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

Anna Garbagnati,[a] Martin Piesch,[a] Michael Seidl,[a] Gábor Balázs,[a] and Manfred Scheer*[a]

Abstract: The oxidation of [(Cp'''Co)(μ,η[5]:η[3]−E)] (E = As (1), P (2); Cp''' = 1,2,4-tri(tert-butyl)cyclopentadienyl) with halogens or halogen sources (I2, PBr3, PCl3) was investigated. For the arsenic derivative, the ionic compounds [(Cp'''Co)(μ,η[5]:η[3]−AsX)][Y] (X = I, Y = [AsBr4]0.5, Y = [CoCl4]2−; X = Br, Y = [CoBrCl2]0.5) were isolated. The oxidation of the phosphorus analogue 2 with bromine and chlorine sources yielded the ionic complexes [(Cp'''Co)(μ-PBr2)(μ-Br)][CoCl4]0.5 (6a), [(Cp'''Co)(μ-PCl2)(μ-Cl)][CoCl4]0.5 (6b) and the neutral species [(Cp'''Co)(μ-PCl2)(μ-Cl)(μ,η[3]:η[1]−P,Cl)] (7), respectively. As an alternative approach, quenching of the dications [(Cp'''Co)(μ,η[3]:η[1]−E)](TEF)2 (TEF = [Al(OC(CH3)2)4], E = As (8), P (9)) with KI yielded [(Cp'''Co)(μ,η[3]:η[1]−As,I)][I] (10), representing the homologue of 3, and the neutral complex [(Cp'''Co)(μ-PCl)(μ,η[3]:η[1]−P,F)] (11), respectively. The use of [(CH3)3NF instead of KI leads to the formation of [(Cp'''Co)(μ-PF2)(μ,η[3]:η[1]−P,F)] (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, 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 Pn ligands (TM-Pn) (n = 1–14)[4,5] followed by the halogenation of the Pn unit and the subsequent substitution of the halogen by organic substituents or other functional groups. However, the halogenation of the TM-Pn complexes has only been scarcely investigated and merely a few examples are known so far.[6,7,8,9,10,11,12] 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 [Ru3Cp*2(PCY3)(μ,η[3]:η[1]−P,X)]RuCp* (X = Cl, Br; Scheme 1 A), which contains an uncommon P5Cl5 ligand.[9]

Scheme 1. Selected examples of halogenated polynitrogen complexes.

Recent studies conducted by our group targeted the halogenation of polynitrogen complexes containing different Pn units such as a P6-containing dimetalla-tetrahedrane,[12] a cyclo-P3N6...
end-deck[8] and a cyclo-P₈-triple-decker complex, 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-P₈ compound combines the features of triple-decker complexes and separated E₄ units. Moreover, no compounds with E–F bonds were accessible by the approaches used so far.

Therefore, the redox-active compounds [(Cp’’’Co)(μ₄-η°⁻⁻-E₄)] (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)(μ₄-η°⁻⁻-P₈)] or for heterobimetallic triple-decker complexes.[15] 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)(μ₄-η°⁻⁻-E₄)][²][EFOX] (E = As (8), P (9), [EFOX] = [AlOC(CF₃)₃]⁺) in good yields.[17] As some successful examples of the halogenation of cationic species have been reported, as for instance [P₂I₉]⁺[EFOX] (Scheme 1 F) resulting from the iodination of [AgI₂]⁻[P₂I₉] (18) and [(CpRu(PPh₃)₃)(μ₄-η°⁻⁻-P₈)]⁺[IFOX] (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 [I(CH₃)₂]⁺[N]F (TMAF). This approach would represent a new method to synthesise compounds containing E–X bonds, representing a milder alternative to the halogenation of polynitrogen 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 PF₅⁻ species. In this respect, a novel approach to fluorine-containing nitrigenoc complexes would be of benefit.

Herein, we present the reactivity of the polynitrogen compounds 1 and 2 towards halogen and halogen sources (I, PBr₃, PCl₃), 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-E₄ compounds (E = P, As) by nucleophilic quenching of the cationic polynitrogen species 8 and 9 by the salts KI and [(CH₃)₂]⁺[N]F, the latter representing a novel approach to fluorine-containing TM-E₄ derivatives.

Results and Discussion

The reaction of 1 with an excess (4 equiv.) of halogen or halogen sources (I, PBr₃, PCl₃) leads to the isostructural compounds [(Cp’’’Co)(μ₄-η°⁻⁻-E₄)]⁺[Y] (Y = I⁻, [AsI₈]⁻[IFOX] (3 a); X = Br, Y = [CoBr₂]⁺[IFOX] (4); X = Cl, Y = [CoCl₂]⁺[IFOX] (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 identified (see the Supporting Information). The cation of the complexes 3 a, 4 and 5 contains a strongly distorted cyclo-As₈ ring 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 As₈X units as middle decks are obtained. Few examples of complexes bearing different arsenic halides are reported in the literature, such as AsX₈ (X = Cl, Br, I)[19] or the remarkable ligand As₁₂ in [(Cp⁶Ru)(μ₄-η°⁻⁻-As₁₂)]⁺[20] which represents a tetramer of [Asl₄]⁻ fragments. However, no examples of polyarsenic subhalides as ligands exists as found in 3 a, 4 and 5. Crystals suitable for X-ray structure analysis were obtained from solutions in C₂H₅Cl, layered with n-pentane at room temperature (3 a, 3 b, 4 and 5). From the reaction solution of 1 with iodine, beside 3 a a few crystals with the same cation but with [CoCl₂]⁺[IFOX] (n = 0, 2, 4) as counterion were isolated (3 b). The solid-state structure of the anion in 3 a ([AsI₈]⁻, Figure 1) was already found in salts with different counterions[9,20] and therefore will

![Figure 1](image-url)  
Figure 1. Molecular structures of 3 a (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.
The As₄ 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: 2.327(5) Å in 4, As₂: As₃: 2.342(5) Å in 5), two are in the range of an As–As single bond and the side-on coordinated As–As bond to the halogen atom is elongated (As₄–As₁: 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 and whose geometries were optimised at the TPSSH/def2-TZVP 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 As₄ 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–As₁A 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 3 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 [Co₂X₆]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.[21]

The ¹H NMR spectrum of 3a (CD₂Cl₂) shows three sharp singlets for the magnetically equivalent Cp" ligands at δ = 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"Co₂]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"Co₂]²⁺ and 3a is approximately 1.5:1, which could partly explain the low yield of isolated 3a. The ¹H NMR spectrum of 4 (CD₂Cl₂) shows three broad signals for the Cp" ligands centred at δ = 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 δ = 0.83 and 0.71 ppm (integral ratio: 18:9) corresponding to the tBu groups of the Cp" ligand and a very broad signal at 4.04 ppm (δ = 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 [Co₂X₆]²⁻ (X = Br, Cl) with the cation. The same phenomenon was described for another salt of the [Co₂X₆]²⁻ anion[26] and this might explain why it is not detected for 3a (where the anion is diamagnetic). The signals of the tBu 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-As₅ 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"Co₂]µ[µ₁η¹⁻E₆]²⁻ (E = As, P; see Scheme 1, 8 and 9),[21] the halogenation of

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[(Cp'''Co)(μ,P{η^2}::P{η^2})] (2; see below) gave different species as compared to 1. Interestingly, a recent investigation concerning the iodination of [(Cp'Me){η^2}E] (Cp' = C_{5}Me_{5}; M = Fe; R = Br; E = As, P) showed likewise different behaviours of the As and P derivatives. The halogenation of 2 leads to different compounds depending on the halogenating agent used, 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 I_{2} is conducted under the same conditions as for 1 (4 equiv. of I_{2}), the only product detected by ^1H NMR spectroscopy of the reaction solution is [(Cp'''Co)] (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 P{η^2} analogue to what was observed for the halogenation of the heavier compound could be isolated. 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)(μ,P{η^2}::P{η^2})] (2) was reacted with PBr_{5} (4 equiv.) at room temperature, the crude reaction mixture shows a silent ^31P(^1H) NMR spectrum, as observed with I_{2} (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 Br_{2} (4 equiv.) at −50°C, [(Cp'''Co)(μ-PBr{Br})] (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 CD_{2}Cl_{2} were recorded, to detect its thermal decomposition (Figure S6).

Surprisingly, a different reaction behaviour was observed when the chlorine source PCl_{5} was used instead. While the VT ^31P(^1H) NMR spectra of the crude reaction mixture showed an unsselective reaction as observed for PBr_{5} (see the Supporting Information), the reaction of 2 and PCl_{5} (4 equiv.) at room temperature, instead leads to the isolation of an analogue of 6a, namely the ionic complex [(Cp'''Co)(μ-PCl{Cl})][Co{BrCl}{Cl}], (6b), and a few crystals of the neutral species [(Cp'''Co)(μ-PCl{Cl})][μ-P{η^2}] (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 I_{2} or PX_{3} (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 PX_{3} 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 (PCl) bridging ligand, with a distance comparable to the one in 6 (P1–P2: 2.608(3) Å; BO: 0.11) and a (P{Cl}) bridging ligand, coordinating in a μ{η^2} 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). The ligand (P{Cl}) was so far only reported in the bimetallic complex [(Cp'''Mo(CO))][μ-P{Cl}]AlCl_{3}]_{2} A similar bridging P{X} unit (X = Cl, Br) stabilised by N-heterocyclic
carbenes was observed in the cations [P₂(IPr)Cl]⁺ [30] and [P₂(I-Pr)Br]⁻ [31]. Compound 7 is extremely sensitive to moisture and air, and despite numerous attempts, it always co-crystallises with the oxidised compound [(CP₃Co)(μ₃-I)][I] (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-P₃ ligand as middle-deck, coordinating in an η⁴ fashion to the (CP₃Co) fragment and in an η¹ mode to a newly formed (CP₃CoI)⁺ unit. The P–P bond lengths in the P₂S unit vary from 2.130(3) Å to 2.183(3) Å, being all in the range 2.16–2.22 Å.

The reaction of 8 with KI (2 equiv.) results in the formation of [{(CP₃Co)(μ₃-I)η¹-AsI}][I] (10) which contains the same cation as 3a, with I⁻ instead of the [As₃I₄]⁻ 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-As₄ 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–II 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 As₃I 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, [{(CP₃Co)(CP₃CoI)μ₃-I}⁻][I] (Scheme 4), the only one that could be isolated among the products formed in this reaction. The structure in the solid state shows a sandwich complex with a square-planar cyclo-P₃ ligand as middle-deck, coordinating in an η² fashion to the (CP₃Co) fragment and in an η¹ mode to a newly formed (CP₃CoI)⁺ unit. The P–P bond lengths in the P₂ unit vary from 2.130(3) Å to 2.183(3) Å, being all in the range 2.16–2.22 Å.

The 'H NMR spectra of 6a,b (CD₂Cl₂) show the characteristic signals for the magnetically equivalent CP' ligands with the integral ratio of 2:18:9, centred at δ = 4.70, 1.21 and 1.02 ppm (6a) and at δ = 4.82, 1.07 and 0.79 ppm (6b). The 31P[1H] NMR spectra show each one singlet at δ = 135.2 ppm (6a) and one at δ = 176.2 ppm (6b), respectively, for the two equivalent P atoms. In the 31P[31P] NMR spectrum of 6a, there are two additional doublets, centred at δ = 139.2 and at 30.9 ppm, with a Jₚₚ 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 31P[1H] NMR spectrum of 7 shows an AMNX spin system with four resonances centred at δ = 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 the bridging P atom, and for the upfield shifted one (P1) a Jₚₚₚₚ coupling of 238 Hz is detected, due to the coupling with P4 (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 31P[1H] NMR spectrum of the dark brown crystals was recorded (CDCl₃), 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 31P[1H] 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 7a). When the same hexane solution was filtered over celite, the 31P[1H] NMR spectrum of the solution showed among some other signals, signals for 7a and 7. By comparing both spectra and with the help of a 31P–31P COSY NMR experiment, the signals corresponding to 7 could be unequivocally attributed (see the Supporting Information for detailed spectra).

The signal of PX₃ (X = Cl, Br) is always detected in the reaction solution, when using PX₃ (X = Cl, Br) as a reagent, due to its dissociation [32,33] but 31P NMR spectroscopic investigations show that also the phosphorus atoms in 2 are partly halogenated to PX₃ (X = Cl, Br).

Since the halogenation of 1 revealed a synthetic way to obtain the halogenated monocatic 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 [{(CP₃Co)(μ₃-I)η¹-AsI}][TEF₂] [20] (E = As (8), P (9)) with weak nucleophiles such as X⁻ (X = I, F) came up.
of a shortened P–P single bond[21] and similar to those observed for the sandwich complex \([\text{Cp}'''\text{Co}(\eta^5\text{-P}_3\text{F}_2)]\).[24] 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 tetrakis(dimethylamino)fluoride ([CH(NMe)₂]₂NF; TMAF). The reaction of 9 with \([\text{CH}_3\text{NF}] \) (2 equiv.) leads to \([\text{[Cp}''''\text{Co}]_2(\mu\text{-P}_3\text{F}_2)]\) (12, Scheme 4) and to the neutral complex \([\text{[Cp}''''\text{Co}]_2(\mu\text{-P}_3\text{F}_2)]\) (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 \([\text{CH}_3\text{NF}] \) (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 XeF₂ resulted in decomposition. There is no direct evidence of the formation of As₉F₉ as the final product of the decomposition, but many new signals are detected in the ³¹P NMR spectra of the reaction solution, while the one of 1 disappeared.

Compound 12 could also be obtained when the monocation \([\text{[Cp}''''\text{Co}]_2(\mu\text{-P}_3\text{F}_2)]\) [BF₄] (1 equiv.) was reacted with \([\text{CH}_3\text{NF}] \) (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 \((\text{PF}_3)\) unit and a \(\mu\text{-P}_3\text{F}_2\) ligand. The \(\text{P}_2\text{F}_2\) ligand contains a P–P bond length in the range of a single bond (P–P=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 \((\text{PF}_3)\) is widely known for both organic[35] and inorganic compounds,[36] the \(\text{P}_2\text{F}_2\) unit has only been reported so far in \(\text{Me}_3\text{SiR}_2\)PF₃ (R=Bu).[37] Therefore 12 represents the first complex bearing such a \(\text{P}_2\text{F}_2\) ligand coordinated to a transition metal.

The \(^{1}H\) NMR spectrum of 10 (CD₂Cl₂) 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 \(\text{Cp}''''\) 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 \(^{31}P\)\(^{1}H\) NMR spectrum of the crystals dissolved in CH₂Cl₂, which show only two resonances centred at −46.9 and −520.7 ppm, corresponding to 2 and \(\text{P}_2\) respectively.[38] To check if the structure of 11 could be stable in solution at lower temperatures, crystals of 11 were dissolved in CD₂Cl₂ at 193 K and a variable temperature \(^{31}P\)\(^{1}H\) NMR spectroscopic investigation was performed. The \(^{31}P\)\(^{1}H\) 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 \(\text{A}_2\text{M}_1\) spin system, which disappear at 253 K. Although these spectra may indicate a dynamic process in solution of the \(\text{cyclo-P}_2\text{As}\) 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 \(^{1}H\) NMR spectrum of dissolved crystals of 12 (CD₂Cl₂) shows six signals for the two magnetically non-equivalent \(\text{Cp}''''\) ligands, together with the signals of the \(\text{Cp}''''\) of 2 which co-crystallise, as minor part, with 12 (ratio 12:2=0.94:0.06).[39] The \(^{31}P\)\(^{1}H\) 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 PF₃ ligand \((\text{P}_3)\) resonates at 303.3 ppm and shows a large coupling to the F atoms \((J_{PF}=1213\) Hz and 1269 Hz). The other three resonances belong to the \(\text{P}_2\text{F}_2, \text{F}_2\) unit. The diffluorinated P atom \((\text{P}_2\text{F}_2)\) resonates at 218.9 ppm \((J_{PF}=1322\) Hz and 1367 Hz). The signal at −51.4 ppm partly overlaps with the signal of compound 2 (co-crystallised with 12). The \(^{19}F\)\(^{1}H\) NMR spectrum of 12 shows an AMXN 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 \(^{31}P\)\(^{19}F\) NMR chemical shifts and coupling constants of 12 were calculated by iterative fitting of the experimental spectra.

Conclusions

In summary, we have shown that \([\text{[Cp}''''\text{Co}]_2(\mu\text{-P}_3\text{F}_2)]\) (1) can easily be oxidised by halogens to obtain the monocationic species 3–5 revealing the formation of two new As–As single bonds to form an unprecedented cyclic arsenic subhalide ligand As₂X (X=I, Br, Cl). An alternative route to the same cationic complexes was achieved by treating the dication \([\text{[Cp}''''\text{Co}]_2(\mu\text{-P}_3\text{F}_2)]\) [TEF₄] (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 As₂ middle-deck, contrary to the formation of the anion \([\text{As}_2\text{I}_3]\) 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 dicaticionic 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 [(CH3)2NF, novel P–F bonds are formed in a controlled way, as observed for compound 12, [(Cp'''CoI2)2(μ-η2:η1-PF6)], which contains a novel and unprecedented P,F-chain ligand. These results open up the possibility of synthesising new polymeric compounds bearing P–X bonds by using mild 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-2162041 ([(Cp'''CoI)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.

Keywords: arsenic • fluorine • halogenation • nucleophilic quenching • phosphorus

[1] D. E. C. Corbridge, Phosphorus: Chemistry, Biochemistry and Technology, 6th ed., CRC Press, Boca Raton, 2013.
[2] a) D. J. Scott, J. Cammarata, M. Schimpf, R. Wolf, Nat. Chem. 2021, 13, 458–464; b) C. M. Hoidn, D. J. Scott, R. Wolf, Chem. Eur. J. 2021, 27, 1886–1902; c) R. Rothfie1der, V. Streifert, U. Lennert, J. Cammarata, D. J. Scott, K. Zeller, R. M. Gschwind, R. Wolf, Angew. Chem. Int. Ed. 2021, 60, 24650–24658.
[3] a) M. B. Geeson, C. C. Cummins, ACS Cent. Sci. 2020, 6, 848–860; b) F. Zhai, T. Xin, M. B. Geeson, C. C. Cummins, ACS Cent. Sci. 2022, 8, 332–339; c) M. B. Geeson, C. C. Cummins, Science 2018, 359, 1383–1385.
[4] M. Caporali, L. Gonsalvi, A. Rossin, M. Peruzzini, Chem. Rev. 2010, 110, 4178–4235.
[5] B. M. Cossart, N. A. Piro, C. C. Cummins, Chem. Rev. 2010, 110, 4164–4177.

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[36] a) S. Kahlal, W. Wang, L. Scoles, K. A. Udachin, J. Saillard, A. J. Carty, *Organometallics* 2001, 20, 4469–4475; b) C. M. Hoidn, J. Leitl, C. G. P. Ziegler, I. G. Shenderovich, R. Wolf, *Eur. J. Inorg. Chem.* 2019, 1567–1574; c) A. M. A. Boshaala, S. J. Simpson, J. Autschbach, S. Zheng, *Inorg. Chem.* 2008, 47, 9279–9292.

[37] G. Fritz, M. Jarmer, E. Matern, *Z. Anorg. Allg. Chem.* 1990, 589, 23–38.

[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, P₄ and [(Cp'''Co)(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″ ligand of a compound that could not be identified so far.