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1,1'-Bis(diphenylphosphino)ferrocene ligand substitution in the benzylidyne-capped cluster $\text{PhCCo}_3(\text{CO})_9$. Synthesis, X-ray structure, and redox reactivity of $\text{PhCCo}_3(\text{CO})_7(\text{dppf})$

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Abstract

The reaction between 1,1'-bis(diphenylphosphino)ferrocene (dppf) and the tricobalt cluster $\text{PhCCo}_3(\text{CO})_9$ (1) yields the disubstituted cluster $\text{PhCCo}_3(\text{CO})_7(\text{dppf})$ (2). The dppf ligand in 2 bridges adjacent cobalt centers via axial coordination. Ligand substitution leading to 2 may be achieved by thermolysis, oxidative decarbonylation using trimethylamine oxide, and by electron-transfer chain (ETC) catalysis using sodium benzophenone ketyl. The isolated yield of 2 ranged from 50 to 70% in all cases. Solution characterization of 2 by FT-IR and ³¹P NMR spectroscopy is presented along with the single-crystal X-ray diffraction results. The dppf-bridged cluster $\text{PhCCo}_3(\text{CO})_7(\text{dppf}) \cdot (\text{toluene})$ crystallized in the monoclinic space group $P2_1/c$ with $a = 13.560(3)$, $b = 17.339(3)$, $c = 21.482(3)$ Å, $\beta = 106.81(1)^\circ$, $V = 4835(1)$ Å³ and $Z = 4$. Block-cascade least-squares refinement yielded $R = 0.0630$ for 5055 ($I > 3\sigma(I)$) reflections. The redox reactivity of 2 was examined by cyclic voltammetry, which revealed the presence of two irreversible oxidations that are attributed to the oxidation of the dppf ligand and the cluster core along with the observation of an irreversible reduction that exhibits cyclic voltammetric curve crossing. All of the redox processes are discussed with respect to existing tricobalt cluster redox chemistry.

1. Introduction

The use of dppf as a ligand in inorganic and organometallic complexes continues to receive much attention. For example, dppf has been employed as an ancillary ligand in hydroformylation [1], hydrosilation [2], and cross-coupling catalysis reactions [3]. Other interesting chemistry reported for dppf-substituted complexes includes the redox properties of a series of rhenium carbonyls [4] and the potential chemotherapeutic activity displayed by platinum(II) derivatives [5].

The majority of dppf-substituted compounds currently known are based on mono- and dinuclear complexes [6]. There exist only two reports on the reactivity of dppf with polynuclear metal clusters. These studies,

which originate from the laboratories of Bruce and Cullen, have dealt with polynuclear Group 8 metal complexes [7]. Given our interest in ligand substitution processes in metal clusters and ligand-modulated cluster reactivity [8,9], we investigated the reaction between dppf and the tricobalt cluster $\text{PhCCo}_3(\text{CO})_9$. This particular cluster was chosen, in part, due to our prior work with $\text{PhCCo}_3(\text{CO})_9$ [10] and the extensive existing literature that would enable reactivity comparisons to be made between the dppf-substituted cluster $\text{PhCCo}_3(\text{CO})_7(\text{dppf})$ and other phosphine-substituted $\text{PhCCo}_3(\text{CO})_7(\text{P})_2$ clusters.

2. Results and discussion

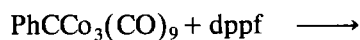
2.1. Synthesis and spectral properties for $\text{PhCCo}_3(\text{CO})_7(\text{dppf})$

Reaction of $\text{PhCCo}_3(\text{CO})_9$ [11] with 1 mol equiv. of dppf [12] in benzene at 60°C proceeds rapidly and is

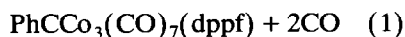
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accompanied by the liberation of CO (2 mol) and the formation of the new phosphine-substituted cluster $\text{PhCCo}_3(\text{CO})_7(\text{dppf})$ (**2**) as the major product (eqn. (1)). TLC analysis revealed the presence of a fast moving brown material ($\sim 5\%$) that has been assigned to the mono-substituted cluster $(\text{PhCCo}_3(\text{CO})_8(\eta^1\text{-dppf}))$. The IR spectrum of this cluster is identical with that reported for $\text{PhCCo}_3(\text{CO})_8(\text{PPh}_3)$ [13]. The mono-substituted dppf cluster was observed to give cluster **2** upon standing in solution in agreement with its proposed structure. No further characterization of this material was undertaken given its solution lability; however, we note that Robinson and Simpson have reported similar behavior in the bis(diphenylphosphino)ethane (dppe) ligand substitution in $\text{RCCo}_3(\text{CO})_9$ clusters [14].



(1)



(2)

Cluster **2** was also observed as the major reaction product by IR and TLC analyses when an equimolar mixture of **1** and dppf was treated with neither Me_3NO [15] or sodium benzophenone ketyl [16]. Since these alternative procedures offer no advantage over the thermolysis reaction, they will not be discussed further.

Cluster **2** was isolated as an orange-red solid by chromatography over silica gel using petroleum ether/ CH_2Cl_2 (3:1) as the eluant. We routinely isolated

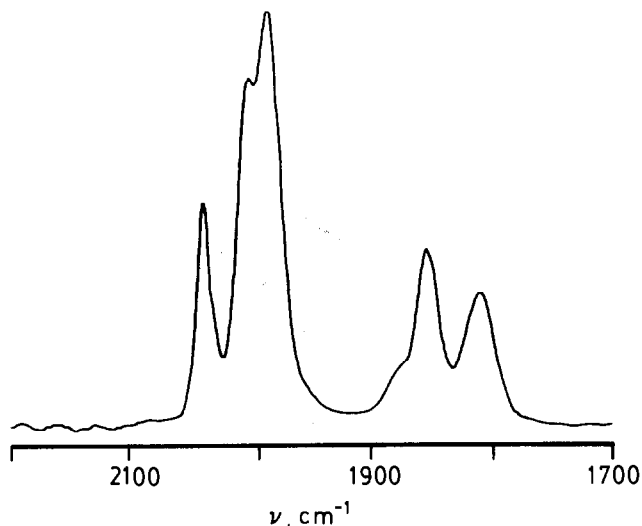


Fig. 1. Infrared spectrum of the carbonyl region for $\text{PhCCo}_3(\text{CO})_7(\text{dppf})$ in dichloromethane at room temperature.

cluster **2** in only 50–70% yield, despite the fact that IR and TLC analyses indicated a higher yield of **2** in the crude reaction mixture (80–90%). Our lowered yield stems from partial cluster decomposition during the chromatographic work-up. The FT-IR spectrum of **2** in CH_2Cl_2 reveals three intense terminal $\nu(\text{CO})$ bands at 2043s, 2006s, and 1987vs cm^{-1} in addition to three bridging carbonyl bands at 1881w, 1857m, and 1812m cm^{-1} (Fig. 1). The adoption of bridging carbonyl groups reflects the tendency of four-vertex *closo* clusters of this genre to relieve steric strain and dissipate donated

TABLE 1. X-Ray crystallographic and data processing parameters for $\text{PhCCo}_3(\text{CO})_7(\text{dppf}) \cdot (\text{toluene})$ (**2**)

Space group	$P2_1/c$, monoclinic
Cell constants	
a (Å)	13.560 (3)
b (Å)	17.339 (3)
c (Å)	21.482 (3)
β (°)	106.81 (1)
V (Å ³)	4835 (1)
Molecular formula	$\text{C}_{48}\text{H}_{33}\text{Co}_3\text{FeO}_7\text{P}_2 \cdot \text{C}_7\text{H}_8$
F.W.	1108.53
Formula units/cell (Z)	4
ρ (g cm^{-3})	1.523
Crystal size (mm^3)	$0.23 \times 0.25 \times 0.45$
Absorption coefficient (μ) (cm^{-1})	14.21
λ (radiation) (Å)	0.71073
Data collection method	ω
Collection range (°)	$3.0 \leq 2\theta \leq 45.0$
Total no. of data collected	6328
No. of independent data, $I > 3\sigma(I)$	5055
R	0.0630
R_w	0.0691
Weights	$w = [\sigma^2(F_o) + F_c^2]^{-1}$

TABLE 2. Positional parameters of the non-hydrogen atoms for $\text{PhCCo}_3(\text{CO})_7(\text{dppf}) \cdot (\text{toluene})$ (**2**) with estimated standard deviations in parentheses

	x	y	z	U^a
Co(1)	2574(1)	800(1)	2662(1)	36(1)
Co(2)	3936(1)	-60(1)	2445(1)	38(1)
Co(3)	2171(1)	-557(1)	2312(1)	46(1)
Fe	3037(1)	1701(1)	738(1)	37(1)
C(1)	2637(7)	1255(5)	3403(4)	47(3)
O(1)	2753(5)	1519(4)	3909(3)	72(3)
C(2)	4046(7)	996(5)	2759(4)	48(4)
O(2)	4653(5)	1455(4)	2997(3)	62(3)
C(3)	5178(9)	-328(6)	2889(5)	60(4)
O(3)	6006(6)	-511(5)	3166(4)	93(4)
C(4)	3380(8)	-1089(6)	2168(5)	63(5)
O(4)	3601(7)	-1707(4)	2063(5)	96(4)
C(5)	1377(8)	-747(5)	1515(5)	53(4)
O(5)	834(7)	-921(4)	1018(4)	88(4)
C(6)	1777(8)	-1320(6)	2733(5)	64(4)
O(6)	1513(7)	-1819(5)	2991(4)	96(4)
C(7)	1252(7)	321(5)	2488(4)	51(4)
O(7)	414(5)	386(4)	2483(3)	65(3)
C(8)	3180(7)	-162(5)	3064(4)	45(3)
C(81)	3401(7)	-404(5)	3743(4)	50(4)
C(82)	4368(11)	-653(8)	4112(6)	108(7)
C(83)	4534(12)	-879(10)	4753(6)	140(9)
C(84)	3748(13)	-867(8)	5030(6)	110(7)
C(85)	2802(10)	-609(8)	4693(5)	89(6)
C(86)	2651(8)	-389(7)	4059(5)	74(5)
P(1)	1903(2)	1831(1)	1973(1)	35(1)
C(11)	622(6)	1757(5)	1384(4)	41(3)
C(12)	312(6)	1079(5)	1062(4)	47(3)
C(13)	-593(7)	1037(6)	549(4)	56(4)
C(14)	-1192(8)	1687(7)	376(5)	63(4)
C(15)	-922(8)	2354(7)	705(5)	71(5)
C(16)	-11(7)	2406(5)	1213(4)	53(4)
C(21)	1697(6)	2672(5)	2443(4)	42(3)
C(22)	2090(7)	3387(5)	2368(4)	51(4)
C(23)	1871(8)	4013(5)	2713(5)	64(4)
C(24)	1281(8)	3922(7)	3121(5)	70(5)
C(25)	900(8)	3208(7)	3196(5)	66(5)
C(26)	1100(7)	2589(5)	2848(4)	52(4)
C(31)	2596(6)	2248(4)	1448(4)	37(3)
C(32)	3698(7)	2289(5)	1585(4)	48(3)
C(33)	3906(8)	2660(5)	1048(5)	60(4)
C(34)	2975(8)	2872(5)	605(5)	58(4)
C(35)	2170(7)	2625(5)	848(4)	47(3)
P(2)	4424(2)	116(1)	1510(1)	32(1)
C(41)	3586(6)	613(4)	817(4)	34(3)
C(42)	3831(7)	1015(5)	294(4)	43(3)
C(43)	2907(7)	1233(5)	-151(4)	51(4)
C(44)	2093(7)	990(5)	64(4)	52(4)
C(45)	2497(6)	605(5)	658(4)	43(3)
C(51)	4599(6)	-819(4)	1162(4)	36(3)
C(52)	3938(7)	-1092(5)	585(4)	48(3)
C(53)	4121(8)	-1810(6)	361(5)	65(4)
C(54)	4933(8)	-2256(5)	702(6)	66(5)
C(55)	5584(8)	-1982(5)	1280(5)	56(4)
C(56)	5425(7)	-1272(5)	1505(4)	52(4)
C(61)	5681(6)	557(5)	1579(4)	39(3)
C(62)	6219(6)	373(5)	1133(4)	43(3)
C(63)	7140(7)	702(5)	1178(5)	55(4)
C(64)	7574(8)	1221(7)	1663(5)	68(4)

TABLE 2. (continued)

	x	y	z	U^a
C(65)	7070(8)	1402(7)	2100(5)	79(5)
C(66)	6124	1073	2069	52
C(91)	1706(16)	5593(12)	1133(7)	161(14)
C(92)	1990	6365	1128	246(22)
C(93)	1234	6937	963	252(28)
C(94)	195	6735	802	257(27)
C(95)	-89	5962	807	189(16)
C(96)	667	5391	973	203(17)
C(97)	462(33)	4651(15)	925(16)	527(45)

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

P-ligand electron density through more effective, $d\pi(\text{Co}) \rightarrow \pi^*(\text{CO})$ backbonding [14,17]. In such a scheme equatorial coordination of the dppf ligand would be prohibited on steric grounds and axial coordination of the dppf ligand is favored (*vide infra*). However, caution must be exercised in such structural assignments because of the possibility of equatorial/axial isomerism, which has led to discrepancies in the reported IR data of phosphine-substituted tricobalt clusters [14,18].

Cluster **2** was next examined by NMR spectroscopy. The room temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** in CDCl_3 displayed a relatively sharp singlet at δ 23.9 (~ 50 Hz at FWHH). Typically, sharp ^{31}P NMR spectra of phosphine-substituted cobalt clusters require thermal decoupling of the ^{59}Co nuclei ($I = 7/2$) from the ^{31}P nuclei [19,20]. This is readily achieved by recording the ^{31}P NMR spectrum at low temperature whereby the molecular correlation time (τ_c) is slowed and the scalar coupling between ^{31}P and ^{59}Co nuclei is diminished. Reduced scalar $^{59}\text{Co}-^{31}\text{P}$ coupling leads to sharper ^{31}P resonances. Attachment of the large ancillary dppf ligand to cluster **1** has presumably reduced the τ_c of **2** to such a degree that a low-temperature ^{31}P NMR measurement is not required. Relaxation studies are currently planned in order to address this phenomenon more fully.

2.2. X-Ray crystallographic structure of $\text{PhCCo}_3(\text{CO})_7(\text{dppf}) \cdot (\text{toluene})$

The structure of **2** was unequivocally determined by single-crystal X-ray diffraction analysis. Dark red crystals of **2** were grown from a toluene solution containing **2** that had been layered with heptane. Compound **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 for **2** are given in Table 1 with the final fraction coordinates listed in Table 2.

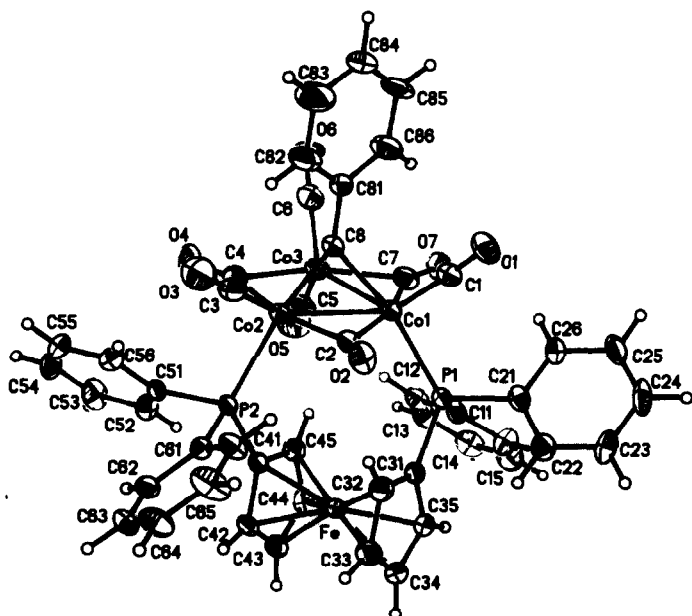


Fig. 2. ORTEP diagram of $\text{PhCCo}_3(\text{CO})_7(\text{dppf})$ with the thermal ellipsoids drawn at the 30% probability level.

The ORTEP diagram in Fig. 2 shows the molecular structure of cluster **2** and clearly establishes the axial disposition of the dppf ligand. Selected bond distances and angles are given in Table 3. The Co–Co bond lengths are all equal within experimental error with a mean value of 2.494 Å. The internal polyhedron of **2** consists of a triangular array of cobalt atoms that is capped by a μ_3 -benzylidyne ligand. The μ_3 -C–Co bond distances range from 1.970(10) Å to 1.947(8) Å with a mean distance of 1.923 Å. Both sets of bond lengths are in close agreement with those reported for the parent cluster $\text{PhCCo}_3(\text{CO})_9$ [21]. The terminal Co–CO bond distances range from 1.742(10) Å to 1.772(9) Å with an average length of 1.760 Å. No physically significant asymmetry is seen in the bridging carbonyl/cobalt bond distances as the μ_2 -C–Co bond lengths reveal a mean length of 1.973 Å. The remaining bond lengths and angles are unexceptional and require no further comment.

2.3. Cyclic voltammetric investigation of $\text{PhCCo}_3(\text{CO})_7(\text{dppf})$

We next turned our attention to the redox behavior of $\text{PhCCo}_3(\text{CO})_7(\text{dppf})$ due to the plethora of redox chemistry reported for the parent cluster $\text{PhCCo}_3(\text{CO})_9$ and its phosphine-substituted derivatives [14,22–24]. The presence of the redox active dppf ligand in **2** is attractive as multiple redox chemistry between the ferrocene moiety and the tricobalt cluster was anticipated. Indeed, such cooperative intramolecular redox

reactivity is of interest as it forms the basis for new mixed-valence complexes [25].

Cyclic voltammetry studies were carried out in CH_2Cl_2 containing 0.2 M tetra-*n*-butyl ammonium perchlorate (TBAP) as the supporting electrolyte at a platinum electrode. Cluster **2** displays two irreversible oxidations at $E_p^a = 0.49$ V and $E_p^a = 1.00$ V at room temperature and a scan rate of 100 mV s^{-1} . No evidence for reversibility of either redox couple was observed when the scan rate was increased to 2 V s^{-1} or when the temperature was lowered to -70°C [20]. The irreversible nature of both oxidations presumably derives from an irreversible chemical reaction that follows the oxidation (*i.e.* an EC process) [27].

The identity of both oxidation couples can be confidently assigned on the basis of existing literature data. The first oxidation process corresponds to oxidation of the iron center (0/+1) in the dppf ligand. Other studies dealing with tricobalt clusters with pendent ferrocenyl moieties display an iron 0/+1 oxidation in the vicinity of 0.6 V [25]. The irreversibility of this iron oxidation is not totally unexpected given the reports on the redox instability of oxidized dppf complexes [6a,n,28]. The remaining oxidation wave at 1.00 V is assigned straightforwardly to the oxidation (0/+1) of the tricobalt core in **2**. The observed potential and irreversible behavior of this redox couple is in excellent agreement with other bridged diphosphine $\text{PhCCo}_3(\text{CO})_7(\text{P})_2$ clusters reported by Robinson and Simpson [14].

The initial cathodic scan cyclic voltammogram of **2** is shown in Fig. 3. Unlike the reported reversible one-electron reduction process for the analogous ligand-bridged clusters $\text{PhCCo}_2(\text{CO})_7(\text{dppm})$ and $\text{PhCCo}_3(\text{CO})_7(\text{dppe})$ [14], cluster **2** exhibits an irreversible reduction. The value of the cathodic peak potential (E_p^c) is -1.47 V. Two weak oxidation waves are observed at -1.18 and 0.59 V upon scan reversal. Increased scan rates and lower solution temperatures did not lead to any noticeable reversibility of the 0/–1 redox couple. The absence of a reoxidation wave for this redox couple indicates the existence of a fast chemical follow-up step that extricates the mono-reduced cluster $\mathbf{2}^-$ from solution before it can be oxidized back to neutral **2**. This process is akin to an ECE or EEC reaction [29]. However, the presence of a cyclic voltammetric curve crossing -1.35 V and -1.24 V on the reverse scan signals the intervention of a possible disproportionation sequence in the redox process. Such a crossover effect has been observed by Heinze and Vahrenkamp [24] in the reduction of related trisubstituted $\text{MeCCo}_3(\text{CO})_6\text{P}_3$ clusters.

The origin of this CV curve crossing phenomenon derives from a diffusion gradient for a reducible species

TABLE 3. Selected bond distances (Å) and angles (°) in $\text{PhCCo}_3(\text{CO})_7(\text{dppf}) \cdot (\text{toluene}) (2)$

<i>Bond distances</i>			
Co(1)–Co(2)	2.519(2)	Co(1)–Co(3)	2.482(2)
Co(1)–C(1)	1.757(9)	Co(1)–C(2)	1.975(10)
Co(1)–C(7)	1.912(10)	Co(1)–C(8)	1.947(8)
Co(1)–P(1)	2.331(2)	Co(2)–Co(3)	2.480(2)
Co(2)–C(2)	1.942(10)	Co(2)–C(3)	1.742(10)
Co(2)–C(4)	1.961(10)	Co(2)–C(8)	1.907(10)
Co(2)–P(2)	2.310(3)	Co(3)–C(4)	1.982(11)
Co(3)–C(5)	1.772(9)	Co(3)–C(6)	1.769(12)
Co(3)–C(7)	2.071(10)	Co(3)–C(8)	1.916(8)
C(1)–O(1)	1.147(11)	C(2)–O(2)	1.154(11)
C(3)–O(3)	1.153(13)	C(4)–O(4)	1.153(13)
C(5)–O(5)	1.147(11)	C(6)–O(6)	1.140(14)
C(7)–O(7)	1.139(13)	C(8)–C(81)	1.463(12)
C(81)–C(82)	1.390(15)	C(81)–C(86)	1.375(17)
C(82)–C(83)	1.387(19)	C(83)–C(84)	1.363(25)
C(84)–C(85)	1.354(19)	C(85)–C(86)	1.373(16)
P(1)–C(11)	1.834(8)	P(1)–C(21)	1.841(9)
P(1)–C(31)	1.814(9)	P(2)–C(41)	1.808(7)
P(2)–C(51)	1.829(8)	P(2)–C(61)	1.834(8)
<i>Bond angles</i>			
Co(2)–Co(1)–Co(3)	59.5(1)	Co(2)–Co(1)–C(1)	125.9(3)
Co(3)–Co(1)–C(1)	130.4(3)	Co(2)–Co(1)–C(2)	49.4(3)
Co(3)–Co(1)–C(2)	108.8(3)	C(1)–Co(1)–C(2)	92.5(4)
Co(2)–Co(1)–C(7)	113.8(3)	Co(3)–Co(1)–C(17)	54.4(3)
C(1)–Co(1)–C(7)	99.7(4)	C(2)–Co(1)–C(7)	163.1(4)
Co(2)–Co(1)–C(8)	48.5(3)	Co(3)–Co(1)–C(8)	49.5(2)
C(1)–Co(1)–C(8)	94.5(4)	C(2)–Co(1)–C(8)	79.4(4)
C(7)–Co(1)–C(8)	88.1(4)	Co(2)–Co(1)–P(1)	120.6(1)
Co(3)–Co(1)–P(1)	121.6(1)	C(1)–Co(1)–P(1)	98.0(3)
C(2)–Co(1)–P(1)	97.6(3)	C(7)–Co(1)–P(1)	92.2(3)
C(8)–Co(1)–P(1)	167.3(3)	Co(1)–Co(2)–Co(3)	59.5(1)
Co(1)–Co(2)–C(2)	50.6(3)	Co(3)–Co(2)–C(2)	110.0(3)
Co(1)–Co(2)–C(3)	134.6(4)	Co(3)–Co(2)–C(3)	135.9(4)
C(2)–Co(2)–C(3)	95.5(4)	Co(1)–Co(2)–C(4)	110.9(3)
Co(3)–Co(2)–C(4)	51.4(3)	C(2)–Co(2)–C(4)	161.3(5)
C(3)–Co(2)–C(4)	98.6(4)	Co(1)–Co(2)–C(8)	49.9(3)
Co(3)–Co(2)–C(8)	49.7(2)	C(2)–Co(2)–C(8)	81.2(4)
C(3)–Co(2)–C(8)	102.9(4)	C(4)–Co(2)–C(8)	83.7(4)
Co(1)–Co(2)–P(2)	119.5(1)	Co(3)–Co(2)–P(2)	117.1(1)
C(2)–Co(2)–P(2)	99.5(3)	C(3)–Co(2)–P(2)	92.0(4)
C(4)–Co(2)–P(2)	92.2(4)	C(8)–Co(2)–P(2)	164.9(2)
Co(1)–Co(3)–Co(2)	61.0(1)	Co(1)–Co(3)–C(4)	111.6(3)
Co(2)–Co(3)–C(4)	50.6(3)	Co(1)–Co(3)–C(5)	119.2(3)
Co(2)–Co(3)–C(5)	118.2(4)	C(4)–Co(3)–C(5)	93.5(5)
Co(1)–Co(3)–C(6)	128.8(4)	Co(2)–Co(3)–C(6)	128.7(3)
C(4)–Co(3)–C(6)	96.7(5)	C(5)–Co(3)–C(6)	99.5(5)
Co(1)–Co(3)–C(7)	48.6(3)	Co(2)–Co(3)–C(7)	109.6(3)
C(4)–Co(3)–C(7)	160.0(4)	C(5)–Co(3)–C(7)	94.8(3)
C(6)–Co(3)–C(7)	99.8(5)	Co(1)–Co(3)–C(8)	50.6(3)
Co(2)–Co(3)–C(8)	49.4(3)	C(4)–Co(3)–C(8)	82.9(4)
C(5)–Co(3)–C(8)	165.5(4)	C(6)–Co(3)–C(8)	94.9(4)
C(7)–Co(3)–C(8)	84.5(4)	Co(1)–C(1)–O(1)	174.3(8)
Co(1)–C(2)–O(2)	80.1(4)	Co(1)–C(2)–O(2)	137.4(8)
Co(2)–C(2)–O(2)	141.1(8)	Co(2)–C(3)–O(3)	178.1(10)
Co(2)–C(4)–O(4)	143.8(9)	Co(3)–C(4)–O(4)	137.5(9)
Co(3)–C(5)–O(5)	174.5(9)	Co(3)–C(6)–O(6)	178.5(9)
Co(1)–C(7)–O(7)	77.0(4)	Co(1)–C(7)–O(7)	146.7(8)
Co(1)–C(8)–O(8)	79.9(3)	Co(2)–C(8)–O(8)	80.9(3)
C(31)–C(35)–C(34)	108.9(8)	Co(2)–P(2)–C(41)	120.6(3)
Co(2)–P(2)–C(61)	110.0(3)	C(41)–P(2)–C(51)	102.2(3)
Co(2)–P(2)–C(61)	118.5(3)	C(41)–P(2)–C(61)	102.5(4)

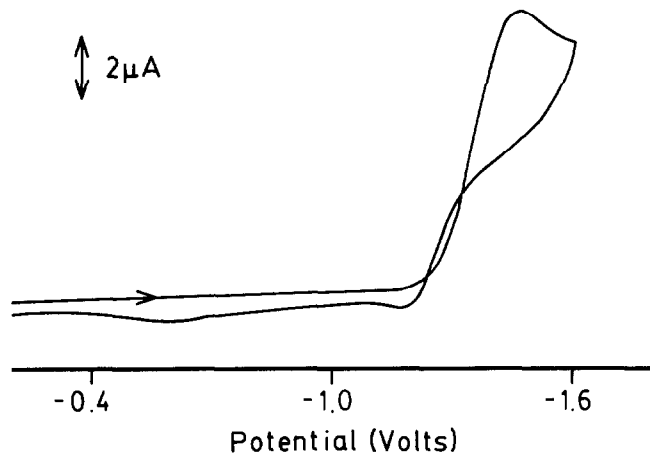


Fig. 3. Initial cathodic-scan cyclic voltammogram of $ca. 3 \times 10^{-3}$ M $\text{PhCCo}_3(\text{CO})_7(\text{dppf})$ in dichloromethane containing 0.2 M TBAP at $v = 0.1 \text{ V s}^{-1}$.

during the reverse scan oxidation process [24,30,36]. Attempts to further probe this redox couple for an isopotential point by repetitive CV scans were unsuccessful due to detrimental electrode passivation. Future electrochemical studies are planned in order to more fully explore the redox pathways associated with the reduction of **2**.

3. Conclusion

The reaction between $\text{PhCCo}_3(\text{CO})_9$ and dppf affords the diphosphine-bridged cluster $\text{PhCCo}_3(\text{CO})_7(\text{dppf})$. The dppf ligand is bound to a pair of cobalt atoms via axial coordination. Electrochemical analysis of $\text{PhCCo}_3(\text{CO})_7(\text{dppf})$ reveals two irreversible oxidation waves, which have been assigned to the oxidation of the iron atom of the dppf ligand and oxidation of the tricobalt cluster core. Reduction of $\text{PhCCo}_3(\text{CO})_7(\text{dppf})$ does not correspond to a simple single-electron redox process (0/−1) as observed for other diphosphine-bridged systems but resembles the CV behavior reported for the trisubstituted clusters $\text{MeCCo}(\text{CO})_6\text{P}_3$.

4. Experimental section

4.1. General

Dicobalt octacarbonyl and chlorodiphenylphosphine were purchased from Pressure Chemical Co. and used as received. $\text{PhCCo}_3(\text{CO})_9$ [11] and dppf [12] were synthesized according to known literature procedures. All reactions were conducted under argon using Schlenk techniques [32]. THF and benzene were distilled from sodium/benzophenone, while CH_2Cl_2 was distilled and stored under argon in Schlenk vessels equipped with high-vacuum teflon stopcocks.

Infrared spectra were recorded on a Nicolet 20SXB FT-IR spectrometer in 0.1 mm NaCl cells. The ^{31}P NMR spectrum was recorded on a Varian 300-VXR spectrometer at 121 MHz with the chemical shift of cluster **2** referenced to external 85% H_3PO_4 , taken to have $\delta = 0$. The positive chemical shift of **2** is to low field of the external standard.

4.2. Synthesis of $\text{PhCCo}_3(\text{CO})_7(\text{dppf})$

Since all the procedures utilized similar amounts of $\text{PhCCo}_3(\text{CO})_9$ and dppf and gave the final product in identical yields, only the thermolysis reaction between $\text{PhCCo}_3(\text{CO})_9$ and dppf is described in detail.

To a 50-ml benzene solution containing 0.2 g (0.39 mmol) of $\text{PhCCo}_3(\text{CO})_9$ was added 0.22 g (~ 0.39 mmol) of dppf. The reaction was stirred at 60°C for $ca.$ 6 h and then examined by IR and TLC analyses, which revealed $> 80\%$ conversion to the desired cluster **2**. The solvent was removed under vacuum and cluster **2** was subsequently isolated by chromatography over silica gel using a 3:1 (v/v) mixture of petroleum ether and CH_2Cl_2 . Single crystals suitable for X-ray diffraction analysis were grown from a toluene solution containing **2** that had been layered with heptane. The remaining material was recrystallized from a CH_2Cl_2 solution of **2** that had been layered with heptane. IR (CH_2Cl_2): $\nu(\text{CO})$ 2043m, 2006s, 1987vs, 1881w, 1857m, and 1812m cm^{-1} . $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 23.9. Anal. Found: C, 55.42; H, 3.44. $\text{C}_{48}\text{H}_{33}\text{Co}_3\text{FeO}_7\text{P}_2 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$ calc.: C, 55.0; H, 3.21%.

4.3. X-Ray crystallography

A dark red crystal of dimensions $0.23 \times 0.25 \times 0.45 \text{ mm}^3$ 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 $25.36 \leq 2\theta \leq 29.66^\circ$. Systematic absences and statistics are consistent with the monoclinic space group $\text{P}2_1/c$. 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 0.934–0.851). The structure was solved by direct methods and refined by a block-cascade least-squares technique. The phenyl rings were refined as rigid groups. All of the hydrogens were located in the difference map, but were allowed to ride at a fixed distance from the attached carbon atom. An isotropic temperature factor was refined for each hydrogen atom, while all other atoms were refined with anisotropic thermal parameters. The function minimized was $\sum w(|F_o| - |F_c|)^2$.

4.4 Electrochemical measurements

Cyclic voltammetry measurements were conducted with a PAR Model 273 potentiostat/galvanostat, equipped with positive feedback circuitry to compensate for IR drop. The CV cell was of airtight design and was based on a three-electrode configuration. The working electrode consisted of a platinum disk (area = 0.0079 cm^2) and a platinum auxiliary electrode, which was coiled around the cobalt/pyrex glass seal. The former electrode was also embedded in a cobalt/pyrex glass seal. A silver wire quasi-reference electrode was used in all CV measurements. All CV potentials are referenced relative to the formal potential of the $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$ couple run under identical conditions, taken to have a $E_{1/2} = 0.306 \text{ V}$ [27].

5. Supplementary material available

Listing 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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