Short Note

Tris(μ_2-carbonyl)-octacarbonyl-triphenylphosphite-tetracobalt

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Abstract: The reaction of [$Co_2(CO)_8$] with an equimolar amount of $P(OPh)_3$] in toluene solution yields *in situ* generated [$Co_2(CO)_7\{P(OPh)_3\}$] **1**. Subsequent heating of **1** provides in a condensation reaction an alternative synthetic access to the tetranuclear cluster [$\{Co_4(\mu_2\text{-}CO)_3(CO)_8\{P(OPh)_3\}$] **2**. Compound **2** has been characterized by IR and ^{31}P NMR spectroscopy, the tetranuclear cluster framework has be ascertained by a single-crystal X-ray diffraction study performed at 100 K.

Keywords: cobalt; carbonyl; triphenylphosphite; crystal structure; molecular cluster.

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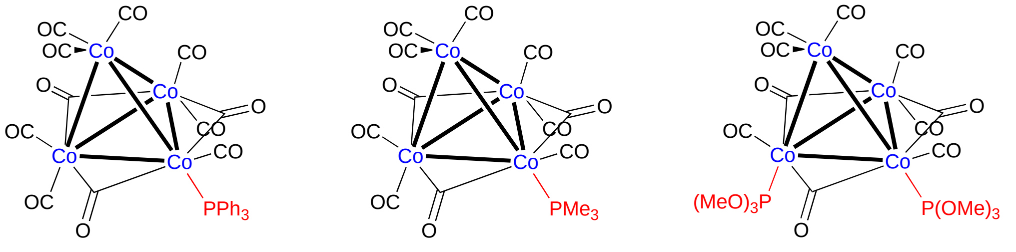
1. Introduction

The tetrahedral carbonyl cluster [$Co_4(\mu_2\text{-}CO)_3(CO)_9$] was first described by Hieber in 1932 and is commonly prepared by decarbonylation of dicobaltoctacarbonyl [1,2]. This 60-electron cluster bearing both terminal and bridging carbonyls has been the object of several crystallographic investigations [3,4] and served as starting material for a number of organic (for example formation of arene clusters [$Co_4(CO)_9$(arene)]) and inorganic transformations [2,5,6]. Among the latter reaction, several papers have been devoted to the kinetics and mechanistic aspects associated to substitution reactions with various phosphine PR_3, diphosphine (such as bis(diphenylphosphino)amine dppa and bis(diphenylphosphino)methane dppm), and phosphite $P(OR)_3$ ligands [7-13] Some examples of structurally characterized mono- and di-substituted derivatives [$Co_4(\mu_2\text{-}CO)_3(CO)_{9\text{-}n}(PR_3)_n$] (n = 1, 2) are depicted in Scheme 1. There is also a report on the crystal structure of [$Co_4(CO)_{10}(PMe_2Pr)_2$] bearing one PR_3 ligand at the apical and the second one at an axial position (see Fig. 4) [14].



tris(μ_2-carbonyl)-octacarbonyl-triphenylphosphine-tetracobalt

I

tris(μ_2-carbonyl)-octacarbonyl-trimethylphosphine-tetracobalt

II

tris(μ_2-carbonyl)-heptacarbonyl-bis(trimethylphosphite)-tetracobalt

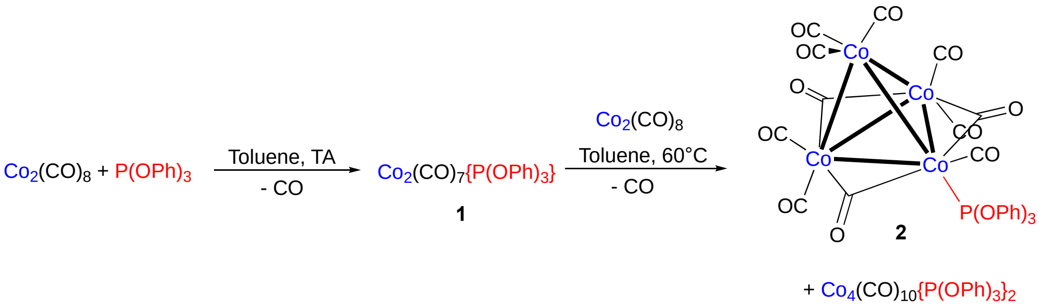
III

Scheme 1. Examples of some phosphine- and phosphite-substituted tetranuclear cobalt clusters.

Note that with $P(OMe)_3$ and $P(OPh)_3$, even formation of tetra-substituted clusters $[Co_4(CO)_8\{P(OR)_3\}_4]$ can be achieved [8]. In the context of our research on $P(OPh)_3$-substituted Co-Co carbonyl complexes towards alkynes producing dicobaltatetrahedranes [15,16], we attempted also to synthetize the monosubstituted dinuclear complex $[Co_2(CO)_7\{P(OPh)_3\}]$ **1** by addition of a stoichiometric amount of $P(OPh)_3$ to a solution of $[Co_2(CO)_8]$ in toluene. The existence of this substitution product has been mentioned in the literature, but apart of its IR spectrum, no further characterization data have been communicated [17]. With objective to isolate this species, we repeated this reaction under similar conditions, but upon heating we isolated instead by serendipity as major component the title compound $[Co_4(\mu_2\text{-}CO)_3(CO)_8\{P(OPh)_3\}]$ **2**.

2. Results

The title compound **2** has been first mentioned in 1975 by Marko et al. and was obtained by treatment of $[Co_4(CO)_9(\text{arene})]$ with triphenylphosphite at 20°C under CO atmosphere along with $[Co_4(CO)_{10}\{P(OPh)_3\}_2]$ and $[Co_4(CO)_9\{P(OPh)_3\}_3]$ [5]. But apart from a detailed IR analysis in solution, no additional characterization data were presented. With the intention to prepare the compound $[Co_2(CO)_7\{P(OPh)_3\}]$, we treated first a solution of $[Co_2(CO)_8]$ in toluene at ambient temperature employing a 1:1 ratio (Scheme 2). IR monitoring revealed formation of **1** (2086, 2034, 1999, 1978 cm^{-1}) along with traces of $[Co_2(CO)_6\{P(OPh)_3\}_2]$ (1978 cm^{-1}, very strong). Formation of this dinuclear bisphosphite complex is also corroborated by an NMR $^{31}P\{^1H\}$ analysis performed on a sample of the reactional mixture which shows a singlet at 167.3 ppm [18]. To complete the reaction, the mixture was then heated for 5h to 60°C. Surprisingly, the IR bands attributed to **1** had disappeared and replaced by novel ones at 2089, 2050, 2042, 2032, 2012 and 1882, 1850, 1839 cm^{-1} the latter being in the characteristic region of bridging carbonyl ligand. The formation of minor amounts of $[Co_4(CO)_{10}\{P(OPh)_3\}_2]$ is suggested by a CO elongation at 2073 cm^{-1} in the IR spectrum.



Scheme 2. Synthesis of the title compound **2**.

A product was isolated after workup in form of dark crystals, whose elemental analysis indicated a composition as $[Co_4(CO)_{11}\{P(OPh)_3\}]$. The IR spectrum of this moderate air-stable product in cyclohexane, shown in Fig. 1, reveals in addition to the ν(CO) vibrations at 2088, 2049, 2043, 2032, 2011 cm^{-1}, three absorptions at 1885, 1856 and 1842 cm^{-1} attributed to bridging carbonyls. These values fit well with those reported in heptane by Marko et al [5]. The infrared band pattern is similar to that reported for $[Co_4(\mu_2\text{-}CO)_3(CO)_8(PPh_3)]$ in heptane, the CO vibrational frequencies being slightly shifted to higher wave numbers due to the weaker electron-donating propensity exerted by $P(OPh)_3$ with respect to PPh_3.

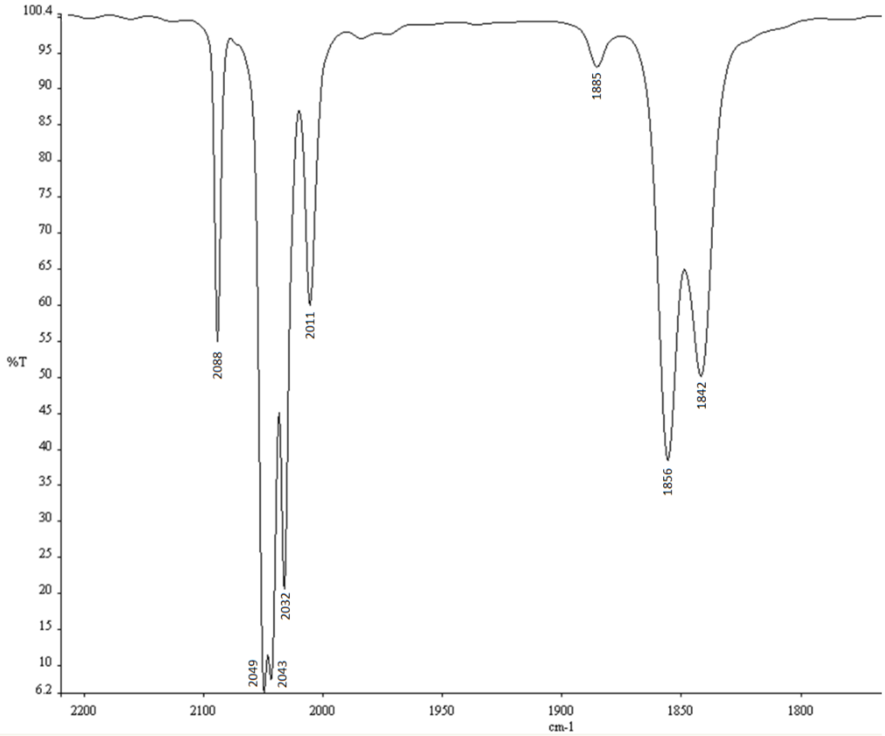


Figure 1. IR spectrum of compound **2** recorded in cyclohexane.

The proton-decoupled ^{31}P-NMR recorded in $CDCl_3$ reveals a strongly broadened singlet at δ 130.4 due to the coordinated triphenylphosphite ligand, suggesting a fluxional behavior in solution (Fig. 2). In line with this hypothesis, we were unable to identify at ambient temperature distinct carbonyl resonances in the proton-decoupled ^{13}C NMR spectrum despite longue data acquisition overnight. Only a broad hump centered at about δ 196 could be observed for the 11 carbonyl groups (Fig. 3). Note that in the literature no ^{31}P or ^{13}C NMR data recorded at ambient temperature are available on related PR_3 and $P(OR)_3$ clusters. There is just one report on $[Co_4(CO)_{11}\{P(OMe)_3\}]$ at low temperature using ^{13}C-enriched CO allowing to differentiate between bridging and terminal carbonyls [19].

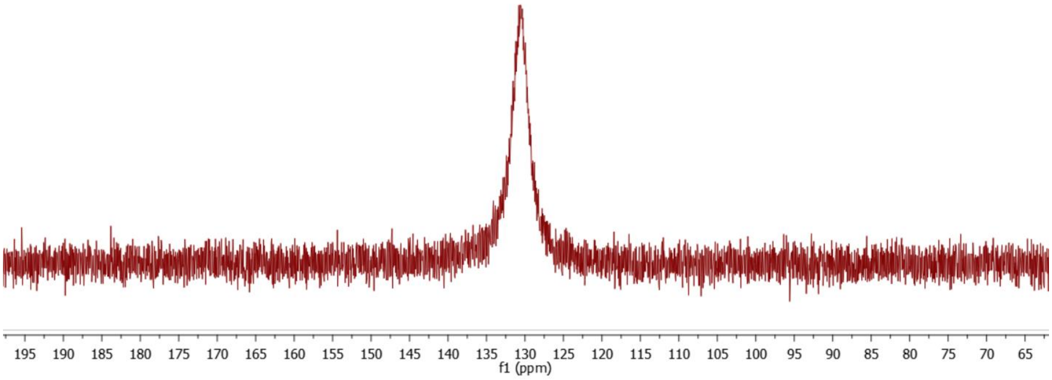


Figure 2. $^{31}P\{^1H\}$ NMR spectrum (161.99 MHz, $CDCl_3$) of compound **2** at 25°C.

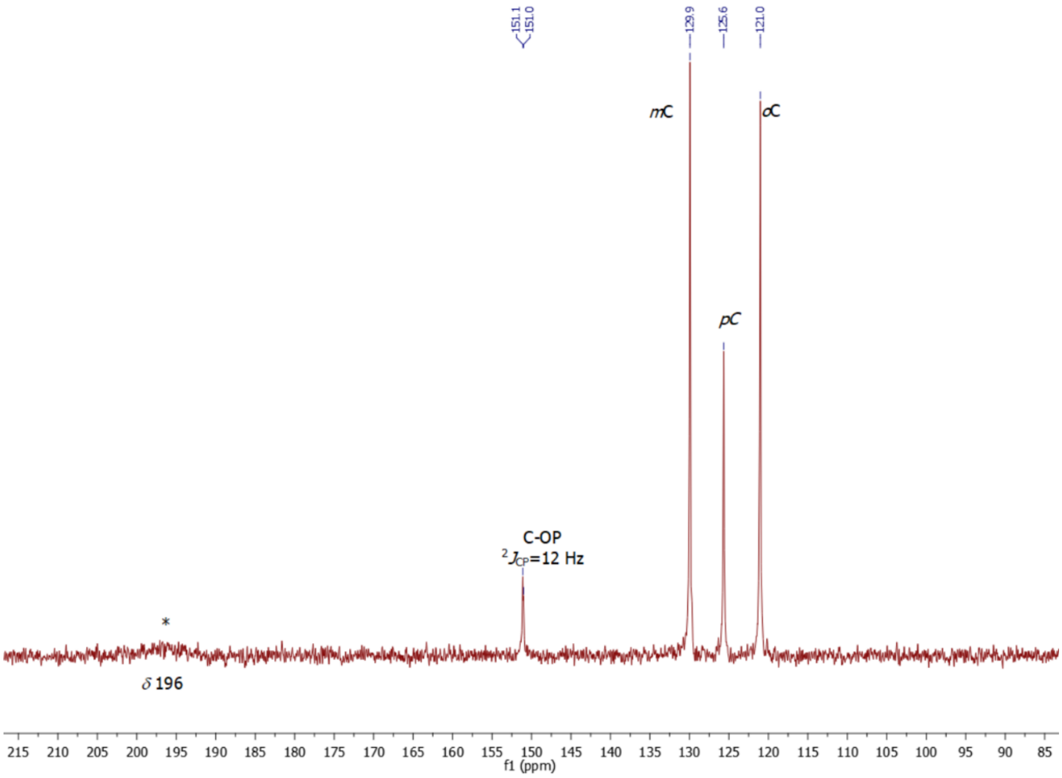


Figure 3. $^{13}C\{^{1}H\}$ NMR spectrum (100.62 MHz, $CDCl_3$) of compound **2** at 25°C.

In order to check whether $[\{Co_4(\mu_2\text{-}CO)_3(CO)_8\{P(OPh)_3\}]$ **2** is isostructural to $[\{Co_4(\mu_2\text{-}CO)_3(CO)_8(PPh_3)]$, we examined the product by an X-ray diffraction study performed at 100 K. Indeed, cluster **2** is crystallizing like its PPh_3 analogue in the monoclinic crystal system but has been refined with space group $P2_1/c$ instead of $P2_1/n$ employed for the latter. Darensbourg and Incorva proposed that *a priori* three isomeric motifs are conceivable for a monosubstituted $[\{Co_4(\mu_2\text{-}CO)_3(CO)_8\mathbf{L}]$ skeleton (Fig. 4) [11].

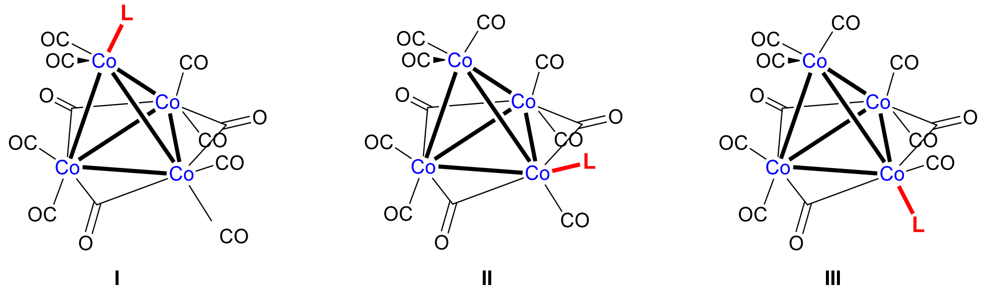


Figure 4. Presentation of the three conceivable isomers of $[\{Co_4(\mu_2\text{-}CO)_3(CO)_8\mathbf{L}]$ bearing **L** at the apical (I), equatorial (II) or axial site (III)

As shown in Fig. 5, the tetrahedral cluster adopts geometry III, since the phosphite ligand occupies an axial site with respect to the basal triangular plane formed by Co1, Co2 and Co3. The Co1 center, which bears the $P(OPh)_3$ ligand is furthermore ligated by one terminal CO ligand and shares two symmetrically bridging carbonyls with the adjacent Co2 and Co3 centers. Co2 and Co3 in turn bear each two terminal Cos and have one shared edge bridged by a μ_2-CO ligand. The fourth vertex of the tetrahedral core is constituted of the Co4 fragment, bearing exclusively three terminal COs. The Co1–P bond is quite colinear with the Co1–Co4 vector, the angle Co4–Co1–P being 166.155(18)°. So, overall the molecular structures of **2** and [{$Co_4(\mu_2\text{-}CO)_3(CO)_8(PPh_3)$] are very similar, the corresponding Co–Co–PPh_3 angle of 174.98(4)° being somewhat more linear.

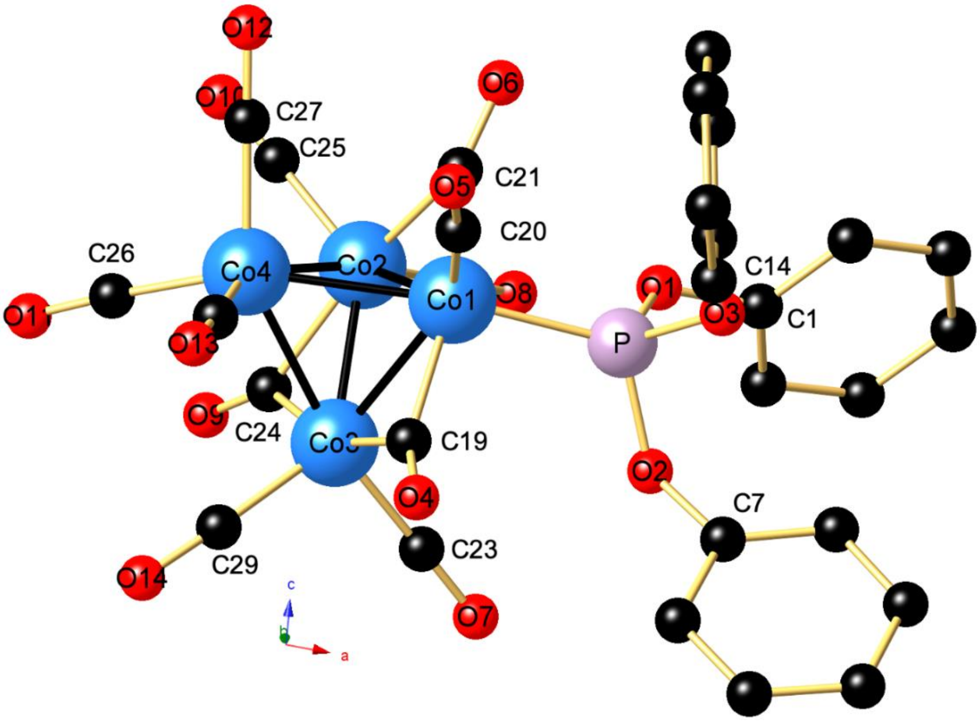


Figure 5. Molecular structure of **2**. Selected angles (deg)**:** All H atoms are omitted for clarity. Co1–Co2–Co3 60.000(11), Co1–Co2–Co4 60.377(11), Co1–Co3–Co2 60.293(11), Co1–Co4–Co3 58.636(10), Co1–Co4–Co2 58.739(10), Co3–Co4–Co2 58.303(10), Co4–Co1–P 166.115(18), Co3–Co1–P 107.614(16), Co2–Co1–P 107.396(17).

The most relevant bond lengths of **2** are listed in Table 1 and compared with those of [$Co_4(\mu_2\text{-}CO)_3(CO)_8(PR_3)$]. It follows that the mean Co–Co bond lengths of **2** is slightly shorter than that of its PPh_3 and PMe_3 analogues and that reported for the parent [$Co_4(\mu_2\text{-}CO)_3(CO)_9$] compound (2.4838 vs. 2.492 Å). Compared with the Co–P distances reported for [$Co_4(\mu_2\text{-}CO)_3(CO)_8(PR_3)$], that of **2** is shortened and matches with the average Co–P distances of [$Co_4(CO)_{10}\{P(OMe)_3\}_2$] shown in Fig. 1 (2.1542(5) vs. 2158(2) Å). The mean Co–C bond length decreases in the order $P(OPh)_3$> PPh_3> PMe_3. Noteworthy is the observation that the terminal Co4–C distances are elongated compared the other ones.

Table 1. Relevant bond lengths (Å) in **2** and crystallographically characterized monosubstituted [$Co_4(\mu_2\text{-}CO)_3(CO)_8(PR_3)$] clusters.

	P(OPh)$_3$	PPh$_3$	PMe$_3$
Co1–Co4	2.5042(4)	2.542(1)	2.532(2)
Co1–Co2	2.4639(4)	2.491(1)	2.485(2)
Co1–Co3	2.4567(4)	2.487(3)	2.474(2)
Co2–Co3	2.4494(4)	2.468(1)	2.449(2)
Co2–Co4	2.5154(4)	2.523(1)	2.529(2)
Co3–Co4	2.5129(4)	2.526(1)	2.530(2)
Average Co-Co	*2.4838*	*2.5062*	*2.4998*
Basal-basal	*2.4567*	*2.482*	*2.469*
Basal-apical	*2.5108*	*2.530*	*2.530*
Co1–P	2.1542(5)	2.246(1)	2.222
Co1-µC19	1.9199(19)	1.908(4)	1.926
Co3-µC19	1.9608(19)	1.976(4)	1.989
Co2-µC24	1.9360(18)	1.929(4)	1.970
Co3-µC24	1.9433(18)	1.951(4)	1.918
Co1-µC21	1.9138(19)	1.887(5)	1.852
Co2-µC21	1.9713(18)	1.971(5)	1.927
Average Co-µC	*1.9409*	*1.937*	*1.930*
Co1-C20	1.786(2)	1.758(5)	1.677
Co2-C22	1.802(2)	1.794(5)	1.759
Co2-C25	1.792(2)	1.778(5)	1.736
Co3-C23	1.8057(19)	1.789(7)	1.849
Co3-C29	1.7854(19)	1.776(5)	1.760
Co4-C26	1.814(2)	1.832(5)	1.606
Co4-C27	1.832(2)	1.827(5)	1.800
Co4-C28	1.831(2)	1.822(5)	1.779
Average Co-C	*1.806*	*1.797*	*1.746*
Apical	*1.826*	*1.827*	*1.728*
Equatorial	*1.7878*	*1.771*	*1.724*
Axial	*1.7937*	*1.792*	*1.804*
CSD reference	This work	BAFFET [11]	MSTCOB [12]

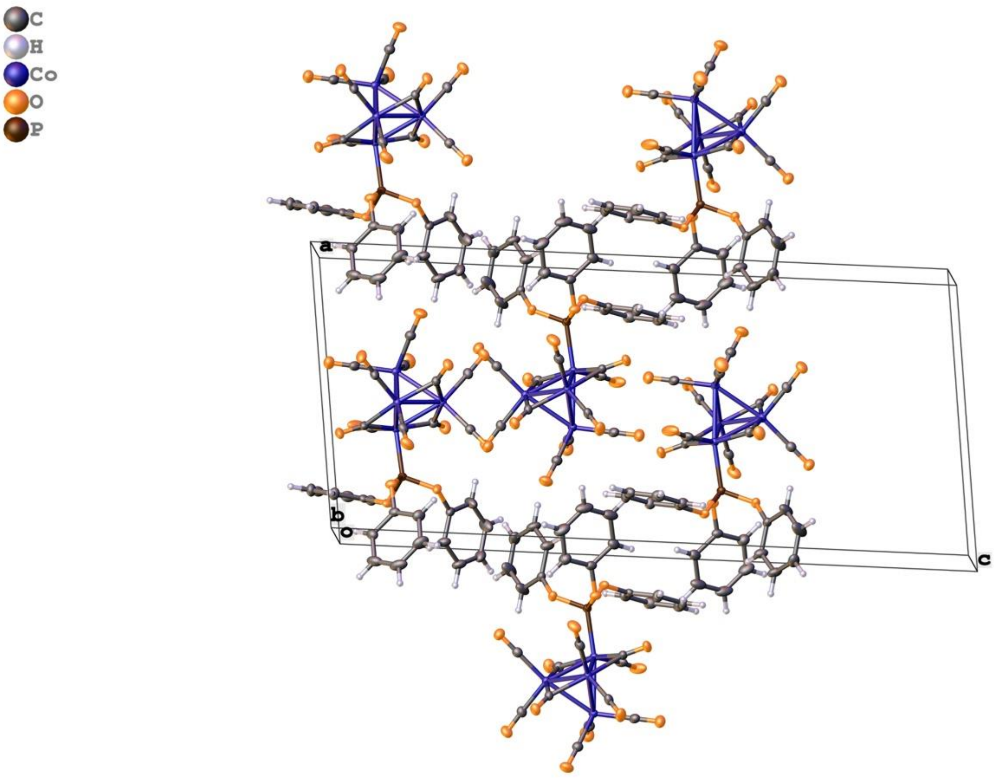


Figure 6. OLEX-generated view of the packing of **2** along the *a* axis

Inspection of the crystal structure reveals the existence of various other weak intermolecular contacts. A partial view of the crystal packing is shown Fig. 6. The shortest contact implies two carbonyl ligands, an axial and a bridging one [d(C23···O9′) = 3.027 Å; symmetry code (′) 1-x, -1/2+y, ½-z]. An apical carbonyl is also involved in two weak interactions with atoms of phenyl rings [d(O11···C4′′) = 3.072 Å; symmetry code (′′) -1+x, y, z] and [d(H11···O11′) = 2.611 Å; symmetry code (′) 1-x, -1/2+y, ½-z]. Note that two intermolecular C-H··π interactions are observed but since all hydrogen atoms were not refined freely, a discussion is not appropriate.

3. Discussion

Several methods have been described in the past to synthesize phosphine and phosphite-substituted tetranuclear clusters $[Co_4(\mu_2\text{-}CO)_3(CO)_{9-n}(PR_3)_n]$. $[\{Co_4(\mu_2\text{-}CO)_3(CO)_8(PMe_3)]$ has been obtained in low yield by reaction of Me_2PCl_3 with $Na[Co(CO)_4]$ (12). More common is the use of a preformed tetranuclear scaffold such as $[Co_4(CO)_{12}]$ or $[Co_4(CO)_9(arene)]$, followed by substitution with $P(OR)_3$ or PR_3 [5,8-11]. Since the elucidation of the mechanism of the formation of **2** was not the objective of this short note, we did not investigate this in detail. However, we can rule out initial formation of $[Co_4(\mu_2\text{-}CO)_3(CO)_9]$ followed by CO/ $P(OPh)_3$ exchange, since formation of $[Co_2(CO)_7\{P(OPh)_3\}]$ **1** is detectable by IR monitoring. We rather suggest that cluster **2** is obtained by initial formation of $[Co_2(CO)_7\{P(OPh)_3\}]$ **1**, which reacts in a thermal cluster condensation reaction with $[Co_2(CO)_8]$ yielding **2**. In the reaction mixture there are also IR vibrations which can be attributed the disubstituted cluster $[\{Co_4(\mu_2\text{-}CO)_3(CO)_3\{P(OPh)_3\}_2]$ [5], but we failed to isolate the compound in pure form.

We have also attempted to condensate $[Co_2(CO)_6\{P(OPh)_3\}_2]$ with $[Co_2(CO)_8]$ in hot toluene. Spectroscopic examination of the reaction mixture revealed indeed formation of cluster **2** along with $[Co_4(CO)_{10}\{P(OPh)_3\}_2]$ and minor amounts of unreacted $[Co_2(CO)_6\{P(OPh)_3\}_2]$. No attempts were undertaken to separate the mixture.

4. Experimental

$P(OPh)_3$ (0.262 mL, 1 mmol) was added to a stirred solution of $Co_2(CO)_8$ (342.0 mg, 1 mmol) in toluene (5 mL). An immediate evolution of gas was observed. The reaction mixture was heated to 60°C for 5h. The solution was cooled to room temperature prior to lowering its temperature to 4°C. The product **2** crystallized as dark plates collected by filtration. Yield: 39%. Anal. Calc. for $C_{29}H_{15}Co_4O_{14}P$ (M.W = 854.14 g.mol^{-1}): C, 40.78; H, 1.77%. Found: C, 40.93; H, 1.84 %. $^{13}C\{^1H\}$ NMR ($CDCl_3$) at 298 K: δ 121.0 (C*o*), 125.6 (C*p*), 129.9 (C*m*), 151.2 (C*ipso*-O, d, $^2J_{PC}$ = 12 Hz), 196 (br, CO) ppm.

Crystal data for $C_{29}H_{15}Co_4O_{14}P$, M = 854.10 g.mol^{-1}, black crystals, crystal size 0.377 × 0.194 × 0.15 mm^3, monoclinic, space group $P2_1/c$; a = 12.5987(10) Å, b =8.9773(9) Å, c = 27.953(2) Å, α = 90°, β = 96.829(3)°, γ = 90°; V = 3139.2(5) Å^3, Z = 4, D_{calc} = 1.807 g/cm^3, T = 100 K, GOF = 1.035; R_1 = 0.0360, wR2 = 0.0957 for 11959 reflections with I > = 2σ (I) and 11959 independent reflections. Largest diff. peak/hole / e Å^{-3} 3.22/-0.67. Data were collected using graphite monochromated MoK$_\alpha$ radiation l = 0.71073 Å and have been deposited at the Cambridge Crystallographic Data Centre as CCDC 2174841. (Supplementary Materials). The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/getstructures. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 (SHELXL, 2015 [20–22]).

5. Conclusions

We have demonstrated direct that addition of $P(OR)_3$ to [$Co_2(CO)_8$] provides and alternative route to [$\{Co_4(CO)_{11}\{P(OAr)_3\}$] species, avoiding the use of quite expensive [$Co_4(CO)_{12}$] as starting material. We have crystallographically evidenced that cluster **2** adopts a structure quite reminiscent to that reported for [$\{Co_4(\mu_2\text{-}CO)_3(CO)_8(PPh_3)$] and bears the $P(OPh)_3$ ligand at the axial site of a Co vertex.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/xxx/s1, CIF file and Check-CIF report.

Author Contributions: I.J. prepared the compound; C.S. and R.S collected the X-ray data and solved the structure; I.J and M.K designed the study, analysed the data and wrote the paper.

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Data Availability Statement: The X-ray data are at CCDC as stated in the paper.

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Conflicts of Interest: The authors declare no conflict of interest

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