Synthesis of Phosphinines from Co^{II}-Catalyzed [2+2+2] Cycloaddition Reactions

Tim Gläsel, Haijun Jiao,* and Marko Hapke*

Cite This: *ACS Catal.* 2021, 11, 13434–13444

Read Online

ACCESS |

Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: The Co^{II}-catalyzed [2+2+2] cycloaddition of functionalized diynes and phosphalkynes resulting in the formation of an array of structurally interesting phosphinines is reported. A combination of 1,2-bis(diphenylphosphino)benzene (dppbenz) and CoI₂ turned out to be the most suitable and active catalyst system under microwave reaction conditions. Chemo-selective cyclizations of phosphalkynes in the presence of nitriles have been observed, and a number of carbonyl functionalities are tolerated as well. The reaction can successfully be conducted with a 1:1 ratio of phosphalkyne/diyne substrate. Model reactions with benzonitrile and diyne demonstrated that Co^{II} catalysts in the presence of bisphosphines prefer carbocyclization, while reduction to lower oxidation states promotes heterocyclization to the corresponding pyridine. A reaction mechanism comprising a Co^{II} oxidation state for the cyclotrimerization process is proposed and rationalized based on control experiments and theoretical calculations.

KEYWORDS: cobalt, [2+2+2] cycloaddition, phosphalkynes, phosphinines, pyridines, reaction mechanism

INTRODUCTION

Catalytic [2+2+2] cycloadditions of alkynes and heterocumulenes, leading to a wealth of functionalized aromatic and heteroaromatic molecules, have become an interesting synthetic strategy for the assembly of complex molecules from structurally simpler precursors since the onset of the first systematic studies.^{1,2} The development also includes the introduction of various catalysts from the whole range of transition metals.³ The large variety of metal complexes available for cyclotrimerizations is also manifested in the diversity of reaction mechanisms.⁴ Cobalt compounds have always taken a front seat in the application of late transition-metal catalysts in cyclotrimerization reactions, especially by cyclopentadienyl (Cp)Co^I-(neutral ligand) complexes like CpCo(CO)₂,⁵ or modified congeners.⁶ A number of *in situ* generated Co^I complexes from the reduction of Co^{II} halides containing bisphosphine or NHC (*N*-heterocyclic carbene) ligands have been utilized for the transformation of triynes to furnish highly substituted benzenes.⁷ Also the isolable complex CoCl(PPh₃)₃ was identified as a useful molecularly defined precatalyst for this transformation under mild conditions.⁸ The reaction scope has also been extended to asymmetric cyclizations by an *in situ* generated chiral Co^I-(P,N ligand) catalyst, affording atropochiral biaryls and triaryls.⁹

While pyridines belong to the core area of heteroaromatic chemistry, phosphinines (also coined phosphabenzenes) have a much shorter history.¹⁰ However, their molecular properties, e.g., in comparison to pyridines,¹¹ in homogeneous catalysis¹²

and coordination chemistry,^{13,14} have stirred significant work over recent decades toward their synthesis and functionalization.¹⁵ *De novo* synthesis of phosphinines by transition-metal-catalyzed reactions besides traditional approaches like the [4+2] cycloaddition of phosphalkynes with 2-pyrones is still rare (Scheme 1, top).

A single example is reported for the reaction of sodium phosphaehtynolate with alkynes to furnish the sodium phosphinin-4-olate in two [2+2] cycloaddition events (Scheme 1, middle).¹⁶ The only known successful transition-metal-catalyzed cyclization of phosphalkynes was reported by Nishibayashi and co-workers, applying FeI₂ without additional ligands, proposing an Fe^{II}/Fe^{IV} catalytic reaction cycle (Scheme 1, middle).¹⁷ However, an excess of the valuable phosphalkyne building block is required in this reaction. The unusual and successful application of an Fe^{II} halide as a catalyst raises the question of whether higher cobalt oxidation states can potentially also be useful in facilitating cyclotrimerization processes. While CpCo^I complexes are established catalysts for pyridine ring assembly under a variety of conditions, a large tendency toward dimerization of the phosphalkynes using

Received: August 3, 2021

Revised: September 7, 2021

Published: October 21, 2021

Scheme 1. Synthesis of Phosphinines (R = Bulky Alkyl or Aryl Groups)

Classical route for phosphinine synthesis via Diels-Alder-type synthesis of phosphaethyne with 2-pyrones:

Consecutive [2+2] cycloadditions of phosphaethyne with alkynes:

Fe^{II}-catalyzed [2+2+2] cycloaddition of diynes and phosphaealkynes:

Co^{II}-catalyzed [2+2+2] cycloaddition of diynes and phosphaealkynes (this work):

FG Functional Groups comprising cyclizations in the presence of, e.g. nitrile, lactone, sulfoxide or ester groups in the substrate

different CpCo^I complexes was observed, leading to the formation of highly stable diphosphabutadienes.¹⁸ This behavior can be traced back to the properties of phosphaealkynes, which rather reflect alkynes than nitriles. Only recently, the successful application of Co^{II} complexes in hydroformylation reactions was reported.¹⁹ In the following, we disclose our results on the unprecedented Co^{II}-catalyzed synthesis of functionalized phosphabenzene. To the best of our knowledge, such type of reaction has never been reported for cobalt-catalyzed cyclotrimerizations to date (Scheme 1, below).²⁰

RESULTS AND DISCUSSION

Initial experiments applied reactions of dipropargylether (**1a**) with the commercially available adamantlyphosphaealkyne (**2a**) in the presence of cobalt salts in different oxidation states (Scheme 2). For CoCl(PPh₃)₃ and Co(acac)₃/dppe (1,2-bis(diphenylphosphino)ethane), neither cyclization (**3a**) nor at least homocyclization of **1a** to the **1a** dimer was observed, and no cyclization products could be isolated at all. Inspired by our current experiments, applying CoI₂ as Co^{II} salt together with dppe as ligand, without the presence of a typical reductant like elemental zinc, led to the successful cyclization furnishing phosphabenzene **3a** with 36% isolated yield at high temperatures under microwave conditions.

This outcome inspired us to investigate the unusual cyclization mode of Co^{II} catalysts in the presence of chelating ligands for phosphaealkyne/diyne substrates in detail, as Co^{II} would present a rather unusual oxidation state to catalyze cyclotrimerizations. Preliminary tests with Co^{II} salts in the presence of a reductant like elemental zinc or manganese did not give any useful yields, distinctly hinting at the requirement of Co^{II} in the active catalyst. However, in the absence of such reductants the reaction proceeded as described above. We have set out to use dipropargyl diethylmalonate (**1b**) as substrate for cyclizations with **2a** using conventional heating as well as microwave conditions (Table 1).²¹

The results in Table 1 were obtained for a 1:1 ratio of **1b**:**2a**, which is remarkable in view of the observation that 2 equiv of phosphaealkyne are required for the Fe-catalyzed reaction.^{17a} Initial tests showed a significant yield (35%) of phosphinine **3b** for dppe as ligand in only one case (entry 9), while under all other conditions (entries 1–3, 5–8), only very small amounts or no product formation was observed. Control experiments with CoCl(PPh₃)₃ under identical conditions did not show any cyclization at all (entry 4). Cyclizations with bisphosphines possessing larger bite angles (entries 10 and 11) or dppe derivatives (entry 12) gave either no or a maximum 20% yield of **3b**. When applying 1,2-bis(diphenylphosphino)benzene (dppbenz) as ligand, essentially all investigated Co^{II} halides successfully performed the [2+2+2] cycloaddition process, with yields of 39% (X = Cl, entry 18), up to 69% (X = Br, entries 13–15) or even 80% (X = I, entry 19) for the desired phosphinine **3b**.

Remarkably, the reaction was usually run at 180–210 °C for a reaction time of 1 to 4 h. A lower temperature (100 °C) requires a significantly longer reaction time to deliver a

Scheme 2. Cobalt Complexes in Different Oxidation States in the Cyclization of **1a** and **2a**

Table 1. Optimization of Reaction Conditions

1b		2a	3b		
[Co], ligand, additive solvent, MW, T, t					
#	[Co] (mol %)	ligand (mol %)	solvent	T (°C)/T (h)	3b (%) ^a
1	CoCl ₂ ·6H ₂ O (10) ^b	dppe (10) toluene	toluene	130/2	7
2	CoBr ₂ (10) ^{b,c}	dppe (10) toluene	toluene	130/9	9
3	[Co(en) ₂ Cl ₂]Cl (20)	dppe (20)	toluene	130/2	
4	CoCl(PPh ₃) ₃ (10)		THF	180/2	
5	CoBr ₂ (20) ^d	dppe (20)	toluene	180/2	7
6	CoBr ₂ (20) ^d	dppe (20)	THF	180/2	12
7	CoBr ₂ (20)	dppe (20)	DCE	180/2	
8	CoBr ₂ (20)	dppe (20)	1,4-dioxane	180/2	
9	CoBr ₂ (20)	dppe (20)	THF	100 ^e /90	35
10	CoBr ₂ (10)	dppp (10)	THF	180/4	20
11	CoBr ₂ (10)	dppb (10)	THF	180/4	
12	CoBr ₂ (10)	dcpe (10)	THF	240/1	10
13	CoBr ₂ (10)	dppbenz (10)	THF	180/4	46
14	CoBr ₂ (10)	dppbenz (10)	THF	210/4	69
15	CoBr ₂ (10)	dppbenz (10)	THF	240/1	69
16	CoBr ₂ (10)	dppbenz (10)	iPrOH ^f	210/4	23
17	CoBr ₂ (10)	dppbenz (10)	EtOH	240/4	29
18	CoCl ₂ (10)	dppbenz (10)	THF	210/4	39
19	CoI ₂ (10) ^g	dppbenz (10)	THF	210/4	80
20	Co(acac) ₃ (10)	dppbenz (10)	THF	210/4	
21	Co(acac) ₃ (10) ^h	dppbenz (10)	THF	210/4	20
22	CoI ₂ (20) ^{i,j}	dppbenz (20)	THF	210/4	35

^aIsolated yield. ^bAddition of 20 mol % Zn. ^cAddition of 20 mol % ZnI₂. ^dAddition of 40 mol % Zn and ZnI₂. ^ePerformed with conventional heating without microwave. ^fPerformed with technical standard purity. ^gShort period of sonication before heating. ^hAddition of 10 mol % Zn. ⁱAddition of 20 mol % of Zn and heating to 60 °C for 1 h. ^jAddition of 20 mol % [Cp₂Fe]PF₆.

reasonable yield (entry 9). The utilization of Co(acac)₃ as Co^{III} salt together with dppbenz under otherwise identical conditions did not yield any **3b**, excluding Co^{III} from being responsible for cyclizations (entry 20). Further corroboration came from an experiment, when under the same conditions 10 mol % elemental zinc was added to the Co(acac)₃/dppbenz mixture, yielding 20% of **3b** (entry 21). It is reasonable to assume a preceding reduction of Co^{III} to Co^{II} by zinc and then cyclization of **1b** with **2a** was possible to occur.

In another control experiment, CoI₂/dppbenz was first reduced with elemental zinc to Co^I, which was then reoxidized with stoichiometric amounts of ferrocenium hexafluorophosphate back to Co^{II}, easily recognizable by color change after addition of each reagent (entry 22). The resulting catalyst solution performed the cyclization with 35% yield of **3b**.

After having evaluated the reaction conditions, we were interested in the scope of substrates utilizing the most efficient

catalyst system.²² Especially the structural variations of the diyne substrates were of high interest (Chart 1). In all transformations investigated, again the favorable 1:1 substrate ratio of functionalized diyne/phosphaalkyne was applied.

Phosphinines **3a** and **3b** were isolated using the optimized catalytic system either from diynes **1a** or **1b** and **2a** in reliably excellent yields. The presence of the carboxylic ester group in

Chart 1. Screening of Substrate Scope for the Synthesis of Phosphinines (Isolated Yields)

^aMicrowave at 160 °C for 16 h. ^bMixture containing two isomers, the shown product **3ja** and the mono-decarboxylated product **3jb** in a ratio of 4:5; see the Supporting Information (SI). ^cProduct formed only in traces. ^dMixture of two regioisomers in a ratio of 10:3, the major isomer is displayed. ^eMicrowave at 140 °C for 4 h. ^fBoth regioisomers combined. ^gMicrowave at 240 °C for 1 h.

the diyne seemed to have a significant influence on the yields. The mono-*tert*-butyl ester product (**3c**) and malonate methyl ester product (**3e**) were obtained with yields around 30%, while the malonate benzyl ester (**3d**) was furnished with a good yield (63%). Tetracarboxylate-substituted diynes were possible to cyclize with **2a**, affording the six-membered ring-annellated phosphinine **3f** with a 30% yield. Cyclization of 4-diacetylated 1,6-heptadiynes gave phosphinine **3g** with at least 50% yield, while a Meldrum's acid-based diyne (substrate for **3h**) gave no product, presumably due to diyne decomposition at such high reaction temperature. The reaction of terminally monosubstituted diynes (**3i**) gave only low yield (23%).

Unsymmetrical malonate esters with large alkyl groups underwent decarboxylation, resulting in a mixture of both, regioisomers **3j** and decarboxylation product, but no complete selective decarboxylation could be achieved. The cyclization of unsubstituted 1,6-heptadiyne only gave traces of product **3k**. Substrates with combined keto/ester functionality, dipropargyl tosylamide or even diynes containing free hydroxyl groups gave phosphinines **3l**, **3m**, and **3n** in isolated yields of up to 49%. The cyclization of sulfonyl-bridged diynes has been rarely investigated but can be accomplished with at least 42% yield (**3o**).²³ Application of a cyanoalkyne to construct a P,N heterocycle, such as **3p**, was investigated but did not furnish the desired product under these reaction conditions. An ester-bridged diyne was successfully transformed at a lower reaction temperature (140 °C) to prevent decomposition, allowing isolation of **3q** as two regioisomers with a total yield of 61%. To elucidate the scope of the reaction, other phosphalkynes were exemplarily investigated as well. Utilizing *tert*-butylphosphaethyne (**2b**) as substrate with **1b** afforded phosphinine **3r** with a good yield (69%). The assembly of the biaryl product **3s** using the novel sterically demanding 2,4,6-triisopropylphenyl phosphaethyne (**2c**) was achieved with a 50% yield, which required heating at 240 °C for 1 h. Finally, deploying the sterically demanding triphenylmethyl phosphaethyne (**2d**) and **1b** furnished the phosphinine **3t** with a lower yield (23%) due to its bulkiness and multiple possible side reactions, exemplarily demonstrated for ruthenium promoted phosphindole formation by Grützmacher and co-workers.²⁴ The complete intermolecular [2+2+2] cycloaddition between phenylacetylene as terminal alkyne and **2a** was also shortly investigated for our Co^{II} catalyst system, but finally resulted repeatedly in the polymerization of phenylacetylene, presumably due also to the high reaction temperatures applied (210 °C under standard conditions).²⁵

To further develop the applicability of our phosphinine synthesis protocol, we have screened propargylated malonitrile derivatives **4a–e** as cyclization components with phosphalkynes **2a–d**. We were especially interested in the chemoselectivity of the cyclization as both C≡N and C≡P were present in the reaction mixtures. Interestingly, only phosphinine formation was observed, thus establishing a systematic access to a novel class of nitrile-substituted phosphinines enabling further derivatization (Chart 2). Under our established catalytic conditions, the transformations took place with satisfying yields for all investigated nitrile-substituted substrates and phosphalkynes **2a/2b** (yields 30–91%), without the formation of any pyridine products. The product isolation was easily done by chromatography as the formed phosphinines **5a–i** are reasonably stable. Isolated nitrile-substituted phosphinine **5f** emerged to be stable at room temperature on air at least for three months, whereas in

Chart 2. Synthesis of Nitrile-Substituted Phosphinines (Isolated Yields)

^aMicrowave heating for 22 min to 240 °C. ^bMicrowave heating for 2 h to 240 °C.

solution or as an oil, decomposition processes could be observed over time. Cyclization of the 2,4,6-triisopropylphenyl-substituted phosphaethyne (**2c**) with malononitrile **4c** gave only 12% yield in the case of malononitrile **5i** at even 240 °C. This phosphalkyne appears to be of less reactivity and sterically very bulky; therefore, inferior results were obtained. Following the decoration with nitrile and ester groups, the synthesized molecules offer interesting potential for further functionalization.

We were able to obtain single crystals of phosphinine **5c** for structural characterization by X-ray diffraction as shown in Figure 1.²⁶ The structure clearly shows the deviation of the heteroaromatic ring with the phosphorus atom compared to a pure carbocyclic ring system with equidistant space between the ring carbons.

The C–C distances are only varying marginally in the range of 1.383(2)–1.395(2) Å, while the bond length between C–5–

Figure 1. Molecular structure of phosphinine **5c**. Displacement ellipsoids correspond to 30% probability. Hydrogen atoms are omitted for clarity.

P–1 (1.7587(14) Å) is significantly elongated compared to the nonannellated phosphinine (1.739 Å), whereas the bond length of C–1–P–1 (1.7293(15) Å) shows a significantly smaller deviation,²⁷ indicating the delocalized character of the six-membered ring system. Comparing the ³¹P NMR shifts from the furnished annellated phosphinines with the unsubstituted pure phosphinine, most cases show little shielding, ranging from 193.1 ppm (**3jb**) to 198.5 ppm (**3a**), in contrast to 206.5

ppm for C_5H_5P .²⁸ Aryl substituents lead to a slight deshielding of the phosphorus atom for **3s** and **3t**, whereas the electron-withdrawing effects of the carbonyl carbon in meta position to phosphorus are resulting in a significantly higher deshielding with a resonance at 245.0 ppm for the lactone **3q**. The nitrile-bearing phosphinines (**5**) are exhibiting slightly shifted resonances, culminating in a ^{31}P NMR signal of 212.2 ppm for **5i**.

Our synthetic protocol was further exemplarily investigated toward the manufacture of synthetically useful amounts of substituted phosphinine **5f**. Allowing slightly longer reaction times and lower temperatures (technical limitation by the used microwave), **5f** was isolated in a 55% yield on a 10 times larger scale without reduction of yield (Scheme 3).

Scheme 3. Large-Scale Preparation of Phosphinine 5f by [2+2+2] Cycloaddition (10-Fold Upscaling, 1.5 mmol)

To expand the synthetic useability, a functional-group-decorated phosphinine was exemplarily assembled, demonstrating the tolerance of the developed phosphinine formation for alkynes and acetals in the backbone (Scheme 4). The

Scheme 4. Synthesis of Alkyne-Functionalized Phosphinines 7a and 7b

reaction of **6** with **2b** resulted in the formation of two regioisomers **7a/7b** in a 1:1 ratio with a 37% yield. In contrast to Meldum's acid-based cyclic diyne (**3h**, Chart 1), the functionalized acetal in **6** proved to be stable enough for the reaction conditions. The formed phosphinine core of **7a/7b** remained intact upon unsuccessful attempts to transform the remaining phenylacetylene substituent, e.g., by $Cp^*RuCl-(COD)$ -catalyzed [3+2] cycloaddition with phenylazide to substituted triazoles. However, the substrate **7** could always be quantitatively recovered.

Co^{II} complexes are commonly used as precursors in cyclotrimerization reactions; however, an *in situ* reduction with elemental zinc is usually mandatory to furnish the catalytically active Co^I -catalyst. Only for a homo-Diels–Alder reaction, Co^{II} catalysis has been proposed by Binger and Albus.²⁰ Adding ZnI_2 as Lewis acid to $CoI_2(PPh_3)_2$ furnished cationic species like $[CoI(PPh_3)_2]^+[ZnI_3]^-$ or $[Co-(PPh_3)_2]^{2+}[ZnI_3]^{2-}$, acting as catalysts for the cyclization. During our study, we recognized that Co^I and Co^{III} complexes are not performing the described cycloaddition reactions but rather a Co^{II} species. This was independently confirmed by either selective oxidation of Co^I or reduction of Co^{III}

complexes to the formal Co^{II} complexes leading in each case to cyclotrimerization activity, as was experimentally proven (Table 1, entries 21 and 22). A 1:1 stoichiometry of CoX_2 /bisphosphine was essential, as a 1:2 ratio with a second ligand was shutting down the catalytic activity completely.

The compatibility of catalytic systems for the transformation of structural variations of a substrate often reveals interesting information on the catalyst itself. For example, we deployed the catalyst system found for phosphinine formation in the reaction of diynes and nitriles, intending to furnish pyridines in the same manner (Table 2). Results quickly showed no formation of the expected pyridine (**9**), but rather homocyclization of **1b** to **1b_dimer** and presumably tri- and oligomers (Table 2, entry 1). For further detailed investigations, we evaluated dppe as ligand, which was also proved suitable for cyclizations with phosphalkynes (e.g., Table 1, entry 9) and also nitriles.²⁹ Initial experiments using solely CoI_2 and dppe without any additive in tetrahydrofuran (THF) solution gave mostly **1b_dimer** with small amounts of the pyridine **9** (10%, Table 2, entry 2). Changing reaction temperature and reaction time did not give general changes; however, lower temperatures and longer times only led to an increase of the formed trimers and oligomers from **1b**.³⁰ It should be noted that pyridine formation with Co^{II} complexes was observed at a significantly lower temperature compared to phosphinine formation. Evaluating cobalt sources showed that use of $CoCl_2$ and even more $CoBr_2$ gave higher yields of pyridine **9** (12 and 20%, Table 2, entries 3 and 4); therefore, we decided to use $CoBr_2$ also due to its better solubility for further experimentation. It is a current matter of discussion how the oxidation state of the active cobalt catalyst plays a distinguished role in the synthesis of nitrogen heterocycles, as it is illustrated by a very recent literature example.³¹ We followed that impetus by adding elemental zinc to investigate the changes in product contribution. The trend observed by several experiments including an increasing amount of zinc is quite clear (Table 2, entries 5–7). Utilizing 4 equiv of zinc finally furnished nearly exclusively the pyridine product **9** with a 80% yield at 180 °C (Table 2, entry 7). Lowering the reaction temperature to 100 °C and prolonging the reaction time under otherwise identical conditions exclusively yielded **9** with a 50% yield (Table 2, entry 8). Control experiments without cobalt (Table 2, entry 9) or without dppe ligand (Table 2, entry 10) gave either no yield or only carbocyclus **1b_dimer** with a 29% yield like in the latter case. The utilization of a ligand-free low-valent cobalt catalyst system from $CoBr_2$ and elemental zinc for the successful cyclotrimerization of a triyne has been observed before, featuring rather a Co^I species as a catalyst than a Co^0 species.⁸ Initial investigation of different reactivities for Co^0 and ligand-free Co^I species as well as $CpCo(CO)_2$ with diynes in the presence of nitriles and phenylacetylene already showed strong deviations in reactivity depending on the oxidation state and ligand presence.³²

Following our experiments, we proposed the involvement of a Co^{II} -bisphosphine complex as starting species in the catalytic cycle. Interestingly, in most cases, the reactions proceeded rather straightforward at high temperatures to afford phosphinines as sole isolable products after work-up. Clearly and in contrast to the Fe-catalyzed cyclization,^{17a} the choice of ligand for cobalt does play a decisive role in the cycloaddition process. A tentative reaction mechanism is displayed in Chart 3. The first step would be generation of the active catalyst

Table 2. Investigation of the Reaction Conditions for Pyridine Formation

Reaction scheme: Diene **1b** reacts with [Co], ligand, additive **PhCN** (4 equiv.) (**8**) in THF under microwave (MW) conditions at temperature *T* for time *t* to yield product **9** and **1b_dimer** (tri- and oligomers).

#	[Co] (mol %)	ligand (mol %)	additive (mol %)	<i>T</i> (°C)/ <i>t</i> (h)	9 (%) ^a	1b_dimer (%) ^a
1	CoI ₂ (10) ^b	dppbenz (10)		210/4	0	52
2	CoI ₂ (10) ^b	dppe (10)		210/4	10	40
3	CoCl ₂ (10)	dppe (10)		180/2	12	33
4	CoBr ₂ (10)	dppe (10)		180/2	20	46
5	CoBr ₂ (20) ^c	dppe (20)	Zn (10)	180/2	23	28
6	CoBr ₂ (20) ^c	dppe (20)	Zn (40)	180/2	30	10
7	CoBr ₂ (20) ^c	dppe (20)	Zn (80)	180/2	80	2
8	CoBr ₂ (20) ^c	dppe (20)	Zn (80)	100/48 ^d	50	
9	no CoX ₂ ^c	dppe (20)	Zn (80)	180/2		
10	CoBr ₂ (20) ^c		Zn (80)	180/2		29

^aFor the complete screening, see Table S2 in the SI. Yield of isolated product. ^bShort period of sonication before heating. ^cCobalt source, ligand, and zinc were heated to 60 °C for 1 h before the substrates were added. ^dPerformed with conventional heating without microwave.

Chart 3. Proposed Reaction Mechanism for the Co^{II}-Catalyzed Synthesis of Phosphinines from Diynes and Phosphaalkynes (L = dppbenz, X = halide)

species by halide dissociation, leading to cationic complex **A**, which upon coordination of diyne **1a** gave a cationic square-pyramidal diyne complex **B**. Subsequently, formation of a

Co^{IV}-cyclopentadiene complex (**C**) would occur via C–C oxidative coupling.³³ Next, coordination of phosphaalkyne to the Co^{IV} center forms intermediate **D** and a formal [2+2] cycloaddition leads to intermediate **E**, which rearranges to seven-membered intermediate **F**. Finally, reductive elimination gives the intermediate **G** as a catalyst–product complex, from which the phosphinine is released and coordination of another diyne starts the next catalytic cycle.

On the basis of this proposal, we carried out density functional theory computations to explore the potential free energy surface and the computational details are given in the Supporting Information. Geometry optimization was carried out in gas phase at the BP86³⁴ level with the all-electron TZVP³⁵ basis set for nonmetal elements as well as the effective core potential (ECP) of Hay and Wadt with double- ζ valence basis set LANL2DZ³⁶ for the iodine atom. All optimized structures were further characterized at the same level either as energy minimums without imaginary frequencies or transition states with only one imaginary frequency by frequency calculations, which provide zero-point vibrational energies and thermal corrections to enthalpy and Gibbs free energy at 298.15 K under 1 atmosphere. On the basis of the BP86 optimized geometries in gas phase, single-point energies at the M06L³⁷ level with the same basis sets under the consideration of solvation effect of THF as solvent based on solute electron density (SMD)³⁸ were computed. The final Gibbs free energies for discussion were calculated from the M06L single-point energies and the thermal correction to Gibbs free energy from B3P86 at 298 and 443 K. In recent studies of cobalt complexes with different spin states,^{39,40} M06L showed the best agreement with experiment in the thermodynamic parameters. All calculations were carried out using the Gaussian 16 program.⁴¹

The reaction is initiated by halide dissociation from the precursor complex CoX₂(dppbenz), further discussed as CoX₂L. First, we computed the structure and stability of the precursor complexes, CoX₂L. For CoX₂L, the quartet spin state is more stable than the doublet spin state by 3.7, 6.5, and 4.7

kcal/mol for X = Cl, Br, and I, respectively. The dissociation Gibbs free energy [$\text{CoX}_2\text{L} = \text{CoX}^+\text{L} + \text{X}^-$] is 66.4, 76.2, and 58.1 kcal/mol for X = Cl, Br, and I, respectively (Chart 4).

Chart 4. Halide Dissociation from CoX_2L

For the monocationic complex **A**, $[\text{CoXL}]^+$, the doublet spin state is more stable than the quartet spin state by 1.1, 6.5, and 0.7 kcal/mol for X = Cl, Br, and I, respectively, revealing the possible exchange of spin states under thermodynamic equilibrium. The quartet ground state of CoX_2L has tetrahedral Co coordination and the low-lying excited double state has distorted planar Co coordination. On the contrary, the doublet ground state of $[\text{CoXL}]^+$ has nearly triangular planar Co coordination and the low-lying excited quartet state has trigonal pyramidal Co coordination. For X = Cl, the nearly triangular planar doublet ground state is more stable than the nonplanar structure by only 2.4 kcal/mol and such a small energy difference indicates the possibility of flexible coordination of the chloride ligand.

Based on these results, we computed the [2+2+2] cyclization of diynes and phosphalkyne using $[\text{CoCIL}]^+$ (**A_{Cl}**) as a catalyst and dipropargylether (**1a**) and *tert*-butylphosphaethyne (**2b**) as substrates. The coordination of **1a** and the subsequent cyclization have several coordination isomers, C–C coupling transition states, and products, and only the most stable isomers are used for discussion (Figure S1). As shown in the potential Gibbs free energy profiles (Chart 5), the formation of complex **B** [**A_{Cl}** + **1a** = **B**] is exergonic by 2.9 kcal/mol, indicating a very weak coordination. The subsequent oxidative C–C coupling via transition state **TS(B/C)** has a Gibbs free energy barrier of 5.8 kcal/mol and the formation of the cobaltacyclopentadiene intermediate (**C**) is exergonic by 19.4 kcal/mol, indicating a thermodynamically and kinetically very easily accessible step. Due to the very close energy between the doublet and quartet states of the precatalyst and active catalyst, we computed the quartet state of complex **B**, which is more stable than the double state by 4.9 kcal/mol. However, the corresponding quartet transition state **TS(B/C)** is less stable than the doublet state by 10.4 kcal/mol, and quartet intermediate **C** is less stable than the doublet state by 13.4 kcal/mol. Thus, our discussion follows the doublet potential energy surface.

Starting from isomer **C**, **2b** coordination to form intermediate **D** is endergonic by 8.2 kcal/mol, and the corresponding **2b** insertion via transition state **TS(D/E)** has a Gibbs free energy barrier of 3.5 kcal/mol and the formation of the insertion product **E** is exergonic by 25.6 kcal/mol. Starting from intermediate **E**, it is not possible to locate the corresponding seven-membered metallacycle (**F**) for reductive elimination, and attempts to optimize intermediate **F** results in the direct formation of the final reductive eliminated product

Chart 5. Gibbs Free Energy (kcal/mol, 298 K) Profiles at M06L-SCRF/TZVP for Intermediates of the Catalytic Cycle (Q for the Energy of the Corresponding Quartet State)

intermediate (G). The rearrangement from E to G is very exergonic by 76.2 kcal/mol and such huge downhill energy might explain the failure of not being able to locate intermediate F. Finally, release of product (3') and regeneration of active catalyst A is endergonic by 13.5 kcal/mol.

The Gibbs free energy profiles in Chart 5 show that from the monocationic A as active catalyst, TS(B/C) represents the highest point (5.8 kcal/mol) and also the rate-determining step, while the total reaction is very exergonic by 99.5 kcal/mol. In addition, we also computed the TS(B/C) for X = Br and I, and the Gibbs free energy is 4.5 and 10.2 kcal/mol, respectively. All of these show that this reaction should be very easy and fast on the basis of the comparably low barriers and X = I should have lower activity due to the highest barrier. However, these results are not in agreement with the rather intense reaction condition (> 200 °C, 4 h) on the one hand, and the finding that X = I is more active than X = Cl and Br on the other hand. Since CoX₂L is found to have the stability order of CoBr₂L > CoCl₂L > CoI₂L, we assumed that the kinetic activity should be associated with their stability. Therefore, we computed the apparent Gibbs free energy barrier starting from CoX₂L, i.e., the Gibbs free energy difference between CoX₂L + 1a and TS(B/C) + X[−] (Chart 6).

Chart 6. Apparent Barrier (443 K, kcal/mol) of the Oxidative Cyclization Step in Dependence on the Halide Counteranion of the Catalytic Species (X = Halide)

It is found that the apparent Gibbs free energy barrier is 82.1, 85.3, and 75.6 kcal/mol for X = Cl, Br, and I at 443 K, respectively (71.1, 74.2, and 68.3 kcal/mol for X = Cl, Br, and I at 298 K, respectively). Such high apparent barriers might explain the need of a rather high temperature and a long reaction time on the one hand, and the identified lowest apparent barrier for X = I might also show the higher activity compared to X = Cl and Br. It is noted that such high apparent barriers are more qualitative than quantitative since it includes

large electrostatic effects between an anion and a cation apart from coordination and excludes the counterions. Nevertheless, their difference can be used to explain the observed difference in activity.

Cyclizations with terminal diynes, as was observed in our syntheses, can lead to homocyclization products. We have therefore investigated the potential coordination of intermediate C and one C≡C bond of substrate 1a with respect to the formation of homocyclization product 1a_dimer (see Scheme 2). The expected η^2 -coordination of the alkyne C≡C bond to C would lead to a similar structure like intermediate D in the case of the phosphalkynes (Chart 5). However, structure optimization of such an intermediate led directly to the corresponding Co^{II}-coordinated product 1a_dimer, analogous to the formation of an intermediate G for the phosphinine product. This step for cyclization of 1a is even more exergonic than for phosphalkyne 2b (−125.7 vs −113.0 kcal/mol). However, the coordination of substrate to C via the heteroatom lone-pair (in the phosphalkyne) vs the η^2 -C≡C coordination (in the diyne) should be more effective, which might explain the beneficial 1:1 substrate ratio for 1 and 2.⁴²

CONCLUSION

For the first time, we report on the efficient synthesis of functionalized phosphinines by Co^{II}-catalyzed [2+2+2] cycloaddition from phosphalkynes and functionalized diynes, allowing a high atom-economical 1:1 ratio of the substrate and yielding the products with up to 91% yield. The reaction tolerates functional groups such as esters, ketones, lactone, sulfone, and even nitriles to be present in the phosphinine products. The cyclization catalyst consists of a cobalt(II)–bisphosphine complex without a reducing agent, and high reaction temperatures are required for successful and fast catalysis. The preference of Co^{II} catalysis for the cyclization of C≡P vs C≡N bonds with diynes in contrast to lower cobalt oxidation states was also proven by test reactions with benzonitrile and diynes. Theoretical studies on the reaction mechanism suggest a unique Co^{II}/Co^{IV} cycle at work in the catalytic cycle on the doublet potential energy surface. The prospects of the unusual Co^{II} oxidation state catalysis for other substrate combinations and more complex molecules are currently evaluated in our laboratory.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.1c03483>.

Detailed experimental information on the synthesis of starting materials and products, computational details, and spectral data for all synthesized compounds (PDF)

AUTHOR INFORMATION

Corresponding Authors

Haijun Jiao – Leibniz Institute for Catalysis e.V. (LIKAT), D-18069 Rostock, Germany; orcid.org/0000-0002-2947-5937; Email: haijun.jiao@catalysis.de

Marko Hapke – Institute for Catalysis (INCA), Johannes Kepler University Linz (JKU), A-4040 Linz, Austria; Leibniz Institute for Catalysis e.V. (LIKAT), D-18069 Rostock, Germany; orcid.org/0000-0001-7454-9184; Email: marko.hapke@jku.at

Author

Tim Gläsel – Institute for Catalysis (INCA), Johannes Kepler University Linz (JKU), A-4040 Linz, Austria

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acscatal.1c03483>

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding

M.H. thanks the JKU for financial support.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank Fabian Fischer for preparative assistance and are indebted to Kirill Faust and Dr. Anke Spannenberg for the determination of the single-crystal X-ray structure analysis of **5c**.

■ DEDICATION

Dedicated to the memory of the authors' wonderful colleague Prof. Paul Kamer.

■ REFERENCES

- (1) *Transition-Metal-Mediated Aromatic Ring Construction*; Tanaka, K., Ed.; John Wiley & Sons: Hoboken, 2013; pp 1–807.
- (2) Reviews: (a) Heller, B.; Hapke, M. The fascinating construction of pyridine ring systems by transition metal-catalyzed [2+2+2] cycloaddition reactions. *Chem. Soc. Rev.* **2007**, *36*, 1085–1094. (b) Varela, J. A.; Saá, C. Recent Advances in the Synthesis of Pyridines by Transition-Metal-Catalyzed [2+2+2] Cycloaddition. *Synlett* **2008**, 2571–2578. (c) Turek, P.; Kotorá, M. Synthesis of pyridines by [2+2+2]-cyclootrimerization of alkynes with nitriles. *Targets Heterocycl. Syst.* **2009**, *13*, 175–200. (c) Shaaban, M. R.; El-Sayed, R.; Elwahy, A. H. M. Construction of fused heterocycles by metal-mediated [2+2+2] cyclootrimerization of alkynes and/or nitriles. *Tetrahedron* **2011**, *67*, 6095–6130. (d) Hua, R.; Abrenica, M. V. A.; Wang, P. Cycloaddition of Alkynes: Atom-Economic Protocols for Constructing Six-Membered Cycles. *Curr. Org. Chem.* **2011**, *15*, 712–729. (e) Okamoto, S.; Sugiyama, Y. account From the Development of Catalysts for Alkyne and Alkyne–Nitrile [2+2+2] Cycloaddition Reactions to Their Use in Polymerization Reactions. *Synlett* **2013**, *24*, 1044–1060. (f) Tanaka, K. Rhodium-Catalyzed [2+2+2] Cycloaddition for the Synthesis of Substituted Pyridines, Pyridones, and Thiopyrimidines. *Heterocycles* **2012**, *85*, 1017–1043. Rhodium: (g) Thakur, A.; Louie, J. Advances in Nickel-Catalyzed Cycloaddition Reactions To Construct Carbocycles and Heterocycles. *Acc. Chem. Res.* **2015**, *48*, 2354–2365. Nickel: (h) Yamamoto, Y. Recent topics of Cp*RuCl-catalyzed annulation reactions. *Tetrahedron Lett.* **2017**, *58*, 3787–3794. Ruthenium: (i) Kotha, S.; Lahiri, K.; Sreevani, G. Design and Synthesis of Aromatics through [2+2+2] Cyclootrimerization. *Synlett* **2018**, *29*, 2342–2361. (j) Pla-Quintana, A.; Roglans, A. Chiral Induction in [2+2+2] Cycloaddition Reactions. *Asian J. Org. Chem.* **2018**, *7*, 1706–1718. (k) Stará, I. G.; Starý, I. Helically Chiral Aromatics: The Synthesis of Helicenes by [2+2+2] Cycloisomerization of π -Electron Systems. *Acc. Chem. Res.* **2020**, *53*, 144–158.
- (3) Hapke, M.; Weding, N.; Kral, K. Cyclootrimerization Reactions of Alkynes. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Wiley-VCH: Weinheim, 2018; Vol. 1, pp 375–409.
- (4) (a) Yamamoto, K.; Nagae, H.; Tsurugi, H.; Mashima, K. Mechanistic understanding of alkyne cyclootrimerization on mono-nuclear and dinuclear scaffolds: [4+2] cycloaddition of the third alkyne onto metallocyclopentadienes and dimetallocyclopentadienes. *Dalton Trans.* **2016**, *45*, 17072–17081. (b) Roglans, A.; Pla-Quintana, A.; Solà, M. Mechanistic Studies of Transition-Metal-Catalyzed [2+2+2] Cycloaddition Reactions. *Chem. Rev.* **2021**, *121*, 1894–1979. (5) Vollhardt, K. P. C. Cobalt-Mediated [2+2+2]-Cycloadditions: A Maturing Synthetic Strategy. *Angew. Chem., Int. Ed.* **1984**, *23*, 539–556. (6) (a) Jonas, K.; Deffense, E.; Habermann, D. Synthesis and Reactions of η^5 -Cyclopentadienylbis(ethene)cobalt. *Angew. Chem., Int. Ed.* **1983**, *22*, 716–717. (b) Geny, A.; Agenet, N.; Iannazzo, L.; Malacria, M.; Aubert, C.; Gandon, V. Air-Stable {(C₅H₅)Co} Catalysts for [2+2+2] Cycloadditions. *Angew. Chem., Int. Ed.* **2009**, *48*, 1810–1813. (c) Hapke, M.; Weding, N.; Spannenberg, A. Highly Reactive Cyclopentadienylcobalt(I) Olefin Complexes. *Organometallics* **2010**, *29*, 4298–4304. (d) Thiel, I.; Jiao, H.; Spannenberg, A.; Hapke, M. Fine-Tuning the Reactivity and Stability by Systematic Ligand Variations in CpCoI Complexes as Catalysts for [2+2+2] Cycloaddition Reactions. *Chem. - Eur. J.* **2013**, *19*, 2548–2554. (e) Thiel, I.; Spannenberg, A.; Hapke, M. Synthesis of Air-Stable and Recyclable CpCoI-Complexes. *ChemCatChem* **2013**, *5*, 2865–2868. (f) Fischer, F.; Pientka, T.; Jiao, H.; Spannenberg, A.; Hapke, M. CpCo(I) precatalysts for [2 + 2 + 2] cycloaddition reactions: synthesis and reactivity. *Catal. Sci. Technol.* **2020**, *10*, 8005–8014. (7) (a) Review: Gläsel, T.; Hapke, M. Cobalt-Catalyzed [2+2+2] Cycloadditions. In *Cobalt in Catalysis and Synthesis*; Wiley-VCH: Weinheim, 2020; Chapter 9, pp 287–335. Review: Original work: (a) Saino, N.; Kogure, D.; Okamoto, S. Intramolecular Cyclo-trimerization of Triynes Catalyzed by N-Heterocyclic Carbene–CoCl₂/Zn or -FeCl₃/Zn. *Org. Lett.* **2005**, *7*, 3065–3067. (b) Saino, N.; Amemiya, F.; Tanabe, E.; Kase, K.; Okamoto, S. A Highly Practical Instant Catalyst for Cyclootrimerization of Alkynes to Substituted Benzenes. *Org. Lett.* **2006**, *8*, 1439–1442. (c) Sugiyama, Y.; Okamoto, S. Catalytic [2 + 2 + 2] cycloaddition polymerization of diyne–nitrile monomers in the presence of CoCl₂·6H₂O/diphosphine/Zn. *J. Polym. Sci., Part A: Polym. Chem.* **2016**, *54*, 345–351. (8) Jungk, P.; Fischer, F.; Thiel, I.; Hapke, M. CoCl(PPh₃)₃ as Cyclootrimerization Catalyst for Functionalized Triynes under Mild Conditions. *J. Org. Chem.* **2015**, *80*, 9781–9793. (9) Jungk, P.; Fischer, F.; Hapke, M. In Situ-Generated Chiral Co(I)-Catalyst for Asymmetric [2+2+2] Cycloadditions of Triynes. *ACS Catal.* **2016**, *6*, 3025–3029. (10) History and general overview: (a) Märkl, G. Aromatic phosphorus heterocycles—synthesis, structure, and reactivity. *Lect. Heterocycl. Chem.* **1972**, *1*, 69–92. (b) Ashe, A. J., III The Route to Phosphabenzene and Beyond. *Eur. J. Inorg. Chem.* **2016**, *2016*, 572–574. (c) Le Floch, P. Six-membered Rings: Phosphinines. In *Phosphorus-Carbon Heterocyclic Chemistry: The Rise of a New Domain*; Pergamon: Oxford, 2001; pp 485–533. (11) (a) Weemers, J. J. M.; Wiecko, J.; Pidko, E. A.; Weber, M.; Lutz, M.; Müller, C. 2,4,6-Triarylphosphinines versus 2,4,6-Triarylpyridines: An Investigation of the Differences in Reactivity between Structurally Related Aromatic Phosphorus and Nitrogen Heterocycles. *Chem. - Eur. J.* **2013**, *19*, 14458–14469. (b) Carrasco, A. C.; Pidko, E. A.; Masdeu-Bultó, A. M.; Lutz, M.; Spek, A. L.; Vogt, D.; Müller, C. 2-(2'-Pyridyl)-4,6-diphenylphosphinine versus 2-(2'-pyridyl)-4,6-diphenylpyridine: an evaluation of their coordination chemistry towards Rh(I). *New J. Chem.* **2010**, *34*, 1547–1550. (12) (a) Weber, L. Phosphorus Heterocycles: From Laboratory Curiosities to Ligands in Highly Efficient Catalysts. *Angew. Chem., Int. Ed.* **2002**, *41*, 563–572. (b) Müller, C.; Vogt, D. Phosphinines as ligands in homogeneous catalysis: recent developments, concepts and perspectives. *Dalton Trans.* **2007**, 5505–5523. (13) Recent reviews: (a) Müller, C.; Broeckx, L. E. E.; de Krom, I.; Weemers, J. J. M. Developments in the Coordination Chemistry of Phosphinines. *Eur. J. Inorg. Chem.* **2013**, *2013*, 187–202. (b) Coles, N. T.; Sofie Abels, A.; Leitl, J.; Wolf, R.; Grützmacher, H.; Müller, C. Phosphinine-based ligands: Recent developments in coordination chemistry and applications. *Coord. Chem. Rev.* **2021**, *433*, No. 213729. (14) Original work: (a) Müller, C.; Pidko, E. A.; Totev, D.; Lutz, M.; Spek, A. L.; van Santen, R. A.; Vogt, D. Atropoisomeric phosphinines:

- design and synthesis. *Dalton Trans.* **2007**, 5372–5375. (b) Müller, C.; Pidko, E. A.; Lutz, M.; Spek, A. L.; Vogt, D. Diphosphinine derivatives of terpyridine: a new class of neutral p-accepting pnp-pincer ligands. *Chem. - Eur. J.* **2008**, *14*, 8803–8807. (c) Müller, C.; Pidko, E. A.; Staring, A. J. P. M.; Lutz, M.; Spek, A. L.; van Santen, R. A.; Vogt, D. Developing a new class of axial chiral phosphorus ligands: preparation and characterization of enantiopure atropisomeric phosphinines. *Chem. - Eur. J.* **2008**, *14*, 4899–4905. (d) Müller, C.; Freixa, Z.; Lutz, M.; Spek, A. L.; Vogt, D.; van Leeuwen, P. W. N. M. Wide-Bite-Angle Diphosphinines: Design, Synthesis, and Coordination Properties. *Organometallics* **2008**, *27*, 834–838. (e) Newland, R. J.; Smith, A.; Smith, D. M.; Fey, N.; Hanton, M. J.; Mansell, S. M. Accessing Alkyl- and Alkenylcyclopentanes from Cr-Catalyzed Ethylene Oligomerization Using 2-Phosphinophosphinine Ligands. *Organometallics* **2018**, *37*, 1062–1073. (f) Chen, X.; Li, Z.; Grützmacher, H. Multidentate Phosphanyl Phosphinines: Synthesis and Properties. *Chem. - Eur. J.* **2018**, *24*, 8432–8437. (g) Cleaves, P. A.; Mansell, S. M. Unexpected Multiple Coordination Modes in Silyl-Bridged Bis(phosphinine) Complexes. *Organometallics* **2019**, *38*, 1595–1605.
- (15) Selected examples: (a) Mao, Y.; Mathey, F. A Phosphinine 2-Carboxaldehyde. *Org. Lett.* **2012**, *14*, 1162–1163. (b) Kostenko, N.; Ericsson, C.; Engqvist, M.; Gonzalez, S. V.; Bayer, A. Palladium(0)-Catalyzed Cross-Couplings of 2-Bromophosphinine. *Eur. J. Org. Chem.* **2013**, *2013*, 4756–4759. (c) Zagidullin, A. A.; Ganushevich, Y. S.; Kafiyatullina, A. G.; Miluykov, V. A.; Sinyashin, O. G. Reactions of 1-ethyl-1,2-diphosphole with acetylenes. *Russ. Chem. Bull.* **2015**, *64*, 1986–1988. (d) Habicht, M. H.; Wossidlo, F.; Weber, M.; Müller, C. 3-Bromo-2-Pyrron: An Alternative and Convenient Route to Functionalized Phosphinines. *Chem. - Eur. J.* **2016**, *22*, 12877–12883. (e) Polezhaev, A. V.; Beagan, D. M.; Cabelof, A. C.; Chen, C.-H.; Caulton, K. G. A substituent-tolerant synthetic approach to N/P-“loaded” heteroarenes. *Dalton Trans.* **2018**, *47*, 5938–5942. (f) Hansmann, M. M. Synthesis of Azaphosphinines by Directed Inverse-Electron-Demand Hetero-Diels–Alder Reactions with Na-(OCP). *Chem. - Eur. J.* **2018**, *24*, 11573–11577. (g) Habicht, M. H.; Wossidlo, F.; Bens, T.; Pidko, E. A.; Müller, C. 2-(Trimethylsilyl)- λ^3 -Phosphinine: Synthesis, Coordination Chemistry, and Reactivity. *Chem. - Eur. J.* **2018**, *24*, 944–952. (h) Mei, Y.; Wu, D. J.; Borger, J. E.; Grützmacher, H. Simple Synthesis of Functionalized 2-Phosphanaphthalenes. *Angew. Chem., Int. Ed.* **2018**, *57*, 5512–5515. (i) Yang, Z.; Chen, H.; Li, B.; Guo, W.; Jie, K.; Sun, Y.; Jiang, D.-e.; Popovs, I.; Dai, S. Topotactic Synthesis of Phosphabenzene-Functionalized Porous Organic Polymers: Efficient Ligands in CO₂ Conversion. *Angew. Chem., Int. Ed.* **2019**, *58*, 13763–13767. (j) Giese, S.; Klimov, K.; Mikeházi, A.; Kelemen, Z.; Frost, D. S.; Steinhauer, S.; Müller, P.; Nyulászi, L.; Müller, C. 2-(Dimethylamino)phosphinine: A Phosphorus-Containing Aniline Derivative. *Angew. Chem., Int. Ed.* **2021**, *60*, 3581–3586.
- (16) Chen, X.; Alidori, S.; Puschmann, F. F.; Santiso-Quinones, G.; Benkő, Z.; Li, Z.; Becker, G.; Grützmacher, H.-F. Sodium Phosphaethynolate as a Building Block for Heterocycles. *Angew. Chem., Int. Ed.* **2014**, *53*, 1641–1645.
- (17) (a) Nakajima, K.; Takata, S.; Sakata, K.; Nishibayashi, Y. Synthesis of Phosphabenzene by an Iron-Catalyzed [2+2+2] Cycloaddition Reaction of Diynes with Phosphaalkynes. *Angew. Chem., Int. Ed.* **2015**, *54*, 7597–7601. (b) Nakajima, K.; Liang, W.; Nishibayashi, Y. Iron-Catalyzed [2 + 2 + 2] Cycloaddition Reactions of Diynes with Oxyphosphaethynes To Construct 2-Phosphaphenol Derivatives. *Org. Lett.* **2016**, *18*, 5006–5009.
- (18) (a) Hitchcock, P. B.; Maah, M. J.; Nixon, J. F. First example of cyclodimerisation of a phosphaalkyne to a 1,3-diphosphacyclobutadiene. Syntheses of complexes of the type $[M(\eta^5-C_5R_5)\{\eta^4-(Bu^tCP)_2\}]$ R = H or Me; M = Co, Rh, or Ir): crystal and molecular structure of η^5 -pentamethylcyclopentadienyl-2,4-di-*t*-butyl-1,3-diphosphacyclobutadienecobalt(I), $[Co(\eta^5-C_5Me_5)\{\eta^4-(Bu^tCP)_2\}]$. *J. Chem. Soc., Chem. Commun.* **1986**, 737–738. (b) Matos, R. M.; Nixon, J. F.; Okuda, J. Cyclodimerisation and addition reactions of Bu^tCP at a cobalt(I) centre. *Inorg. Chim. Acta* **1994**, *222*, 13–20.
- (19) Hood, D. M.; Johnson, R. A.; Carpenter, A. E.; Younker, J. M.; Vinyard, D. J.; Stanley, G. G. Highly active cationic cobalt(II) hydroformylation catalysts. *Science* **2020**, *367*, 542–548.
- (20) Only single reports describe the use of Co(II) salts without reductant in a related Homo-Diels–Alder reaction as a special variant of the [2+2+2] cycloaddition: Binger, P.; Albus, S. Deltacyclopentadiene formation catalysed by cationic Co(II) complexes. *J. Organomet. Chem.* **1995**, *493*, C6–C8.
- (21) The complete screening table can be found in the SI, pp 21–23.
- (22) By using CoI₂ as cobalt(II) source, sonication was applied to reaction mixture before heating for a short time at room temperature for better solubilization of the commercially available pellets/balls of CoI₂.
- (23) (a) Grigg, R.; Scott, R.; Stevenson, P. Rhodium-catalysed [2 + 2 + 2]-cycloadditions of acetylenes. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1357–1364. (b) Kotha, S.; Sreevani, G. A Short Synthetic Route to Benzosultine-sulfone using Rongalite and [2+2+2]-Cyclo-trimerization. *ChemistrySelect* **2017**, *2*, 10804–10808.
- (24) Cordaro, J. G.; Stein, D.; Grützmacher, H. A synthetic cycle for the ruthenium-promoted formation of 1H-phosphindoles from phosphaalkynes. *J. Am. Chem. Soc.* **2006**, *128*, 14962–14971.
- (25) Control of the reaction progress by ³¹P NMR spectroscopy showed no formation of the expected phosphinine product at all.
- (26) Deposition Number CCDC 2024641 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.
- (27) Jonas, V.; Frenking, G. The molecular structure of phosphabenzene. A theoretically predicted correction to the experimentally determined C–C bond lengths. *Chem. Phys. Lett.* **1993**, *210*, 211–215.
- (28) Elschenbroich, C.; Six, J.; Harms, K.; Frenking, G.; Heydenrych, G. η^1 -Coordination of Phosphinine C₅H₅P and Arsenine C₅H₅As to Ruthenium(II) and Osmium(II). *Eur. J. Inorg. Chem.* **2008**, *2008*, 3303–3309.
- (29) As examples for nitriles, see: (a) Chang, H.-T.; Jeganmohan, M.; Cheng, C.-H. Cobalt-Catalyzed Intramolecular [2+2+2] Cyclootrimerization of Nitrilediynes: An Efficient Route to Tetra- and Pentacyclic Pyridine Derivatives. *Org. Lett.* **2007**, *9*, 505–508. (b) Sugiyama, Y.; Okamoto, S. Regioselective Syntheses of Substituted Pyridines and 2,2'-Bipyridines by Cobalt-Catalyzed [2+2+2] Cycloaddition of α,ω -Diynes with Nitriles. *Synthesis* **2011**, 2247–2254.
- (30) For the complete screening table see the SI, pp 42–43.
- (31) Wang, C.-S.; Sun, Q.; García, F.; Wang, C.; Yoshikai, N. Robust Cobalt Catalyst for Nitrile/Alkyne [2+2+2] Cycloaddition: Synthesis of Polyarylpyridines and Their Mechanochemical Cyclodehydrogenation to Nitrogen-Containing Polyaromatics. *Angew. Chem., Int. Ed.* **2021**, *60*, 9627–9634.
- (32) Chiusoli, G. P.; Pallini, L.; Terenghi, G. Different chemoselectivities in cobalt(0)- and cobalt(I)-catalyzed cyclocotrimerization of C $\equiv$ C and C $\equiv$ N triple bonds. *Transition Met. Chem.* **1984**, *9*, 360–362.
- (33) The formation of a CpCo(V) species has been proposed singularly in the cyclootrimerization towards pyridines as a cobalt(V) carbene: Miclo, Y.; Garcia, P.; Evanno, Y.; George, P.; Sevrin, M.; Malacria, M.; Gandon, V.; Aubert, C. Synthesis of Orthogonally Protected Angular Nitrogen Polyheterocycles via CpCo-Catalyzed Pyridine Formation. *Synlett* **2010**, 2314–2318.
- (34) Perdew, J. P. Density-functional approximation for the correlation energy of the inhomogeneous electron gas. *Phys. Rev. B* **1986**, *33*, 8822–8824.
- (35) Schäfer, A.; Huber, C.; Ahlrichs, R. Fully optimized contracted Gaussian basis sets of triple zeta valence quality for atoms Li to Kr. *J. Chem. Phys.* **1994**, *100*, 5829–5835.
- (36) Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. *J. Chem. Phys.* **1985**, *82*, 299–310.

(37) Zhao, Y.; Truhlar, D. G. A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions. *J. Chem. Phys.* **2006**, *125*, No. 194101.

(38) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *J. Phys. Chem. B.* **2009**, *113*, 6378–6396.

(39) Liu, J.; Wei, Z.; Jiao, H. Catalytic Activity of Aliphatic PNP Ligated $\text{Co}^{\text{III/I}}$ Amine and Amido Complexes in Hydrogenation Reaction—Structure, Stability and Substrate dependence. *ACS Catal.* **2021**, *11*, 4593–4605.

(40) Wei, Z.; Tian, X.; Bender, M.; Beller, M.; Jiao, H. Mechanisms of Co^{II} and Acid Jointly Catalyzed Domino Conversion of CO_2 , H_2 and CH_3OH to Dialkoxymethane—A DFT Study. *ACS Catal.* **2021**, *11*, 6908–6919.

(41) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams, J.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. et al. *Gaussian 16*, revision A.03; Gaussian Inc.: Wallingford, CT, 2016.

(42) The overall formation of carbocycle **1a_dimer** is exergonic by 125.6 kcal/mol, even significantly more exothermic than that of the formation of phosphinine **3a'** (99.5 kcal/mol), compare Chart 5.