-core is, experiments with deuterated dimethyl fumarate showed that the olefin ligand does not stay coordinated during catalysis but indeed re-coordinates after the reaction (Scheme 3). The reisolation of the complex after the cycloaddition reaction or the control experiment and analysis showed that a mixture of **3a** and [D_6]-**3a** was obtained in each case.

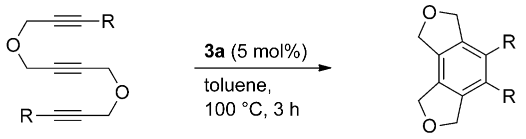
Interestingly, **3a** cannot be recycled if used in catalytic reactions under photochemical conditions, although excellent product yields have been obtained under these conditions.[15] Thus, it seems that light has a greater influence on the stability

Scheme 3. Ligand exchange of the dimethyl fumarate ligand for the deuterated analogue during cycloaddition and substitution reaction as control experiments (see the Supporting Information for details). Reaction conditions: 1) Cycloaddition: as in Scheme 2 plus [D_6]-dimethyl fumarate (2 equiv.); 2) Substitution: toluene, $t = 3$ h, $T = 100$°C, [D_6]-dimethyl fumarate (2 equiv.).

of the resting state of the catalyst than temperature. An explanation could be that the olefin ligand dimethyl fumarate isomerises into its *cis* form dimethyl maleate under irradiation with light, which does not coordinate as effectively to the cobalt centre, allowing the generation of the respective air-sensitive bisphosphite complex $[CpCo\{P(OEt)_3\}_2]$. Gandon et al. have reported a similar observation: even if starting from **1** and with pure dimethyl maleate as a ligand, only the respective dimethyl fumarate complex **4** could be isolated in 73% yield.[3a] Therefore, the amount of air-stable complex **3a** decreases with every cycle of the recycling experiments in favour of the air-sensitive complexes $[CpCo\{P(OEt)_3\}_2]$ and $[CpCo(cis\text{-}MeO_2CCH{=}CHCO_2Me)\{P(OEt)_3\}]$ (**3f**), which are not recoverable.[10] The robustness of the precatalyst has been proven by the performance of the cycloaddition test reaction with **3a** in non-dried and non-degassed toluene without any loss of product yield. The reaction could even be run in solvent taken straight from the bottle and air with only a slight decrease in yield.[14] Under these circumstances, however, the decomposition of the complex during the reaction under air was observed, not allowing a recycling of the precatalyst as described above.

To examine the substrate scope of the new catalysts, we applied **3a** in a number of different cyclotrimerisation reactions. As we are especially interested in the synthesis of pyridines, we investigated the intermolecular cycloaddition reaction between several diynes and nitriles. As shown in Table 1, the reactions with diyne **5a**, which results in a five-membered ring in the backbone of the product, always resulted in better yields than the corresponding reactions with **5b**. The loss in yield on switching from **6a** to **b** to **c** can be attributed to the steric hindrance of the bulky groups close to the nitrile moiety.

We also investigated the intramolecular [2+2+2] cycloaddition reaction of the two triynes **13** and **15** to their respective benzene derivatives **14** and **16**. Both conventional heating and microwave irradiation were applied, resulting in moderate to good yields in the range of those published for **4** (Scheme 4).[3a]

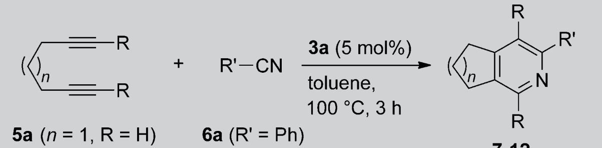


13 (R = H)
15 (R = Ph)

14 (R = H): 1) 36%, 2) 74%
16 (R = Ph): 1) 87%, 2) 52%

Scheme 4. Intramolecular [2+2+2] cycloaddition reaction with **3a**; 1) triyne (1 mmol), **3a** (5 mol%), toluene (3 mL), $T=100\,^{\circ}C$, $t=3$ h; 2) triyne (1 mmol), **3a** (5 mol%), DMF (3 mL), microwave irradiation, $T=200\,^{\circ}C$, $t=10$ min.

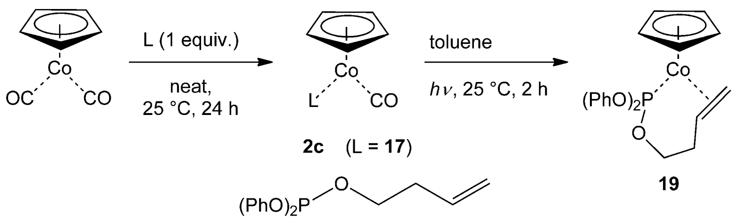
Table 1. Substrate screening for the intermolecular [2+2+2] cycloaddition of diynes and nitriles with **3a**.



5a (*n* = 1, R = H)
5b (*n* = 2, R = H)
6a (R' = Ph)
6b (R' = *i*Pr)
6c (R' = *t*Bu)
7-12

Entry	Diyne	Nitrile	Product	Isolated yield [%]
1	**5a**	**6a**	**7**	94
2	**5a**	**6b**	**8**	57
3	**5a**	**6c**	**9**	71
4	**5b**	**6a**	**10**	63
5	**5b**	**6b**	**11**	40
6	**5b**	**6c**	**12**	38

As $CpCo^I$-complexes with olefin and phosphite ligands have proven to be excellent catalysts for the [2+2+2] cycloaddition reaction even under mild conditions,[4] we were interested in the application of potentially chelating ligands with an intramolecular phosphite–olefin combination, which should be advantageous for the coordination resulting from the chelate effect, stabilising the CpCo core (Scheme 5). Therefore, we synthesised a suitable phosphite ligand (**17**) with a linear olefin attached.[16] The corresponding complex **2c** with one remaining CO ligand was prepared in very good yields starting from **1**, as described above. For the isolated complex **2c**, three slightly separated signals can be seen in the ^{31}P NMR spectrum, corresponding presumably to conformers of **2c** from different arrangements of the phosphite phenyl groups. Subsequent irradiation with light and the release of the second CO ligand led to a successful chelating coordination of the olefin moiety. Analogous substitution reactions with $[CpCo(H_2C{=}CHSiMe_3)_2]$ or [CpCo(cod)] and **17** led only to phosphite-coordinated complexes, namely $[CpCo(H_2C{=}CHSiMe_3)(\mathbf{17})]$ or $[CpCo(\mathbf{17})_2]$. Therefore, the described route starting from **1** is the only possibility to date to synthesise complexes with chelating phosphite–olefin ligands; to the best of our knowledge, **19** represents the first $CpCo^I$-complex with a chelating phosphite–olefin ligand.



2c (L = **17**)
17
19

Scheme 5. Synthesis of complex **19** with a chelating phosphite–olefin ligand.

To obtain a better idea of the effect of the chelating ligand, we investigated the catalytic activity of the two complexes **2c** and **19** in the same cycloaddition [2+2+2] test setup (see Scheme 2). As indicated in Figure 3, the ligand combination of phosphite–olefin (**19**) is, again, more efficient than the phosphite-CO combination (**2c**), providing complete conversion in a short reaction time. If one compares the catalytic activity of **19** with those of complexes containing non-chelating phos-

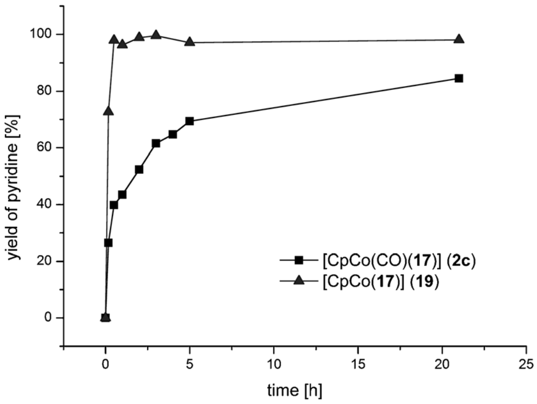


Figure 3. Evaluation of the catalytic activity of **2c** and **19** in the cycloaddition test reaction (Scheme 2).

phite–olefin ligand variations such as **3a**–**c**, no visible stabilising effect resulting from chelation can be detected. Therefore, the effect of the chelating ligand on the catalytic performance is significantly less than that of a strongly coordinating monodentate ligand such as CO.

In summary, we have described a novel and facile synthetic strategy towards the class of [CpCo(olefin)(phosphite)] complexes with a variety of phosphites and olefin ligands from commercially available CpCo$(CO)_2$ (**1**). Precatalysts of the structure [CpCo(dimethyl fumarate)(phosphite)] (**3a**–**b**) were air-stable and recyclable complexes, which were active in the inter- and intramolecular [2+2+2] cycloaddition reaction for the synthesis of pyridines and benzenes. The reaction times were short, non-dried toluene was used as the solvent and no inert gas atmosphere was required, demonstrating the robustness of the precatalyst. Additionally, the effect of a chelating phosphite–olefin ligand combination was investigated and the catalytic activity of the respective complex compared with complexes containing non-chelating ligands.

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Keywords: catalysis · cobalt · cycloaddition · alkenes · phosphite

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[9] CCDC 928416 (**3a**) and 928415 (**3b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[10] An experiment using dimethyl maleate as the olefin with opposite configuration of the double bond compared with the fumaric acid ester resulted in the observation of a mixture of 59% [CpCo(*cis*-MeO$_2$CCH=CHCO$_2$Me){P(OEt)$_3$}] (**3f**), 17% [CpCo{P(OEt)$_3$}$_2$], 6% **3a** and 17% dimethyl maleate, which were identified in the NMR spectra.
[11] If **2b** was used, mostly [CpCo{P(OPh)$_3$}$_2$] was recovered, whereas **2a** did not yield any bisphosphite complex.
[12] The activity of **3e** has been described before, providing high reactivity in cyclotrimerisations at 50 °C (see Ref. [4]).
[13] The recollection of precatalyst **4** after the first run of the cycloaddition reaction was only 43%, according to Ref. [3a].
[14] For detailed information, see the Supporting Information.
[15] After the first reaction, varying amounts of catalyst **3a** were isolated, allowing a second run, after which no catalyst was recovered at all.
[16] Synthesized by using a modified procedure: H. Ingenuin, P. C. William, F. C. Lanoue, *Vol. US2834798*, SHEA CHEMICAL CORP, Columbia, United States, **1958**.

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