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Fine-Tuning the Reactivity and Stability by Systematic Ligand Variations in CpCo^I Complexes as Catalysts for [2+2+2] Cycloaddition Reactions

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Abstract: CpCo^I-olefin-phosphite and CpCo^I-bisphosphite complexes were systematically prepared and their reactivity in [2+2+2] cycloaddition reactions compared with highly active [CpCo($H_2C{=}CHSiMe_3$)$_2$] (**1**). Whereas **1** is an excellent precursor for the synthesis of [CpCo(olefin)(phosphite)] complexes (**2a**–**f**), [CpCo(phosphite)$_2$] complexes (**3a**–**e**) were prepared photochemically from [CpCo(cod)]. The complexes were evaluated in the cyclotrimerization reaction of diynes with nitriles yielding pyridines. For [CpCo(olefin)(phosphite)], as well as some of the [CpCo(phosphite)$_2$] complexes, reaction temperatures as low as 50 °C were sufficient to perform the cycloaddition reaction. A direct comparison showed that the order of reactivity for the complex ligands was olefin$_2$ > olefin/phosphite > phosphites$_2$. The complexes with mixed ligands favorably combine reactivity and stability. Calculations on the ligand dissociation from [CpCo(olefin)(phosphite)] proved that the phosphite is dissociating before the olefin. [CpCo($H_2C{=}CHSiMe_3$){P(OPh)$_3$}] (**2a**) was investigated for the co-cyclization of diynes and nitriles and found to be an efficient catalyst at rather mild temperatures.

Keywords: cobalt · cycloaddition · cyclopentadienyl ligands · olefin ligands · P ligands

Introduction

Transition-metal-catalyzed [2+2+2] cycloadditions have matured into a versatile methodology for constructing new carbo- and heterocyclic structures including enantio- and stereoselectivities.[1] The application in the assembly of complex structures such as natural products highlights [2+2+2] cycloadditions as an important tool for strategic reactions.[2] Next to a large number of transition-metal complexes known to catalyze these reactions, group 9 complexes, in particular CpCo^I complexes, still represent the predominantly used catalysts.[1u,2] Besides [CpCo(PPh$_3$)$_2$] and [CpCo(CO)$_2$] with σ-donating ligands, π-donating olefin ligands have also been established for these precatalysts as demonstrated by the Jonas catalyst [CpCo($H_2C{=}CH_2$)$_2$] and [CpCo(cod)] (cod = 1,5-cyclooctadiene). Recently, catalysts containing two different donor ligands were reported. For example, Butenschön et al., reported a catalyst with an ethylene ligand and a Cp-tethered phosphine ligand for [2+2+2] cycloadditions in aqueous medium,[3] as well as Aubert and Gandon who described the synthesis and application of [CpCo(CO)(dialkyl fumarate)] complexes, which can be prepared from [CpCo(CO)$_2$] and are air-stable solids.[4] Nevertheless, all the regularly applied catalysts, except the Jonas catalyst, need either fairly high reaction temperatures or/and irradiation to become catalytically active.

Our group focused on the preparation of new and reactive CpCo^I-olefin complexes for [2+2+2] cycloadditions. We recently reported the synthesis and the catalytic activity of [CpCo($H_2C{=}CHSiMe_3$)$_2$] (**1**), which was demonstrated presumably to be the most active precatalyst for Co-catalyzed cycloadditions for the preparation of pyridines and also a great precursor for the synthesis of a variety of [CpCo(olefin)$_2$] complexes.[5,6] However, the thermal instability of **1**, which degrades rapidly above −30 °C, is a critical drawback making the handling of the catalyst somewhat tricky. This degradation forms stable tetranuclear CpCo-cluster complexes, which are inactive in cycloadditions under ambient conditions.[7] To improve the stability of precatalyst **1** without interfering too strongly with its capability to rather easily generate the catalytically active species, we set out to prepare CpCo^I complexes with one olefin ligand substituted by a ligand that would be able to provide sufficient stability and reactivity. Apart from the fact that a large number of phosphites with different electronic and steric properties are commercially available, we chose phosphites for our goals for additional other reasons: Phosphites should coordinate less strongly since they are more electron-deficient σ-donors and also allow a weaker π-backbonding compared with the corresponding phosphine analogues.[8] On the other hand they should bind tighter to the metal than olefins.

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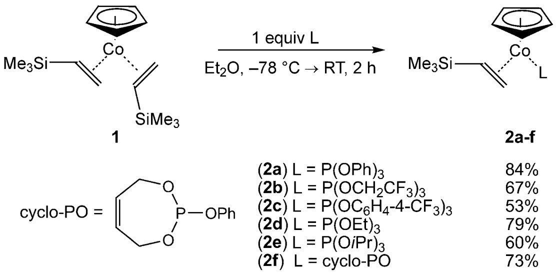
Results and Discussion

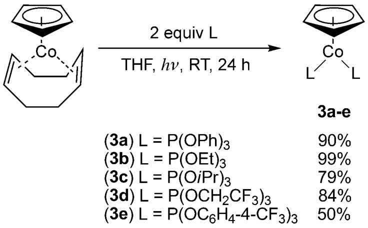
Following the observation of the ease of ligand displacement in **1**, we investigated the reaction of **1** with one equivalent of $P(OPh)_3$ to substitute one olefin ligand. This reaction proceeded very smoothly and the mixed $[CpCo(H_2C{=}CHSiMe_3)\{P(OPh)_3\}]$ complex (**2a**) could be obtained in excellent yield (84%). To our surprise the corresponding bisphosphite $[CpCo\{P(OPh)_3\}_2]$ complex (**3a**) could not be obtained in pure form even with an excess of $P(OPh)_3$ or prolonged reaction times.[9] As it turned out, this reaction was highly suitable to systematically prepare a large array of mixed $[CpCo(H_2C{=}CHSiMe_3)\{P(OR)_3\}]$ complexes for the first time, allowing a broad variety of phosphites with different electronic properties (Scheme 1). The yields are high to very high and the products can be easily isolated. Complexes **2a–f** proved to be stable at room-temperature under inert conditions, depicting the first successful step towards stable and active precatalysts for [2+2+2] cycloadditions.



Scheme 1. New mixed $CpCo^I$-olefin-phosphite complexes obtained through a substitution reaction from **1** (the yields are that of isolated product).

To obtain a complete series of the complexes **1**, **2**, and **3**, as well as to clarify the influence of the phosphite ligand, we wanted to prepare the respective $[CpCo\{P(OR)_3\}_2]$ complexes, and in addition, investigate their catalytic properties. Due to the fact, that only very few $[CpCo\{P(OR)_3\}_2]$ complexes are known[10,11] and to our best knowledge none of them have been tested in catalytic [2+2+2] cycloadditions, we initially turned our attention to the published synthesis of $[CpCo\{P(OPh)_3\}_2]$ (**3a**). Werner et al. were the first to describe the synthesis of **3a**,[10] followed by a modified procedure by McKinney et al.[11] Unfortunately, further experimental work proved none of these conditions suitable as a general approach for the synthesis of $[CpCo\{P(OR)_3\}_2]$ complexes.[12] Therefore, a new, general and efficient method for preparing $[CpCo\{P(OR)_3\}_2]$ complexes with different electronic properties was sought. We took advantage from our experience with photocatalytic reactions and succeeded in developing a photochemical substitution reaction as a route to various $[CpCo\{P(OR)_3\}_2]$ complexes (Scheme 2). In contrast to **1**, [CpCo(cod)] proved to be a suitable starting material for these substitution reactions.[13]

[CpCo(cod)] can be easily activated at low and ambient temperature through irradiation by releasing the COD ligand; this opens the possibility for the coordination of new potentially stronger coordinating phosphite ligands. To our delight, we noted that this substitution proceeded smoothly and led to quantitative conversion after 24 h at room temperature (Scheme 2). Generally, these new complexes can then be isolated in very high to excellent yields by a short filtration over aluminum oxide, as shown for complexes **3b** and **3c** with electron-rich phosphites and complexes **3d** and **3e** with electron-deficient phosphites.[14,15] These complexes are stable and can easily be handled under inert conditions.[15]



Scheme 2. New photochemical route for the synthesis of the $CpCo^I$-bisphosphite complexes **3a–e** from [CpCo(cod)] (the yields are that of the isolated product).

We were able to obtain crystals of **3a** and **3e** from a saturated pentane solution at 4 °C suitable for X-ray structure analysis.[16] Figure 1 shows the molecular structures of the $CpCo^I$-bisphosphite complexes. The structural features of the complexes with respect to their substitution at the phosphites are very similar, which is displayed, for example, by the Co–P bond distances (**3a**: 2.0389(5) and 2.0486(4) Å; **3e**: 2.0435(6) and 2.0428(6) Å) and the P1-Co-P2 angles (**3a**: 95.78(2)°; **3e**: 94.62(2)°).

Having a large array of new potential precatalysts (**2a–f** and **3a–e**) in our hands which showed high stability at room temperature, we tested their catalytic performance in the [2+2+2] reaction between 1,6-heptadiyne (**4**) and benzonitrile, giving pyridine **8** (Figure 2).[17] We chose 50 °C as the reaction temperature to test the activity at rather mild conditions and were pleased to detect a very high catalytic activity towards the synthesis of pyridines.

Figure 2 (top) shows that most of complexes **2a–f** provide complete conversions after short reaction times, except for **2f**, which reaches conversions between 60 and 70% only after $t > 20$ h. It can therefore be concluded that the nature of the phosphite ligand did not play a large role in providing high reactivity, but rather in stabilizing the complex by coordinating more strongly to the cobalt center than the olefin ligands in **1**. The catalytic performance of **3a–e** was investigated in the same catalytic screening setting as **2a–f** (Figure 2, bottom). The outcome showed that in most cases the phosphite ligands coordinate stronger to the cobalt center, resulting in a lower reactivity compared with **2a–f**. However, the most active complex **3c** shows almost full conversion of the substrate already after 3 h.

Comparing the reactivity of the complexes one can see that the electronic properties of the phosphite ligands do play a large role. Whereas electron-rich phosphites such as

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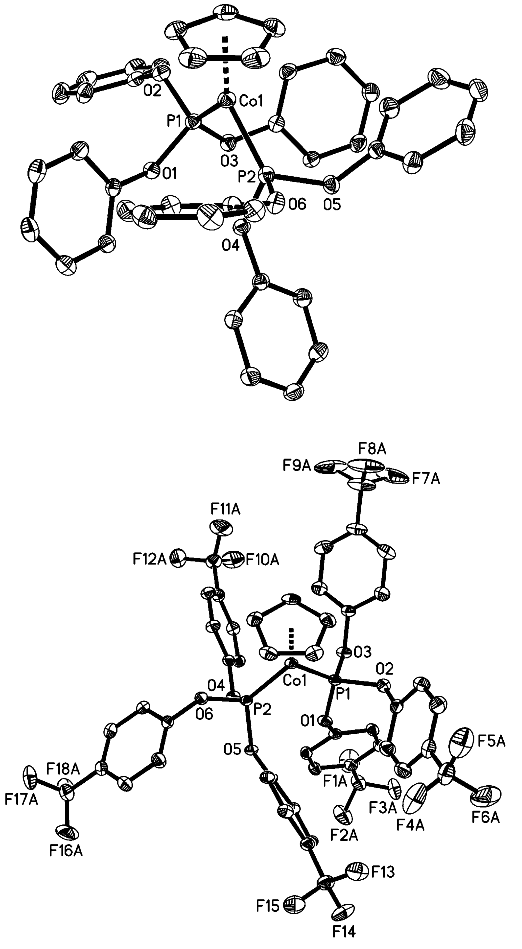


Figure 1. ORTEP drawings of the molecular structure of **3a** (top) and **3e** (bottom). Ellipsoids are drawn at the 30% level. Hydrogen atoms are omitted for clarity.

$P(OiPr)_3$ and $P(OEt)_3$ (**3c** and **3b**) lead to easily activated complexes, which reach quantitative conversions to the pyridine derivative, more electron-deficient phosphites such as $P(OPh)_3$ (**3a**) only reach conversions up to 20% after 24 h. The introduction of electron-withdrawing groups as in the case of $P(OC_6H_4\text{-}4\text{-}CF_3)_3$ even leads to a complete loss of activity of the respective complex **3e**. Ligand $P(OCH_2CF_3)_3$ is an exception being rather electron-deficient but reaching conversions up to 33% in 24 h under these conditions (**3d**).

Due to the now possible and unprecedented access to three complex types with either only olefin or phosphite and also the mixed ligand combination, it was possible to directly compare the performance of these catalysts. The comparative reactivity profile of complexes **1**, **2a**, and **3a** for the [2+2+2] cycloaddition in Figure 2 at different temperatures and within different time frames is displayed in Figure 3.[17] Whereas complex **1** is most active, accomplishing the reaction at 0 °C in a very short time (within minutes), the chart shows very clearly that the stable complex **2a** still maintains a significantly high reactivity as precatalyst, leading to completion of the pyridine formation already at 50 °C within an hour and also showing some reactivity at temperatures as low as 0 °C. Complex **3a** requires 100 °C for completion of the cycloaddition reaction and a much longer reaction time (24 h). However, the reaction temperature here is still lower or at least in the same range than for many other CpCo complexes used as catalysts. This comparison explicitly shows the stabilizing influence of the phosphite ligands. It was also possible to perform the cycloaddition reaction with **2a** and **3a** in non-dried and non-degassed toluene without any loss in the product yield.[18] The combination with one olefin ligand therefore leads to a unique complex that offers higher thermal stability compared with the purely olefin-li-

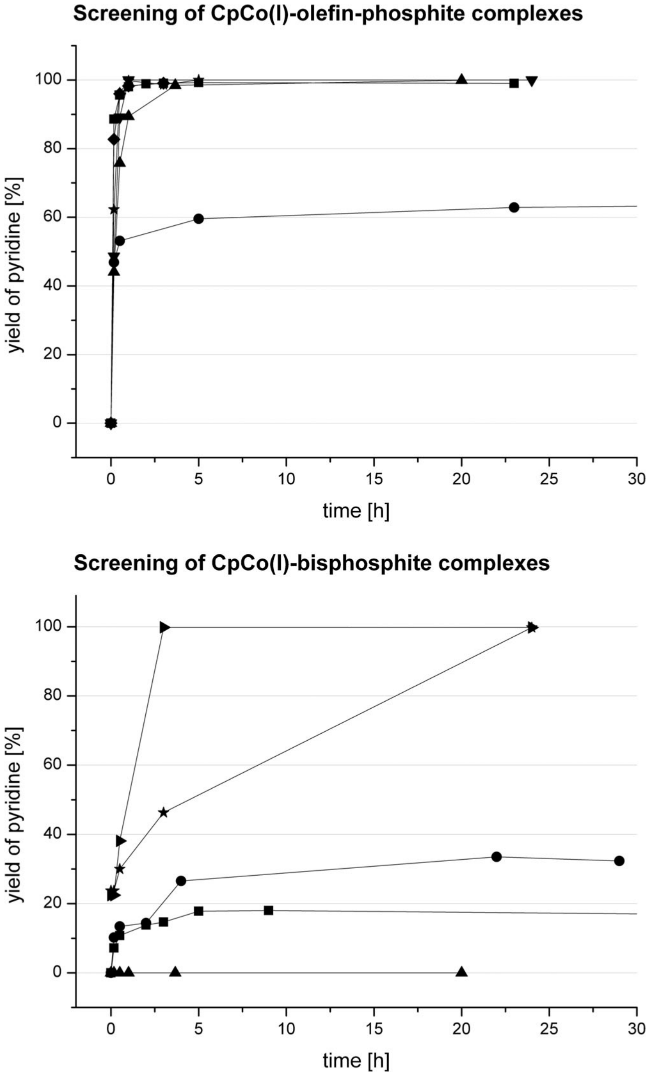


Figure 2. Screening experiments of co-cyclotrimerization reactions with $CpCo^I$-olefin-phosphite complexes (**2a–f**; top) and $CpCo^I$-bisphosphite complexes (**3a–e**; bottom) as catalysts (the yields were determined by GC analysis):[17] Complexes **2a–f** (top): ■ = $[CpCo(H_2C{=}CHSiMe_3)\{P(OPh)_3\}]$ (**2a**); ▲ = $[CpCo(H_2C{=}CHSiMe_3)\{P(OCH_2CF_3)_3\}]$ (**2b**); ▼ = $[CpCo(H_2C{=}CHSiMe_3)\{P(OC_6H_4\text{-}4\text{-}CF_3)_3\}]$ (**2c**); ★ = $[CpCo(H_2C{=}CHSiMe_3)\{P(OEt)_3\}]$ (**2d**); ◆ = $[CpCo(H_2C{=}CHSiMe_3)\{P(OiPr)_3\}]$ (**2e**); ● = $[CpCo(H_2C{=}CHSiMe_3)(cyclo\text{-}PO)]$ (**2f**). Complexes **3a–e** (bottom): ■ $[CpCo\{P(OPh)_3\}_2]$ (**3a**); ★ = $[CpCo\{P(OEt)_3\}_2]$ (**3b**); ▶ = $[CpCo\{P(OiPr)_3\}_2]$ (**3c**); ● = $[CpCo\{P(OCH_2CF_3)_3\}_2]$ (**3d**); ▲ = $[CpCo\{P(OC_6H_4\text{-}4\text{-}CF_3)_3\}_2]$ (**3e**).

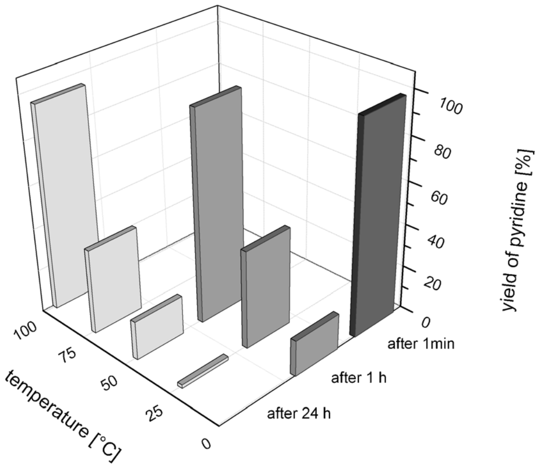


Figure 3. Temperature-dependent yields of pyridine (**8**) determined for [CpCo($H_2C{=}CHSiMe_3$)$_2$] (**1**, dark grey), [CpCo($H_2C{=}CHSiMe_3$){P(OPh)$_3$}] (**2a**, grey), and [CpCo{P(OPh)$_3$}$_2$] (**3a**, light grey), respectively.[17]

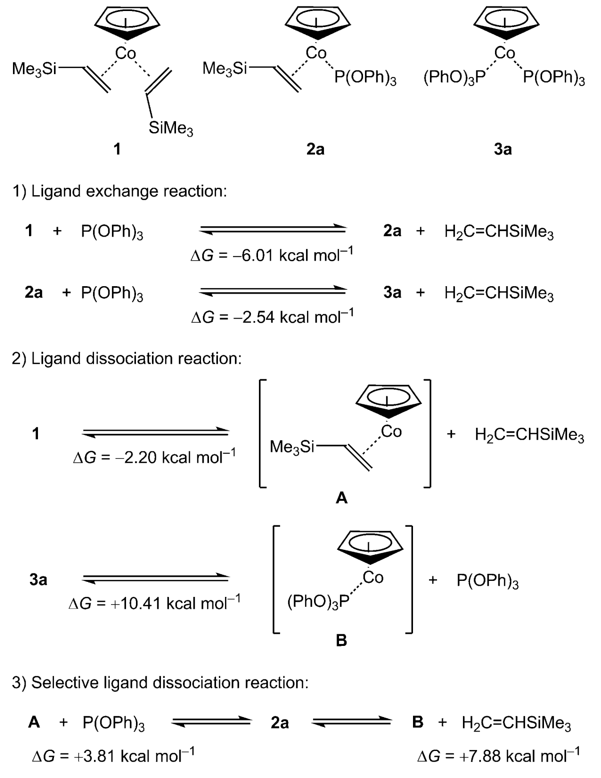


Figure 4. Calculations on the formation of the new complexes and free energies of ligand dissociation from **1**, **2a**, and **3a** at BP86/TZVP level.

gated **1**, but still provides significant reactivity for cycloaddition reactions.

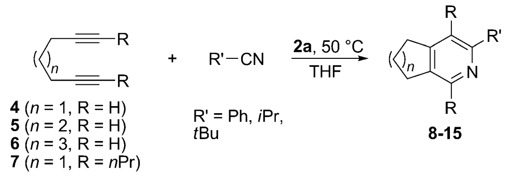
To fortify our experimental results we were interested to further evaluate the influence of the phosphite ligand for the reactivity and stability features of these complexes by using DFT calculations. We performed DFT calculations on the formation of the complexes as well as the ligand dissociation, being the initial step of the catalytic cycle (Figure 4). In our calculations we used the real-size complexes and ligands and the computational details are given in the Supporting Information.

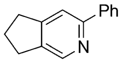
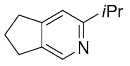
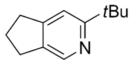
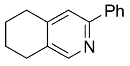
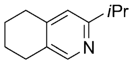
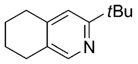
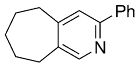
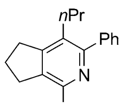
At first we computed the stepwise exchange reaction of one olefin ligand in **1** by one phosphite ligand at a time to form **2a** and **3a**, respectively. P(OPh)$_3$ has three isomers; the isomer with C_1 symmetry is more stable than the C_3 as well as C_s isomer by 1.34 and 0.94 kcal mol^{-1}, respectively. Therefore, the C_1 isomer was used for our energetic comparison. It was found that the formation of **2a** is highly favorable, as indicated by the computed negative free energy (−6.01 kcal mol^{-1}). For the formation of **3a**, however, the negative free energy (−2.54 kcal mol^{-1}) still indicates a favorable process, but to a lesser extent when compared with the formation of **2a**.

The stability of complexes **1**, **2a**, and **3a** towards ligand dissociation has also been computed. It is found that the 16-electron complex [CpCo($H_2C{=}CHSiMe_3$)] (**A**) has a triplet ground state, which is more stable than the corresponding singlet state by 11.84 kcal mol^{-1}; the computed dissociation free energy is −2.20 kcal mol^{-1}, revealing the instability of complex **1** at ambient conditions. This reflects the experimentally discovered instability of complex **1** above −30 °C. For complex **3a**, the monophosphite complex [CpCo{P(OPh)$_3$}] (**B**) has a triplet ground state as well, which is 16.4 kcal mol^{-1} more stable than the singlet state. The computed dissociation free energy of complex **3a** is 10.41 kcal mol^{-1}, indicating its high stability towards dissociation, which is in agreement with our experimental findings. For complex **2a**, both the olefin and phosphite ligand can dissociate. Here the selectivity depends solely on the dissociation free-energies. It is found that the phosphite dissociation of complex **2a** leading to the formation of complex **A** needs lower free energy than the olefin dissociation with the formation of complex **B** (3.81 vs. 7.88 kcal mol^{-1}). This indicates that complex **2a** dissociates selectively into complex **A**, subsequently leading to the active catalyst. This also explains why the reactivity of the mixed complexes did not largely depend on the type of phosphite ligand, as Figure 2 (left) showed, since in each case the phosphite is dissociating first, leading to the same intermediate. The computed first ligand dissociation free energies reveal that the stability of the complexes increases in the following order: **1** (−2.20 kcal mol^{-1}) < **2a** (3.81 kcal mol^{-1}) < **3a** (10.41 kcal mol^{-1}). This stability order correlates well with our experimental observations as discussed above.

Since complex **2a** proved to be one of the most active but at the same time rather stable CpCo^I catalysts, we expanded the substrate scope for cycloadditions with **2a** as precatalyst to different diynes and various nitriles (Table 1).[19] Pyridines possessing annellated five- and six-membered rings were isolated in moderate to excellent yields (Table 1, entries 1–6). The reactions of 1,7-octadiyne (**5**) with PhCN, *i*PrCN, and *t*BuCN (Table 1, entries 4, 5, and 6) generally gave lower yields compared with the corresponding reactions with 1,6-heptadiyne (**4**) (Table 1, entries 1, 2, and 3). However, the

Table 1. Investigation of **2a** as catalyst for cycloaddition reactions between diynes and nitriles.

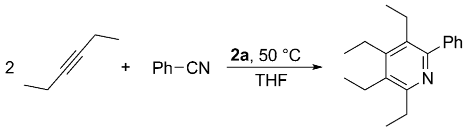


Entry	Nitrile	Diyne	Product[a]	Yield [%][b]
1	PhCN	**4**	 **8**	98[c], 97[d]
2	*i*PrCN	**4**	 **9**	96
3	*t*BuCN	**4**	 **10**	49
4	PhCN	**5**	 **11**	67
5	*i*PrCN	**5**	 **12**	46
6	*t*BuCN	**5**	 **13**	35
7	PhCN	**6**	 **14**	0
8	PhCN	**7**	 **15**	42[e]

[a] General procedure: Diyne (1 mmol), nitrile (5 mmol), and $[CpCo(H_2C{=}CHSiMe_3)\{P(OPh)_3\}]$ (**2a**, 5 mol %) were dissolved in dry THF (3 mL) and stirred at 50 °C for 3 h. [b] Yield of the isolated product. [c] GC yield. [d] $[CpCo(H_2C{=}CHSiMe_3)\{P(OPh)_3\}]$ (**2a**, 1 mol %). [e] Yield after 6 h.

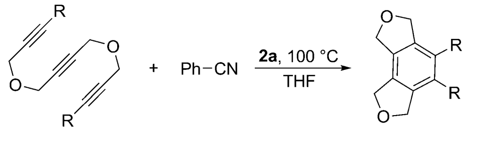
very bulky *t*BuCN gave lower yields in both cases (Table 1, entries 3 and 6). The conversion of internal diynes needs longer reaction times and results in lower yields, probably due to steric hindrance, as was demonstrated with diyne **7** (Table 1, entry 8). The use of 1,8-nonadiyne (**6**) resulted in the intermolecular [2+2+2] cycloaddition between two nitriles and two diynes and the formation of a macrocyclic bispyridine instead of **14** (Table 1, entry 7).[20]

We also investigated the intermolecular cycloaddition reaction between 3-hexyne (**16**) and benzonitrile, yielding the respective pyridine **17** in very good yield (Scheme 3). In addition, the intramolecular cycloaddition reaction was demonstrated exemplarily for terminal and internal triynes (**18** and **19**), yielding the benzene derivatives (Scheme 4). In the latter reaction moderate yields are achieved at a reaction temperature of 100 °C, which in the case of **20** are slightly lower compared with reactions with other cobalt catalysts under more extreme conditions.[4]



16 **17** 80%

Scheme 3. Investigation of **2a** as catalyst for an intermolecular cycloaddition reaction between 3-hexyne (**16**) and benzonitrile (isolated product yield).



18 (R = H)
19 (R = Ph)

20 (R = H) 41%
21 (R = Ph) 39%

Scheme 4. Application of **2a** as catalyst for the intramolecular cycloaddition reaction of triynes **18** and **19**, leading to carbocyclic products (isolated product yield).

Conclusion

We have described new and efficient synthetic routes to a large number of novel $CpCo^I$-complexes containing either olefin-phosphite ligand combinations ($[CpCo(H_2C{=}CHSiMe_3)\{P(OR)_3\}]$) or two phosphite ligands ($[CpCo\{P(OR)_3\}_2]$) by selective substitution from $[CpCo(H_2C{=}CHSiMe_3)_2]$ (**1**) or by photochemical exchange reactions from [CpCo(cod)], respectively. The screening of the catalytic activity in [2+2+2] cycloadditions showed that $[CpCo\{P(OEt)_3\}_2]$ (**3b**) and $[CpCo\{P(O\mathit{i}Pr)_3\}_2]$ (**3c**) are the most reactive bisphosphite complexes at a reaction temperature as mild as 50 °C. However, the mixed $CpCo^I$-olefin-phosphite complexes exhibited much higher catalytic activities but were also stable compounds at room temperature. This highly beneficial combination of stability and high catalytic activity was proven by comparison of the reaction temperatures for $[CpCo(H_2C{=}CHSiMe_3)_2]$ (**1**), $[CpCo(H_2C{=}CHSiMe_3)\{P(OPh)_3\}]$ (**2a**) and $[CpCo\{P(OPh)_3\}_2]$ (**3a**). Computational results showed that in the mixed complexes $[CpCo(H_2C{=}CHSiMe_3)\{P(OR)_3\}]$, the dissociation of the phosphite ligand is preferred compared to the olefin. Also, the reactivity and stability differences between $[CpCo(H_2C{=}CHSiMe_3)_2]$ (**1**) and $[CpCo\{P(OR)_3\}_2]$ can be demonstrated. The synthetic scope in pyridine synthesis from diynes and nitriles was investigated for **2a** in intramolecular as well as intermolecular reactions, demonstrating the high utility of this new precatalyst. The concept of using two different ligands for complexes of the type $[CpCo(L^1)(L^2)]$ to combine the properties of the respective complexes $[CpCo(L^1)_2]$ and

$[CpCo(L^2)_2]$ proved to be very useful for the development of new, reactive and stable CpCo^I-precatalysts.

Experimental Section

General procedure for the synthesis of $[CpCo(H_2C{=}CHSiMe_3)\{P(OR)_3\}]$: To a solution of $[CpCo(H_2C{=}CHSiMe_3)_2]$ (**1**) in diethyl ether a solution of the respective phosphite (1 equiv) in THF (2 mL) was slowly added at −78 °C. The solution was stirred at −78 °C for 2 h before it is slowly warmed to room temperature. The solution was filtered over a small amount of neutral Al_2O_3 (Brockman Type I), which was washed with THF (10 mL). After removal of the solvent under reduced pressure the resulting red-black oil was dried under vacuum.

General procedure for the synthesis of $[CpCo\{P(OR)_3\}_2]$: A solution of [CpCo(cod)] (232 mg, 1 mmol) and the respective phosphite (2 mmol) in THF (6 mL) was irradiated with light (two 460 W lambs) in a thermostated Schlenk-type vessel under argon for 24 h. The solution was filtered over a small amount of neutral Al_2O_3 (Brockman Type I), which was washed with diethyl ether (10 mL). After removal of the solvent under reduced pressure the resulting deep red oil/solid was dried under vacuum.

General procedure for the catalytic trial: 1,6-Heptadiyne (114 μL, 1 mmol), benzonitrile (515 μL, 5 mmol) and dodecahydrotriphenylene (DHT, 36 mg, 0.15 mmol) as internal standard were dissolved in THF (2 mL). A solution of the respective complex (5 mol% regarding the diyne) in THF (1 mL) was added and the reaction mixture stirred at 50 °C. At given times small aliquots of the reaction mixture (0.1 mL) were taken for GC analysis.

Substrate screening: Diyne (1 mmol), nitrile (5 mmol) and $[CpCo(H_2C{=}CHSiMe_3)\{P(OPh)_3\}]$ (**2a**, 26 mg, 5 mol%) were dissolved in dry THF (3 mL). The solution was stirred at 50 °C for 3 h before the solvent was removed under reduced pressure. Column chromatography (*n*-hexane/ethyl acetate 6:1, v/v) afforded the respective pyridines as white solids or clear oils. The compounds were identified by NMR spectroscopy and MS and comparison with reported data.

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[9] A similar observation was described by Brookhart et al., who were trying to substitute the trimethylvinylsilane ligands of $[(Me_5C_5)Co(H_2C{=}CHSiMe_3)_2]$ with trimethylphosphite: a) C. P. Lenges, P. S. White, M. Brookhart, *J. Am. Chem. Soc.* **1998**, *120*, 6965; b) C. P. Lenges, M. Brookhart, B. E. Grant, *J. Organomet. Chem.* **1997**, *528*, 199. They remarked that a large excess (10-fold) of trimethylphosphite (and higher temperatures) were necessary to remove the second trimethylvinylsilane ligand of $[(Me_5C_5)Co(H_2C{=}CHSiMe_3)\{P(OMe)_3\}]$ to yield $[(Me_5C_5)Co\{P(OMe)_3\}_2]$. Substitution reactions with N-donor ligands such as pyridine and 2,2′-bipyridine were also reported: c) C. P. Lenges, P. S. White, W. J. Marshall, M. Brookhart, *Organometallics* **2000**, *19*, 1247.

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[12] Essentially, cobaltocene was heated at reflux with the phosphite at high temperatures over long reaction times. We investigated various other routes for the synthesis of **3a** under reducing conditions in the presence of $P(OPh)_3$ but only the application of NaK (sodium/potassium alloy) was found effective, albeit yielding **3a** in a lower yield than the original procedure. Interestingly, all experiments involving the reduction of cobaltocene with pure alkali metals (Li, Na, or K) led to no reaction at all, not even a decomposition of the phosphite ligands was observed.

[13] We also investigated the direct synthesis of complex **2a** from [CpCo(cod)] (1 mmol), $P(OPh)_3$ (1 mmol), and $H_2C{=}CHSiMe_3$ (10 mmol) in THF using irradiation for 24 h. Analysis of the obtained reaction product showed that a 2:1:2 mixture of [CpCo(cod)]/**2a**/**3a** was produced (see the Supporting Information).

[14] Experiments using phosphites with large aryl- (e.g., tris-(2,4-*tert*-butylphenyl)phosphite) or large alkyl groups (e.g., tris-(dimethyl-*tert*-butylsilyl)phosphite) gave no reaction at all, which could be attributed to the steric bulkiness of these phosphites.

[15] Whereas complex **3a** and **3e** are solids, complexes **3b–d** are red oils.

[16] CCDC-879909 (**3a**) and 879908 (**3e**) 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.

[17] Figures 2 and 3 are displayed in color in the Supporting Information.

[18] For more details and comparison with the reaction in anhydrous solvents see the Supporting Information.

[19] The reaction of diynes with nitriles was investigated with catalyst systems of different metals. Selected original work: a) Y. Yamamoto,

K. Kinpara, R. Ogawa, H. Nishiyama, K. Itoh, *Chem. Eur. J.* **2006**, *12*, 5618; b) Y. Zhou, J. A. Porco, J. K. Snyder, *Org. Lett.* **2007**, *9*, 393; c) H.-T. Chang, M. Jeganmohan, C.-H. Cheng, *Org. Lett.* **2007**, *9*, 505; d) B. L. Gray, X. Wang, W. C. Brown, L. Kuai, S. L. Schreiber, *Org. Lett.* **2008**, *10*, 2621; e) J.-C. Hsieh, C.-H. Cheng, *Chem. Commun.* **2008**, 2992; f) L. Sripada, J. A. Teske, A. Deiters, *Org. Biomol. Chem.* **2008**, *6*, 263; g) A. Goswami, K. Ohtaki, K. Kase, T. Ito, S. Okamoto, *Adv. Synth. Catal.* **2008**, *350*, 143; h) A. Kadlkova, M. Kotora, *Molecules* **2009**, *14*, 2918; i) C. Wang, X. Li, F. Wu, B. Wan, *Angew. Chem.* **2011**, *123*, 7300; *Angew. Chem. Int. Ed.* **2011**, *50*, 7162.

[20] GC-MS and HRMS (ESI) analysis showed signals ($[M+H^+]$ found: m/z 447.2794) corresponding to a macrocyclic bispyridine yielded by the cycloaddition of two molecules of 1,8-nonadiyne and two molecules of benzonitrile ($[M+H^+]$ calcd: m/z 447.2795).

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