Synthesis and Multiple Subsequent Reactivity of Anionic cyclo-E₃ Ligand Complexes (E = P, As)

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Dedicated to Professor Matthias Driess on the occasion of his 60th birthday

Abstract: A synthetic pathway for the synthesis of novel anionic sandwich complexes with a cyclo-E₃ (E = P, As) ligand as an end deck was developed giving [Cp''Co(n₃-E₃)]⁻ (Cp'' = 1,2,4-tri-tert-butylcyclopentadienyl, E = P (5)), As (6)) in good yields suitable for further reactivity studies. In the reaction with the chlorophosphanes R₂PCL (R = Ph, Cy, 'Bu), neutral complexes with a substituted cyclo-E₃P (E = P, As) ligand in [Cp''Co(n₃-E₃-E₃P)] (E = P (7a-c), As (9a-c)) were obtained. These compounds can be partially or completely converted into complexes with a cyclo-E₃ (E = P, As) ligand with an exocyclic [PR₃] unit in [Cp''Co(n₃:E₃-E₃P)][E = P (8a-c), As (10a-c)]. Additionally, the insertion of the chlorosilylene [LSCI] (L = (Bu₃)2SiPh) into the cyclo-E₃ ligand of [5] and [6] was achieved and the novel heteroatomic complexes [Cp''Co(n₃-E₃E₃SiL)] (E = P (11), As (12)) could be isolated. The reaction pathway was elucidated by DFT calculations.

Introduction

During the last decades, the conversion of white phosphorus and yellow arsenic in the coordination sphere of transition metal complexes has been widely investigated yielding a plethora of polyoxogen (Eₙ) complexes. While neutral complexes with cyclic Eₙ ligands are well known, anionic derivatives are rather limited for E = P, but completely unknown for E = As. Two principal routes for the synthesis of the P derivatives have been reported. One is the reduction of a suitable halogen-containing precursor in the presence of white phosphorus. Cummins et al. reported the first derivative [Na(thf)][(DippO₂)₂Nb(n₃-P₃)] (A, Scheme 1) obtained that way in 2009. [2] [K(18-c-6)][Cp''Fe(n₃-P₃)] (B, Scheme 1) reported by Wolf et al. was also obtained by the reduction of the related bromo dimer [(Cp''Fe)(μ₃-n₃-B₃)] in the presence of P₃. [3] A similar pathway is the reaction of an isolated anionic precursor with P₄, for example, in the reaction of the cobaltate [K(18-c-6)(thf)]₅[[PHDI]Co(n₃-1,5-cod)] with P₄ yielding [K(18-c-6)][PHDI]Co(n₃-P₄) (C, Scheme 1). [4] Another route is the abstraction of P atoms from neutral precursors, for example, by the reaction of [(PHDI)Co(n₃-P₃)] (D) with cyanides under formation of [K(18-c-6)][(PHDI)Co(CN)(n₃-P₃)] (E, Scheme 1). [4] A drawback of the mentioned procedures is the partially low yield synthesis and that they can hardly be scaled up in most of the cases. In contrast, we recently showed that one P atom of [M(n₃-P₃)] (M = Cp''Co (F), Cp''Ta(CO)₅ (G): Cp'' = 1,2,4-tri-tert-butylcyclopentadienyl) can be abstracted by NaNHC to yield [[(NaNHC)₃]Co(CP''(n₃-P₃))] (H, Scheme 1) and [[(NaNHC)₃]Co(CP''(n₃-P₃))] (I, Scheme 1) in very good yields. [5, 6] However, the laborious synthesis of the starting materials F and G represents a slight drawback in this approach. The anion [Cp''Co(n₃-P₃)] was also observed by the reduction of F with alkali metals in the presence of crown ether or as a side product in the functionalization of F with main group nuclophiles. Figueroa et al. could show that a cyclo-P₃ ligand in molybdenum complexes, for example, in [(CNA₄D₄m)Mo₂(CO)(n₃-P₃)] (J, stays intact upon reduction under formation of the dianionic complex [K₂(db-18-c-6)][(CNA₄D₄m)Mo(CO)(n₃-P₃)] (K, Scheme 1). [7] The subse-
quent chemistry of these anionic complexes is only barely explored. Compound C can be quenched with chlorophosphines to form neutral complexes with a disubstituted five-membered P,R ligand.[14] Compound A can be reacted with electrophiles, for example, AsCl3, to give the landmark access to AsP,[3] or with the neutral phosphinidenep Cp*P[W(CO)3] to form the anionic complex [Na[18-c-6](thf)]-[DippO]NB(m,η2-C5H4-P=Cp)(W(CO)3)][15,16]. The first reaction can be considered as a transfer of a cyclo-P3 unit to an As atom after reduction of AsCl3. There is only one other example reported where a complete homoatomic cyclo-C5 ligand is transferred, namely a cyclo-C5 ligand from [Cp*Fe(m,η4-E5)] (E = P, As) to Ru and Os in the reaction with [Cp*MP(CO)3][M = Ru, Os] yielding [Cp*M(m,η4-E5)] (M = Ru, Os; E = P, As).[10] Moreover, Di Vaira et al. were able to transfer cyclo-C5S (E = P, As) units from cobalt to rhodium centers.[11] A subsequent investigation of the reactivity of the cyclo-P3 complexes E, H and I has not been reported yet due to their limited accessibility. The anion H containing a cyclo-P3 ligand might be an interesting starting material for quenching reactions with main group electrophiles. Although the yield of 79% is quite high, the laborious and resource-consuming synthesis of P is a limiting factor.[5] Additionally, the salt elimination in reactions with, for example, chlorophosphines, is less favored if the [1H(NHC)P]+ cation is present compared to alkali metal ions. Therefore, the question arises as to whether it is possible to synthesize [Cp*Co(η1-P3)] in a more efficient way and with an alkali metal as counterion. Moreover, the access to compounds of the heavier homologue arsenic to receive first anionic cyclo-As3 ligand is still a challenge. Thus, we took pains to synthesize the As analogue complex of A via the route described by Cummins et al. for the P derivative,[2] however, without success. In search of different approaches, the idea came up to combine the features of transfer reactions and reductive reaction conditions. Hence, [Cp*Ni(η3-E3)] (E = P (1), As (2)) seems to be a suitable starting material including a cyclo-η3 ligand which is accessible in gram scale.[12,13] [Cp*Ni(η4-E4)] (E = P, As) can be reacted with the cobalt toluene complex [Cp*Co(μ,η1-C5H5)] to yield the heterobimetallic triple-decker complexes [Cp*Co]-[Cp*Ni](μ,η1-C5H5)] (E = P (3), As (4)) in gram scale.[12,14] The investigation of their redox chemistry reveals an interesting fact, namely that in the monocations [(Cp*Co)-Cp*Ni](μ,η1-C5H5)] (E = P, As; [FAI] = FAI[OC6F5Co(C5F5)3]) the [Cp*M] fragments are not strongly bound to the E3 ligand and a rearrangement process takes place under formation of the homometallic species [(Cp*Co)(μ,η4-E4)][FAI] and [(Cp*Ni)(μ,η4-E4)][FAI].[15] On the other hand, the reduction of 3 and 4 yields the monoanionic triple-decker complexes [K(thf)]-[(Cp*Co)(Cp*Ni)(μ,η4-E4)] (E = P, As), which retain their heterobimetallic character. Herein we report the reaction of 3 and 4 with an excess of potassium leading to [Cp*Co(Cp*Ni)(η4-E4)] (E = P (5), As (6)). In high yields, the latter being the first anionic cyclo-As3 ligand complex, and their reactivity towards chlorophosphines and chlorosilylenes to obtain first cyclo-E3 heterolele ligands with P/As/Si sequences.

Results and Discussion

The reduction of 3 and 4 with an excess of elemental potassium (Scheme 2) leads to [K(thf)]-[(Cp*Co)(η3-E3)] (E = P, n = 0.7 (5); E = As, n = 0.8 (6)), KcP” and a black precipitate.[15] After workup, a 1:0.8 mixture of KCp” and [S] and a 1:0.7 mixture of KCp” and [6] can be obtained as a red and a green solid in yields of 69 and 63%, respectively. The content of thf was determined by 1H NMR spectroscopy. Addition of 18-c-6 and recrystallization from a concentrated thf solution of [S]/[6] layered with n-hexane at room temperature yields large colorless single crystals of [K(18-c-6)][Cp*Co(Cp*Ni)(η4-E4)] (E = P (5), As (6)), respectively, which can be separated under the microscope giving analytically pure [K(18-c-6)][S] and [K(18-c-6)][6] in isolated yields of 23 and 15%, respectively. Since the anion [Cp*Co(η3-P3)]- was already reported with [1H(NHC)P]+ as a counterion,[15] only the structure of the novel arsenic derivative [6] will be discussed in the following. The structure in the solid state (Figure 1) reveals a sandwich complex with a cyclo-As3 ligand as an end deck. The As–As distances are 2.3876(4) and 2.3969(4) Å and in the range between single and double bonds[16,17] which is in agreement with the calculated Wiberg Bond Indices (WBIs) of 1.07 for all As–As bonds. The novel anion [6] is isoelectronic to the neutral nickel complex [Cp6Ni(η3-As3)] (Cp8 = C5H5)[Pr6H3][18] Cp6[12] and represents the first anionic complex with a cyclo-As3 ligand as end deck. As already mentioned, a few subsequent reactions of anionic complexes with a cyclo-E3 (E = P, As) ligand were only investigated for the phosphorus niobium complex A reported by Cummins.[12,19]

Scheme 2. Reaction of 1/2 with [(Cp*Co)(μ,η1-C5H5)] to the heterobimetallic triple-decker complexes 3/4; reduction to [K(thf)]-[S]/[K(thf)]-[6] and complexation with 18-c-6 (Cp* = 1,2,4-tri tert-butylcyclopentadienyl).
Due to the much higher yields of [K(thf)0.7][5] and [K(thf)0.8][6] and the fact that KCp\(^{\text{H}}\) does not disturb much the reaction with chlorine-containing electrophiles, mixtures of [K(thf)0.7][5] and [K(thf)0.8][6] with KCp\(^{\text{H}}\), respectively, were used for the subsequent reactivity investigations.

Firstly, the reactivity of [K(thf)0.7][5] towards the chlorophosphines R\(_2\)PCI (R = Ph, Cy, iBu) was studied. The reaction of [K(thf)0.7][5] with an excess of \(\text{R}_2\)PCI in thf at \(-80^\circ\text{C}\) leads to an immediate color change from dark red to brown in all cases. After warming to room temperature, the solvent was removed in vacuo and the residue extracted with \(n\)-pentane. After filtration from a large amount of white solid (KCP\(^{\text{H}}\) + KC), the solvent was removed in vacuo and NMR spectra in \(\text{D}_2\)toluene were recorded. The \(^{31}\text{P}[\text{H}]\) NMR spectra each reveal the complete conversion of [5] and the formation of two types of complexes [\(\text{CP}^{\text{H}}\)\(\text{Co}(\eta^1-\text{P}_2\text{R}_3)\)] (R = Ph (7a), Cy (7b), iBu (7c)) and [\(\text{CP}^{\text{H}}\)\(\text{Co}(\eta^1-\text{P}_1\text{P}_2\text{R}_3)\)] (R = Ph (8a), Cy (8b), iBu (8c)) in ratios of 1:0.2 (7a:8a), 1:0.01 (7b:8b) and 1:0.01 (7c:8c), respectively (Scheme 3). For R = Ph, instead of unused Ph\(_2\)PCI, small amounts of Ph\(_2\)P, Ph\(_3\)P, and (PhP)\(_3\) can be detected, while for R = Cy, iBu unused R\(_3\)PCI can be detected in the \(^{31}\text{P}[\text{H}]\) NMR spectra. For R = iBu, Cy, a column-chromatographic workup was conducted. For R = iBu, clean 7c was the only obtained fraction, while for R = Cy, a first weak red fraction of 8b and a second brown fraction of 7b could be separated. Finally, single crystals of 7b, 7c and 8a (details cf. SI) could be obtained.

The molecular structure of 7b/7c (Figure 2) reveals a neutral complex with a disubstituted cyclo-P\(_2\)R\(_3\) ligand, while P1 is bent out of the plane (P2−P3−P4) by 2.1583(5) Å (7b), 2.1810(8) Å (7c) and P1−P−P distances (P1−P2 2.1545(5) Å (7b), 2.1756(8) Å (7c)) and two slightly longer P−P distances within the P\(_3\) unit coordinated to cobalt (P2−P3 2.2011(6) Å (7b), 2.2023(8) Å (7c) and P3−P4 2.2029(6) Å (7b), 2.2017(8) Å (7c). All P−P bonds are in the range of single bonds,\(^{17}\) underlined by WBIs in the range of 0.99 and 1.04. The molecular structure of 8a in the solid state reveals a cyclic P\(_2\)ligand with an exocyclic [PPh\(_3\)] unit which is \(\eta^1\) coordinated to the Co atom together with one side of the cyclo-P\(_2\) unit in \(\eta^2\) fashion, respectively. The phosphorus ligand shows two shorter P−P distances (P1−P2 2.1777(15) Å, P3−P4 2.1316(17) Å) and two longer ones (P2−P3 2.2309(15) Å, P2−P4 2.2372(15) Å). The P3−P4 distance lies between a single and a double bond, indicated by a WBI of 1.14, while all other P−P distances are in the range of single bonds (WBIs of 0.95–0.96).

Moreover, the reactivity of the arsenic derivative [6] towards chlorophosphines was investigated. The reaction of [K(thf)0.8][6] with R\(_3\)PCI (Ph, Cy, iBu) in thf at \(-80^\circ\text{C}\) leads to an immediate color change from dark green to brown. After workup, NMR spectra in \(\text{D}_2\)toluene of these reactions were recorded. The reaction with Ph\(_2\)PCI is again less selective. The \(^{31}\text{P}[\text{H}]\) NMR spectrum shows the formation of [\(\text{CP}^{\text{H}}\)\(\text{Co}(\eta^1\text{AsPPh}_3)\)] (9a), [\(\text{CP}^{\text{H}}\)\(\text{Co}(\eta^1\text{AsPPh}_3)\)] (10a) in a ratio of

**Scheme 3.** Reaction of [K(thf)0.7][5] and [K(thf)0.8][6] with R\(_3\)PCI (R = Ph, Cy, iBu) and [(Bu\(_3\)N)\(_2\)]PCI. The yields correspond to the isolated crystalline material.
1:3.5 beside Ph₃P, Ph₅P₂ and (PhP)₃, while the ¹H NMR spectrum additionally shows signals for \([\text{Cp}^{”}\text{Co}(\mu\eta^1-\eta^1-\text{As}_3\text{Cl}_2)]\). For \(R = \text{Cy}\), only the two products \([\text{Cp}^{”}\text{Co}(\eta^1-\eta^1-\text{As}_3\text{PCy}_3)]\) (9b) and \([\text{Cp}^{”}\text{Co}(\eta^1-\eta^1-\text{As}_3\text{PCy}_3)]\) (10b) are detected in the \(^{31}\text{P}[[\text{H}]\) NMR spectrum in a ratio of 8.5:1. For \(R = \text{Bu}\) \([\text{Cp}^{”}\text{Co}(\eta^1-\eta^1-\text{As}_3\text{PBU}_3)]\), (9c) can be detected as the major product beside traces (1:0.01) of \([\text{Cp}^{”}\text{Co}(\eta^1-\eta^1-\text{As}_3\text{PBU}_3)]\) (10c).

The reaction mixtures were purified by column chromatography yielding analytically clean 9b, 9c and 10a, with 10b, however, being contaminated with 9b. During this workup, no fraction of 9a and 10c, respectively, could be obtained, probably due to a complete conversion of 9a to 10a caused by the reaction time and by chromatographic workup. Moreover, 10c was only present in very small amounts in the reaction mixture.

After crystallization, 9b could be isolated in 7%, 9c in 6%, 10a in 44% and 10b in 12% (mixture of 9b:10b 1:3, cf. Scheme 3) yields. The molecular structures of 9b and 9c in the solid state (Figure 2) each reveal unprecedented four-membered cycles consisting of three As atoms and one P atom, with all As atoms being coordinated to Co1. The PR₃ unit deviates from the plane (As₁–A₂–As₃) by 33° (9b) and 32° (9c). The P–As bonds (P₁–As₁ 2.2967(5) Å (9b), 2.3052(8) Å (9c) and P₁–As₃ 2.3002(5) Å (9b), 2.3113(7) Å (9e)) are in the range of single bonds, indicated by WBIs of 0.95 (9b) and 0.94 (9c). The As–As bonds (As₁–As₂ 2.4381(3) Å (9b), 2.4404(4) Å (9c) and As₂–As₃ 2.4264(3) Å (9b), 2.4196(5) Å (9c)) are also in the range of slightly shortened single bonds, underlined by WBIs of 1.01/1.02 (9b) and 1.01/1.02 (9c). The molecular structure of 10a/10b reveals a cyclo-As₃ ligand with an exocyclic [PR₃] unit. One side of the As₁ unit coordinates in an η¹ fashion and the [PR₃] unit in an η¹ fashion to the cobalt atom. The P₁–As₁ distance is 2.3111(8) Å (10a) and 2.2991(11) Å (10b) (WBI of 0.94 and 0.97), respectively. The As₃ unit shows two As–As distances in the range of single bonds (As₁–As₂ 2.4699(5) Å (10a), 2.4731(6) Å (10b), As₁–As₃ 2.4644(5) Å (10a), 2.4717(7) Å (10b); WBIs of 0.94/0.93 (10a) and 0.94/0.94 (10b)).

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Figure 2. Molecular structure of 7b, 7c, 8a, 9b, 9c, 10a and 10b in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50% probability level.
sample at 60°C, 7b can be successively transferred into 8b, for example, ratios of 32:1 after one hour and of 0.75:1 after 86 hours were observed (Figure 3). Directly after the reaction of [5] with Bu₃P, the presence of 7e and 8c in a ratio of 86:1 is observed in the 3¹P[¹H] NMR spectrum. After four days, the ratio changed to 24:1 and after nine days to 22:1. Tempering of the sample at 60°C leads after one hour to a ratio of 17:1, which does not change further upon longer thermolysis times (after 14 hours still the same ratio). The behavior of the reaction of the arsenic compound [6] is quite similar (cf. SI).

In order to elucidate the reaction pathway and clarify the outcome of the reactions that are so strongly dependent on the substituents on the chlorophosphanes, DFT calculations were performed for the model reaction of [CP₄Co(η⁴−E₂)]⁻ (E = P, As; E-1) with the phosphenium ion PMe₃⁺ (E-2). The optimization of the starting material, products, intermediates and transition states was performed at the BP86/def2-SVP level of theory and the energies were calculated at the B3LYP/def2-TZVP level of theory including solvent effects and dispersion correction D3BJ.[50] The complete pathway was calculated only for the methyl-substituted phosphonium ion (PMe₃⁻), while for the other substituents (Ph, Cy, Bu) only the products [CP₄Co(η⁴−E₂PR₃)]⁻ (P-1), [CP₄Co(η⁴−E₂-PR₃)] (P-2) and the highest transition state TS-2 between P-1 and P-2 were optimized. A combined summary of the essential steps is depicted in Figure 4 (for the phosphorus species; for the arsenic species cf. SI). The first step displays the addition of the [PMe₃⁻] unit at the cyclo-E₂ ligand in E-1 leading to the intermediate Int-1. Over the transition state TS-1 with a barrier of 33 (P) and 35 kJ mol⁻¹ (As), respectively, the products P-1 are formed. The energy of P-1 was set arbitrarily to 0. It has to be noted that for E = P, an additional intermediate and transition state could be modeled, representing a rotation of the [PMe₃⁻] unit along the P-P bond before the optimization leads to P-1 (cf. SI). The [PMe₃⁻] unit migrates to one E atom over the transition state TS-2, which is 126 (P) and 138 kJ mol⁻¹ (As), respectively, higher in energy and the products P-2 are formed. Again, for E = P, further intermediates and transition states could be modeled which are all lower in energy than TS-2 and mainly represent rotation processes of the [PMe₃⁻] unit (cf. SI). Compared to P-1, the final products P-2 are lower in energy by 28 and 39 kJ mol⁻¹ for E = P and As, respectively, and the conversion of P-1 into P-2 is exothermic overall. For the other substituents on the electrophile (Ph, Cy, Bu), the formation of all six products P-2 is exothermic related to their respective P-1. The cyclohexyl-substituted species are less favored (−26 (P) and −30 kJ mol⁻¹ (As)), followed by the tert-butyl-substituted ones (−33 (P) and −35 kJ mol⁻¹ (As)) and the phenyl-substituted ones which are the most favored ones (−36 (P) and −47 kJ mol⁻¹ (As)).[51] Nevertheless, the highest transition state (TS-2) between P-1 and P-2 determines how easy the conversion of P-1 into P-2 can take place. The highest energy shows the tert-butyl derivative (170 (P) and 176 kJ mol⁻¹ (As)), followed by the cyclohexyl derivative (141 (P) and 145 kJ mol⁻¹ (As)) while the phenyl-substituted derivative shows the lowest activation barrier (126 (P) and 128 kJ mol⁻¹ (As)). The results are in good agreement with the experimental observations from the reactions of the Cₚ‴ derivatives [5] and [6] with R₃P, (Ph, Cy, Bu). The conversion of the phenyl-substituted species 7a and 9a into 8a and 10a proceeds much faster at room temperature and for short thermolysis times and only 8a and 10a could be isolated finally. The cyclohexyl derivatives 7b and 9b can be partially converted at room temperature only after a long time or after long thermolysis times into 8b and 10b, while no full conversion was observed within the investigated time range. For the tert-butyl derivatives 7c and 9c, only traces of 8c and 10c can be detected after a long time at room temperature or after thermolysis.

An insertion of a chlorophosphane or an in situ generated phosphonium ion starting from a chlorophosphane into a cyclo-P₃ ligand was only reported for the reaction of the anionic cobalt complex [K(18-c-6)]{[(PPhDI)Co(η⁴-P₃)]} yield-
ing \( ([\text{PHDI}]\text{Co}(\eta^1-\text{P},\text{R},\text{R}))\)\(^{[4,22]} \) reported by Wolf et al. and by ourselves for the reaction with the neutral nickel complex \([\text{Cp}^\text{a}^-\text{Ni}(\eta^1-\text{P},\text{R},\text{R})]\) yielding cationic species of the type \([\text{Cp}^\text{a}^-\text{Ni}(\eta^1-\text{P},\text{R},\text{R})]\)\(^{[-23]} \). The latter complexes are isoelectronic and isostructural to 7a–c but represent the final products of their reactions and no further rearrangements to species along the lines of 8a–c were found, which are formed after an unprecedented ring contraction reaction. A similar structural motif of the latter complexes was already reported for the cationic rhodium complex \([\text{[triphos}]\text{Rh}(\eta^1-\text{P},\text{R},\text{R})]\)\(^{[1]} \) with overall P–P distances closely related to those observed for 8a\(^{[24]} \). Note that, for \([\text{Cp}^\text{a}^-\text{Fe}(\eta^1-\text{P},\text{GeL},\text{L})]\) (L = (BuN)\(_2\)CPh), a migration of one exocyclic germyleme fragment towards the \text{Cp}^\text{a}^-\text{Fe} unit was observed.\(^{[25]} \)

The mixed phosphorus and arsenic complexes 9a–c and 10a–c expand the series of rare examples of complexes comprising mixed polypnictogen ligands, namely, EP\(_3\) (E = As, Sb)\(^{[23]} \) \([\text{Cp}^\text{a}^-\text{Co}((\eta^1-\text{E},\text{AsL},\text{L})\text{W}(\text{CO})_8])\]\(^{[9]} \) \([\text{Cp}^\text{a}^-\text{Fe}(\mu_3,\eta^1-\text{P},\text{AsL},\text{L})]\) \((x + y = 4)\), \([\text{Cp}^\text{a}^-\text{Fe}(\eta^1-\text{P},\text{AsL},\text{L})]\) \((x + y = 5)\)\(^{[20]} \) and \([\text{Cp}^\text{a}^-\text{Mo}(\text{CO})_8(\mu_3,\eta^1-\text{E},\text{EE}))\] \((\text{EE}’ = \text{P, As, Sb, Bi})\)\(^{[21]} \) were reported.

In order to investigate if this reactivity pattern of \([5]\) and \([6]\) can be extended to other halogen-containing species, the reaction of \([\text{K(thf)}_3][5]\) and \([\text{K(thf)}_3][6]\) with the chlorosilylene \([\text{LSiCl}]\) \((\text{L} = (\text{BuN})_2\text{CPh})\) (Scheme 3) was studied. The reactions were conducted at \(-80^\circ\text{C}\) in thf, while a color change was first observed upon warming to room temperature form dark red to brown and from dark green to brown-green, respectively. After workup, \([\text{Cp}^\text{a}^-\text{Co}(\eta^1-\text{E},\text{SiL},\text{L})]\) \((\text{L} = (\text{BuN})_2\text{CPh}, \text{E} = \text{P})\) (11), As (12) could be isolated in crystalline yields of 29 and 18%, respectively. Crystals suitable for X-ray single crystal structure analysis could be obtained from a concentrated solution of 11 in \(\alpha\)-difluorobenzene layered with n-pentane at \(-30^\circ\text{C}\) and from a concentrated solution of 12 in a mixture of n-pentane and toluene at \(-30^\circ\text{C}\). The molecular structures in the solid state (Figure 5) reveal that the silylene has been inserted into the cyclo-E\(_4\) ligand and novel four-membered rings consisting of three pnictogen atoms and one Si atom are formed. All three E atoms are coordinated to Co1, while Si1 is bent out of the plane by 30\(^\circ\) (11/12). The Si1–E1 distance amounts to

Figure 4. Calculated reaction mechanism for the reaction of \(\text{Cp}^\text{a}^-\text{Co}E^-\) (E=1) with Me,\(\text{P}^+\) (E=2) at the B3LYP-D3B/[\text{def2-TZVP}] level of theory (for details see SI). Solvent effects were included via the polarizable continuum model (CPM). Energy values are referenced to P-1. Additional intermediates and transition states are omitted for clarity (cf. SI). The relative energy of the transition states for \([\text{Cp}^\text{a}^-\text{P},\text{R},\text{E}](\text{R} = \text{Bu}, \text{Cy}, \text{Ph}; \text{TS}-2)\) and the final products P-2 are also given.

Figure 5. Molecular structure of 11 and 12 in the solid state.\(^{[21]} \) Hydrogen atoms and solvent molecules are omitted for clarity. Thermal ellipsoids are drawn with 50% probability level.
2.1682(17) Å (11) and 2.2853(14) Å (12), Si1–E3 distance to 2.1696(18) Å (11) and 2.2775(14) Å (12), the E1–E2 bond to 2.2283(19) Å (11) and 2.4417(8) Å (12), and the E2–E3 bond to 2.0323(18) Å (11) and 2.4243(8) Å (12). All mentioned distances are in the range between single and double bonds, confirmed by the calculated WBIs in the range of 1.01 and 1.08 (11) and 0.98 and 1.09 (12), respectively. Compound 11 and 12 represent the first complexes including a four-membered cycle consisting of three pnictogen atoms and one silicon atom and add to the row of pnictogen silicon heterocycles, for example, [(LSi)2P]2[29] reported by the groups of H. W. Roessky and Driess in 2011 and its heavier analogue [(LSi)2As] reported 2016 by our group.[29] The latter synthetic approach gave also access to the inorganic benzene derivatives [(LSi)2E] (E = P, As).[29] P. Roessky et al. recently showed that the chlorosilylene [LiSiCl] (L = (BuN)2CPh) can be used for a substitution of P atom in [Cp*Fe{η2-P}2] to form [Cp*Fe{η2-P2}].[30] However, compound 12 represents the first example where an As3Si heterocycle acts as a ligand for a transition metal complex.

The 31P{1H} NMR of 11 in [D6]thf shows a doublet of doublets centered at δ = −66.6 ppm and two overlapping doublets centered at δ = −75.0 ppm with an integral ratio of 1:1:1 with JPP coupling constants of 213 and 262 Hz. The signal at −75.0 ppm additionally reveals silicon satellites with a JPS coupling constant of 109 Hz. The related 35Si{1H} NMR spectrum shows a triplet of doublet centered at δ = −24.6 ppm with a JPS coupling constant of 109 Hz and a JPP coupling constant of 12 Hz. The 29Si{1H} NMR spectrum of 12 in CD2Cl2 shows one singlet centered at δ = −51.6 ppm.

As a proof of principle and to check whether the complexes with a cyclo-E, ligand and the exocyclic [PR3] unit can be further functionalized, [Cp′Co{η2-P}3As(PPh3)](10a) was reacted with the in situ generated phosphonium ion PPh3+ [halide abstraction from PCl3 with Ti[TEF], (TEF) = [Al(OCCF3)3]], cf. Eq. (1)). The 31P{1H} NMR spectrum of the reaction solution in CD2Cl2 shows the formation of [Cp′Co{η2-P}3As(PPh3)][TEF] (13), beside starting material and small amounts of decomposition products. After workup and crystallization, 13 could be isolated in 33% crystalline yield.

Single crystals of 13 suitable for X-ray single-crystal structure analysis could be obtained from a concentrated solution in CH2Cl2 layered with n-pentane at room temperature. The molecular structure (Figure 6) reveals that the PPh3+ has been inserted into the cyclo-As3 ligand of 10a. One As–As edge of the As3P3H2 cycle coordinates in η2 fashion to the cobalt atom together with the exocyclic [PPPh3] unit in η1 fashion. The P2 atom deviates from the plane of the arsenic atoms by approx. 21° (fold angle As1-As2-As3-P2). All E–E distances are in the range of single bonds, only the As1–As2 bond is slightly elongated (2.5758(5) Å). The 1H NMR spectrum of 13 in CD2Cl2 shows five signals for the Cp′ ligand indicating that the rotation of the Cp′ is hindered (usually, three signals are observed). The 31P{1H} spectrum in CD2Cl2 shows two doublets centered at δ = 2.4 and −27.1 ppm with an JPP coupling constant of 41 Hz.

**Conclusion**

We have shown that it is possible to obtain access to the anionic complex [Cp′Co{η2-P}3]− [5] in a much easier preparative way and in reasonable preparative scale for further reactivity studies. In addition, the approach could be successfully extended to the analogous arsenic species [Cp′Co{η2-As}3]− [6], representing the first anionic compound with a cyclo-As3 ligand as end deck. Both compounds could be electrophilically quenched with chlorophosphines to yield compounds with a substituted cyclo-As3P3H2 ligand in [Cp′Co{η2-E}3PR3] (E = P (7a–c), As (9a–c)) in a first step. These complexes tend to undergo an unusual ring contraction reaction from a four-membered cyclic ligand to complexes with an cyclo-E3 ligand with an exocyclic [PR3] unit in [Cp′Co{η2-PR3}] (E = P (8a–c), As (10a–c)). This transformation proceeds at room temperature in solution or at elevated temperatures and is dependent on the substituents on the used chlorophosphane. Such behavior was not observed before for other complexes with a P3R3 ligand. Moreover, the complexes 9a–c and 10a–c add to the only scarcely known complexes containing mixed phosphorus and arsenic ligands, but here with As as major component. Therefore, the use of [6] presents a unique possibility to obtain As-rich derivatives. The conversion processes could be monitored by NMR spectroscopy and the reaction pathway could be elucidated by DFT calculations. Furthermore, this synthetic concept was extended to other halogen-containing...
main group compounds such as the chlorosilylene [LSiCl] (L = (BuN),CPh). That way, the first cyclic PSi and unprecedented As,Si rings were formed in [Cp""CO(η""2-E,SiL)] (E = P (11), As (12)), contributing to the rare family of known pnicogen–silicon heterocycles. Furthermore, it could be shown that the complexes with a cyclo-E3 ligand and an exocyclic [PR3] unit are still reactive and can be further functionalized. As a proof of principle, an in situ generated PPh3+ could be inserted into the cyclo-As3 ligand in 10a yielding the cationic complex 13 which contains a novel mixed As3(PPh3)3 ligand coordinating in an η2:η1 fashion. This shows that the initially formed products have big potential for subsequent reactivity.

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Conflict of interest

The authors declare no conflict of interest.

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[1] a) C. M. Hoidn, D. J. Scott, R. Wolf, Chem. Eur. J. 2021, 27, 1886–1902; b) F. Scalambra, M. Peruzzini, A. Romerosa in Advances in Organometallic Chemistry (Ed.: P. J. Pérez), Academic Press, San Diego, 2019, pp. 173–222; c) M. Caporalí, L. Gonsalvi, A. Rossin, M. Peruzzini, Chem. Rev. 2010, 110, 4178–4235; d) M. Scidl, G. Balázs, M. Scheer, Chem. Rev. 2019, 119, 8406–8434.

[2] B. M. Cossairt, M.-C. Diawara, C. C. Cummins, Science 2009, 323, 602.

[3] U. Chakraborty, J. Leitl, B. Mühldorf, M. Bodensteiner, S. Pelties, R. Wolf, Dalton Trans. 2018, 47, 3693–3697.

[4] C. M. Hoidn, T. M. Maier, K. Traubisch, J. J. Weigand, R. Wolf, Angew. Chem. Int. Ed. 2019, 58, 18931–18936; Angew. Chem. 2019, 131, 19107–19112.

[5] M. Piesch, S. Reichl, M. Scidl, G. Balázs, M. Scheer, Angew. Chem. Int. Ed. 2019, 58, 16563–16568; Angew. Chem. 2019, 131, 16716–16721.

[6] F. Riedlberger, S. Todisco, P. Mastrorilli, A. Y. Timoshkin, M. Scidl, M. Scheer, Chem. Eur. J. 2020, 26, 16251–16255.

[7] M. Piesch, M. Scidl, M. Scheer, Chem. Sci. 2020, 11, 6745–6751.

[8] K. A. Mandla, M. L. Neville, C. E. Moore, A. L. Rheingold, J. S. Figueroa, Angew. Chem. Int. Ed. 2019, 58, 15329–15333; Angew. Chem. 2019, 131, 15473–15477.

[9] M. Piesch, M. Scidl, M. Stubenhofer, M. Scheer, Chem. Eur. J. 2019, 25, 6311–6316.

[10] B. Rink, O. J. Scherer, G. Wolmershäuser, Chem. Ber. 1995, 128, 71–73.

[11] M. Di Vaira, F. Mani, S. Moneti, M. Peruzzini, L. Sacconi, P. Stopponi, Inorg. Chem. 1985, 24, 2230–2236.

[12] M. Piesch, S. Reichl, C. Riesinger, M. Seidl, G. Balázs, M. Scheer, Chem. Eur. J. 2021, 27, https://doi.org/10.1002/chem.202100844.

[13] E. Madl, G. Balázs, E. V. Peresypkina, M. Scheer, Angew. Chem. Int. Ed. 2016, 55, 7702–7707; Angew. Chem. 2016, 128, 7833–7838.

[14] M. Piesch, F. Dielmann, S. Reichl, M. Scheer, Chem. Eur. J. 2020, 26, 1518–1524.

[15] The black residue of the reaction was dissolved in concentrated nitric acid, neutralized with KOH and filtered. The obtained green solid (Ni(OH)2) was dissolved in a concentrated ammonia solution. After addition of an alcoholic solution of diacetyl dioxime, a pink precipitate of the related nickel complex was obtained.

[16] P. Pytkko, M. Atsumi, Chem. Eur. J. 2009, 15, 12770–12779.

[17] P. Pytkko, M. Atsumi, Chem. Eur. J. 2009, 15, 186–197.

[18] O. J. Scherer, J. Braun, P. Walther, G. Wolmershäuser, Chem. Ber. 1992, 125, 2661–2665.

[19] a) A. Velian, B. M. Cossairt, C. C. Cummins, Dalton Trans. 2016, 45, 1891–1895; b) A. Velian, C. C. Cummins, Chem. Sci. 2012, 3, 1003; c) B. M. Cossairt, C. C. Cummins, Angew. Chem. Int. Ed. 2010, 49, 1595–1598; Angew. Chem. 2010, 122, 1639–1642.

[20] For the calculations, the in situ generated phosphonium ion was used as a model system instead of the obviously much more complicated reaction of the chlorophosphane with [P2(CH2)3Co]− under salt elimination.

[21] In some cases, the conversion of P-I into P-II does not proceed in one step over TS-2. Since TS-2 represents the highest barrier, no further intermediates and transition states were modeled.

[22] C. G. P. Ziegler, T. M. Maier, S. Pelties, C. Taube, F. Hennersdorf, A. W. Ehlers, J. J. Weigand, R. Wolf, Chem. Sci. 2019, 10, 1302–1308.

[23] C. Riesinger, L. Dutsch, G. Balázs, M. Bodensteiner, M. Scheer, Chem. Eur. J. 2020, 26, 17165–17170.

[24] P. Barbaro, A. Ienco, C. Mealli, M. Peruzzini, O. J. Scherer, G. Schmitt, F. Vizza, G. Wolmershäuser, Chem. Eur. J. 2003, 9, 5195–5210.

[25] R. Yadav, B. Goswami, T. Simler, C. Schoo, S. Reichl, M. Scheer, P. W. Roesky, Chem. Commun. 2020, 56, 10207–10210.

[26] C. Schwarzmaier, M. Bodensteiner, A. Y. Timoshkin, M. Scheer, Angew. Chem. Int. Ed. 2014, 53, 290–293; Angew. Chem. 2014, 126, 295–299.

[27] L. Dutsch, C. Riesinger, G. Balázs, M. Scheer, Chem. Eur. J. 2021, 27, https://doi.org/10.1002/chem.202100663.

[28] a) S. Inoue, W. Wang, C. Präsang, M. Asay, E. Iiran, M. Driess, J. Am. Chem. Soc. 2011, 133, 2868–2871; b) S. S. Sen, S. Khan, H. W. Roesky, D. Kratzer, K. Meindl, J. Henn, D. Stalke, J.-P. Demers, A. Lange, Angew. Chem. Int. Ed. 2011, 50, 3222–3225; Angew. Chem. 2011, 123, 2370–2373.

[29] A. E. Seitz, M. Eckhardt, A. Erlebach, E. V. Peresypkina, M. Sierka, M. Scheer, J. Am. Chem. Soc. 2016, 138, 10433–10436.

[30] R. Yadav, T. Simler, S. Reichl, B. Goswami, C. Schoo, R. Koppe, M. Scheer, P. W. Roesky, J. Am. Chem. Soc. 2020, 142, 1190–1195.

[31] Deposition Numbers CCDC 2068508, 2068509, 2068510, 2068511, 2068512, 2068513, 2068514, 2068515, 2068516, 2068517, 2068518, and 2068519 contain 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.

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