

Carbonyl clusters with a capping methylidyne phosphonate ligand Crystal structure of $[\text{Co}_3(\text{CO})_9\{\eta^1-\mu_3-[\text{CP}(\text{O})(\text{OEt})_2]\}]^1$

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Received 27 January 1997

Abstract

The bridging methylidyne clusters $[\text{Co}_3(\text{CO})_9\{\eta^1-\mu_3-[\text{CP}(\text{O})(\text{OR})_2]\}]$ **1** (R = Et) and **3** (R = SiMe₃) with α -phosphoryl substituents have been synthesized by reaction of $\text{Cl}_3\text{C}-\text{P}(\text{O})(\text{OR})_2$ with $\text{Co}_2(\text{CO})_8$, followed by protonation. Cluster **3** was also obtained by the reaction of **1** with Me₃SiBr. The structure of **1** has been determined by X-ray crystallography. The donor properties of the P=O function toward Lewis acids such as $[\text{Cp}_2\text{MCl}]^+$ (M = Ti, Zr) were used to assemble early–late metal systems. © 1997 Elsevier Science S.A.

Keywords: Cluster; Cobalt; Phosphonate; Titanium; Zirconium

1. Introduction

Although tricobalt carbonyl clusters of the type $[\text{Co}_3(\mu_3-\text{CR})(\text{CO})_9]$, in which the methylidyne ligand is stabilized by the Co_3 face, have been known since the early 1960s and investigated to a considerable extent (see for example Refs. [1,2]), the properties and the reactivity of this class of complexes continue to attract much interest. The first cluster of this type $[\text{Co}_3(\mu_3-\text{CMe})(\text{CO})_9]$ was obtained in 1958 by Cotton and coworkers by treatment of the alkyne complex $[\text{Co}_2(\text{HCCCH})(\text{CO})_6]$ with sulphuric acid in methanol [3]. This approach was subsequently used to prepare a series of other clusters of the type $[\text{Co}_3(\mu_3-\text{CCH}_2\text{R})(\text{CO})_9]$; however, it is restricted to complexes with a CH_2 group on the apical carbon. A more general route has been developed later [4]. It involved the reaction of $\text{Co}_2(\text{CO})_8$ with α, α, α -trihalo compounds and to a certain extent dihalomethyl compounds. Somewhat surprisingly, among all the CR units reported (e.g. R = H, alkyl, aryl, halogen, carbonyl, formyl and even substituents with functional groups), there appears to be only a few

examples in which the methylidyne carbon atom is directly attached to a phosphorus atom, although μ_3 -methylidyne compounds of this type could allow e.g. to evaluate the influence of the phosphorus centre on the cluster–ligand bonding. Most of the derivatives described are ylide-type species ($\mu_3\text{-CPR}_3$), formed by ligand substitution reaction at non-metal sites [5], whereas the other triangular clusters capped by a $\mu_3\text{-CP}$ unit have been obtained by coordination of $\text{C}\equiv\text{P}$ moieties to three metal centres [6] or observed as by-products in the formation of $[\{\text{Ru}_3(\text{CO})_{11}\}_2(\text{Ph}_2\text{PC}\equiv\text{CPh}_2)]$ [7]. We sought to prepare triangular clusters containing an $\text{M}_3(\mu_3-\text{CR})$ unit associated with a phosphonate-type ligand which could confer interesting chemical or physical properties, such as assembling capability or solubility in water. Thus, in addition to the possibility of combining the reactivity of $\text{Co}_3(\mu\text{-CR})$ -type clusters with that of phosphonate derivatives, the formation of larger polymetallic structures by coordination of the phosphoryl group to oxophilic metal centres could be envisaged.

2. Results and discussion

The reaction of $[\text{Co}_2(\text{CO})_8]$ with $\text{Cl}_3\text{C}-\text{P}(\text{O})(\text{OEt})_2$ (1.6:1 ratio) in THF at 50 °C afforded after acidification

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¹ Dedicated to Professor G. Huttner on the occasion of his 60th birthday, with our sincere congratulations and warmest wishes.

and purification $[\text{Co}_3(\text{CO})_9\{\eta^1-\mu_3-[\text{CP}(\text{O})(\text{OEt})_2]\}]$ **1** as a burgundy solid (Scheme 1). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** contains a signal in the expected region for a phosphonate group (δ 29.4 ppm), whereas the IR spectrum exhibits four $\nu(\text{CO})$ absorptions at 2111m, 2069s, 2065s and 2047s cm^{-1} , characteristic for a $\text{Co}_3(\text{CO})_9$ core. Interestingly, the $\nu(\text{P}=\text{O})$ vibration in **1** undergoes a shift to lower frequencies of 50 cm^{-1} compared to that observed for $\text{Cl}_3\text{C}-\text{P}(\text{O})(\text{OEt})_2$ (1230 and 1280 cm^{-1} respectively). In order to establish the nature of the bonding interactions in this cluster, an X-ray diffraction study was performed on a single crystal of **1** obtained from a pentane solution at 4°C . Crystal data are given in Table 1. Selected bond distances and bond angles with estimated standard deviations are listed in Table 2 and fractional coordinates and isotropical parameters are reported in Table 3.

The structure is shown in Fig. 1. An equilateral Co_3 triangle is symmetrically capped by the C(10) carbon atom from the $\text{C}-\text{P}(\text{O})(\text{OEt})_2$ group. If the two ethoxy substituents are not taken into account, a pseudo mirror plane passing through the Co(3), C(10), P and O(10) exists in the complex. The value of the P–C(10) bond distance, $1.767(2)\text{ \AA}$, is much longer than that found in the anion $[\text{Fe}_2\text{Co}(\text{CO})_9(\mu_3-\text{C}-\text{PMe}_3)]^-$, $1.715(3)\text{ \AA}$, where the carbon of the $\text{C}-\text{PMe}_3$ group caps an Fe_2Co triangle [5a] and only slightly longer than in $[\text{FeCo}_2(\text{CO})_9(\mu_3-\text{C}-\text{PMe}_2\text{CH}_2\text{CH}_2\text{PMe}_2\text{Fe}(\text{CO})_4)]$, $1.742(3)\text{ \AA}$, where the carbon of the $\text{C}-\text{PMe}_2\text{R}$ group caps an FeCo_2 triangle [5c]. The value of the P–O(10) bond distance, $1.468(2)\text{ \AA}$, is shorter than those P–O(11) and P–O(12), $1.580(2)$ and $1.587(2)\text{ \AA}$, consistent with its double bond character.

Recent work by Roundhill and coworkers [8] and Knight and coworkers [9] has shown that phosphonic acids or anionic phosphonate moieties on phosphine

Table 1
Crystallographic data of complex **1**

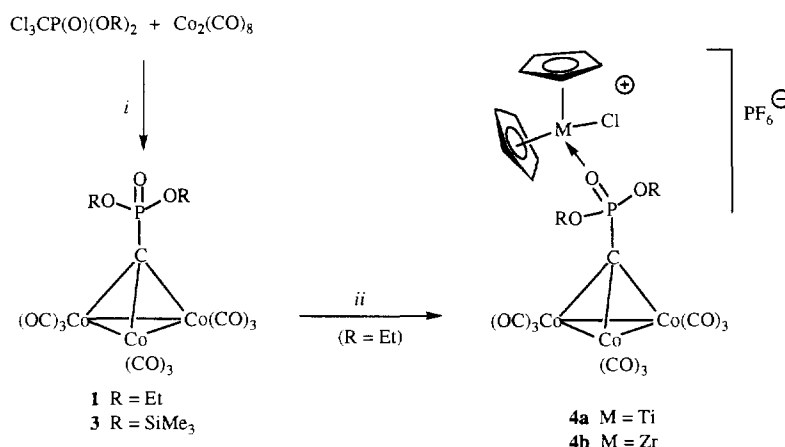
Formula	$\text{C}_{14}\text{H}_{10}\text{Co}_3\text{O}_{12}\text{P}$
Mw	578.00
Crystal system	triclinic
Space group	$P\bar{1}$
a (\AA)	8.108(2)
b (\AA)	9.047(2)
c (\AA)	15.554(3)
α (deg)	90.03(1)
β (deg)	96.02(2)
γ (deg)	113.13(3)
V (\AA^3)	1042.3(5)
Z	2
D_{calcd} (g cm^{-3})	1.842
$F(000)$	572
λ (\AA)	0.71073
μ (Mo K α) (cm^{-1})	24.94
Max, min transmission factors	1.00–0.758
Number of variables	311
G.O.F. ^a	1.11
$R(F_o)^b$	0.0237
$R_w(F_o)^c$	0.0274

^a G.O.F. = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{observns}} - N_{\text{var}})]^{1/2}$.

^b $R = \sum \|F_o| - F_c\| / \sum |F_o|$.

^c $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$.

ligands could render organometallic complexes water-soluble. Their synthetic strategy involved the formation of bis(trimethylsilyl) phosphonic esters by reaction of phosphonates with Me_3SiBr which was followed by hydrolysis under basic conditions to yield the corresponding phosphonic salts. Therefore we sought to prepare $[\text{Co}_3(\text{CO})_9\{\eta^1-\mu_3-[\text{CP}(\text{O})(\text{OSiMe}_3)_2]\}]$ **3** by treatment of **1** with Me_3SiBr , or by the reaction of $\text{Cl}_3\text{C}-\text{P}(\text{O})(\text{OSiMe}_3)_2$ **2** with $[\text{Co}_2(\text{CO})_8]$ under the same reaction conditions as those reported above for the preparation of **1**. IR monitoring showed the appearance



i) THF, 50°C ; ii) Cp_2MCl_2 (M = Ti, Zr), TIPF_6 , CH_2Cl_2 , -30°C to room temp.

Scheme 1.

Table 2
Selected bond lengths (Å) and angles (deg) for **1**

Co(1)–Co(2)	2.485(1)
Co(1)–Co(3)	2.485(1)
Co(2)–Co(3)	2.487(1)
Co(1)–C(10)	1.897(3)
Co(2)–C(10)	1.898(2)
Co(3)–C(10)	1.895(2)
P–O(10)	1.468(2)
P–O(11)	1.580(2)
P–O(12)	1.587(2)
P–C(10)	1.767(2)
O(11)–C(11)	1.460(4)
O(12)–C(13)	1.464(3)
C(11)–C(12)	1.477(5)
C(13)–C(14)	1.494(5)
Co(1)–Co(2)–Co(3)	60.0(1)
Co(2)–Co(1)–Co(3)	60.1(1)
Co(1)–Co(3)–Co(2)	60.0(1)
Co(1)–Co(2)–C(10)	49.1(1)
Co(1)–Co(3)–C(10)	49.1(1)
Co(2)–Co(1)–C(10)	49.1(1)
Co(2)–Co(3)–C(10)	49.1(1)
Co(3)–Co(1)–C(10)	49.0(1)
Co(3)–Co(2)–C(10)	49.0(1)
Co(1)–C(10)–Co(3)	81.9(1)
Co(2)–C(10)–Co(3)	81.9(1)
Co(1)–C(10)–Co(2)	81.8(1)
C(1)–Co(1)–C(10)	145.0(1)
C(2)–Co(1)–C(10)	102.1(1)
C(3)–Co(1)–C(10)	102.1(1)
C(4)–Co(2)–C(10)	141.3(1)
C(5)–Co(2)–C(10)	101.4(1)
C(6)–Co(2)–C(10)	104.2(1)
C(7)–Co(3)–C(10)	103.2(1)
C(8)–Co(3)–C(10)	102.0(1)
C(9)–Co(3)–C(10)	142.2(1)
Co(1)–C(10)–P	126.8(1)
Co(2)–C(10)–P	129.5(1)
Co(3)–C(10)–P	135.9(1)
O(10)–P–C(10)	114.7(1)
O(11)–P–C(10)	102.6(1)
O(12)–P–C(10)	106.1(1)
O(10)–P–O(11)	115.8(1)
O(10)–P–O(12)	113.4(1)
O(11)–P–O(12)	102.9(1)
P–O(11)–C(11)	117.8(2)
P–O(12)–C(13)	121.4(2)

of four $\nu(\text{CO})$ absorptions at 2111m, 2081s, 2062s and 2046s cm^{-1} as expected for a $\text{Co}_3(\text{CO})_9$ core. The resulting brown mixture was treated with aqueous hydrochloric acid (10%) and the product was thoroughly extracted with pentane and burgundy crystals were obtained at 4 °C. Both the mass spectrum and the elemental analysis are in a good agreement with the proposed structure of **3** and the ^1H NMR spectrum shows the presence of a singlet at δ 0.6 ppm that can be assigned to the methyl protons of the Me_3SiO groups. A broad signal was observed at δ 33 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum.

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^4$) for the non-hydrogen atoms of the complex **1**

Atom	x	y	z	U_{eq}^a
Co(1)	2235.1(4)	4011.6(3)	2969.8(2)	278(1)
Co(2)	3652.3(4)	2211.3(4)	3601.6(2)	298(1)
Co(3)	375.4(4)	1098.8(4)	3074.0(2)	295(1)
P	3067.3(8)	1965.5(7)	1456.1(3)	277(2)
O(1)	1728(3)	5513(3)	4560(1)	724(11)
O(2)	–371(3)	4522(3)	1668(1)	627(10)
O(3)	5481(3)	6638(2)	2484(1)	594(9)
O(4)	3441(3)	2844(3)	5446(1)	763(12)
O(5)	7401(3)	4229(3)	3343(2)	698(10)
O(6)	4278(4)	–766(3)	3616(2)	1038(15)
O(7)	7(3)	–2261(3)	2988(2)	819(12)
O(8)	–2605(3)	629(3)	1706(2)	786(11)
O(9)	–1191(3)	1334(3)	4677(1)	775(12)
O(10)	4947(2)	2991(2)	1346(1)	424(7)
O(11)	2533(2)	92(2)	1346(1)	393(7)
O(12)	1639(2)	2256(2)	773(1)	374(6)
C(1)	1893(3)	4928(3)	3953(2)	415(10)
C(2)	616(3)	4331(3)	2178(2)	399(10)
C(3)	4244(3)	5624(3)	2672(2)	379(10)
C(4)	3549(3)	2594(3)	4742(2)	446(11)
C(5)	5953(3)	3477(3)	3442(2)	433(11)
C(6)	4000(4)	365(4)	3612(2)	560(13)
C(7)	136(4)	–975(3)	3029(2)	477(11)
C(8)	–1461(4)	830(3)	2238(2)	465(11)
C(9)	–612(3)	1228(3)	4062(2)	445(11)
C(10)	2427(3)	2167(3)	2487(1)	265(8)
C(11)	2783(5)	–536(3)	527(2)	481(12)
C(12)	2924(5)	–2100(3)	662(2)	563(14)
C(13)	2177(4)	3617(3)	206(2)	473(12)
C(14)	2424(5)	3101(5)	–667(2)	584(15)

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

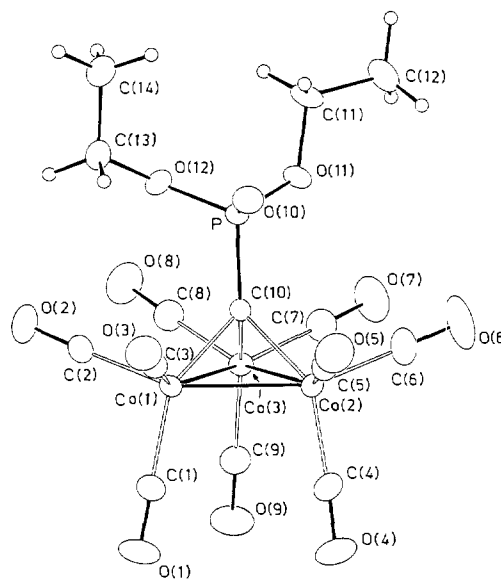


Fig. 1. View of the molecular structure of $[\text{Co}_3(\text{CO})_9(\eta^1\text{-}\mu_3\text{-}[\text{CP}(\text{O})(\text{OEt})_2])] \mathbf{1}$ together with the atomic numbering system.

The reaction of **1** with Me_3SiBr (ratio 1:2) in CH_2Cl_2 also produced, after extraction with pentane, a burgundy crystalline material which has the same spectral characteristics as those of **3**. The ^1H NMR spectrum confirms the disappearance of the signals due to the OEt groups. Further investigations are being carried out in order to confirm the structure of **3**.

Ligands bearing P=O functions are frequently used in coordination chemistry. Although numerous reports have been devoted to phosphine oxide ligands, phosphoryl derivatives have been much less studied (for examples of phosphoryl ligands see Ref. [10]). Therefore, we explored the possibility of coordinating the phosphonate group in **1** to an early transition metal and thus access novel early–late polymetallic systems. Treatment of $[\text{Cp}_2\text{MCl}]^+$ ($\text{M} = \text{Ti}, \text{Zr}$), formed in situ by addition of TIPF_6 to a CH_2Cl_2 solution of Cp_2MCl_2 , with **1** (1:1 ratio) yielded $[\text{Co}_3(\text{CO})_9\{\eta^1-\mu_3-[\text{CP}(\text{O})(\text{OEt})_2]\}\{\text{Cp}_2\text{MCl}\}]^+\text{PF}_6^-$ **4a** ($\text{M} = \text{Ti}$) and **4b** ($\text{M} = \text{Zr}$) (Scheme 1). In the IR spectra the expected $\nu(\text{CO})$ absorptions between 2120 and 2020 cm^{-1} are observed whereas the disappearance of the $\nu(\text{P}=\text{O})$ vibration, which was observed at 1230 cm^{-1} in **1** but could not be unambiguously assigned in the products, was noticed. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra show a small shift to lower fields of the signals compared to that of **1** ($\Delta\delta = 5\text{--}6\text{ ppm}$), which is consistent with the coordination of the P=O function to the metal centre M by the oxygen. The two Cp ligands in each compound are non-equivalent as shown in the ^1H NMR spectra where they give two signals in a 1:1 ratio. All the data collected are consistent with the proposed structure (Scheme 1).

Replacement of CO in **1** readily occurs at room temperature in toluene or pentane–toluene mixture (1/1 ratio) in the presence of an excess of phosphine and yields the monosubstituted derivatives $[\text{Co}_3(\text{CO})_8\text{L}\{\eta^1-\mu_3-[\text{CP}(\text{O})(\text{OEt})_2]\}]$ **5a** ($\text{L} = \text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{Ph}$) and **5b** ($\text{L} = \text{PPh}_3$). It is notable that methinyl octacarbonyl clusters of the type $\text{CCo}_3(\text{CO})_8\text{L}$ ($\text{Y} = \text{aryl}, \text{alkyl}, \text{halide}, \text{etc.}$ and $\text{L} = \text{phosphine}, \text{arsine}, \text{phosphite}$) are usually prepared from $\text{YCCo}_3(\text{CO})_9$ by ligand exchange in boiling hexane or at room temperature under u.v. irradiation or in the presence of the appropriate Pt^0L_4 complex [11,12]. After extraction with hexane, clusters **5** have been characterized by IR and ^{31}P NMR spectroscopy (see Section 3). The carbonyl stretching frequencies are very similar to those reported for $\text{YCCo}_3(\text{CO})_8\text{L}$ where $\text{Y} = \text{halide}$ [2,11,12], which is in agreement with the electron withdrawing nature of the phosphonate group. However, it is not yet possible to unambiguously establish whether the substitution occurred in the equatorial or apical positions. The presence of bridging carbonyls is not noticed. In the case of **5a** the $\nu(\text{C}=\text{O})$ frequency of the ketone is observed at 1673 cm^{-1} , thus showing no interaction of this group

with the Co_3 core. The ^{31}P NMR spectra show in both cases the presence of a sharp singlet at ca. $\delta = 33\text{ ppm}$ for the $-\text{P}(\text{O})(\text{OEt})_2$ unit. Broad signals centred at $\delta = 31\text{ ppm}$ (**5a**) and 45 ppm (**5b**), can be assigned to coordinated phosphine, whereas the presence of free phosphine is also observed. Similar features have already been observed and were attributed to an extensive phosphine dissociation and rapid ligand exchange in solution [11,13].

3. Experimental section

All manipulations and reactions were carried out using standard Schlenk-vessel techniques under an atmosphere of dinitrogen (Air liquide, R-grade), which had been purified by passage over BASF R3-11 catalyst and 4 \AA molecular sieves. Solvents were distilled under an atmosphere of dinitrogen from phosphorus pentoxide (dichloromethane), potassium (tetrahydrofuran), sodium (toluene, pentane, diethyl ether). The ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded, at 300.1 MHz and 121.5 MHz respectively, on a Bruker AM300 instrument. Spectra were referenced internally using residual protio solvent resonances (^1H) relative to tetramethylsilane ($\delta = 0\text{ ppm}$) or externally using 85% H_3PO_4 in H_2O (^{31}P) with downfield chemical shifts reported as positive. Mass spectra were measured on a Fisons ZAB-HF spectrometer (Université Louis Pasteur, R. Hueber). Infrared spectra were recorded on a IFS 66 Bruker FTIR spectrometer. Elemental C, H and N analyses were performed by the Service de microanalyses du CNRS. Infrared spectra were recorded on an IFS 66 Bruker FTIR spectrometer.

3.1. Preparation of $[\text{Co}_3(\text{CO})_9\{\eta^1-\mu_3-[\text{CP}(\text{O})(\text{OEt})_2]\}]$ (**1**)

A THF (150 ml) solution of $\text{Co}_2(\text{CO})_8$ (10.0 g, 29 mmol) and $\text{Cl}_3\text{CP}(\text{O})(\text{OEt})_2$ (3.15 ml, 17.85 mmol) was gently heated to 50°C until the evolution of CO had ceased (about 3 h). The resulting brown mixture was poured into 100 ml of aqueous hydrochloric acid (10%). The product was extracted with pentane ($3 \times 200\text{ ml}$) and this extract was washed three to five times with distilled water until the water was colourless. The organic layer was dried over MgSO_4 and the solvent removed under pressure affording **1** as a brown-purple microcrystalline solid. Burgundy crystals suitable for an X-ray diffraction study were obtained from a pentane solution at 4°C . Yield: 4.8 g (28%). IR $\nu(\text{CO})$ and $\nu(\text{P}=\text{O})$: see text. ^1H NMR (CDCl_3): δ 1.36 (6H, t, $J_{\text{HH}} 7\text{ Hz}$, Me), 4.22 (4H, quint., $J_{\text{HH}} = J_{\text{PH}} 7\text{ Hz}$, CH_2); ^{31}P NMR (CDCl_3): δ 29.4. Mass spectrum: m/z 578 (M^+), 550 ($\text{M}^+ - \text{CO}$), 522 ($\text{M}^+ - 2\text{CO}$), 494 ($\text{M}^+ - 3\text{CO}$), 466 ($\text{M}^+ - 4\text{CO}$), 438 ($\text{M}^+ - 5\text{CO}$), 410 ($\text{M}^+ -$

6CO), 382 ($M^+ - 7CO$), 354 ($M^+ - 8CO$), 326 ($M^+ - 9CO$).

3.2. Preparation of $Cl_3C-P(O)(OSiMe_3)_2$ (**2**)

A CH_2Cl_2 solution (50 ml) of $Cl_3CP(O)(OEt)_2$ (2.1 g, 8.5 mmol) and Me_3SiBr (3.06 g, 20 mmol) was stirred for 3 days at room temperature. After the solvent had been removed, the residue was distilled under reduced pressure and **2** was obtained as a moisture-sensitive colourless liquid, b.p. = 85–87 °C/1 mmHg. Yield: 2.48 g (85%). 1H NMR ($CDCl_3$): δ 0.25 (18H, s, Me); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -12.1.

3.3. Preparation of $[Co_3(CO)_9\{\eta^1-\mu_3-[CP(O)(OSiMe_3)_2]\}]$ (**3**)

Method a. A THF (100 ml) solution of $Co_2(CO)_8$ (2.0 g, 5.85 mmol) and $Cl_3CP(O)(OSiMe_3)_2$ **2** (3.56 mmol) was treated and worked up in a similar manner as reported for the preparation of **1**, affording **3** as a burgundy crystalline material. Yield: 0.9 g (23%).

Method b. A CH_2Cl_2 solution of **1** and Me_3SiBr (2 molar equiv.) was stirred for 2 days at room temperature. The solvent was removed under reduced pressure and the residue extracted with pentane. The resulting brown-red solution afforded **3** in low yield (ca. 15%) as a burgundy crystalline material upon cooling to 0 °C.

1H NMR ($CDCl_3$): δ 0.6; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 33. Mass spectrum: m/z 666 (M^+), 638 ($M^+ - CO$), 610 ($M^+ - 2CO$), 594 ($M^+ - 2CO - O$), 582 ($M^+ - 3CO$), 566 ($MH^+ - 3CO - O$), 554 ($M^+ - 4CO$), 538 ($M^+ - 4CO - O$). Elemental analysis: calc. for $C_{16}H_{18}Co_3O_{12}PSi_2$: C, 28.84; H, 2.72; found: C, 28.74; H, 3.00.

3.4. Preparation of $[Co_3(CO)_9\{\eta^1-\mu_3-[CP(O)(OEt)_2]\}] [Cp_2TiCl]PF_6$ (**4a**)

Cp_2TiCl_2 (0.29 g, 1.18 mmol) and $TiPF_6$ (0.40 mg, 1.18 mmol) were placed in a Schlenk tube at -40 °C and CH_2Cl_2 (30 ml) was added. The mixture was stirred for 5 min at this temperature and a pre-cooled CH_2Cl_2 (10 ml, -40 °C) solution of **1** (0.685 g, 1.18 mmol) was added dropwise. The reaction mixture was stirred for 30 min at below -25 °C and was allowed to warm to room temperature. After filtration over a Celite pad and removal of the volatiles, the residue was washed with Et_2O (2 × 20 ml) and pentane (2 × 30 ml) and **4a** was obtained as a red-burgundy solid. Yield: 0.931 g, 85%. 1H NMR (CD_2Cl_2): δ 6.57 (s, 5H, Cp), 6.49 (s, 5H, Cp), 4.39 (m, 4H, OCH_2), 1.42 (m, 6H, CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 35.06, -144.45 (sept, J_{PF} 708 Hz). Calc. for $C_{24}H_{12}ClCo_3F_6O_{12}P_2Ti$: C, 30.78; H, 2.15; found: C, 31.39; H, 2.48.

3.5. Preparation of $[Co_3(CO)_9\{\eta^1-\mu_3-[CP(O)(OEt)_2]\}] [Cp_2ZrCl]PF_6$ (**4b**)

This compound was prepared in a similar manner to **4a**. Yield: 81%. 1H NMR (CD_2Cl_2): δ 6.48 (s, 5H, Cp), 6.41 (s, 5H, Cp), 4.35 (m, 4H, OCH_2), 1.41 (m, 6H, CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 34.3, -144.5 (J_{PF} 708 Hz). Calc. for $C_{24}H_{12}ClCo_3F_6O_{12}P_2Zr$: C, 29.42; H, 2.06; found: C, 29.53; H, 2.36.

3.6. CO-substitution reactions

To a toluene or pentane–toluene (ratio 1/1) solution of **1** were added 2.5 molar equiv. of $Ph_2PCH_2C(O)Ph$. The solution turned immediately green-brown and evolution of CO was observed. After the volatiles were removed under reduced pressure, the residue was extracted with hexane, affording $[Co_3(CO)_8\{Ph_2PCH_2C(O)Ph\}\{\eta^1-\mu_3-[CP(O)(OEt)_2]\}]$ **5a**. IR $\nu(CO)$ (hexane): 2085s, 2059w, 2046vs, 2037s, 2024vs, 2014vs, 1997sh, 1673s. $^{31}P\{^1H\}$ NMR (hexane- C_6D_6): δ 33.5, 31 (broad), -17.25 (broad).

$[Co_3(CO)_8(PPh_3)\{\eta^1-\mu_3-[CP(O)(OEt)_2]\}]$ **5b** was obtained in a similar manner from **1** and PPh_3 . IR $\nu(CO)$ (hexane): 2086s, 2063w, 2051vs, 2041w, 2033s, 2027vs, 2010w, 1998w. $^{31}P\{^1H\}$ NMR (hexane- C_6D_6): δ 45 (very broad), 33, -5 (broad).

3.7. Crystal structure determination of (**1**)

Suitable crystals were obtained by recrystallization from pentane at 4 °C. The intensity data were collected on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Mo K α radiation and the θ -2 θ scan technique at room temperature. Crystallographic data are summarized in Table 1. 6088 unique reflections were measured (with θ in the range 3–30°) and 3832, having $I > 2\sigma(I)$, were used in the refinement. An empirical correction for absorption was applied. The structure was solved by direct and Fourier methods and refined by full-matrix least squares procedures, with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms. All hydrogen atoms were clearly localized in the final ΔF map and refined isotropically. The SHELX-76 and SHELXS-86 systems of computer programs were used [14]. The R and R_w values were 0.0237 and 0.0274 respectively.

Selected bond distances and angles are given in Table 2 and atomic coordinates for the non-hydrogen atoms are given in Table 3. Atomic coordinates, thermal parameters and a complete list of bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

We are grateful to the Centre National de la Recherche Scientifique (CNRS), the Consiglio Nazionale delle Ricerche (CNR, Roma), the Commission of the European Communities (contract CHRX-CT93-0277) for financial support and to the European Science Foundation (Network "Metal Clusters") for a short visit grant to C.G.

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