

Halogenation and Nucleophilic Quenching: Two Routes to E–X Bond Formation in Cobalt Triple-Decker Complexes (E = As, P; X = F, Cl, Br, I)

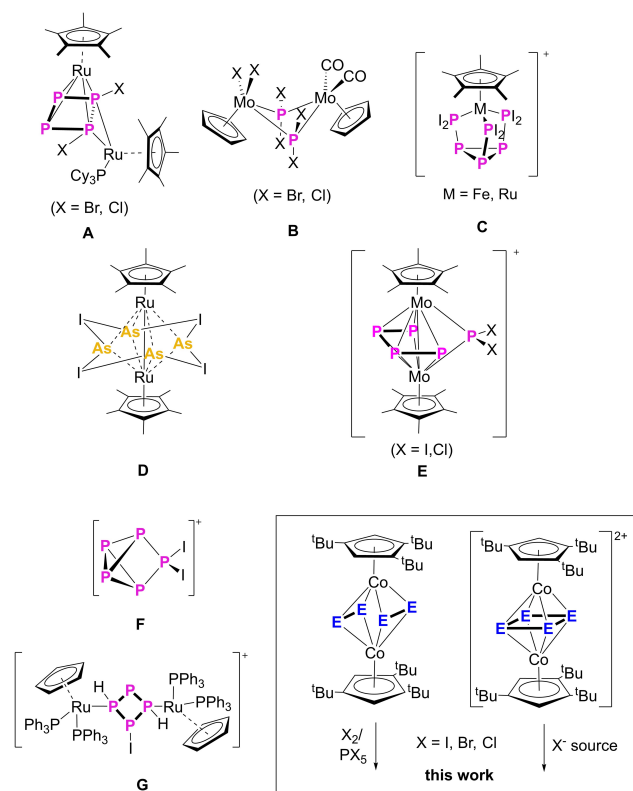
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Abstract: The oxidation of $[(Cp^*Co)_2(\mu, \eta^2: \eta^2-E_2)]$ (E = As (1), P (2)); Cp^{*} = 1,2,4-tri(*tert*-butyl)cyclopentadienyl) with halogens or halogen sources (I₂, PBr₅, PCl₅) was investigated. For the arsenic derivative, the ionic compounds $[(Cp^*Co)_2(\mu, \eta^4: \eta^4-As_4X)] [Y]$ (X = I, Y = [As₆I₈]_{0.5} (3a), Y = [Co₂Cl_{6-n}I_n]_{0.5} (n = 0, 2, 4; 3b); X = Br, Y = [Co₂Br₆]_{0.5} (4); X = Cl, Y = [Co₂Cl₆]_{0.5} (5)) were isolated. The oxidation of the phosphorus analogue 2 with bromine and chlorine sources yielded the ionic complexes $[(Cp^*Co)_2(\mu-PBr_2)_2(\mu-Br)] [Co_2Br_{6.0.5}]$ (6a), $[(Cp^*Co)_2(\mu-PCl_2)_2(\mu-Cl)] [Co_2Cl_{6.0.5}]$ (6b) and the neutral species $[(Cp^*Co)_2(\mu-PCl_2)(\mu-PCl)(\mu, \eta^1: \eta^1-P_2Cl_3)]$ (7), respectively. As an

alternative approach, quenching of the dications $[(Cp^*Co)_2(\mu, \eta^4: \eta^4-E_4)] [TEF]_2$ (TEF = [Al{OC(CF₃)₃}]₄⁻, E = As (8), P (9)) with KI yielded $[(Cp^*Co)_2(\mu, \eta^4: \eta^4-As_4I)] [I]$ (10), representing the homologue of 3, and the neutral complex $[(Cp^*Co)(Cp^*Co)_2(\mu, \eta^4: \eta^1-P_4)]$ (11), respectively. The use of [(CH₃)₄N]F instead of KI leads to the formation of $[(Cp^*Co)_2(\mu-PF_2)(\mu, \eta^2: \eta^1: \eta^1-P_3F_2)]$ (12) and 2, thereby revealing synthetic access to polyphosphorus compounds bearing P–F groups and avoiding the use of very strong fluorinating reagents, such as XeF₂, that are difficult to control.

Introduction

White phosphorus is the most reactive allotrope of the element and the starting material for producing organophosphorus compounds^[1] through conversion to PCl₃ or POCl₃, which are, in turn, converted to P-containing fine chemicals.^[1] Among the direct functionalisation of P₄^[2] and of phosphates,^[3] which is still in its infancy, a potential alternative way is the functionalisation of polyphosphorus compounds obtained from a transition-metal-mediated conversion of P₄ to P_n ligands (TM-P_n) (n = 1–14),^[4,5,6] followed by the halogenation of the P_n unit and the subsequent substitution of the halogen by organic substituents or other functional groups. However, the halogenation of the TM-P_n complexes has only been scarcely investigated and merely a few examples are known so far.^[7,8,9,10,11] Such reactions would enable access to a plethora of halogen-containing TM compounds and open up new research areas. For instance, the ruthenium-mediated halogenation of white phosphorus results in the formation of $[RuCp^*(PCy_3)(\mu, \eta^2: \eta^4-P_4X_2)RuCp^*]$ (X = Cl, Br; Scheme 1 A), which contains an uncommon P₄Cl₂ ligand.^[8]



Scheme 1. Selected examples of halogenated polynpnictogen complexes.

Recent studies conducted by our group targeted the halogenation of polynpnictogen complexes containing different P_n units such as a P₂-containing dimetalla-tetrahedrane,^[12] a *cyclo*-P₅-

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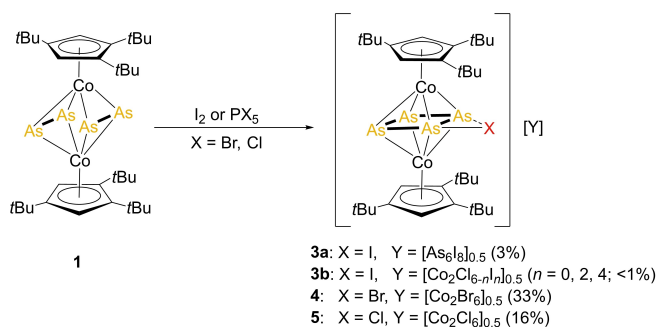
end-deck^[9] and a *cyclo*-P₆-triple-decker complex,^[13] which resulted in neutral or cationic halogenated species (Scheme 1 B–E). Regarding the differences that emerged from these results, the question arose as to what would happen when the TM-P_n compound combines the features of triple-decker complexes and separated E_n units. Moreover, no compounds with E–F bonds were accessible by the approaches used so far.

Therefore, the redox-active compounds [(Cp^{'''}Co)₂(μ,η²:η²-E₂)₂] (E = As (1), P (2); Cp^{'''} = 1,2,4-tri(*tert*-butyl)cyclopentadienyl)^[14] came into the focus of our research. A former investigation of these complexes showed that they exhibit a unique redox chemistry different from the usual behaviour observed for triple-decker complexes such as [(CpMo)₂(μ,η⁶:η⁶-P₆)^[15] or for heterobimetallic triple-decker complexes.^[16] The oxidation and reduction of 1 and 2 both lead to the formation of two additional E–E bonds, highlighting a way to obtain the corresponding dications [(Cp^{'''}Co)₂(μ,η⁴:η⁴-E₄)](TEF)₂ (E = As (8), P (9), [TEF] = [Al{OC(CF₃)₃]₄) in good yields.^[17] As some successful examples of the halogenation of cationic species have been reported, as for instance [P₅I₂]⁺ (Scheme 1 F) resulting from the iodination of [Ag(η²-P₄)₂]⁺,^[10] and [(CpRu(PPh₃)₂)₂(μ,η¹:η¹-P₄H₂)]⁺ (Scheme 1 G),^[11] we were interested in the comparison of the halogenation of the neutral compounds 1 and 2 with the well accessible corresponding cationic species 8 and 9. Moreover, the cationic compounds offer the possibility to “quench” the Lewis acidity of the cations with nucleophilic halides, which would enlarge the group of halogen sources by milder and non-hazardous reagents such as KI or [(CH₃)₄N]F (TMAF). This approach would represent a new method to synthesise compounds containing E–X bonds, representing a milder alternative to the halogenation of polypnictogen compounds. Especially for fluorination reactions, our former results showed that the use of XeF₂, even at low temperature, leads to the complete decomposition of polyphosphorus complexes to yield PF₆[−] species. In this respect, a novel approach to fluorine-containing pnictogen complexes would be of benefit.

Herein, we present the reactivity of the polypnictogen compounds 1 and 2 towards halogen and halogen sources (I₂, PBr₅, PCl₅), leading to the formation of the new cationic and neutral species containing E–X bonds. Furthermore, we present an alternative and new way to synthesise functionalised TM-E_n compounds (E = P, As) by nucleophilic quenching of the cationic polypnictogen species 8 and 9 by the salts KI and [(CH₃)₄N]F, the latter representing a novel approach to fluorine-containing TM-E_n derivatives.

Results and Discussion

The reaction of 1 with an excess (4 equiv.) of halogen or halogen sources (I₂, PX₅, X = Br, Cl) leads to the isostructural compounds [(Cp^{'''}Co)₂(μ,η⁴:η⁴-As₄X)](Y) (X = I, Y = [As₆I₈]_{0.5} (3a); X = Br, Y = [Co₂Br₆]_{0.5} (4); X = Cl, Y = [Co₂Cl₆]_{0.5} (5); Scheme 2). The rather low yields are probably due to the harsh reaction conditions that lead to fragmentations of the starting material into several products and species, not all of which could be



Scheme 2. Reaction of 1 with I₂ or PX₅ (X = Br, Cl). Isolated yields are given in parentheses.

identified (see the Supporting Information). The cation of the complexes 3a, 4 and 5 contains a strongly distorted *cyclo*-As₄ ligand with an *exocyclic* halide attached to one of the As–As edges. In all the reactions, two new As–As bonds are formed and new triple-decker complexes with unprecedented cyclic As₄X units as middle decks are obtained. Few examples of complexes bearing different arsenic halides are reported in the literature, such as AsX₃ (X = Cl, Br, I)^[18] or the remarkable ligand As₄I₄ in [(Cp^{*}Ru)₂(μ,η⁴:η⁴-As₄I₄)],^[9] which represents a tetramer of {AsI} fragments.^[19] However, no examples of polyarsenic subhalides as ligands exists as found in 3a, 4 and 5. Crystals suitable for X-ray structure analysis were obtained from solutions in CH₂Cl₂ layered with *n*-pentane at room temperature (3a, 3b, 4 and 5). From the reaction solution of 1 with iodine, beside 3a a few crystals with the same cation but with [Co₂Cl_{6-n}I_n]_{0.5} (n = 0, 2, 4) as counterion were isolated (3b). The solid-state structure of the anion in 3a ([As₆I₈]^{2−}, Figure 1) was already found in salts with different counterions^[9,20] and therefore will

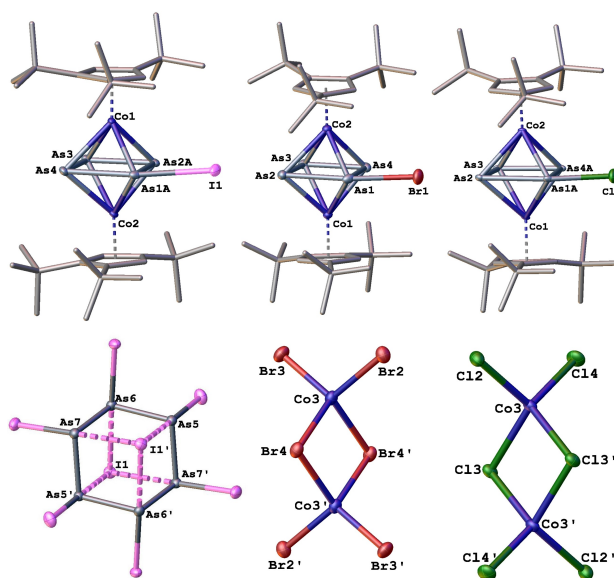


Figure 1. Molecular structures of 3a (left), 4 (middle) and 5 (right) with thermal ellipsoids at the 50% probability level. In the case of disorder, only the major parts are depicted. Hydrogen atoms and solvent molecules are omitted for clarity.

not be further discussed (see the Supporting Information for further details). The solid-state structures reveal triple-decker sandwich complexes with a planar cyclic As_4 unit with an additional side-on bond to a halogen atom X (X=I, Br, Cl) as a ligand coordinating in an $\eta^4:\eta^4$ fashion to two $\{Cp''Co\}$ fragments.

The As_4 units in **3a**, **4** and **5** possess a trapezoidal shape (Figure 1). One of the As–As bonds is shortened (As3–As4: 2.330(8) Å in **3a**, As2–As3: 2.337(5) Å in **4**, As2: As3: 2.342(5) Å in **5**), two are in the range of an As–As single bond^[21] and the side-on coordinated As–As bond to the halogen atom is elongated (As4–As1 A: 2.699(3) Å in **3a**, As1: As2: 2.702(19) Å in **4**, As1–As2: 2.737(8) Å in **5**). The As–X bond lengths are elongated compared to their respective single bonds (As1A–I1: 2.837 Å, As1–Br1: 2.656(3) Å, As1A–Cl1: 2.447(12) Å; lit.: As–I: 2.54 Å, As–Br: 2.35 Å, As–Cl: 2.20 Å).^[21] DFT calculations that were performed with the ORCA program^[22] and whose geometries were optimised at the TPSSh^[23]/def2-TZVP^[24] level of theory starting from the X-ray structure coordinates reproduce well the geometric parameters of the cations in **3**, **4** and **5**. The calculations show that, although two As–As distances are rather long, they can be considered as bonding interactions built up by delocalised multi-centred interactions (see the Supporting Information).

The intrinsic bonding orbitals representing the bonding within the As_4I unit in **3** are depicted in Figure 2. The description of the bonding in **3** is in agreement with the calculated Mayer bond orders (BOs) which show a BO of 0.53 for each As2A–As3 and As1A–As2A bond (labelling according to Figure 1). The BOs corresponding to the As1A–I1 and As2A–I1 bonds are 0.48 and 0.44, respectively. The analyses of the intrinsic bonding orbitals (IBOs) and BOs in the cation of **5** show a similar bonding situation as in **3**, with the exception that the Cl atom is bound to only one arsenic atom (BO 0.61) and there is only a weak interaction with the second As atom (BO 0.16; for details see Supporting Information). This is also confirmed by the electron localisation function and interaction region indicator (see the Supporting Information). The dianions of **4** and **5**, with the formula $[Co_2X_6]^{2-}$ (X=Br, Cl), suggest that part of the starting material is completely converted during the oxidation process, resulting in the halogenation of the metal atoms. Their solid-state structures were already described in products with different counterions.^[25]

The 1H NMR spectrum of **3a** (CD_2Cl_2) shows three sharp singlets for the magnetically equivalent Cp'' ligands at $\delta=4.67$, 1.49 and 1.46 ppm (integral ratio: 2:18:9). However, in the 1H NMR spectrum of the reaction solution, three additional singlets were observed corresponding to the side product $[Cp''CoI_2]$ which was isolated and fully characterised as the main product of the iodination of the P analogue compound **2** (see below and the Supporting Information). The ratio between $[Cp''CoI_2]$ and **3a** is approximately 1.5:1, which could partly explain the low yield of isolated **3a**. The 1H NMR spectrum of **4** (CD_2Cl_2) shows three broad signals for the Cp'' ligands centred at $\delta=4.28$, 0.93 and 0.81 ppm with an integral ratio of 2:9:18. In the case of **5**, there are two broad singlets centred at $\delta=0.83$ and 0.71 ppm (integral ratio: 18:9) corresponding to the *t*Bu groups

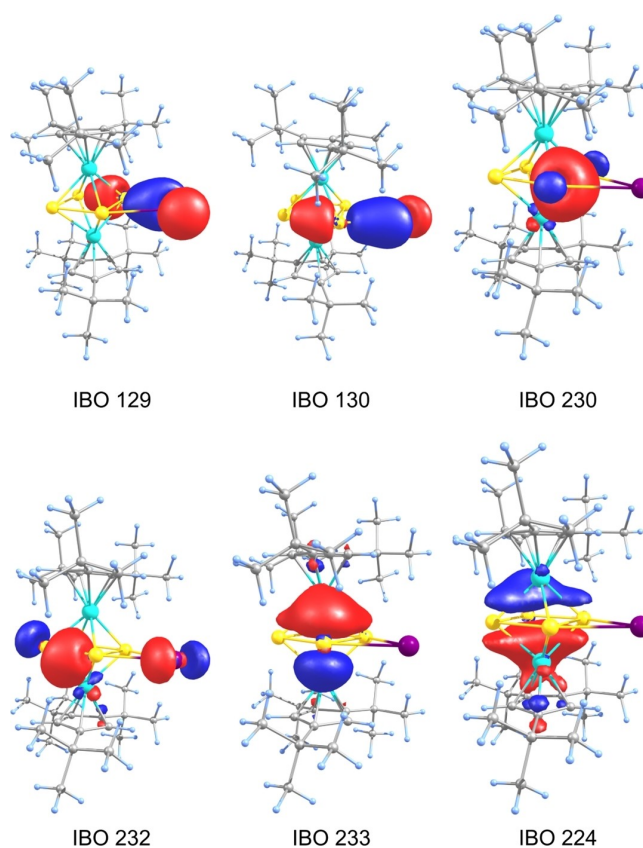


Figure 2. Selected intrinsic bonding orbitals representing the bonding within the As_4I unit in the cation of **3** at the D4-TPSSh(CPCM)/def2-TZVP level of theory.

of the Cp'' ligand and a very broad signal at 4.04 ppm ($\omega_{1/2}=312$ Hz) which is assigned to the H atoms bound directly to the Cp ring. The broadening of the signals in **4** and **5** might be caused by the contact-interaction shift of the paramagnetic anion $[Co_2X_6]^{2-}$ (X=Br, Cl) with the cation. The same phenomenon was described for another salt of the $[Co_2Cl_6]^{2-}$ anion^[26] and this might explain why it is not detected for **3a** (where the anion is diamagnetic). The signals of the *t*Bu groups in **4** and **5** are shifted upfield by approximately 0.5 ppm compared to the starting material, while for the iodine derivative they are in line with the educt.^[14]

Even if the cations formed by the two-electron oxidation of **1** or by the halogenation of the sandwich complex are not comparable, there are still some similarities. In both cases, triple-decker complexes with a *cyclo-As₄* or *cyclo-As₄X* ligand are isolated as the result of the formation of two new As–As bonds. The main differences are the more reactive reagents used in the reactions when a halogen is the oxidating agent, resulting in the partial decomposition of the starting material under formation of the corresponding anions. While the oxidation with silver salts leads to the same results for both the As- (**1**) and the P-containing (**2**) derivatives, namely the formation of two additional E–E bonds, with the formation of the corresponding mono and dications $[(Cp''Co)_2(\mu_4\eta^4:\eta^4-E_4)]^{+/2+}$ (E=As, P; see Scheme 1, **8** and **9**),^[17] the halogenation of

[[Cp^{'''}Co]₂(μ,η²:η²-P₂)₂] (**2**; see below) gave different species as compared to **1**. Interestingly, a recent investigation concerning the iodination of [Cp^{*}M(η⁵-E₅)] (Cp^{*} = C₅Me₅; M = Fe, Ru; E = As, P) showed likewise different behaviours of the As and P derivatives.^[9] The halogenation of **2** leads to different compounds depending on the halogenating agent used, in contrast to what was observed for the halogenation of the heavier analogue **1**, which led to analogous species. As mentioned above, when the reaction between **2** and I₂ is conducted under the same conditions as for **1** (4 equiv. of I₂), the only product detected by ¹H NMR spectroscopy of the reaction solution is [Cp^{'''}Co]₂ (see the Supporting Information for further details). The ³¹P{¹H} NMR spectrum of the reaction solution at room temperature was silent but a few crystals of P₂I₄ could be isolated.^[27] The variable temperature ³¹P{¹H} NMR spectrum of the reaction solution showed two broad singlets centred at δ = 348.9 and 183.4 ppm (integral ratio: 1:1) indicating the formation of a diamagnetic compound which is only stable between 213 and 233 K and could not be isolated, despite numerous attempts.

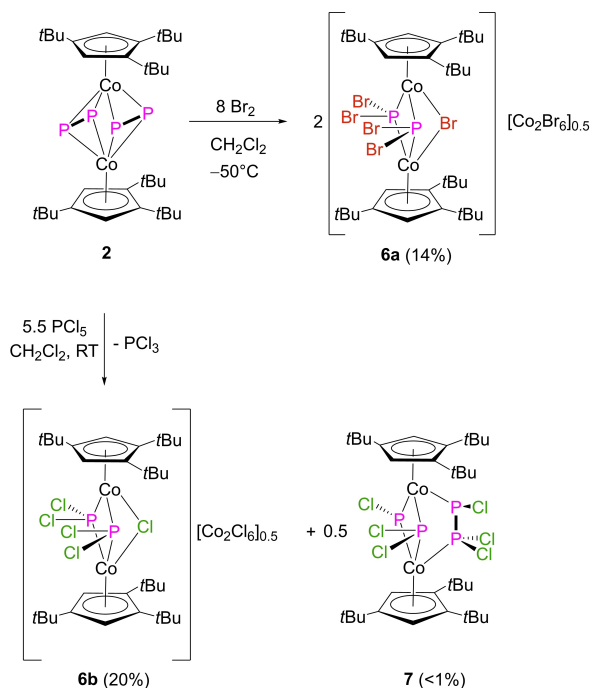
When the P-starting material [[Cp^{'''}Co]₂(μ,η²:η²-P₂)₂] (**2**) was reacted with PBr₅ (4 equiv.) at room temperature, the crude reaction mixture shows a silent ³¹P{¹H} NMR spectrum, as observed with I₂ (see above). On the other hand, the variable temperature NMR spectra of the reaction solution showed many different signals, indicating that, contrarily to the iodine case, lower temperature is not a way to better control the reaction outcome (see Figure S31 in the Supporting Information). Nevertheless, when **2** was reacted with Br₂ (4 equiv.) at -50 °C, [[Cp^{'''}Co]₂(μ-PBr₂)₂(μ-Br)][Co₂Br₆]_{0.5} (**6a**) could be isolated (Scheme 3). As the diamagnetic compound **6a** could not be

isolated, nor detected, at 25 °C, but only at -50 °C, variable temperature ³¹P{¹H} NMR spectra (233–293 K) of crystals of **6a** in CD₂Cl₂ were recorded, to detect its thermal decomposition (Figure S6).^[28,17]

Surprisingly, a different reaction behaviour was observed when the chlorine source PCl₅ was used instead. While the VT ³¹P{¹H} NMR spectra of the crude reaction mixture showed an unselective reaction as observed for PBr₅ (see the Supporting Information), the reaction of **2** and PCl₅ (4 equiv.) at room temperature, instead leads to the isolation of an analogue of **6a**, namely the ionic complex [[Cp^{'''}Co]₂(μ-PCl₂)₂(μ-Cl)][Co₂Cl₆]_{0.5} (**6b**), and a few crystals of the neutral species [[Cp^{'''}Co]₂(μ-PCl₂)(μ-PCl)(μ,η¹:η¹-P₂Cl₃)] (**7**; Scheme 3). **7** can be isolated after extraction with *n*-hexane and, together with **6b**, represents the only isolated species among a plethora of compounds formed in this reaction.

The reaction of **2** with 1 to 3 equivalents of I₂ or PX₅ (X = Cl, Br) leads, according to the ³¹P NMR spectroscopy to intractable mixtures from which no specific compounds could be identified nor isolated.

The structures of **6a,b** and **7** in the solid state (Figure 3 and the Supporting Information) show dinuclear complexes bearing halogen-containing phosphorus ligands. For the monocations in **6a,b** the two {Cp^{'''}Co} fragments are connected by two bridging PX₂ units and an additional X⁻ ion (**6a**: X = Br; **6b**: X = Cl). The distance between P1 and P2 (**6a**: 2.696(17) Å, **6b**: 2.688(9) Å) is clearly too long to be considered as a bond. This is supported by DFT calculations (see the Supporting Information) which show a bond order of 0.10 for the P1–P2 bond. The neutral compound **7** bears a {PCl} and a {PCl₂} bridging ligand, with a distance comparable to the one in **6** (P1–P2: 2.608(3) Å; BO: 0.11) and a {P₂Cl₃} bridging ligand, coordinating in a μ,η¹:η¹ fashion to the two metal fragments. The P3–P4 bond length (2.240(3) Å) in the latter is in the range of a P–P single bond, which is in line with the results of the DFT calculations (BO: 0.95).^[21] The ligand {P₂Cl₃} was so far only reported in the bimetallic complex [[Cp^{*}Mo(CO)₃]₂(μ-P₂Cl₃)] [AlCl₄].^[29] A similar bridging P₂X₃ unit (X = Cl, Br) stabilised by N-heterocyclic



Scheme 3. Reaction of **2** with Br₂ and PCl₅. Isolated yields are given in parentheses.

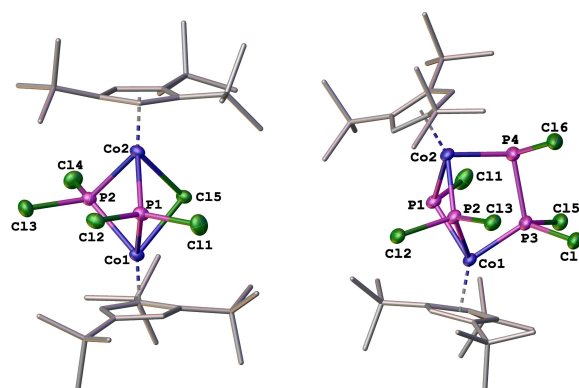


Figure 3. Molecular structure of the cation of **6b** (left) and of the neutral compound **7** (right) with thermal ellipsoids at the 50% probability level. Due to the disorder in **7**, only the major part is depicted. Hydrogen atoms and the solvent molecules are omitted for clarity.

carbenes was observed in the cations $[\text{P}_2(\text{IPr})_2\text{Cl}_3]^+{}^{[30]}$ and $[\text{P}_2(\text{IPr})_2\text{Br}_3]^+{}^{[31]}$. Compound **7** is extremely sensitive to moisture and air, and despite numerous attempts, it always co-crystallises with the oxidised compound $[(\text{Cp}'''\text{Co})_2(\mu\text{-P}(\text{Cl})_2)(\mu\text{-P}(\text{Cl}))(\mu,\eta^1:\eta^1\text{-P}_2\text{OCl}_3)]$ in an approximate ratio of 89:11 (see the Supporting Information).

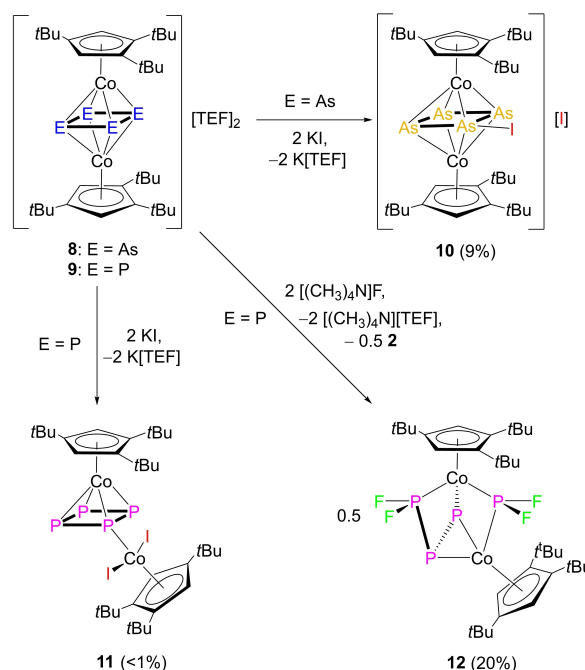
The ^1H NMR spectra of **6a,b** (CD_2Cl_2) show the characteristic signals for the magnetically equivalent Cp''' ligands with the integral ratio of 2:18:9, centred at $\delta=4.70$, 1.21 and 1.02 ppm (**6a**) and at $\delta=4.82$, 1.07 and 0.79 ppm (**6b**). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra show each one singlet at $\delta=135.2$ ppm (**6a**) and one at $\delta=176.2$ ppm (**6b**), respectively, for the two equivalent P atoms. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **6a**, there are two additional doublets, centred at $\delta=139.2$ and at 30.9 ppm, with a $^2J_{\text{PP}}$ coupling constant of 21 Hz which may be assigned to an unidentified side-product (approximate ratio **6a**/side product: 70:30) with two non-equivalent P atoms (see the Supporting Information). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **7** shows an AMNX spin system with four resonances centred at $\delta=211.6$, 160.5, 147.4 and -22.4 ppm (integral ratio: 1:1:1:1). The signals of the two P atoms connected with a single bond resonate at $\delta=160.5$ (P^{M}) and at $\delta=147.4$ (P^{N}) ($^1J_{\text{PMPN}}=358$ Hz). The other two resonances belong to the bridging P atoms, and for the upfield shifted one (P^{X}) a $^2J_{\text{PMPX}}$ coupling of 238 Hz is detected, due to the coupling with P^{M} (see the Supporting Information for further details). Although crystals of **7** could be obtained several times, the characterisation of this compound was rather problematic. When the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the dark brown crystals was recorded (CD_2Cl_2), a very complex spectrum was obtained, showing that other compounds co-crystallise with **7**. If the hexane solution used to extract **7** was filtered over silanised silica gel, a clean $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum was obtained showing an AMNX spin system. However, this spectrum is too complex for compound **7** and probably belongs to a different compound that could not be crystallised (compound **7_{silica}**). When the same hexane solution was filtered over celite, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the solution showed among some other signals, signals for **7_{silica}** and **7**. By comparing both spectra and with the help of a $^{31}\text{P},^{31}\text{P}$ COSY NMR experiment, the signals corresponding to **7** could be unequivocally attributed (see the Supporting Information for detailed spectra).

The signal of PX_3 ($\text{X}=\text{Cl}, \text{Br}$) is always detected in the reaction solution, when using PX_5 ($\text{X}=\text{Cl}, \text{Br}$) as a reagent, due to its dissociation,^[32,33] but ^{31}P NMR spectroscopic investigations show that also the phosphorus atoms in **2** are partly halogenated to PX_3 ($\text{X}=\text{Cl}, \text{Br}$).

Since the halogenation of **1** revealed a synthetic way to obtain the halogenated monocationic species **3–5**, albeit with rather low yields, and the halogenation of **2** exhibited some difficulties in the detection and isolation of the resulting products due to the moderate selectivity of the reactions, especially with iodine, the question arose as to whether it would be possible to find an alternative and a milder way to form new P–X bonds, including the possibility of accessing fluorinated species. Therefore, the idea of quenching the cationic species $[(\text{Cp}'''\text{Co})_2(\mu,\eta^4:\eta^4\text{-E}_4)][\text{TEF}]_2$ ^[17] ($\text{E}=\text{As}$ (**8**), P (**9**)) with weak nucleophiles such as X^- ($\text{X}=\text{I}, \text{F}$) came up.

The reaction of **8** with KI (2 equiv.) results in the formation of $[(\text{Cp}'''\text{Co})_2(\mu,\eta^4:\eta^4\text{-As}_4\text{I})][\text{I}]$ (**10**) which contains the same cation as **3a**, with I^- instead of the $[\text{As}_6\text{I}_8]^{2-}{}_{0.5}$ anion in slightly higher yields (**3a**: 3%, **10**: 9%; Scheme 4). The solid-state structure of the cation in **10** (see the Supporting Information) reveals the same strongly distorted *cyclo*- As_4 middle deck with an iodine attached to one As–As edge as in **3a,b**. The As–As bond lengths are comparable to the one observed in **3a** (bond lengths in **10**: As1–As2: 2.620(4) Å, As2–As3: 2.443(4) Å, As3–As4: 2.395(4) Å, As4–As1: 2.592(4) Å). The As1–I distance of 3.095 Å is elongated compared to the one in **3a** and to an As–I single bond.^[21] It has to be mentioned, that the disorder of the As_4I unit in the solid state structure of **3a** might affect the accuracy of the As–I distances (see the Supporting Information). Solid state effects and/or anion–cation interactions can also influence these distances. The ESI mass spectrum of freshly dissolved crystals of **10** reveals the molecular ion peak at m/z 1010.9. The structural features of the cation in **10** are the same as for the cation in **3a**, therefore it will not be further discussed.

When the phosphorus analogue **9** was reacted under the same conditions with KI (2 equiv.), the iodide attacked the Co atom of only one of the two metal fragments, resulting in a few crystals of compound **11**, $[(\text{Cp}'''\text{Co})(\text{Cp}'''\text{CoI}_2)(\mu,\eta^4:\eta^1\text{-P}_4)]$ (Scheme 4), the only one that could be isolated among the products formed in this reaction. The structure in the solid state (Figure 4) reveals a sandwich complex with a square-planar *cyclo*- P_4 ligand as middle-deck, coordinating in an η^4 fashion to the $\{\text{Cp}'''\text{Co}\}$ fragment and in an η^1 mode to a newly formed $\{\text{Cp}'''\text{CoI}_2\}$ unit. The P–P bond lengths in the P_4 unit vary from 2.130(3) Å to 2.183(3) Å, being all in the range



Scheme 4. Reaction of **8** and **9** with KI and $[(\text{CH}_3)_4\text{N}]\text{F}$. Isolated yields are given in parentheses.

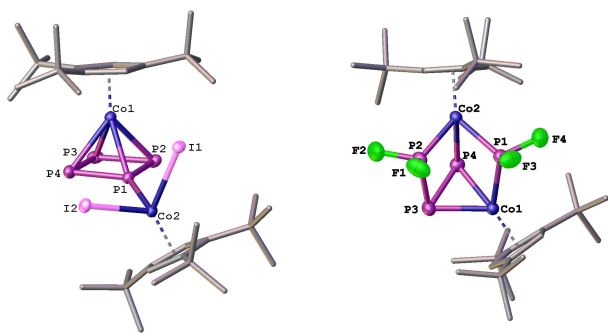


Figure 4. Molecular structures of **11** (left) and **12** (right) in the solid state with thermal ellipsoids at the 50% probability level. In case of disorder, only the major parts are depicted. The hydrogen atoms and solvent molecules are omitted for clarity.

of a shortened P–P single bond^[21] and similar to those observed for the sandwich complex $[\text{Cp}^*\text{Co}(\eta^4\text{-P}_4)]$.^[34] The sum of the internal P–P–P bond angles is close to 360° for both compounds.

With the same procedure, **9** was reacted with the nucleophilic fluorinating agent tetramethylammonium fluoride ($[(\text{CH}_3)_4\text{N}]\text{F}$; TMAF). The reaction of **9** with $[(\text{CH}_3)_4\text{N}]\text{F}$ (2 equiv.) leads to $[(\text{Cp}^*\text{Co})_2(\mu\text{-PF}_2)(\mu, \eta^2: \eta^1: \eta^1\text{-P}_3\text{F}_2)]$ (**12**, Scheme 4) and to the neutral complex $[(\text{Cp}^*\text{Co})_2(\mu, \eta^2: \eta^1\text{-P}_2)]$ (**2**). It could therefore formally be described as a disproportionation of **9** into **12** and **2**. The attempt to isolate the heavier As analogue of **12** by reacting **8** (1 equiv.) with $[(\text{CH}_3)_4\text{N}]\text{F}$ (2 equiv.) resulted in the isolation of a few crystals of the neutral species **1**. This could suggest that quenching of **8** with TMAF also proceeds as a disproportionation reaction, but no crystalline material of the fluorinated As derivative could be isolated. Attempts to fluorinate **1** with XeF_2 resulted in decomposition. There is no direct evidence of the formation of AsF_6^- as the final product of the decomposition, but many new signals are detected in the ^1H NMR spectra of the reaction solution, while the one of **1** disappeared.

Compound **12** could also be obtained when the mono-cation $[(\text{Cp}^*\text{Co})_2(\mu, \eta^4: \eta^4\text{-P}_4)][\text{BF}_4]^{[17]}$ (1 equiv.) was reacted with $[(\text{CH}_3)_4\text{N}]\text{F}$ (1 equiv.) under the same conditions (see the Supporting Information). The solid-state structure of **12** (Figure 4) reveals a cage-like complex with two $\{\text{Cp}^*\text{Co}\}$ fragments connected via a bridging $\{\text{PF}_2\}$ unit and a $\mu, \eta^2: \eta^1: \eta^1\text{-P}_3\text{F}_2$ ligand. The P_3 ligand contains a P–P bond length in the range of a single bond (P3–P4: 2.202(12) Å) and a shortened one (P2–P3: 2.126(12) Å), which is in the range of a P=P double bond. Whereas the difluorophosphine ligand (PF_2) is widely known for both organic^[35] and inorganic compounds,^[36] the P_3F_2 unit has only been reported so far in $\text{Me}_3\text{SiR}_2\text{P}_3\text{F}_2$ ($\text{R} = t\text{Bu}$).^[37] Therefore **12** represents the first complex bearing such a P_3F_2 ligand coordinated to a transition metal.

The ^1H NMR spectrum of **10** (CD_2Cl_2) is comparable with the one observed for the analogous compound **3a**, the different anion is responsible for a slight shift of the characteristic signals of the magnetically equivalent Cp^*

ligands. Three sharp singlets, with an integral ratio of 2:18:9, are centred at $\delta = 4.79$, 1.35 and 1.15 ppm. Compound **11** decomposes in solution at room temperature as monitored by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the crystals dissolved in CH_2Cl_2 , which show only two resonances centred at -46.9 and -520.7 ppm, corresponding to **2** and P_{4r} , respectively.^[38] To check if the structure of **11** could be stable in solution at lower temperatures, crystals of **11** were dissolved in CD_2Cl_2 at 193 K and a variable temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic investigation was performed. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 193 K shows three multiplets centred at $\delta = 155.4$, 129.3 and 42.3 (integral ratio: 2:1:1), corresponding to an A_2BM spin system. At 213 K, the spectrum shows two multiplets at $\delta = 158.6$ and 44.1 ppm (integral ratio: 2:2), corresponding to an A_2M_2 spin system, which disappear at 253 K. Although these spectra may indicate a dynamic process in solution of the *cyclo*- P_4 ligand, the low yield of **11** and the resulting low resolution of the spectrum do not allow to make any educated guess about the stability of **11** in solution at low temperatures or to prove it.

The ^1H NMR spectrum of dissolved crystals of **12** (CD_2Cl_2) shows six signals for the two magnetically non-equivalent Cp^* ligands, together with the signals of the Cp^* of **2** which co-crystallises, as minor part, with **12** (ratio **12**:**2** = 0.94:0.06).^[39] The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows an AMXZ spin system with four signals at $\delta = 303.3$, 218.9, 46.0 and -51.4 ppm. The signal of the P atom from the bridging PF_2 ligand (P^A) resonates at 303.3 ppm and shows a large coupling to the F atoms ($^1J_{\text{PF}} = 1213$ Hz and 1269 Hz). The other three resonances belong to the P_3F_2 unit. The difluorinated P atom (P^M) resonates at 218.9 ppm ($^1J_{\text{PF}} = 1322$ Hz and 1367 Hz). The signal at -51.4 ppm partly overlaps with the signal of compound **2** (co-crystallised with **12**). The $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **12** shows an AMNX spin system, with four signals centred at $\delta = 13.2$, -13.0 , -17.4 and -34.9 ppm, corresponding to the four non-equivalent fluorine atoms (see the Supporting Information for additional coupling constants). The $^{31}\text{P}/^{19}\text{F}$ NMR chemical shifts and coupling constants of **12** were calculated by iterative fitting of the experimental spectra.

Conclusions

In summary, we have shown that $[(\text{Cp}^*\text{Co})_2(\mu, \eta^2: \eta^2\text{-As}_2)]$ (**1**) can easily be oxidised by halogens to obtain the mono-cationic species **3–5** revealing the formation of two new As–As single bonds to form an unprecedented cyclic arsenic subhalide ligand As_xX ($\text{X} = \text{I}, \text{Br}, \text{Cl}$). An alternative route to the same cationic complexes was achieved by treating the dication $[(\text{Cp}^*\text{Co})_2(\mu, \eta^4: \eta^4\text{-As}_4)][\text{TEF}]_2$ (**8**) with KI. Quenching of this dication with a weak nucleophile such as I^- resulted in the analogous compound **10**, in higher yields. The use of this milder nucleophile resulted in a more selective halogenation “limited” to the As_4 middle-deck, contrary to the formation of the anion $[\text{As}_6\text{I}_6]^{2-}$ obtained when the stronger elemental iodine was used as reagent. In the case of the P analogue

complexes **2** and **9** (to **1** and **8**), the reaction of the neutral compound **2** towards halogens and halogen sources led to an outcome different from the one for the complexes obtained by quenching of the dicationic species **9** by weak nucleophiles. However, it was possible to obtain new polyphosphorus compounds bearing P–X bonds. Moreover, with this method and by using a mild fluoride source such as $[(\text{CH}_3)_4\text{N}]\text{F}$, novel P–F bonds are formed in a controlled way, as observed for compound **12**, $[(\text{Cp}^*\text{Co})_2(\mu\text{-PF}_2)(\mu, \eta^2: \eta^1: \eta^1\text{-P}_3\text{F}_2)]$, which contains a novel and unprecedented P_3F_2 -chain ligand. These results open up the possibility of synthesising new polypnictogen compounds bearing P–X bonds by using milder reagents and less harsh reaction conditions, thereby enabling the formation of novel P–F bonds.

Deposition Numbers CCDC-2162030 (**3a**), CCDC-2162031 (**3b**), CCDC-2162032 (**4**), CCDC-2162033 (**5**), CCDC-2162034 (**6a**), CCDC-2162035 (**6b**), CCDC-2162036 (**7**), CCDC-2162037 (**10**), CCDC-2162038 (**11**), CCDC-2162039 (**12**) and CCDC-2162014 ($[(\text{Cp}^*\text{Co})_2]$) 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.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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- [38] The ESI mass spectrum of a solution of the crystals of **11** showed a peak at m/z 708.3 which could be assigned to **2**. Our hypothesis is that in solution at room temperature **11** decomposes to **2**, P_4 and $[(Cp^{III}Co)_2(I)_2]$, but the latter compound could not be detected e.g. by ESI mass spectrometry.
- [39] The 1H NMR spectrum shows three additional signals of a Cp^{III} ligand of a compound that could not be identified so far.

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