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Bis(dimethylphosphino)ethane substitution in $\text{PhCCo}_3(\text{CO})_9$: Synthesis and X-ray structure of the phosphine-bridged cluster $\text{PhCCo}_3(\text{CO})_7(\text{dmpe})$

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Abstract

The bidentate phosphine ligand bis(dimethylphosphino)ethane (dmpe) reacts with $\text{PhCCo}_3(\text{CO})_9$ (1) to initially yield $\text{PhCCo}_3(\text{CO})_7(\text{dmpe})$ (2). The dmpe ligand in 2 bridges adjacent cobalt centers in the equatorial plane as shown by FT-IR and ^{31}P NMR spectroscopy and single-crystal X-ray diffraction analysis. The phosphine-bridged cluster $\text{PhCCo}_3(\text{CO})_7(\text{dmpe})$ crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 9.142(1)$, $b = 16.140(2)$, $c = 16.903(3)$ Å, $V = 2494.7(5)$ Å³ and $Z = 4$. Block-cascade least-squares refinement yielded $R = 0.0702$ for 2151 reflections. Reaction of 2 with additional dmpe is shown to yield the known cluster $\text{PhCCo}_3(\text{CO})_5(\text{dmpe})_2$ (3) as a result of dmpe chelation at the unsubstituted cobalt center in 2. ^{31}P NMR analysis reveals that bridging dmpe in 2 undergoes an equatorial \rightarrow axial rearrangement during the formation of 3 in agreement with the solid-state structure.

Introduction

The stabilization of polynuclear metal clusters using phosphine ligands continues to receive wide attention [1–9]. Research in this area is driven, in part, by the expectation that contiguous metal centers held together by a bridging phosphine ligand(s) may afford novel catalytic systems capable of multisite substrate activation [10–14]. Several polynuclear phosphine(phosphido)-bridged systems have been reported to function as active catalysts in reactions where the unsubstituted parent cluster is unstable. For example, Bonnet and co-workers have shown that phosphido-bridged ruthenium clusters function as intact polynuclear entities in the hydrogenation of cyclohexanone to cyclohexanol [15,16]. The phosphine-bridged cobalt clusters $\text{MeCCo}_3(\text{CO})_7(\text{L-L})$ (where L-L = diphosphine) stabilize and activate the cluster in the hydroformylation of 1-pentene [17] and styrene [18]. Finally, evidence has been presented that the hydroformylation of 1-pentene in the

presence of $\text{Co}_4(\text{CO})_{10}(\mu_4\text{-PPh})_2$ proceeds through an intact phosphinated cluster [19]. While the normal/branched aldehyde ratio in this latter reaction is significantly different from reactions employing $\text{Co}_4(\text{CO})_{10}(\mu_4\text{-PPh})_2$, $\text{Co}_2(\text{CO})_8$, and $\text{Co}_2(\text{CO})_8$ /diphosphine, arguing against a common intermediate, independent studies involving bona fide diphosphine-substituted clusters based on $\text{Co}_4(\text{CO})_{10}(\mu_4\text{-PPh})_2$ are clearly required in order to assess the nature of the catalytically active species.

As part of our interest in the chemistry associated with the tricobalt cluster $\text{PhCCo}_3(\text{CO})_9$ (**1**) [20,21], we report our results on the reaction between **1** and the bidentate phosphine ligand bis(dimethylphosphino)ethane (dmpe). While many mono and bidentate phosphine-substituted clusters based on **1** have been prepared and characterized [22–29], no prior studies exist where dmpe has been used as a ligand. We have previously shown that dmpe, with its smaller methyl groups, reacts with the tetracobalt cluster $\text{Co}_4(\text{CO})_{10}(\mu_4\text{-PPh})_2$ in a chelating fashion [30]. This binding mode of dmpe was unexpected given that the reaction between $\text{Co}_4(\text{CO})_{10}(\mu_4\text{-PPh})_2$ and diphos yields a bridged diphosphine cluster [31]. Another impetus for this study rests with the recently reported X-ray structure of $\text{PhCCo}_3(\text{CO})_5(\text{dmpe})_2$ [32]. There it was shown that one dmpe ligand functioned in a bridging capacity while the second dmpe ligand was observed to chelate at a single cobalt center. Since it was unknown which coordination mode was initially involved in the substitution reaction, we decided to examine this reaction further.

In this paper we describe the synthesis, spectral and crystallographic characterization of $\text{PhCCo}_3(\text{CO})_7(\text{dmpe})$ (**2**). The bridging dmpe ligand in **2** adopts an equatorial substitution position and is subsequently transformed into an axial coordination mode upon further dmpe substitution.

Results and discussion

I. Synthesis and spectral properties for $\text{PhCCo}_3(\text{CO})_7(\text{dmpe})$

Reaction of 1 mol equiv. of dmpe with $\text{PhCCo}_3(\text{CO})_9$ [33] in THF at room temperature gives the diphosphine-substituted cluster $\text{PhCCo}_3(\text{CO})_7(\text{dmpe})$ (**2**). FT-IR analysis confirmed the essentially quantitative conversion to **2**, which was subsequently isolated in > 90% yield by chromatography using silica gel and CH_2Cl_2 /petroleum ether. The FT-IR spectrum of **2** in CH_2Cl_2 , which is shown in Fig. 1a, exhibits two very intense terminal carbonyl bands at 2051 and 1996 cm^{-1} , along with weaker carbonyl bands at 1975sh, 1939vw, 1851vw, and 1823vw cm^{-1} . The IR spectral properties of **2** closely match those reported for $\text{PhCCo}_3(\text{CO})_7(\text{diphos})$ [23]. However, Aime and co-workers have noted discrepancies in the IR spectral data in the related diphosphine cluster $\text{MeCCo}_3(\text{CO})_7(\text{dppm})$, presumably the result of equatorial/axial isomers [34]. On the basis of these data, we felt it was necessary to further characterize **2** in order to unequivocally establish the coordination of the dmpe ligand.

The *in situ* $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2**, obtained from **1** and a slight excess of dmpe, was next examined. These results are shown in Fig. 2a. There the major ^{31}P resonance at δ 20.3 is readily assigned to the dmpe ligand in **2** which functions to bridge adjacent cobalt centers. A chelating dmpe ligand would be expected to display two inequivalent ^{31}P resonances in addition to exhibiting a large nuclear deshielding typical of a 5-membered ring (*vide infra*) [30,35].

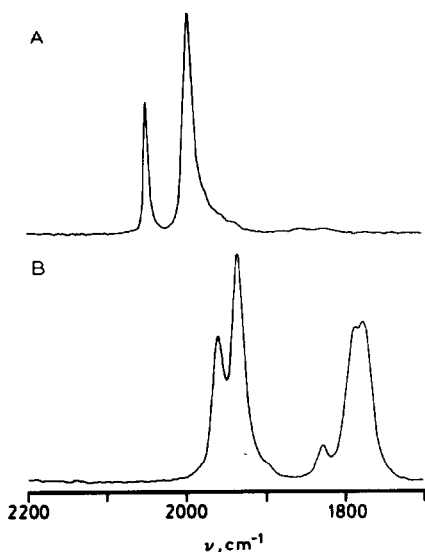


Fig. 1. Infrared spectra of the carbonyl region for (A) $\text{PhCCo}_3(\text{CO})_7(\text{dmpe})$ and (B) $\text{PhCCo}_3(\text{CO})_5(\text{dmpe})_2$ in dichloromethane at room temperature.

While it would be instructive to discuss the observed ^{31}P chemical shift for **2** in terms of Garrou's ring-effect parameter Δ_R [35], this cannot be done at this time due to the absence of ^{31}P NMR data for the model diphosphine cluster $\text{PhCCo}_3(\text{CO})_7\text{L}_2$ (where $\text{L} = \text{monodentate phosphine } \text{PMe}_3 \text{ or } \text{PMe}_2\text{Ph}$). The minor ^{31}P resonances at δ 44.3, 32.2, and 0.8, which display an integral ratio of 1:1:2, respectively, are readily assigned to the bisphosphine cluster **3**. The two ^{31}P resonances which integrate for 1P each are ascribed to the nonequivalent phosphines associated with the chelating dmpe ligand. The remaining high-field ^{31}P

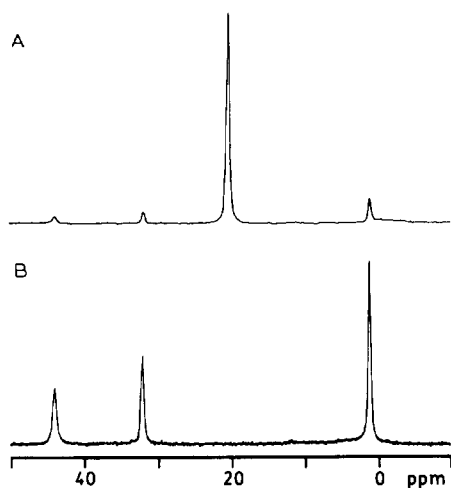


Fig. 2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of (A) $\text{PhCCo}_3(\text{CO})_7(\text{dmpe})$ and (B) $\text{PhCCo}_3(\text{CO})_5(\text{dmpe})_2$ in CDCl_3 at 213 K.

Table 1

X-Ray crystallographic and data processing parameters for $\text{PhCCo}_3(\text{CO})_7(\text{dmpe})$ (**2**)

Space group	$P2_12_12_1$ /orthorhombic
Cell constants	
<i>a</i> , Å	9.142 (1)
<i>b</i> , Å	16.140(2)
<i>c</i> , Å	16.903(3)
<i>V</i> , Å ³	2494.7(5)
Molecular formula	$\text{C}_{20}\text{H}_{21}\text{Co}_3\text{O}_7\text{P}_2$
F.W.	612.13
formula units/cell (<i>Z</i>)	4
ρ , g cm^{-3}	1.63
Crystal size, mm	$0.3 \times 0.1 \times 0.1$
Absorption coefficient (μ), cm^{-1}	21.31
λ (radiation), Å	0.71073
Data collection method	ω
Collection range, deg	$3.0 \leq 2\theta \leq 50.0^\circ$
Total no. of data collected	3080
no. of independent data, $I > 3\sigma(I)$	2151
<i>R</i>	0.0702
<i>R</i> _w	0.0617
Weights	$w = (\sigma^2(F_o) + 0.00074F_c^2)^{-1}$

resonance is assigned to the bridging dmpe moiety. No unusual temperature dependence was observed as the sample containing **2** was warmed back to room temperature from 213 K which suggests that the dmpe ligand is nonfluxional. However, at this stage our data are consistent with either an equatorially or axially disposed dmpe ligand. Therefore, we resorted to X-ray diffraction analysis in order to address the spatial orientation of the dmpe ligand in **2**.

II. X-Ray crystallographic structure of $\text{PhCCo}_3(\text{CO})_7(\text{dmpe})$

The structure of **2** has been confirmed by a single-crystal X-ray diffraction study. Black crystals of **2** were grown from a CH_2Cl_2 solution containing **2** that had been layered with heptane. **2** exists as discrete molecules in the unit cell with no unusually short inter- or intramolecular contacts. The X-ray data collection and processing parameters of **2** are given in Table 1 with the final fractional coordinates listed in Table 2.

The ORTEP diagram in Fig. 3 clearly establishes the equatorial disposition of the bridging dmpe ligand. Selected bond distances and angles are given in Table 3. The internal polyhedron of **2** consists of a triangular array of cobalt atoms capped by a μ_3 -CPh group. The mean value for the Co–Co (2.477 Å) and μ_3 -C–Co (1.928 Å) distances agree well with those reported for the parent cluster **1** [36], which suggests that the dmpe ligand exerts no extenuating steric perturbations on the cluster framework. The Co–CO distances range from 1.742(16) to 1.818(16) Å with a mean distance of 1.773 Å. The remaining distances and angles are unexceptional and require no further comment. Scheme 1 illustrates the reaction for **1** → **2**.

III. Conversion of $\text{PhCCo}_3(\text{CO})_7(\text{dmpe})$ into $\text{PhCCo}_3(\text{CO})_5(\text{dmpe})_2$

Reaction of **1** or **2** with excess dmpe yields the bis-dmpe cluster **3** without the observation of spectroscopic intermediates (IR monitoring). A brief report has

Table 2

Positional parameters of the non-hydrogens atoms for $\text{PhCCo}_3(\text{CO})_7(\text{dmpe})$ (**2**) with esd's in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ^a
Co(1)	3108(2)	1070(1)	1723(1)	42(1)
Co(2)	1740(2)	1484(1)	2927(1)	41(1)
Co(3)	1601(2)	40(1)	2436(1)	41(1)
P(1)	4420(4)	2182(2)	1512(2)	53(1)
P(2)	2861(4)	2550(2)	3448(2)	52(1)
C(1)	4399(18)	406(9)	1265(9)	65(6)
O(1)	5234(13)	-30(7)	959(7)	97(5)
C(2)	1804(21)	1319(10)	994(9)	75(7)
O(2)	950(16)	1471(9)	526(8)	129(7)
C(3)	344(18)	2046(9)	2444(11)	75(6)
O(3)	-571(16)	2407(8)	2128(10)	138(7)
C(4)	944(15)	1242(8)	3835(10)	59(6)
O(4)	478(14)	1057(8)	4459(7)	94(5)
C(5)	1295(18)	-547(10)	3305(10)	67(6)
O(5)	1025(18)	-919(7)	3872(8)	117(7)
C(6)	2201(14)	-780(9)	1807(10)	55(6)
O(6)	2523(11)	-1302(6)	1392(8)	88(5)
C(7)	-185(18)	244(7)	2005(8)	49(5)
O(7)	-1244(10)	375(7)	1715(8)	85(5)
C(8)	3309(14)	714(6)	2776(6)	32(4)
C(10)	5959(10)	552(5)	3034(5)	54(5)
C(11)	7127	407	3547	81(7)
C(12)	6860	198	4335	66(6)
C(13)	5425	134	4610	68(6)
C(14)	4258	279	4097	51(5)
C(9)	4525	488	3309	33(4)
C(15)	3544(22)	2948(10)	877(11)	83(8)
C(16)	6128(19)	2023(11)	951(13)	85(8)
C(17)	4126(25)	2358(11)	4227(12)	105(9)
C(18)	1631(23)	3283(9)	3900(11)	87(7)
C(19)	5059(22)	2807(11)	2329(11)	85(7)
C(20)	3950(18)	3219(8)	2813(11)	75(7)

^a Equivalent isotropic *U* defined as one third of the trace of the orthogonalised U_{ij} tensor.

appeared which unequivocally established the existence of distinct bridging and chelating dmpe ligands in **3** [32]. At that time it was unclear which dmpe coordination mode was initially favored; however on the basis of our results reported here we can confidently assume that the initial dmpe ligand in **2** adopts a bridging role in the equatorial plane. Interestingly enough, reaction of **2** with additional dmpe promotes an equatorial → axial interchange of the bridging dmpe ligand. Other researchers have also noted similar diphosphine interconversions [23,34]. Such a process has been interpreted in terms of thermodynamic/kinetic control. Here clusters with axially oriented bridging phosphines represent thermodynamic products. The reaction leading to **3** is shown in Scheme 1.

We have included the IR and ³¹P NMR spectra of **3** in Figs. 1b and 2b, respectively, for comparative purposes. The IR spectrum of **3** has been reported [32] and the ³¹P NMR of **3** was already described (*vide infra*). We note that there is a ca. 20 ppm shift to higher field for the axially bridged dmpe ligand in **3** relative to the

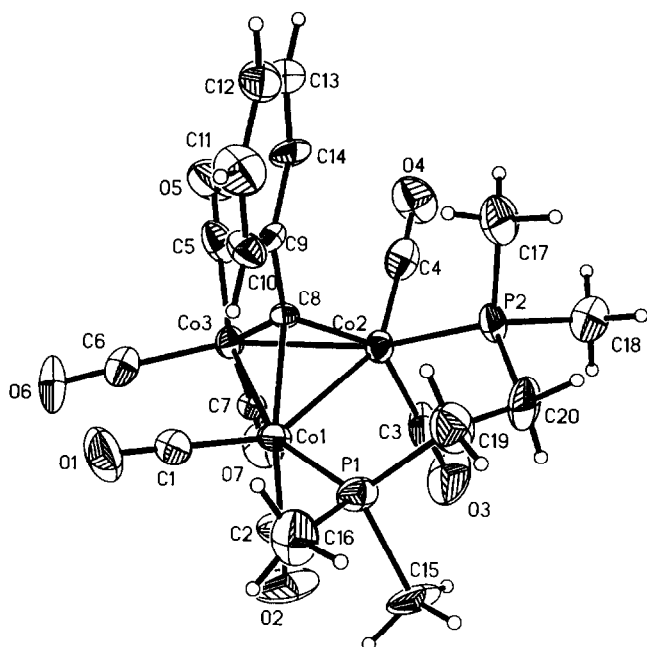


Fig. 3. ORTEP diagram of $\text{PhCCo}_3(\text{CO})_7(\text{dmpe})$ with the thermal ellipsoids drawn at the 30% probability level.

equatorial bridged dmpe ligand in **2**. To our knowledge, this high field shift has not been previously reported for such a ligand interconversion.

Conclusion

The reaction between **1** and dmpe is facile and provides high yields of $\text{PhCCo}_3(\text{CO})_7(\text{dmpe})$ and $\text{PhCCo}_3(\text{CO})_5(\text{dmpe})_2$. The exact degree of dmpe substitution in **1** depends on the initial molar ratio of **1** and dmpe. It has been shown by ^{31}P and X-ray diffraction analysis that the first dmpe ligand bridges adjacent cobalt centers in the equatorial plane. **2** undergoes substitution by a second dmpe ligand at the unique center, coupled with an equatorial \rightarrow axial interconversion of the bridging dmpe ligand.

Experimental section

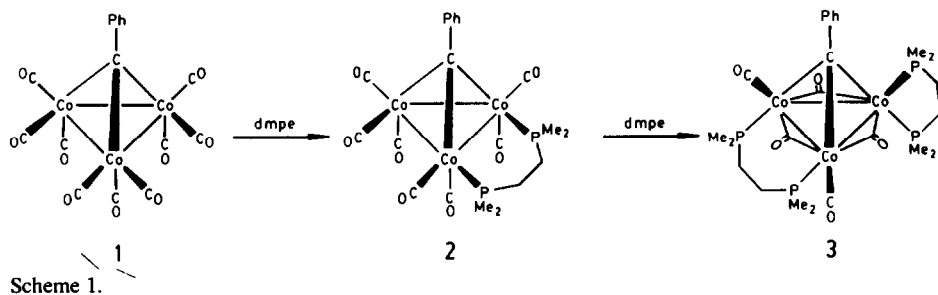
General

Dicobalt octacarbonyl and dmpe were purchased from Pressure Chemical and Strem Chemical, respectively, and used as received. $\text{PhCCo}_3(\text{CO})_9$ was prepared according to the procedure given by Seyferth and co-workers [33]. $\text{PhCCo}_3(\text{CO})_5(\text{dmpe})_2$ was prepared according to the recently published procedure [32] or by treatment of **2** with excess dmpe. All reactions were conducted under argon using Schlenk techniques [37]. THF and heptane were distilled from sodium/benzophenone ketyl, while CDCl_3 was distilled from P_2O_5 . All distilled solvents were stored under argon in Schlenk vessels.

Table 3

Selected bond distances (Å) and angles (deg) in $\text{PhCCo}_3(\text{CO})_7(\text{dmpe})$ (2)

<i>Bond distances</i>			
Co(1)–Co(2)	2.481(3)	Co(1)–Co(3)	2.472(2)
Co(1)–P(1)	2.188(4)	Co(1)–C(1)	1.772(16)
Co(1)–C(2)	1.760(17)	Co(1)–C(8)	1.880(11)
Co(2)–C(3)	2.477(2)	Co(2)–P(2)	2.188(4)
Co(2)–C(3)	1.766(17)	Co(2)–C(4)	1.742(16)
Co(2)–C(8)	1.915(11)	Co(3)–C(5)	1.771(17)
Co(3)–C(6)	1.784(15)	Co(3)–C(7)	1.818(16)
Co(3)–C(8)	1.988(12)	P(1)–C(15)	1.822(18)
P(1)–C(16)	1.844(19)	P(1)–C(19)	1.808(19)
P(2)–C(17)	1.780(22)	P(2)–C(18)	1.803(18)
P(2)–C(20)	1.818(17)	C(1)–O(1)	1.160(19)
C(2)–O(2)	1.138(22)	C(3)–O(3)	1.152(22)
C(4)–O(4)	1.176(21)	C(5)–O(5)	1.157(21)
C(6)–O(6)	1.135(19)	C(7)–O(7)	1.106(19)
C(8)–C(9)	1.476(14)	C(19)–C(20)	1.463(26)
<i>Bond angles</i>			
Co(2)–Co(1)–Co(3)	60.0(1)	Co(2)–Co(1)–P(1)	100.9(1)
Co(3)–Co(2)–P(1)	159.4(1)	Co(2)–Co(1)–C(1)	149.0(5)
Co(3)–Co(1)–C(1)	100.2(5)	P(1)–Co(1)–C(1)	93.4(5)
Co(2)–Co(1)–C(2)	99.9(6)	Co(3)–Co(1)–C(2)	96.7(6)
P(1)–Co(1)–C(2)	94.0(6)	C(1)–Co(1)–C(2)	106.5(7)
Co(2)–Co(1)–C(8)	49.8(3)	Co(3)–Co(1)–C(8)	52.2(4)
P(1)–Co(1)–C(8)	110.6(4)	C(1)–Co(1)–C(8)	99.4(6)
C(2)–Co(1)–C(8)	143.0(7)	Co(1)–Co(2)–Co(3)	59.8(1)
Co(1)–Co(2)–P(2)	107.8(1)	Co(3)–Co(2)–P(2)	154.0(1)
Co(1)–Co(2)–C(3)	97.0(6)	Co(3)–C(3)–C(3)	106.9(5)
P(2)–Co(2)–C(3)	96.9(5)	Co(1)–Co(2)–C(4)	150.8(4)
Co(3)–Co(2)–C(4)	93.6(4)	P(2)–Co(2)–C(4)	91.0(5)
C(3)–Co(2)–C(4)	102.8(7)	Co(1)–Co(2)–C(8)	48.6(3)
Co(3)–Co(2)–C(8)	51.9(3)	P(2)–Co(2)–C(8)	102.3(4)
C(3)–Co(2)–C(8)	144.4(7)	C(4)–Co(2)–C(8)	106.6(5)
Co(1)–Co(3)–Co(2)	60.2(1)	Co(1)–Co(3)–C(5)	148.5(5)
Co(2)–Co(3)–C(5)	103.5(5)	Co(1)–Co(3)–C(6)	92.1(5)
Co(2)–Co(3)–C(6)	151.9(5)	C(5)–Co(3)–C(6)	98.4(7)
Co(2)–C(3)–C(7)	100.6(4)	Co(2)–Co(3)–C(7)	90.6(4)
C(5)–Co(3)–C(7)	106.7(7)	C(6)–Co(3)–C(7)	99.9(6)
Co(1)–Co(3)–C(8)	48.4(3)	Co(2)–Co(3)–C(8)	49.3(3)
C(5)–Co(3)–C(8)	100.2(6)	C(6)–Co(3)–C(8)	109.7(5)
C(7)–Co(3)–C(8)	136.3(5)	Co(1)–P(1)–C(15)	114.3(6)
Co(1)–P(1)–C(16)	115.7(6)	C(15)–P(1)–C(16)	99.4(9)
Co(1)–P(1)–C(19)	120.7(6)	C(15)–P(1)–C(19)	102.3(8)
C(16)–P(1)–C(19)	101.4(9)	Co(2)–P(2)–C(17)	117.7(6)
Co(2)–P(2)–C(18)	113.3(6)	C(17)–P(2)–C(18)	101.8(9)
Co(2)–P(2)–C(20)	119.1(6)	C(17)–P(2)–C(20)	100.6(9)
C(18)–P(2)–C(20)	101.6(7)	Co(1)–C(1)–O(1)	179.3(7)
Co(1)–C(2)–O(2)	179.1(10)	Co(2)–C(3)–O(3)	179.6(13)
Co(2)–C(4)–O(4)	176.3(13)	Co(3)–C(5)–O(5)	176.7(15)
Co(3)–C(6)–O(6)	176.9(12)	Co(3)–C(7)–O(7)	177.2(14)
Co(1)–C(8)–Co(2)	81.6(4)	Co(1)–C(8)–Co(3)	79.4(4)
Co(2)–C(8)–Co(3)	78.8(5)	Co(1)–C(8)–C(9)	136.6(8)
Co(2)–C(8)–C(9)	130.0(7)	Co(3)–C(8)–C(9)	129.3(7)
C(8)–C(9)–C(10)	119.1(5)	C(8)–C(9)–C(14)	120.7(5)
P(1)–C(19)–C(20)	117.2(14)	P(2)–C(20)–C(19)	116.1(11)



Scheme 1.

Infrared spectra were recorded on a Nicolet 20SXB FT-IR spectrometer in 0.1 mm NaCl cells. The ^{31}P NMR spectra were recorded on a Varian 300-VXR spectrometer at 121 MHz. The ^{31}P NMR chemical shifts are referenced to external 85% H_3PO_4 with positive chemical shifts to low field of the external standard. The microanalysis was performed by Atlantic Microlab, Atlanta, GA.

Synthesis of $\text{PhCCo}_3(\text{CO})_7(\text{dmpe})$

To 50 mL of a THF solution containing 0.2 g (0.39 mmol) of $\text{PhCCo}_3(\text{CO})_9$, was added 0.06 g (0.04 mmol) of dmpe . After the reaction had been stirred for 1 h at room temperature, the color of the reaction solution changed from dark brown to green and TLC examination of the solution revealed the absence of starting material. The solvent was removed from the green solution under vacuum and the desired product was purified by chromatography under argon using silica gel and 1:1 (v/v) mixture of petroleum ether and methylene chloride. The resulting material was recrystallized from CH_2Cl_2 /heptane to give 0.22 g (0.36 mmol, 93% yield) of $\text{PhCCo}_3(\text{CO})_7(\text{dmpe})$. Single crystals suitable for X-ray diffraction analysis were obtained from the same solvent system. IR (CH_2Cl_2): 2051s, 1996vs, 1975sh, 1939vw, 1851vw, and 1823vw cm^{-1} . Anal. Found: C, 39.54; H, 3.42. $\text{C}_{20}\text{Co}_3\text{H}_{21}\text{O}_7\text{P}_2$ calcd.: C, 39.24; H, 3.46%.

X-Ray crystallography

A black crystal of dimensions $0.25 \times 0.11 \times 0.11$ mm was mounted on a Nicolet R3M/ μ update of a $\text{P}2_1$ diffractometer. Cell constants were obtained from a least-squares refinement of 25 reflections in the range $20.03 \leq 2\theta \leq 28.99^\circ$. Systematic absences and statistics are consistent with the space group $\text{P}2_12_12_1$ (orthorhombic). Two standard reflections were monitored periodically during the data collection and no statistically significant changes were observed. Lorentz and polarization corrections and a ψ -scan based empirical absorption correction were applied (transmission factors 0.757 to 0.592). The structure was solved by direct methods and refined by a block-cascade least-squares technique. The phenyl ring was refined as a rigid group. All hydrogen atoms were located in the difference map, but were allowed to ride at a fixed distance from the attached carbon atoms. An isotropic temperature factor was refined for each hydrogen atom, while all other atoms were refined with anisotropic thermal parameters. The function minimized was $\sum w(|F_o| - |F_c|)^2$.

Supplementary material available. Listings of observed and calculated structure factor amplitudes and tables of anisotropic thermal parameters, and idealized

hydrogen parameters. Ordering information will be supplied by the authors upon request.

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