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1. Introduction

Metal phosphides have been studied extensively in the past 20 years, largely because they exhibit not only a broad range of physical properties such as magnetism and data storage [1-3], superconductivity [4], magnetocaloric effect [5], magnetoresistance [6], optoelectronics or luminescence [7–9], but also interesting chemical properties, including lithium intercalation [10,11], improved performances for lithium ion batteries [12,13], or catalytic activity [1,14–17]. In particular, metal phosphides have been used as hydrotreatment catalysts for reactions such as hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrodeoxygenation (HDO). While Ni₂P exhibits the best activities in both HDS [18] and HDO [16], MoP and WP give the best results in HDN [19,20]. Moreover, CoP is quite active in HDS [21,22], and Co₂P shows promising results in HDO [16].

Traditionally, metal phosphides have been synthesized by reacting toxic phosphines or phosphorus pentachloride with metals or metal salts [23,24]. More recently, nanometric phosphides, such as FeP [25], CoP [26], Co₂P [26,27], Ni₂P [27-30] and Cu₃P [27-29] have been obtained by solvothermal methods with a rather large polydispersity. The addition of surfactants to control the size and shape of the nanoparticles (NPs) was introduced later

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ABSTRACT

Crystalline cobalt phosphides were synthesized by using three different, low oxidation-state organometallic clusters as precursors, $[Co_4(CO)_{10}(\mu-dppa)]$, $[Co_4(CO)_{10}(\mu_4-PPh)_2]$ and $[Co_4(CO)_8(\mu-dppa)_2]$ (dppa = Ph₂PNHPPh₂), which are characterized by Co/P ratios of 2:1, 2:1 and 1:1, respectively. Depending on their Co/P ratio, these clusters are suitable single-source precursors to form CoP and Co₂P without the need to add any other reagent or surfactant. The thermal behavior of these three clusters was investigated under different conditions. The results show how their Co/P ratios, the nature of the atmosphere used for their thermal activation and the temperature control the nature and composition of the resulting phases.

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[30]. Dendritic nanostructured Ni₂P [31], and Co₂P nanorods [32] were successfully synthesized under such conditions. Brock et al. have obtained MnP, FeP, and CoP nanocrystals [33,34] by using an organometallic route. The reaction of $[Mn_2(CO)_{10}]$ with $P(SiMe_3)_3$ in trioctylphosphine oxide with an additional surfactant led to stabilized MnP nanospheres of tunable size. Similar approaches led to FeP and CoP NPs. Park et al. developed an original access to a number of transition metal phosphides, by thermal decomposition of a continuously delivered metal-phosphine complex to the reacting mixture [35,36]. Reactions of the corresponding metal-carbonyl, metal-acetylacetonate or metallocene complex with trioctylphosphine (TOP) resulted in Mn, Fe, Co and Ni metal-phosphine complexes, precursors to MnP, FeP, Co₂P and Ni₂P nanorods, respectively. More recently, the formation of metal phosphides was reported where metallic NPs are first formed in situ and then reacted with an adjusted concentration of TOP to form the desired phosphides, through a nanoscale Kirkendall effect (difference of diffusion rate between two types of atoms). Ni₂P nanocrystals [37] or hollow nanospheres could be synthesized in this manner, as well as a broad range of transition metal phosphides that were not accessible before, such as PtP₂, Rh₂P, Au₂P₃, Pd₅P₂, and PdP₂ [38]. The same group reported the synthesis of Rh₂P nanocrystals with various shapes (cubes, triangles, multipods) [39] using the same sequence of reactions. Various transition metal phosphides have been prepared using this methodology, not only as nanocrystals, but also as bulk, thin films and foils [40]. A detailed investigation of the transition steps from ϵ -Co to Co₂P,





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and to CoP NPs was reported by Robinson and co-workers [41]. In all these cases, the NPs were coated with organic surfactants, rendering them soluble in a variety of solvents. Detrimental to applications in catalysis is that the accessibility of the active sites is drastically reduced by the coating.

In principle, uncoated NPs should represent heterogeneous catalysts of choice, due to their high surface area and to their easier recyclability than homogeneous catalysts. Noteworthy is, however, that many nanosized metal phosphides were prepared on inorganic supports, as this may help stabilizing the NPs, enhance their catalytic performances, and make them easier to separate from the reaction mixture [42]. Metal salts (phosphates or phosphites) [20,43,44] were used to produce Ni₂P, CoP, Fe₂P, MoP, WP supported on SiO₂. Organometallic precursors were also applied to the formation of supported metal phosphide NPs. Lukehart et al. prepared a silica composite by grafting organometallic complexes at the surface of a xerogel [45], Fe₂P, RuP, Co₂P, Rh₂P, Ni₂P, Pd₄P₂, and PtP₂ phases could be obtained after thermal treatment under a hydrogen atmosphere. Generally, molecular clusters were found to be suitable precursors for the preparation of inorganic NPs [46-55] (pure metals; metal oxides; carbide, silicide, chalcogenide or pnictide alloys; or metallic alloys), which find applications in catalysis [56]. The formation of the appropriate active phases requires a good knowledge of the reactivity and mechanism of decomposition of the precursor clusters.

Our group has previously synthesized cobalt phosphide NPs in the channels of mesoporous SBA-15 silica by grafting the functionalized ligand (Ph₂P)₂N(CH₂)₃Si(OMe)₃ to the surface of silica and then reacting it with a cobalt carbonyl cluster stabilized by a bridging dppa ligand, $[Co_4(CO)_{10}(\mu-dppa)]$ (dppa = Ph₂PNHPPh₂) [57]. Thermal activation at 800 °C afforded well-dispersed cobalt phosphide NPs inside the channels. In principle, the advantage of using low oxidation-state clusters is that no drastic reduction step is required to access NPs. We then began an investigation on the synthesis of metal phosphide NPs starting from well-characterized metal phosphine carbonyl clusters characterized by different metal M/P ratios [58]. Their composition and the close proximity of the M and P atoms make such clusters potentially interesting suitable single source precursors to metal phosphide, without addition of any other reagent or surfactant. However, our investigations show that the control of the nature of the phases thus formed is not as straightforward as believed and depends much on the reaction conditions, i.e. atmosphere, temperature, and stoichiometry of the precursors.

In the present work, we investigate the synthesis of highly crystalline cobalt phosphide NPs from three different tetranuclear P-substituted carbonyl cobalt clusters. These precursors are characterized by different metal to phosphorus ratios, namely Co/ P = 2 in $[Co_4(CO)_{10}(\mu-dppa)]$ (1) and $[Co_4(CO)_{10}(\mu_4-PPh)_2]$ (2), and Co/P = 1 in $[Co_4(CO)_8(\mu-dppa)_2]$ (3) (Fig. 1). We studied their

thermal behavior under different atmospheres and determined the best conditions to obtain Co₂P or CoP particles.

2. Experimental section

2.1. General considerations

All molecular clusters were synthesized using standard Schlenk techniques and dry, distilled solvents. Once synthesized and purified, they were kept under Ar in Schlenk tubes, but could be handled in air for a few days without problem. The infrared spectra were recorded on Thermo Nicolet 6700 FT-IR and Thermo Nicolet 380 FT-IR instruments in transmission mode, using CH₂Cl₂ as solvent. Elemental analyses were done by the "Service d'analyse, de mesures physiques, et de spectroscopies optiques" of the University of Strasbourg, France. Thermogravimetric and thermodifferential analyses (TGA and TDA, respectively) were carried out using a SDT Q600 TA instrument in air or with a 50 mL min⁻¹ N₂ or H₂/Ar (5/95%) stream, between ambient temperature and 900 °C with a heating rate of 2 °C min⁻¹. Powder X-ray diffraction patterns (PXRD) were collected on a PANalytical MPD X'Pert Pro diffractometer operating with Cu-K α radiation (λ = 0.15418 nm) equipped with an X'Celerator real-time strip detector (active length = 2.122° 2θ). The powder patterns were collected with a flat sample holder at 295 K in the range of $15 < 2\theta < 70^\circ$ with a step of $0.017^\circ 2\theta$, and a time/step of 300 s.

High temperature X-ray diffraction (HT-XRD) data were collected on a PANalytical MPD X'pert Pro diffractometer operating with X-ray monochromatic radiation of Cu-K α_1 (λ = 0.15406 nm) equipped with an X'Celerator real-time multiple strip detector (active length = 2.122° 2 θ). The powder patterns were collected in the range of 15 < 2 θ < 70°, with a step of 0.017° 2 θ , and a time/step of 600 s. High-temperature X-ray powder data were obtained using an Anton Paar HTK high-temperature chamber under air or helium atmospheres.

The SEM images were recorded on a Jeol 6700F operating at 3 kV with a camera distance of 8 mm. The topological images were observed by using backscattered electron signal (BSE) with LEI (secondary and back-scattered electrons) and SEI (secondary electrons) modes. Chemical analyses were recorded with an EDX probe (the minimum size is 1 μ m³), operating at 15 kV (camera distance: 15.2 mm) with LEI and composition (COMPO) modes. Data for cobalt, phosphorus and oxygen were collected, even though oxygen content cannot be quantified precisely. The precision on the EDX measured values is lowered by the roughness of the sample and by the size of the probe, which might analyze surrounding neighbors. High oxygen measured values, however, indicate that the analyzed sample contains oxygen.



Fig. 1. Structure of the molecular clusters 1, 2 and 3.

2.2. Synthesis of the precursors

The clusters $[Co_4(CO)_{12}]$ [59], $[Co_4(CO)_{10}(\mu$ -dppa)], $[Co_4(CO)_8(\mu$ -dppa)_2] [60] and $[Co_4(CO)_{10}(\mu_4$ -PPh)_2] [61,62] were prepared according to the published procedures. Additional details are provided below.

2.2.1. [Co₄(CO)₁₀(μ-dppa)], **1**

In a typical synthesis, 6.87 g (17.8 mmol) of dppa in 500 mL of CH₂Cl₂ were added to a solution of $[Co_4(CO)_{12}]$ (10.2 g, 17.8 mmol) in 500 mL of CH₂Cl₂. The phosphine dppa was added in slight excess to avoid the presence of residual $[Co_4(CO)_{12}]$ and form rather small amounts of cluster **3**, which is easier to separate from **1** than $[Co_4(CO)_{12}]$. The reaction mixture was stirred for 2 h at room temperature and monitored by TLC and IR spectroscopy. $[Co_4(CO)_{10}(\mu - dppa)]$ was separated by column chromatography (silica gel) with dichloromethane/pentane (1:1) under argon. After removal of the solvent under reduced pressure, a dark brown-red powder was obtained (11.7 g, 73%). *Anal.* Calc. for $C_{34}H_{21}Co_4NO_{10}P_2$: C, 45.28; H, 2.33; N, 1.55; Co, 26.16. Found: C, 44.75; H, 2.61; N, 1.51%. IR (CH₂. Cl₂): v_{CO} 2068 (s), 2030 (s), 2015 (s), 1991 (sh), 1856 (w), 1823 (m), 1794 (m) cm⁻¹.

2.2.2. [Co₄(CO)₁₀(μ₄-PPh)₂], **2**

Typically, $[Co_2(CO)_8]$ (3.30 g, 9.70 mmol) was reduced over Na amalgam in THF to form Na[Co(CO)_4] overnight. The solution was then filtered with a cannula to separate it from the Na amalgam, and cooled down to -78 °C. Upon slow addition of PhPCl₂ (1.2 mL, 9.0 mmol) at -78 °C, a deep red mixture was obtained. The mixture was stirred for 2 h at -78 °C, then allowed to warm up to room temperature, and stirred overnight. Purification by chromatography through a silica gel column using a mixture of dichloromethane/pentane (1:1) as eluent gave the desired product in 16% yield. Anal. Calc. for $C_{22}H_{10}Co_4O_{10}P_2$: C, 36.10; H, 1.38. Found: C, 35.86; H, 1.67%. IR (CH₂Cl₂): v_{CO} 2040 (vs), 2031 (s), 2015 (s), 1872 (w) cm⁻¹.

2.2.3. [Co₄(CO)₈(μ-dppa)₂], 3

Using a similar procedure to that for **1**, a mixture of $[Co_4(CO)_{12}]$ (2.35 g, 4.10 mmol) and dppa (3.15 g, 8.17 mmol) in a ~1:2 ratio in CH₂Cl₂ at room temperature resulted in a dark green solution. Here, $[Co_4(CO)_{12}]$ was added in a slight excess to avoid leaving unreacted dppa, because the resulting small amounts of cluster **1** thus formed are easier to separate from **3** than dppa. The desired product was purified by chromatography through a silica gel column, using a mixture of dichloromethane/pentane (1:1) as eluent. After removal of the solvent under reduced pressure, a black-green powder was obtained (3.63 g, 72%). *Anal.* Calc. for C₅₆H₄₂Co₄N₂O₈. P₄: C, 54.61; H, 3.41; N, 2.27. Found: C, 54.09; H, 3.58; N, 2.21%. IR (CH₂Cl₂): v_{CO} 2011 (s), 1976 (vs), 1830 (w), 1788 (m, br), 1777 (m, br) cm⁻¹.

2.3. Synthesis of CoP, Co₂P and thermal decomposition products

The clusters (*ca.* 40 mg) were deposited on a gold sheet, held on an alumina crucible, to avoid any contact between the samples and alumina, thus forbidding migration from one to the other at high temperatures. The clusters were then treated at 650 or 800 °C for 2 h, under an air, N₂ or H₂/N₂ (5/95%) stream, in a Hermann Moritz oven. The ramp was set to 2 °C/min to obtain a sample as homogeneous as possible as the temperature increases, thus avoiding diffusion issues at high temperatures.

3. Results

3.1. Thermogravimetric analyses

We first investigated the thermal behavior of the clusters under air or inert atmosphere (N₂ stream) using thermogravimetric analysis (TGA). Below 100 °C, the TGA curves differ slightly following the nature of the clusters (Figs. S1-3) (Supporting information). Indeed, for clusters 1 and 3, there is a slight weight loss possibly accounting for desorption of trace of water possibly originating from a weak hygroscopic character of the clusters (Figs. S1 and S3) which contain amine groups unlike cluster 2 and for which decomposition starts directly at about 120 °C (Fig. S2). The corresponding TGA curves for compound **1** up to 900 °C are plotted in Fig. S1. A first product was detected after 500 °C, corresponding to 54.3% of the initial mass under air, and 56.6% under N₂. Another step around 800 °C precedes the final plateau of the curve at 48.9% of the initial mass, in both cases, which is not consistent with the formation of pure cobalt phosphides. To identify the phases obtained by decomposition of **1** under oxidizing or inert atmosphere, powder XRD patterns of the products were collected. The PXRD



Fig. 2. XRD powder patterns of (A) 1, (B) 2 and (C) 3 under air and N₂ stream.

data (Fig. 2A) revealed the presence of a mixture of $Co_3(PO_4)_2$ (JCPDS 04-008-8058) and Co_3O_4 (JCPDS 04-008-3317) both under air and N₂. The similar final weight losses suggest that products with the same composition were obtained in both cases after calcination.

In the case of **2**, the evolution of the sample mass is different under air or under N₂ (Fig. S2). The first weight loss is sharper under air, with a first plateau at 220 °C, while the first plateau appears at 400 °C under N₂. Even if the weight loss profiles are different, the composition of the powder at the end is the same, i.e. a mixture of $Co_3(PO_4)_2$ and Co_3O_4 according to XRD (Fig. 2B), like in the case of **1**.

The TGA curve of **3** is shown in Fig. S3 (Supporting information). It is similar to that of **1** but the difference in behavior between air and N₂ is larger than in the case of **1**. Again a product is obtained around 500–550 °C (51.5% of the initial mass under N₂, and 53.5% under air), with a gradual weight loss above 600 °C in both cases. The XRD measurements indicated the formation of $Co_2(P_2O_7)$ (JCPDS 04-011-1928) and $Co_3(PO_4)_2$ (JCPDS 04-008-8058) (Fig. 2C).

The TGA-TDA curves obtained under reducing atmosphere (H_2/Ar) are presented in Fig. 3. Below 100 °C the same phenomenon is



Fig. 3. TGA curves of (A) 1, (B) 2 and (C) 3 under H₂/Ar stream.

observed as under air and N₂ atmosphere (see above). For the three compounds, all steps are exothermic. Moreover, the TGA curves exhibit a much steeper weight loss than under air or nitrogen and the product corresponding to the final plateau is obtained at lower temperatures of 600, 550 and 650 °C for 1, 2 and 3, respectively. Compound 2 exhibits a particularly steep weight loss and low temperature of decomposition (Fig. 3B). The weight loss is almost complete at 210 °C. It was not possible to analyze by powder X-ray diffraction the final products obtained after calcination in the set-up we used owing to the very small amount of product available. Nevertheless, starting from 1, the weight of product is 34.0% at 600 °C and 33.1% at 900 °C (Fig. 3A). This fits rather well with the expected mass for pure Co_2P starting from $[Co_4(CO)_{10}($ µ-dppa)]: 33.0%. Similarly, the mass of 40.5% at 650 °C and 39.9% at 900 °C for **2**, corresponds very well to the rapid transformation of $[Co_4(CO)_{10}(\mu_4-PPh)_2]$ in Co₂P (expected 40.7%). Finally, compound **3** exhibits a variation of mass (Fig. 3C) of 38.7% at 500 °C. 31.3% at 650 °C, and 29.3% at 900 °C which is fully consistent with the formation of CoP (expected 29.2%), in accordance with the Co/P ratios in the starting clusters.

3.2. Temperature-resolved X-ray diffraction

We also performed temperature-resolved XRD measurements under air in order to follow *in situ* the formation of intermediate crystalline phases during calcination. The data were collected at temperatures corresponding to the different plateau of the TGA curves.

Typically, in the case of cluster **1**, we recorded XRD patterns at 200, 500, and 800 °C (Fig. 4A). No crystalline phase was detected at 200 °C. The oxide Co_3O_4 (JCPDS 04-008-3317) is the first phase observed at 500 °C along with $Co_3(PO_4)_2$ (JCPDS 04-008-8058). This is fully consistent with the products obtained after TGA up to 900 °C: cobalt phosphate and cobalt oxide.

In the case of cluster **2**, XRD were recorded at 250, 500 and 800 °C (Fig. 4B). No crystalline phase was observed below 500 °C. As for cluster **1**, cobalt phosphate crystallizes only after 500 °C, whereas cobalt oxide is already crystalline at this temperature. No diffraction occurred at 250 °C though.

XRD patterns were recorded at 200, 600 and 800 °C for cluster **3** (Fig. 4C). As previously observed, two different cobalt phosphates were obtained at 800 °C: $Co_2(P_2O_7)$ (JCPDS 04-011-1928) and $Co_3(-PO_4)_2$ (JCPDS 04-008-8058), the former being the only phase detected at 500 °C. Again, no crystalline phase was observed at 200 °C.

As we noticed that oxidation of cobalt occurs in air and N_2 , we monitored the sample evolution by temperature-resolved XRD measurements (Fig. 5) under He atmosphere. Indeed, He is known to be more O_2 -free than N_2 , and it does not diffuse X-rays as much as Ar.

In the case of **1** (Fig. 5A), it appears that the first crystalline phase detected is cubic Co metal (JCPDS 04-003-6596), around 500 °C. The crystalline Co₂P phase (JCPDS 04-007-1524) appears only around 600–650 °C, but it crystallizes in larger quantities than Co at higher temperatures. Nevertheless, Co₃(PO₄)₂ (JCPDS 04-008-8058) is still formed in large enough quantities to be detected above 700 °C. It should be noted that the reflection peaks observed at 35.6° (-202), 35.8° (121) and 36.8° (-131) have high relative intensities of 23%, 26% and 40%, respectively. Such high level of crystallinity suggests that cobalt phosphate forms already at lower temperatures, although it was not detected in this range of 2θ at the temperatures we explored.

Both cubic Co and Co_2P were formed when heating up the cluster **2** (Fig. 5B), but the intensity of the Co peaks seems relatively higher than in the case of cluster **1**. In addition, if Co_2P is apparently present, its characteristic peaks are poorly resolved, espe-



Fig. 4. Temperature-resolved XRD of samples (A) 1, (B) 2, (C) 3 between 200 and 800 $^\circ\text{C}$ under air.

cially the main peak at 40° (112). Moreover, as in the case of **1**, cobalt phosphate $Co_3(PO_4)_2$ (JCPDS 04-008-8058) is formed in quantities large enough to be detected at 650 °C. The main peak of this phase appears at 2θ = 25.9° (012) and the relative intensity of the observed peaks between 35° and 38° is about 25–40%.

Cluster **3** yields neither cubic Co nor $Co_3(PO_4)_2$, according to Fig. 5C. Indeed, Co_2P appears at around 650 °C and $Co_2(P_2O_7)$ (JCPDS 04-011-1928) is detected at 800 °C. The peak (220) at 35.2° has a weak relative intensity (19%).

The three clusters were treated at 650 and 800 °C under a slightly reducing atmosphere in an oven. The black powders obtained were first analyzed by means of XRD. Cluster **1** yielded crystalline Co_2P (JCPDS 04-007-1524), as shown in Fig. 6, both at 650 and 800 °C. The thermal treatment of cluster **2** under reducing atmosphere showed the formation of Co_2P (JCPDS 04-007-1524) too (Fig. 7).

These results are consistent with the TGA data and with the composition of the clusters. Cluster **3** gives CoP (JCPDS-01-089-4862) but small additional peaks in the 2θ range 40-44 degrees



Fig. 5. Temperature-resolved XRD of samples (A) **1**, (B) **2**, (C) **3** between 200 and 800 °C under He ("|" indicates where alumina peaks from the sample holder have been removed).



Fig. 6. XRD of cluster 1 calcined at 650 and 800 °C under H₂/N₂.



Fig. 7. XRD of cluster 2 calcined at 650 and 800 °C under H₂/N₂.



Fig. 8. XRD of cluster 3 calcined at 650 and 800 °C under H₂/N₂.

indicate the presence of Co_2P impurities at 650 and 800 °C alike (Fig. 8).

3.3. Scanning electron microscopy

The SEM technique was used to characterize the morphology and composition of the samples after temperature-resolved XRD measurements under atmospheres leading to the formation of cobalt phosphides.

A representative area of a sample of cluster **1** treated at 800 °C under He showed particles with a size ranging from 50 nm to more than 1 μ m (Fig. 9A). Higher magnification (Fig. 9B) revealed bright zones that can be ascribed to Co metal in low quantities in the bulk. It was identified by using X-ray dispersive microprobe analysis (EDX). The compositions deduced from EDX performed on spots 1 and 2 in Fig. 9B are given in Table 1.

Table 1

Chemical composition of spot 1 and 2 from Fig. 9B.

Spot 1		Spot 2	
Element	Atom (%)	Element	Atom (%)
O-K	3.17	O-K	36.13
P-K	0.88	P-K	16.31
Co-K	95.95	Co-K	47.56
Total	100.00	Total	100.00

Global chemical composition of Fig. 10B.

Global	
Element	Atom (%)
O–K P–K Co–K Total	14.12 14.28 71.60 100.00

In the case of cluster **2**, the phase seems to be rich in cobalt, according to EDX measurements (Table 2). Yet, the sample appears much more homogeneous than **1** or **3**, suggesting the formation of NPs too small to be observed individually by SEM (Fig. 10).

As shown by the temperature-resolved XRD study, the behavior of **3** is significantly different from that of **1**. Indeed, the NPs formed are agglomerated in a crust of several μ m (Fig. 11A). Magnification combined with EDX probe analysis of the chemical composition of the crust surface (Fig. 11B) revealed the presence of NPs with a size of hundreds nm and a ratio Co/P ~ 2.4. The particles are held together by a phase with a lower Co/P ratio of *ca*. 1. The elemental analysis data are presented in Table 3.

Finally, analyzes where performed also on the samples decomposed under reducing atmosphere. When treated thermally under H_2/N_2 , cluster **1** yields a homogeneous solid both at 650 and 800 °C (Fig. 12). The chemical compositions from EDX are given in Table 4. The cluster **2** was thermally treated at 650 °C under H_2/N_2 . The chemical analysis from EDX was carried out on two distinct spots of the sample (Fig. 13A).

The results given in Table 5 indicate a homogenous Co/P ratio of 2. At 800 °C, cluster **2** gives particles which seem more separated than at 650 °C (Fig. 13B). Their composition however seems as homogeneous as at 650 °C (Table 6).

The SEM observations and the EDX analyses of all samples together with the higher homogeneity of the product resulting from the calcination of **2** under H_2/N_2 support the interpretation of the PXRD results presented above. When cluster **3** was calcined at 650 °C under H_2/N_2 , it gave a mixture of two products. The first phase corresponds to the grey zone in Fig. 14A. The sample seems



Fig. 9. SEM images of cluster 1 thermally treated under He at 800 °C in (A) LEI and (B) COMPO modes.



Fig. 10. SEM images in COMPO mode of cluster 2 thermally treated under He at 800 °C, (B) being magnified by a factor 10 compared to (A).



Fig. 11. SEM images of cluster 3 thermally treated under He at 800 °C in (A) LEI and (B) COMPO modes.

Table 3					
Chemical composition	of spot	1 and 2	from	Fig.	11B.

Spot 1		Spot 2		
Element	Atom (%)	Element	Atom (%)	
O-K	16.90	O-K	55.78	
P-K	23.89	P-K	20.50	
Co-K	59.21	Co-K	23.71	
Total	100.00	Total	100.00	

to be made of this "grey" phase (spot 1), in which "white" particles are dispersed (spot 2). The "spot 2" in Fig. 14B was observed when zooming on the part where "white" grains can be seen just above the "spot 1". The chemical compositions of "spot 1" and "spot 2" are given in Table 7 and correspond to a Co/P ratio of *ca.* 1 and 2, respectively. At 800 °C, cluster **3** yields the same mixture of crystalline phases, but the micrometric crystals seem more faceted than at 650 °C. The backscattered electron signals are similar on Fig. 15A for both phases, meaning that the difference in atomic numbers in the two phases is quite small. The chemical compositions of this sample measured on spots 1 and 2 from Fig. 15B are

Table 4Global chemical composition of Fig. 12.

Global composition (A)		Global compos	ition (B)
Element	Atom (%)	Element	Atom (%)
O-K	15.88	O-K	4.85
P–K	30.66	P-K	22.32
Co-K	53.46	Co-K	72.83
Total	100.00	Total	100.00

given in Table 8. These values are consistent with those observed for the lower temperature sample.

4. Discussion

The study in the bulk state of three cobalt carbonyl clusters containing phosphorus assembling ligands provided useful informations towards the understanding of their behavior at high temperatures (500–800 °C). Owing to the low oxidation-state of the metal atoms in these clusters and after CO loss under a neutral



Fig. 12. SEM images in COMPO mode of cluster 1 calcined at 650 °C (A) and 800 °C (B) under H₂/N₂.



Fig. 13. SEM images in COMPO mode of cluster 2 calcined at 650 °C (A) and 800 °C (B) under H₂/N₂.

Table 5Chemical composition of spot 1 and 2 from Fig. 13A.

Spot 1		Spot 2	
Element	Atom (%)	Element	Atom (%)
O-K	24.02	O-K	12.59
P-K	24.93	P-K	28.15
Co-K	51.05	Co-K	59.26
Total	100.00	Total	100.00

Table 6Global chemical composition of Fig. 13B.

Global	
Element	Atom (%)
O-K	10.88
P–K	25.35
Co-K	63.77
Total	100.00

atmosphere like He or N_2 , direct formation of metals and/or, in our case, of metal phosphides was anticipated. Actually, an additional reducing agent was required, as shown above. The nature of the atmosphere used during calcination revealed to be a major factor in determining the phases obtained, beside the Co/P ratio in the starting clusters. Table 9 summarizes the different phases obtained during this study. Our experimental results shed light on the mechanisms of decomposition of the clusters in the different atmospheres used.

In the case of cluster **1**, between 90 and 150 °C in air, we expect loss of the carbonyl groups, accounting for 31% of the total mass of the cluster. But the weight loss is lower than expected. Indeed, the residual mass is 85% of the initial mass and we thus assume that

Table 7
Chemical composition of spot 1 and 2 from Fig. 14A and B, respectively

Spot 1		Spot 2		
Element	Atom (%)	Element	Atom (%)	
O-K	14.76	O-K	9.53	
P-K	39.71	P-K	33.67	
Co-K	45.53	Co-K	56.80	
Total	100.00	Total	100.00	

some oxidation occurs. This is confirmed by the strong exothermic peak observed on the TDA curve at that temperature, Fig. S1 (Supporting information). The next step between 150 and 450 °C corresponds to the loss of the remaining organic parts of the molecules: phenyl groups and nitrogen. Then the expected product would basically be the fragment Co₄P₂. However, the mass obtained (55%) is higher than expected (33%), again due to oxidation. The last step (between 550 and 750 °C) leads to a mixture of Co₃(PO₄)₂ and Co₃O₄, accounting for 49.8% of the starting mass, as suggested by XRD carried out on the powder afterwards. It seems that the oxide phase is obtained in a crystalline state at a lower temperature than the phosphate phase. The ratio between the two main peaks of each phase indicates that the proportion of each phase is 69% of Co₃(PO₄)₂ and 31% of Co₃O₄. The formation of phosphate confirms our assumption that phosphorus mainly remains in the sample.

The overall behavior is similar under N₂. The respective values at each step are slightly different though, owing to the slower oxidation process compared to air. Nevertheless, the final mass is the same as in air, except for a small step just before 900 °C the origin of which remains unclear. The final mass is 49.5% of the initial mass with a composition of 79% of $Co_3(PO_4)_2$ and 21% of Co_3O_4 , according to XRD.

An approximation of the quantity of cobalt oxide and cobalt phosphate formed starting from cluster **1** is plotted in Fig. S4 (Sup-



Fig. 14. SEM images in COMPO mode of cluster 3 calcined at 650 °C under H₂/N₂, (B) being magnified by a factor 10 compared to (A).



Fig. 15. SEM images of cluster 3 calcined at 800 °C under H₂/N₂ in (A) COMPO and (B) LEI modes.

Table 8			
Chemical composition	of spot 1	and 2 from	Fig. 15B.

Spot 1		Spot 2	
Element	Atom (%)	Element	Atom (%)
O-K	9.43	O-K	9.97
P–K	30.43	P-K	43.00
Co-K	60.14	Co-K	47.03
Total	100.00	Total	100.00

Table 9

Phases obtained depending on the starting cluster, after calcination under different atmospheres at 800 $^\circ\text{C}.$

$Co_4(CO)_{10}(\mu-dppa)$ $Co_4(CO)_8(\mu-dppa)_2$ $Co_4(CO)_{10}(\mu_4-PPI)_2$	1) ₂
Air $Co_3O_4 + Co_3(PO_4)_2$ $Co_3(PO_4)_2 + Co_2(P_2O_7)$ $Co_3O_4 + Co_3(PO_4)_2$	2
N_2 $Co_3O_4 + Co_3(PO_4)_2$ $Co_3(PO_4)_2 + Co_2(P_2O_7)$ $Co_3O_4 + Co_3(PO_4)_2$	2
He $Co_2P + Co + Co_3(PO_4)_2$ $Co_2P + Co_2(P_2O_7)$ $Co_2P + Co + Co_3(PO_4)_2$	O ₄) ₂
partially crystalline	
H_2/N_2 Co_2P $CoP + Co_2P$ Co_2P	

porting information). It is based on the TGA final mass assuming that only crystalline $Co_3(PO_4)_2$ and Co_3O_4 are formed. It is also assumed that only cobalt fully remains after the calcinations process, phosphorus being possibly lost, even in very small quantities [45]. The reaction process is summarized by equation

$$3Co_4(CO)_{10}(\mu - dppa) \rightarrow 4xCo_3O_4 + 4(1 - x)Co_3(PO_4)_2 \tag{1}$$

If we consider final masses of 49.4% (under air) or 49% (under N₂), as found by TGA, we find $x \approx 0.26$ (air) and $x \approx 0.28$ (N₂), which means that cobalt phosphate is the main phase in both cases. The parameters in the equation above are then:

$$3Co_4(CO)_{10}(\mu-dppa) \rightarrow 1.04\ Co_3O_4 + 2.96\ Co_3(PO_4)_2\ (air) \eqno(2)$$

$$3Co_4(CO)_{10}(\mu-dppa) \rightarrow 1.12 \ Co_3O_4 + 2.88 \ Co_3(PO_4)_2 \ (N_2) \eqno(3)$$

This leads to a phosphate/oxide ratio of 74/26 under air and 72/28 under N₂, which is in rather good agreement with the XRD data by comparing the peak intensity ratios (69/31 under air, 79/21 under N₂).

For sample **2**, it is noticeable that it is thermally stable up to 110 °C. Under air, the first step leads to 71.2% of the initial weight, whereas there is no such plateau under N₂. The loss of the carbonyl groups occurs quite abruptly, between 130 and 200 °C. The expected weight is 61.7%, without reaction with the atmosphere, but we measured 71.2%. This difference can be explained by a

simultaneous oxidation of the cobalt atoms while the carbonyl ligands are lost. The second step leads to a second plateau. At higher temperature, the same crystalline phases as for sample **1** are found: $Co_3(PO_4)_2$ and Co_3O_4 for 53.6% of the initial mass. Intensities comparison gave a ratio of phosphate to oxide of 65/35.

Under N₂, the decomposition path is somewhat different, and no plateau is observed before CO loss, hence giving a mass of 62.4% at the end of the CO loss (around 245 °C). But the weight loss continues when the temperature rises, meaning that phenyl groups leave soon after. However, the expected weight of 40.7% for Co₂P is not reached. The final mass is actually 51.8%, corresponding to a mixture of Co₃(PO₄)₂ and Co₃O₄, with a ratio of 70/ 30 evaluated by XRD.

The same assumption as above leads to Eq. (4) and the plot shown in Fig. S5 (Supporting information):

$$3Co_4(CO)_8(\mu_4 - PPh_2)_2 \rightarrow 4xCo_3O_4 + 4(1-x)Co_3(PO_4)_2 \tag{4}$$

Under air, the fit gives $x \approx 0.58$, under air and $x \approx 0.65$ under N₂:

$$3Co_4(CO)_8(\mu_4 - PPh_2)_2 \rightarrow 2.32 \ Co_3O_4 + 1.68 \ Co_3(PO_4)_2 \ (air) \ (5)$$

$$3Co_4(CO)_8(\mu_4 - PPh_2)_2 \rightarrow 2.6 Co_3O_4 + 1.4 Co_3(PO_4)_2 (N_2)$$
 (6)

The phosphate to oxide ratios deduced from those equations are 42/58 under air (65/35 by XRD) and 35/65 under N₂ (70/30 by XRD), which does not match the results found by XRD as well as for **1**. Noteworthy here is that the direct comparison of the XRD peak intensities of two phases exhibiting different diffusion factors without reference to a standard is a crude approximation. However oxide and phosphate are not that different to lead to an inversion of the phosphate to oxide ratio.

In the case of cluster **3**, after solvent desorption below 90 °C, carbonyl groups are the first to leave. The expected weight afterwards is 81.8%. However, we measured 95.6% and 95.5% under air and N₂, respectively. It is actually not easy to precisely attribute each step to one fragment of the molecule, since some oxidation occurs at the same time and the weight loss curve shows no real plateau. The plateau at 900 °C, at 45.3% in air and 46.2% under N₂, corresponds to a mixture of $Co_2(P_2O_7)$ and $Co_3(PO_4)_2$ identified by XRD. The ratio between the main peaks gave approximately 12% of $Co_3(PO_4)_2$ and 88% of $Co_2(P_2O_7)$ in air; 21% of $Co_3(PO_4)_2$ and 79% of $Co_2(P_2O_7)$ under nitrogen. The product is still transforming above 900 °C, probably due to phosphorus loss and some oxygen gain, thus decreasing the quantity of $Co_2(P_2O_7)$ while increasing that of $Co_3(PO_4)_2$. We assume that the reaction that occurs is as follows, with *x* increasing with temperature:

$$\operatorname{Co}_{4}(\operatorname{CO})_{8}(\mu - \operatorname{dppa})_{2} \rightarrow 2\left[\frac{2}{3}x\operatorname{Co}_{3}(\operatorname{PO}_{4})_{2}\right] + 2(1 - x)\operatorname{Co}_{2}(\operatorname{P}_{2}\operatorname{O}_{7})$$
(7)

Assuming that only two crystalline phases were formed and that all Co remains after the reaction, we used the Eq. (7) that fits the plot in Fig. S6 (Supporting information). Hence, we found $x \approx 0.35$ (air) and $x \approx 0.23$ (N₂). The effective equations can be written as:

$$Co_4(CO)_8(\mu - dppa)_2 \rightarrow 0.47 \ Co_3(PO_4)_2 + 1.30 \ Co_2(P_2O_7) \ (air) \tag{8}$$

$$Co_4(CO)_8(\mu - dppa)_2 \rightarrow 0.31 \ Co_3(PO_4)_2 + 1.50 \ Co_2(P_2O_7) \ (N_2) \tag{9}$$

These coefficients lead to $Co_3(PO_4)_2/Co_2(P_2O_7)$ ratios of 27/73 (12/88 by XRD) in air and 17/83 (21/79) under N₂.

Overall, these results are in rather good agreement with the proportions of phases deduced from XRD analysis on the final products. The ratio of the main peaks intensity gave the results shown in Table 10–12 for cluster **1**, **2** and **3**, respectively, along with a summary of the previously mentioned proportions between oxides and phosphates. The order of magnitude is correct. Yet the fit to our simple model seems to lead to a slight underestimation of the phosphate phases compared with the XRD analysis. This underlines the relative uncertainty of the model.

The results obtained by temperature-resolved XRD under air confirmed these results but precise comparison with TGA related data above is not straightforward. Indeed, we used a slightly different heating rate in temperature-resolved XRD, due to acquisition time required at 200 and 500 or 600 °C. In the case of clusters **1** and **2** (Table 10 and Table 11), the ratios observed with HT-XRD suggest that Co_3O_4 crystallizes at lower temperatures than $Co_3(PO_4)_2$, because cobalt oxide is largely predominant at 500 °C, while cobalt phosphate becomes predominant at 800 and 900 °C. The fit above can then be consistent with that observation only if the amorphous part of the powder is taken into account at all temperatures.

According to the results shown in Table 12, the linear fit for cluster **3** is in reasonable agreement with the results from XRD. The values for $Co_2(P_2O_7)$ are apparently slightly too low. The HT-XRD suggests that $Co_2(P_2O_7)$ crystallizes at higher temperatures than $Co_3(PO_4)_2$, because the ratio $Co_3(PO_4)_2$ to $Co_2(P_2O_7)$ varies from 19/81 to 12/88 under air, indicating that the relative amount of $Co_3(PO_4)_2$ decreases when the temperature increases, while the relative amount of $Co_2(P_2O_7)$ increases with temperature.

Air or N₂ are not suitable atmospheres to form cobalt phosphides. We could monitor the evolution of the crystalline phases from room temperature to 800 °C by HT-XRD under He. Some of the phases obtained under air or N₂ were observed again, but cobalt phosphide was identified too. Approximations of the proportion of each phase were done, based on the XRD main peak intensities.

Table 10

Proportion of the crystalline phases obtained after TGA or HT-XRD for cluster **1**. The linear fits correspond to Eqs. (2) and (3) in the text.

$Co_3(PO_4)_2/Co_3O_4$	Co ₄ (CO) ₁₀ (µ-dppa)		
	500 °C	800 °C	900 °C
XRD after TGA (N ₂) Linear fit (N ₂) XRD after TGA (air) Linear fit (air)	0/100 - 0/100 -	- 76/24 - 74/26	79/21 72/28 69/31 74/26

Table 11

Proportion of the crystalline phases obtained after TGA or HT-XRD for cluster **2**. The linear fits correspond to Eqs. (5) and (6) in the text.

$Co_3(PO_4)_2/Co_3O_4$	$Co_4(CO)_{10}(\mu_4$ -PPh) ₂		
	500 °C	800 °C	900 °C
XRD after TGA (N ₂) Linear fit (N ₂) XRD after TGA (air) Linear fit (air) HT-XRD (air)	0/100 - 0/100 - 12/88	- 37/63 - 42/58 60/40	70/30 35/65 65/35 42/58 –

Table 12

Proportion of the crystalline phases obtained after TGA or HT-XRD for cluster **3**. The linear fits correspond to Eqs. (8) and (9) in the text.

$Co_3(PO_4)_2/Co_2(P_2O_7)$	Co ₄ (CO) ₈ (µ-dppa) ₂		
	600 °C	800 °C	900 °C
XRD after TGA (N ₂)	-	-	12/88
Linear fit (N ₂)	-	3/97	27/73
XRD after TGA (air)	-	-	21/79
Linear fit (air)	-	20/80	17/83
HT-XRD (air)	19/81	12/88	-

In the case of cluster **1**, cubic cobalt is detected at temperature as low as 500 °C. Indeed, it is known that cobalt crystallizes at rather low temperatures. However, the formation of crystalline cobalt phosphide Co_2P can be observed around 650 °C. Then, there is 75% of Co and 25% of Co_2P . At 700 °C though, the signature of cobalt phosphate appears, owing to partial oxidation during the heating treatment.

The proportions of phases are shown in Table 13. Finally, at 800 °C, crystalline Co_2P is present as more than half of the overall sample. Cobalt phosphate is around 1/5, and cubic cobalt about 1/4 of the crystalline phases. The relative quantity of Co decreases when the temperature increases, while those of cobalt phosphate and phosphide increase.

The SEM pictures give credit to such results. Indeed, spot 1 in Fig. 9B was recorded on a bright zone (composed of atoms with higher atomic numbers) very rich in Co (almost 100% of Co), while oxygen is not even present in that phase (about 3%). One should keep in mind that oxygen cannot be quantified accurately by EDX spectroscopy, but the low measured value suggests a metallic nature of the particles and a very small amount of oxides. Thus this is consistent with the XRD results, showing Co metal as a crystalline phase. The grey part (spot 2) is made on average of atoms with lower atomic numbers, namely Co, P and O (in significant amount). The Co/P ratio is different from 2 because the volume of the EDX probe is about 1 μ m³, thus a part of cubic Co is included, therefore the amount of Co detected is more important. It is also consistent with the identification of Co₂P and Co₃(PO₄)₂ by XRD.

Once again, the behavior of cluster **2** is rather similar to that of cluster **1**. Cubic cobalt is observed by XRD at 500 °C and higher while crystalline Co_2P is identified above 600 °C. At 650 °C, cobalt

Table 13

Relative proportion of crystalline phases detected for cluster 1 under He.

Cluster 1	$Co_4(CO)_{10}(\mu$ -dppa)		
% (°C)	Co ₃ (PO ₄) ₂	Со	Co ₂ P
200	-	-	_
400	-	-	-
500	-	100	-
600	-	100	-
650	-	75	25
700	15	52	33
800	21	24	55

Table 14
Relative proportion of crystalline phases detected for cluster 2 under He.

Cluster 2	$Co_4(CO)_{10}(\mu_4\text{-PPh})_2$		
% (°C)	Co ₃ (PO ₄) ₂	Со	Co ₂ P
200	-	-	_
400	-	-	-
500	-	100	-
600	-	48	52
650	32	30	38
700	37	34	29
800	47	44	9

phosphate is obtained. Then, from 650 to 800 °C, only the proportions vary (Table 14). At 650 °C, each phase accounts for *ca*. 1/3 of the crystalline powder. When the temperature is increased, the amounts of cobalt phosphate and cubic cobalt increase too, while that of cobalt phosphide decreases. At 800 °C, cobalt and cobalt phosphate account for 47% and 44% respectively, while Co₂P is only 9%. So unlike in the case of cluster **1**, the main crystalline phase is not cobalt phosphide, but Co₃(PO₄)₂ despite an identical Co/P ratio in the precursor cluster.

SEM observations in composition mode confirmed that the sample is rather homogeneous (Fig. 10A). The EDX spectroscopy indicates the presence of *ca*. 72% of Co for 14% of P. This analysis is in quite good agreement with that found by XRD. The important part of cubic cobalt in the crystalline part of the sample, and the ratios Co to P in cobalt phosphate and phosphide (3 to 2 and 2 to 1 respectively) contribute to the high proportion of Co.

The behavior of cluster **3** is easier to understand under He atmosphere. Indeed, only two crystalline phases were observed. Co₂P is formed around 650 °C. It remains the only crystalline phase at 700 °C. At 800 °C however, the cobalt phosphate $Co_2(P_2O_7)$ appears. The stoichiometry of the starting cluster corresponds to a Co/P ratio of 1:1 like in $Co_2(P_2O_7)$. At 800 °C, the XRD peak intensities suggest a mixture of about 50% of cobalt phosphate and 50% of cobalt phosphate [Table 15]. Hence, any other phosphate phase is amorphous. Actually, $Co_2(P_2O_7)$ is known to crystallize very slowly and at high temperatures (600 °C from salt precursors) [63] while Co_2P crystallizes around 650 °C, according to our observations.

SEM observations support these results. The bright NPs (spot 1 on Fig. 11B) are made of Co and P, with a ratio around 2:1, which is consistent with the crystalline Co₂P detected by XRD. The phase at spot 2 is oxygen-rich and has a lower Co:P ratio close to 1, therefore it appears less bright. This can be ascribed to Co₂(P₂O₇), as detected by XRD above 800 °C. The SEM observations indicate that the main phase is Co₂(P₂O₇) although it is not fully crystalline at 800 °C. According to XRD, the amount of crystalline phase is similar to that of Co₂P and the rest is amorphous.

As expected, the He gas protects the sample better against oxidation than N₂, since we could identify cobalt phosphide in all cases. However, it is obvious that a neutral atmosphere is not sufficient to yield cobalt phosphide without forming phosphates. Therefore we used a slightly reducing atmosphere consisting of H_2/N_2 (5/95%) which appears to be the key to yield cobalt phosphide from our clusters. Indeed, according to XRD (Fig. 6), cluster 1 forms Co₂P both at 650 and 800 °C. Heating to 800 °C improves the crystallinity of the product. The crystallite size was evaluated by using the Scherrer equation $S = \frac{K \cdot \lambda}{\beta \cdot \cos \theta}$, where *K* is a shape factor equal to 0.9 for spherical crystallite, λ is the wavelength of the Xray used, β is the difference of the full width at half maximum (FWHM) between peaks of the studied material and a standard which gives the resolution of the instrument, and θ the corresponding Bragg angle of the diffraction peak analyzed. Applied on the d_{020} reflections it leads to an average size of 17 nm at 650 °C, and 46 nm at 800 °C.

Table 15			
Relative proportion of crystalline ph	ases detected for a	cluster 3 under	He

Cluster 3	$Co_4(CO)_8(\mu$ -dppa) ₂		
% (°C)	$Co_2(P_2O_7)$	Co ₂ P	
200	-	-	
400	-	-	
500	-	-	
600	-	-	
650	-	100	
700	-	100	
800	49	51	

Mapping of the composition by SEM showed that this sample originating from cluster 1 was rather homogeneous (Fig. 12). Moreover, as expected, the EDX measurements give a molar ratio Co/P about 2:1 (Table 4). When it comes to cluster 2 with the same Co/P ratio as 1, XRD (Fig. 7) confirms the formation of crystalline Co₂P. The use of the Scherrer equation leads to an average crystallite size of 28 nm at 650 °C and 35 nm at 800 °C. Compared to 1, the crystallite size varies not much between 650 and 800 °C. Actually, cluster 2 decomposed at much lower temperature than 1 and 3 (Fig. 3) and the product exhibits a composition close to that of Co₂P (Fig. 13, Table 5 and Table 6) which is then already well crystallized at 650 °C. One reason why cluster 2 decomposes more rapidly than clusters **1** and **3** might be attributed to the coordination mode of the P atom of the μ_4 -PPh ligand. Indeed, the Co-P bond energy in cluster **2** might be weaker than in the case of the single bonds found in clusters 1 and 3. Also the chemical nature of the phosphine might be important.

Cluster **3** shows once again a different behavior, owing to its composition. Indeed, the phases obtained both at 650 and 800 °C under H_2/N_2 are cobalt phosphides Co_2P and CoP (Fig. 8). XRD peak intensities suggest that CoP is the main phase, accounting for 79% at 650 °C (21% for Co_2P) and for 68% at 800 °C (32% for Co_2P). However, one should notice that its quantity decreases when the temperature increases, while the amount of Co_2P increases. This is undoubtedly connected to the thermal stability of CoP [64]. Indeed, the CoP phase is stable at temperatures as high as *ca*. 1000 °C, while Co_2P can still exist at 1380 °C. The average size of the crystallites determined using the Scherrer equation are about 14 nm for CoP at 650 °C, and around 30 nm at 800 °C. The size of the Co_2P crystallites could not be estimated in this sample, because the reflection peak used in the case of compound **1** does not appear on the diffractogram, Co_2P being the minor component.

The SEM observations corroborate these first results. At 650 °C, two different regions were observed on the pictures (Fig. 14) using the composition mapping mode: the relative brightness of the regions of spots 1 and 2 suggests that the average atomic number is higher in spot 2 than in spot 1. The "grey" part seems to be the main phase. The EDX spectroscopy (Table 7) suggests a Co/P ratio close to 1:1 for spot 1, which is consistent with CoP. On the other hand, spot 2 gives a ratio close to 2:1, which points toward Co₂P. At 800 °C, the phenomenon is quite similar, that is a "grey" phase (predominant), and "white" and faceted crystals (Fig. 15). Here again, the elemental analysis from EDX is clear: "white" crystals have a ratio Co to P of 2:1, corresponding to Co₂P, and the "grey" part is CoP (Co to $P \approx 1:1$).

5. Conclusions

The study of the thermal behavior of three tetranuclear Co-P organometallic carbonyl clusters under different atmospheres revealed that a slightly reducing atmosphere is necessary to obtain cobalt phosphide only, and completely avoid the formation of cobalt phosphate. The combined use of TGA, (temperature-resolved) XRD and SEM allowed us to understand the influence of the precur-

sor and the atmosphere on the phase formed. While two clusters (1, 2) with the appropriate stoichiometry led to Co_2P only, the third cluster (3) gave a mixture of CoP and Co₂P, since a lack of phosphorus allows the formation of well faceted Co₂P crystallites. Finally, cluster 2 decomposed at lower temperatures than cluster 1. This suggests that using the μ_4 -PPh ligand is more efficient than dppa to obtain cobalt phosphide at lower temperature. Thus, although the chemical nature of the phosphide phases can be controlled, no monodisperse size could be obtained. To overcome this issue, we currently develop new methods using the decomposition of similar metal clusters dispersed into inorganic porous matrices, under appropriate atmosphere.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.09.019.

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