

Ligand substitution in $\text{HC(O)CCo}_3(\text{CO})_9$ with 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd): Diphosphine ligand fluxionality, decarbonylation of the formyl moiety and competitive P–Ph bond cleavage reactivity

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Abstract

The reaction of the formyl-capped cluster $\text{HC(O)CCo}_3(\text{CO})_9$ (**1**) with the diphosphine ligand 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd) in the presence of added Me_3NO leads to the production of the disubstituted cluster $\text{HC(O)CCo}_3(\text{CO})_7(\text{bpcd})$ (**2**). Thermolysis of **2** in toluene at 60 °C gives the methylidyne-capped cluster $\text{HCCo}_3(\text{CO})_7(\text{bpcd})$ (**4**) and the phosphido-bridged cluster $\text{Co}_3(\text{CO})_7[\mu_2, \eta^2, \eta^1\text{-P(Ph)C=C(PPh}_2\text{)C(O)CH}_2\text{C(O)}]$ (**5**). Cluster **4** has been independently prepared from $\text{HCCo}_3(\text{CO})_9$ and bpcd and shown to serve as the precursor to **5**. The new clusters **2**, **4**, and **5** have been isolated and characterized in solution by IR and NMR (¹H and ³¹P) spectroscopies and their solid-state structures have been established by X-ray diffraction analyses. Both clusters **2** and **4** contain 48e- and exhibit triangular Co_3 cores with a chelating and bridging bpcd ligand in the solid state, respectively. The structure of **5** provides unequivocal support for the loss of the methylidyne capping ligand and P–Ph bond cleavage attendant in the activation of **4** and confirms the presence of the face capping seven-electron $\mu_2, \eta^2, \eta^1\text{-P(Ph)C=C(PPh}_2\text{)C(O)CH}_2\text{C(O)}$ ligand in the final product. The fluxionality displayed by the bpcd ligand in clusters **2** and **4** and the decarbonylation behavior of the formyl moiety in the former cluster are discussed relative to related alkylidyne-capped Co_3 derivatives.

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Keywords: Tetrahedral clusters; Ligand substitution; P–Ph bond cleavage; Decarbonylation

1. Introduction

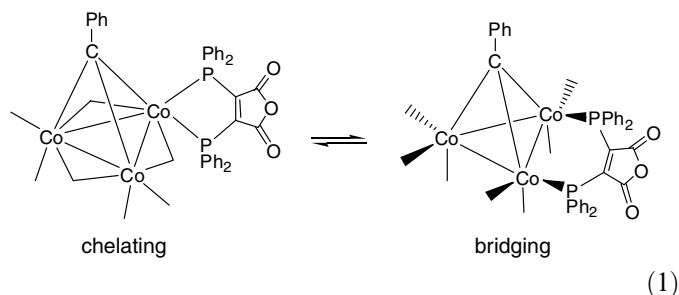
Coordination of the diphosphine ligands 2,3-bis(diphenylphosphino)maleic anhydride (bma) and 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd) to the tetrahedrane clusters $\text{RCCo}_3(\text{CO})_9$ [$\text{R} = \text{Ph, Fc, Me, Cl}$] affords the corresponding diphosphine-substituted clusters

$\text{RCCo}_3(\text{CO})_7(\text{P-P})$ [1–4]. This genre of trimetallic clusters continues to command our attention due to the novel reactivity that these systems exhibit as a result of the ancillary diphosphine ligand. For example, the nondissociative diphosphine isomerization displayed by the bma and bpcd ligands at many different cluster motifs allows for facile interconversion between the chelating and bridging forms of the cluster; this isomerization behavior is depicted in Eq. (1) for $\text{PhCCo}_3(\text{CO})_7(\text{bma})$. The fluxional process involving these and related diphosphine ligands points to the under appreciated and generally overlooked fact that tertiary phosphines are capable of participation

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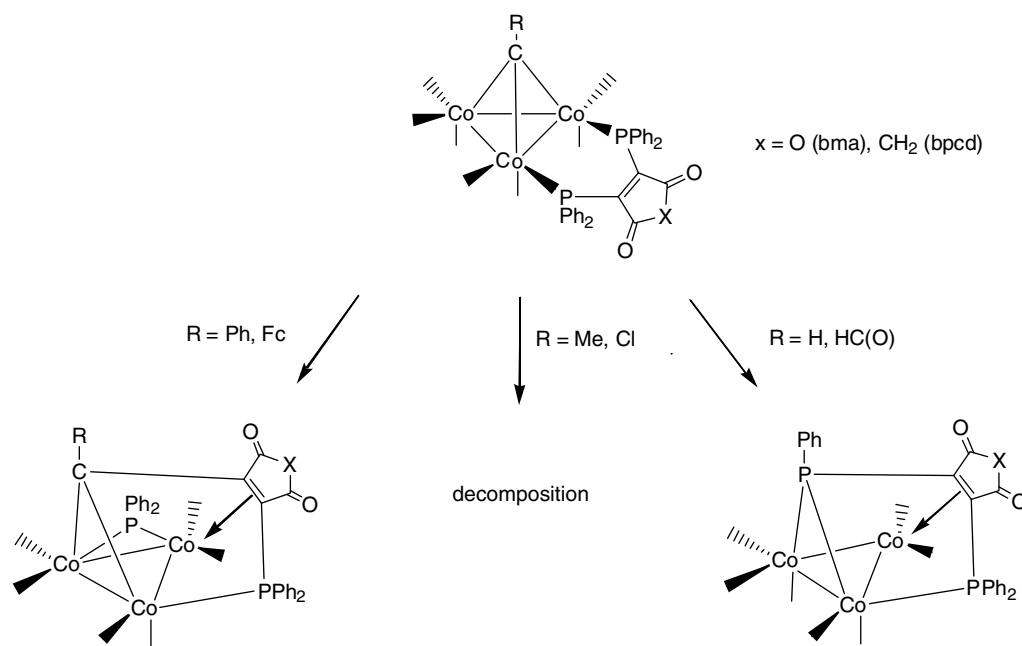
in nondissociative terminal-bridge-terminal phosphine ligand scrambling about a polynuclear metal cluster [5]. Such a dynamic phosphine exchange allows for the net permutation of a given phosphine moiety between metal centers, avoiding the generation of a high-energy, unsaturated cluster through a dissociative release of the phosphine moiety, followed by its recoordination to the cluster polyhedron. The migratory behavior that has been proposed for these phosphine isomerizations parallels that of the CO ligand, whose fluxionality at numerous metal clusters is a well-established phenomenon [6]



Apart from the dynamics associated with the diphosphine isomerization, the tetrahedrane clusters $\text{RCCo}_3(\text{CO})_7(\text{bma})$ and $\text{RCCo}_3(\text{CO})_7(\text{bpcd})$ have also been found to undergo facile cluster/diphosphine activation over the temperature range 30–60 °C, with the exact mode of reaction being influenced by the capping R group. Scheme 1 summarizes the known reactivity pathways for the tricoordinate cluster family, where three different modes of reaction have been found. When the capping RC group is Ph or ferrocenyl (Fc), the $\text{RCCo}_3(\text{CO})_7(\text{P-P})$ clusters decompose with the formation of the benzylidene- and ferrocenylidene-capped clusters $\text{Co}_3(\text{CO})_6[\mu_2, \eta^2, \eta^1\text{-C(R)C=C(PPh}_2\text{)C(O)XC(O)}]$ -

($\mu_2\text{-PPh}_2$) [1,2], while the Me- and Cl-capped derivatives display gross decomposition under comparable thermolysis conditions [5]. The last manifold for cluster/ligand activation involves the clusters $\text{HC(O)CCo}_3(\text{CO})_7(\text{P-P})$ and $\text{HCCo}_3(\text{CO})_7(\text{P-P})$, whose reaction chemistry serves as the basis of this report. The course of reactivity for the H- and HC(O)-capped clusters $\text{RCCo}_3(\text{CO})_7(\text{bpcd})$ is illustrated in lower right-hand portion of Scheme 1. Here the formal loss of the capping carbyne moiety and one of the phenyl groups from the diphosphine ligand furnishes the phosphido-bridged cluster $\text{Co}_3(\text{CO})_7[\mu_2, \eta^2, \eta^1\text{-P(Ph)C=C(PPh}_2\text{)C(O)CH}_2\text{C(O)}]$. These data suggest that subtle steric and electronic effects strongly influence the final product outcome in the thermolysis reactions of these $\text{RCCo}_3(\text{CO})_7(\text{P-P})$ clusters in a manner that is not fully understood at this time. Definitive proof for the enhanced diphosphine ligand reactivity in $\text{RCCo}_3(\text{CO})_7(\text{bma})$ and $\text{RCCo}_3(\text{CO})_7(\text{bpcd})$ derives from the synthesis of the related clusters containing the archetypal diphosphine ligand (*Z*)- $\text{Ph}_2\text{PCH=CHPPh}_2$. The structurally similar clusters $\text{RCCo}_3(\text{CO})_7[(\text{Z})\text{-Ph}_2\text{PCH=CHPPh}_2]$ [7] have been shown to be stable under conditions comparable to those used to promote the transformations illustrated in Scheme 1.

Herein we present our data on the ligand substitution in the tricoordinate clusters $\text{HC(O)CCo}_3(\text{CO})_9$ and $\text{HCCo}_3(\text{CO})_9$, with the diphosphine ligand bpcd, which initially give the cluster compounds $\text{RCCo}_3(\text{CO})_7(\text{bpcd})$ and ultimately furnish the phosphido-bridged cluster $\text{Co}_3(\text{CO})_7[\mu_2, \eta^2, \eta^1\text{-P(Ph)C=C(PPh}_2\text{)C(O)CH}_2\text{C(O)}]$ (5) upon thermolysis. The solution spectroscopic data and the X-ray diffraction structures of clusters 2, 4, and 5 confirm the identities of the substitution products and allow for the delineation of a working reaction sequence leading to cluster 5.



2. Experimental

2.1. General methods

The starting clusters $\text{HC(O)CCo}_3(\text{CO})_9$ and $\text{HCCo}_3(\text{CO})_9$ were synthesized from $\text{Co}_2(\text{CO})_8$ (Strem Chemical Co.) according to the procedure of Seyferth [8], while the diphosphine ligand *bpcd* was prepared from 4,5-dichloro-4-cyclopenten-1,3-dione and $\text{Ph}_2\text{PSiMe}_3$ [9,10]. All reaction and NMR solvents were distilled under argon from a suitable drying agent and stored in Schlenk storage vessels [11]. The combustion analyses were performed by Atlantic Microlab, Norcross, GA.

All reported infrared data were recorded on a Nicolet 20 SXB FT-IR spectrometer in 0.1 mm amalgamated NaCl cells, using PC control and OMNIC software, while the ^1H (300 MHz) and ^{31}P NMR (121 MHz) spectra were recorded on a Varian 300-VXR spectrometer. The ^{31}P NMR data were acquired in the proton-decoupled mode and are reported relative to external H_3PO_4 , taken to have $\delta = 0$.

2.2. Reaction between $\text{HC(O)CCo}_3(\text{CO})_9$ (**1**) and *bpcd* in the presence of Me_3NO

To 0.094 g (0.20 mmol) of $\text{HC(O)CCo}_3(\text{CO})_9$ and 0.093 g (0.20 mmol) of *bpcd* in 20 mL of CH_2Cl_2 at 0 °C was added 34 mg (0.45 mmol) of Me_3NO in one portion under argon flush. The reaction solution was stirred with warming to room temperature (<1 h) at which time TLC analysis revealed the presence of new spot ($R_f = 0.40$ in CH_2Cl_2) belonging to cluster **2**. The solvent was removed

under vacuum and the crude product was purified by low-temperature (−78 °C) column chromatography over silica gel using CH_2Cl_2 /petroleum ether (1:1) as the eluent. The black-green solid that was obtained was then recrystallized from CH_2Cl_2 and heptane. Yield of **2**: 0.12 g (68%). IR (CH_2Cl_2): $\nu(\text{CO})$ 2071 (vs), 2022 (vs), 1753 (w, symm dione), 1718 (m, antisymm dione), 1650 (b, vw, formyl) cm^{-1} . ^1H NMR (CD_2Cl_2 ; 298 K): δ 3.28 (s, 2H, CH_2), 7.25–7.42 (m, 20H, aryl), 10.43 (s, CHO). ^{31}P NMR (THF; 298 K): δ 43 (broad); (THF; 187 K): δ 64.19 (chelating, 45%), 37.39 (bridging, 55%). Anal. Calcd. (found) for $\text{C}_{38}\text{H}_{23}\text{Co}_3\text{O}_{10}\text{P}_2$: C, 52.59 (52.62); H, 2.60 (2.88).

2.3. Reaction between $\text{HCCo}_3(\text{CO})_9$ (**3**) and *bpcd* in the presence of Me_3NO

To 0.22 g (0.50 mmol) of $\text{HCCo}_3(\text{CO})_9$ and 0.23 g (0.50 mmol) of *bpcd* in 30 mL of CH_2Cl_2 was added 75 mg (1.0 mmol) of Me_3NO . The solution immediately changed from purple to black and stirring was continued for an additional 0.5 h, after which the solvent was removed under vacuum. Pure **4** was isolated by low-temperature (−78 °C) column chromatography using CH_2Cl_2 as the eluent. Yield: 0.10 g (23%). Due the relative instability of **4**, the product was spectroscopically characterized in solution. IR (CH_2Cl_2): $\nu(\text{CO})$ 2063 (vs), 2008 (vs), 1748 (w, symm dione), 1717 (m, antisymm dione) cm^{-1} . ^1H NMR (CD_2Cl_2 ; 298 K): δ 3.29 (s, 2H, CH_2), 7.35–7.49 (m, 20H, aryl), 10.99 (s, $\mu_3\text{-CH}$). ^{31}P NMR (THF; 298 K): δ 51 (broad); (THF; 187 K): δ 65.57 (chelating, 58%), 41.20 (bridging, 42%).

Table 1

X-ray crystallographic data and processing parameters for the tricobalt clusters **2**, **4**, and **5**

Compound number	2	4	5
CCDC entry number	277904	277905	277906
Space group	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$	Monoclinic, Cc
<i>a</i> (Å)	8.854(2)	11.5588(9)	10.395(1)
<i>b</i> (Å)	19.468(5)	12.493(1)	33.233(4)
<i>c</i> (Å)	20.867(5)	12.797(1)	9.204(1)
α (°)		98.268(1)	
β (°)	92.895(4)	100.914(1)	108.501(2)
γ (°)		101.228(1)	
<i>V</i> (Å ³)	3593(1)	1748.1(2)	3014.3(6)
Molecular formula	$\text{C}_{38}\text{H}_{23}\text{Co}_3\text{O}_{10}\text{P}_2$	$\text{C}_{37}\text{H}_{23}\text{Co}_3\text{O}_9\text{P}_2$	$\text{C}_{30}\text{H}_{17}\text{Co}_3\text{O}_9\text{P}_2$
Formula weight	878.29	850.28	760.17
Formula units per cell (<i>Z</i>)	4	2	4
D_{calcd} (Mg/m^3)	1.624	1.615	1.675
λ (Mo $K\alpha$) (Å)	0.71073	0.71073	0.71073
Absorption coefficient (mm^{-1})	1.517	1.554	1.791
Maximum/minimum transmission	0.6249/0.8675	0.2849/0.4418	0.554/0.889
Total reflections	15,341	11,012	9580
Independent reflections	5159	7730	4924
Data/restraints/parameters	5159/0/478	7730/0/460	4924/2/397
<i>R</i>	0.0354	0.0300	0.0486
<i>R_w</i>	0.0741	0.0810	0.1175
GOF on F^2	0.938	1.038	1.033
Weights	$[0.04F^2 + (\sigma F)^2]^{-1}$	$[0.04F^2 + (\sigma F)^2]^{-1}$	$[0.04F^2 + (\sigma F)^2]^{-1}$
Largest difference in peak and hole ($e/\text{Å}^3$)	0.498 and −0.348	0.472 and −0.351	0.747 and −0.870

2.4. Synthesis of $\text{Co}_3(\text{CO})_7[\mu_2, \eta^2, \eta^1\text{-P(Ph)C}\equiv\text{C(PPh}_2\text{)C(O)CH}_2\text{C(O)}]$ (**5**) from the thermolysis of cluster **2**

To 0.10 g (0.10 mmol) of $\text{HC(O)CCo}_3(\text{CO})_7(\text{bpcd})$ in a Schlenk tube was added 20 mL of toluene, after which the vessel was heated at 60 °C for 3.0 h. Upon cooling the reaction was analyzed by TLC analysis, which revealed the complete consumption of cluster **2** and the presence of cluster **5** and decomposed material that remained at the origin of TLC plate. **5** was subsequently isolated by column chromatography at room temperature using CH_2Cl_2 as the eluent. The resulting green solid was recrystallized from a CH_2Cl_2 solution of **5** that had been layered with hexane. Yield: 0.030 g (39%). IR (CH_2Cl_2): $\nu(\text{CO})$ 2072 (vs), 2028 (vs), 1712 (m, symm dione), 1686 (m, antisymm dione) cm^{-1} . $^1\text{H NMR}$ (CDCl_3 ; 298 K): δ 3.38 (AB quartet, 2H, CH_2 , $J_{\text{H-H}} = 20$ Hz), 7.18–8.20 (m, 15H, aryl). $^{31}\text{P NMR}$ (THF; 187 K): δ 171.58 (s, phosphido), 23.25 [s, Ph_2P - (dione)]. Anal. Calcd. (found) for $\text{C}_{30}\text{H}_{17}\text{Co}_3\text{O}_9\text{P}_2 \cdot 1/5\text{hexane}$: C, 48.18 (48.29); H, 2.57 (2.45).

2.5. X-ray structural determinations

Tables 1 and 2 contain the X-ray data and processing parameters and selected bond distances and angles, respectively, for clusters **2**, **4**, and **5**. The reported X-ray data were collected on a Bruker SMART™ 1000 CCD-based diffractometer at 213 K. The frames were integrated with the available SAINT software package using a narrow-frame algorithm [12], and the structures were solved and refined using the SHELXTL program package [13]. The molecular structures were checked by using PLATON [14], and solved by direct methods with all nonhydrogen atoms refined anisotropically. All carbon-bound hydrogen atoms were assigned calculated positions and allowed to ride on the attached heavy atom, unless otherwise noted.

3. Results and discussion

3.1. Synthesis, bpcd fluxional behavior, and molecular structure of $\text{HC(O)CCo}_3(\text{CO})_7(\text{bpcd})$ (**2**) and $\text{HCCo}_3(\text{CO})_7(\text{bpcd})$ (**4**)

Treatment of an equimolar mixture of $\text{HC(O)C-Co}_3(\text{CO})_9$ and bpcd in CH_2Cl_2 with a slight excess of Me_3NO at room temperature led to an immediate reaction and formation of the disubstituted cluster $\text{HC(O)CCo}_3(\text{CO})_7(\text{bpcd})$. Attempts to purify cluster **2** at room temperature by column chromatography led to extensive decomposition of **2**, necessitating the use of low-temperature (−78 °C) chromatography over silica gel using CH_2Cl_2 /petroleum ether as the eluent. Isolated samples of $\text{HC(O)CCo}_3(\text{CO})_7(\text{bpcd})$ are thermally and air sensitive in both the solid state and in solution; **2** has been observed to undergo slow decarbonylation to furnish the hydrogen-capped cluster $\text{HCCo}_3(\text{CO})_7(\text{bpcd})$ (**4**) on prolonged stor-

Table 2
Selected bond distances (Å) and angles (°) for the tricobalt clusters **2**, **4**, and **5**^a

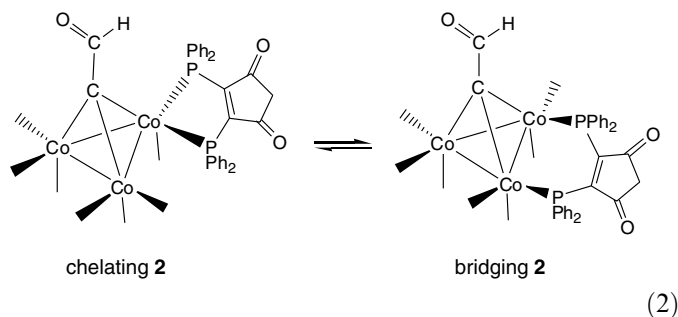
Cluster 2			
Bond distances			
Co(1)–Co(2)	2.4944(7)	Co(1)–Co(3)	2.4933(7)
Co(2)–Co(3)	2.4922(8)	Co(1)–P(1)	2.220(1)
Co(1)–P(2)	2.203(1)	Co(1)–C(30)	1.795(4)
Co(1)–C(37)	1.884(3)	Co(2)–C(33)	1.793(4)
Co(2)–C(31)	1.800(4)	Co(2)–C(32)	1.833(4)
Co(2)–C(37)	1.921(3)	Co(3)–C(36)	1.786(4)
Co(3)–C(34)	1.805(4)	Co(3)–C(35)	1.806(4)
Co(3)–C(37)	1.932(3)	C(37)–C(38)	1.444(4)
C(1)–C(2)	1.502(4)	C(1)–C(5)	1.514(4)
C(2)–C(3)	1.336(4)	C(3)–C(4)	1.510(4)
C(4)–C(5)	1.510(4)	P(1)···P(2)	3.108(2)
Bond angles			
C(37)–Co(1)–P(2)	114.3(1)	C(37)–Co(1)–P(1)	106.1(1)
P(2)–Co(1)–P(1)	89.28(4)	P(2)–Co(1)–Co(3)	156.97(3)
P(1)–Co(1)–Co(3)	110.47(3)	P(2)–Co(1)–Co(2)	97.17(3)
P(1)–Co(1)–Co(2)	155.34(3)	C(2)–P(1)–Co(1)	104.1(1)
C(3)–P(2)–Co(1)	103.7(1)	C(3)–C(2)–P(1)	118.6(2)
C(2)–C(3)–P(2)	117.8(2)	C(38)–C(38)–Co(1)	140.7(2)
C(38)–C(37)–Co(2)	129.1(2)	C(38)–C(37)–Co(3)	122.2(2)
Cluster 4			
Bond distances			
Co(1)–Co(2)	2.4740(4)	Co(1)–Co(3)	2.4937(4)
Co(2)–Co(3)	2.4837(4)	Co(1)–P(1)	2.2052(5)
Co(2)–P(2)	2.1889(5)	Co(1)–C(30)	1.770(2)
Co(1)–C(31)	1.814(2)	Co(1)–C(37)	1.890(2)
Co(2)–C(36)	1.773(2)	Co(2)–C(35)	1.797(2)
Co(2)–C(37)	1.873(2)	Co(3)–C(32)	1.789(2)
Co(3)–C(34)	1.791(2)	Co(3)–C(33)	1.827(2)
Co(3)–C(37)	1.918(2)	C(1)–C(5)	1.520(2)
C(1)–C(2)	1.500(3)	C(2)–C(3)	1.505(3)
C(3)–C(4)	1.518(3)	C(4)–C(5)	1.357(3)
P(1)···P(2)	3.493(1)		
Bond angles			
C(37)–Co(1)–P(1)	109.50(6)	P(1)–Co(1)–Co(2)	102.72(2)
P(1)–Co(1)–Co(3)	158.20(2)	C(37)–Co(2)–P(2)	99.78(6)
P(2)–Co(2)–Co(1)	103.19(2)	P(2)–Co(2)–Co(3)	149.59(2)
C(4)–P(1)–Co(1)	119.01(6)	C(5)–P(2)–Co(2)	112.88(6)
C(5)–C(4)–P(1)	126.4(1)	C(4)–C(5)–P(2)	124.6(1)
Cluster 5			
Bond distances			
Co(1)–Co(2)	2.562(1)	Co(1)–Co(3)	2.576(1)
Co(2)–Co(3)	2.5441(9)	Co(1)–P(1)	2.146(1)
Co(2)–P(2)	2.146(1)	Co(2)–P(2)	2.199(2)
Co(1)–C(24)	1.776(8)	Co(1)–C(25)	1.785(7)
Co(1)–C(26)	1.797(7)	Co(2)–C(27)	1.793(6)
Co(2)–C(28)	1.814(6)	Co(3)–C(29)	1.777(6)
Co(3)–C(30)	1.786(5)	Co(3)–C(1)	2.055(5)
Co(3)–C(5)	2.069(4)	C(1)–C(2)	1.435(7)
C(1)–C(2)	1.477(7)	C(2)–C(3)	1.522(7)
C(3)–C(4)	1.517(9)	C(4)–C(5)	1.478(7)
Bond angles			
P(1)–Co(2)–P(2)	89.86(5)	C(1)–Co(3)–C(5)	40.7(2)
C(5)–P(1)–C(6)	109.4(2)	C(5)–P(1)–Co(2)	101.3(2)
C(6)–P(1)–Co(2)	126.4(2)	C(5)–P(1)–Co(1)	111.7(2)
C(6)–P(1)–Co(1)	128.5(2)	Co(2)–P(1)–Co(2)	73.29(4)
C(27)–Co(2)–P(2)	108.9(2)	C(28)–Co(2)–P(2)	105.9(2)
C(24)–Co(1)–P(1)	103.6(2)	C(25)–Co(1)–P(1)	99.7(2)
C(26)–Co(1)–P(1)	139.0(2)	C(27)–Co(2)–P(1)	97.3(2)
C(28)–Co(2)–P(1)	152.2(2)		

^a Numbers in parentheses are estimated SDs in the least significant digits.

age at room temperature under argon (*vide infra*). The transformation of **2** to **4** is inhibited under CO (1 atm).

$\text{HC(O)CCo}_3(\text{CO})_7(\text{bpcd})$ was characterized in solution by IR and NMR spectroscopies. The IR spectrum for **2** exhibits two strong signature terminal $\nu(\text{CO})$ bands at 2071 and 2022 cm^{-1} typical of diphosphine-substituted clusters $\text{RCCo}_3(\text{CO})_7(\text{P-P})$ [7,15]. The two lower frequency carbonyl stretches at 1753 and 1718 cm^{-1} belong to the vibrationally coupled C=O groups of the dione ring [16]. The ^1H NMR spectrum of **2** in CD_2Cl_2 shows resonances at δ 3.28 (s), 7.25–7.42 (m), and 10.43 (s) for the methylene, aromatic, and formyl hydrogens, respectively. Cluster **2** reveals the presence of a single, broad ^{31}P resonance at room temperature in THF at ca. δ 49, whose location is strongly suggestive of a bridging bpcd ligand. Cooling this sample to 187 K led to the production of two sharp ^{31}P resonances at δ 64.19 and 37.39 attributed to the bpcd chelating (45%) and bridging (55%) isomers of **2**. Samples of cluster **2** that were cycled several times over the temperature range of 187–298 K afforded ^{31}P NMR spectral changes consistent with a reversible equilibrium between the isomeric bpcd clusters, as depicted below in Eq. (2) and previously demonstrated by us for $\text{PhCCo}_3(\text{CO})_7(\text{bma})$ [1]. The K_{eq} value at 187 K is 1.22 in favor of the bridging isomer. The observation of a single ^{31}P resonance for the chelating isomer of **2** indicates that the two phosphorus atoms are bound at the two equatorial sites, as expected for a cluster having idealized C_s symmetry. An alternative coordination mode for the bpcd ligand at a single cobalt center in cluster **2** would involve the binding of the diphos-

phine ligand at the one unique axial site and one of the two equatorial sites [1,3,17]. In the cases of such chelating isomers, two distinct ^{31}P resonances are observed in the absence of diphosphine equilibration between the equatorial and axial sites. This rocking motion of the diphosphine ligand serves to equilibrate the two phosphine moieties between the equatorial and axial sites, giving rise to a weighted-average ^{31}P resonance [18]



The molecular structure for **2** was established by X-ray crystallography. The ORTEP diagram of **2** is depicted in the left-hand portion of Fig. 1. Cluster **2** contains 48-valence electrons and displays a chelating bpcd ligand that is attached to the Co(1) center. The three cobalt atoms in **2** form an equilateral triangle that is capped by the μ_3 -CCH(O) moiety. The three Co–Co bonds exhibit a mean distance of 2.4933 Å, consistent with those distances in the nonacarbonyl clusters $\text{RCCo}_3(\text{CO})_9$ [19] and numerous phosphine-substituted clusters $\text{RCCo}_3(\text{CO})_{9-n}\text{P}_n$ and $\text{RCCo}_3(\text{CO})_7(\text{P-P})$ [20]. The Co(1)–P(1) [2.203(1) Å] and

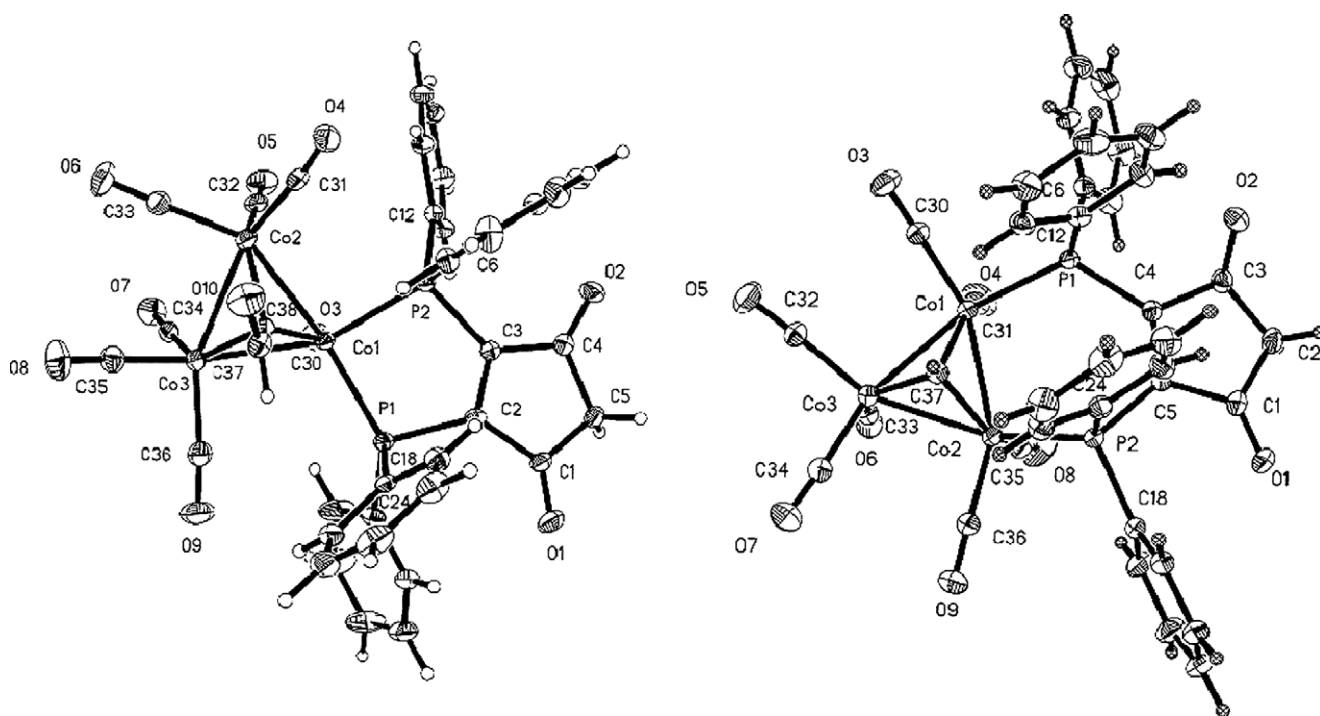


Fig. 1. Thermal ellipsoid plots of $\text{HC(O)CCo}_3(\text{CO})_7(\text{bpcd})$ (**2**; left) and $\text{HCCo}_3(\text{CO})_7(\text{bpcd})$ (**4**; right) showing the thermal ellipsoids at the 50% probability level.

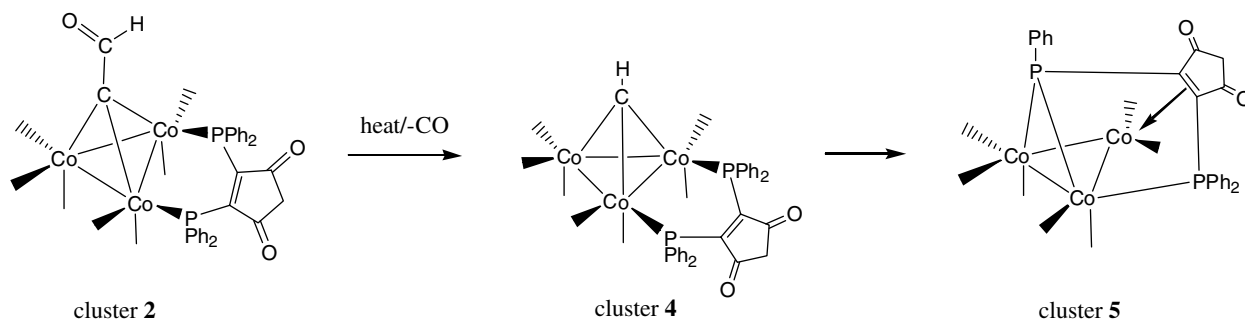
Co(1)–P(2) [2.220(1) Å] bond distances and the P(1)–Co(1)–P(2) bond angle of 89.28(4)° are unexceptional with respect to other bpcd-substituted compounds.

The chelation of the bpcd ligand in cluster **2** is of interest because the vast majority of structurally characterized diphosphine-substituted clusters $\text{RCCo}_3(\text{CO})_7$ (P–P) contain a bridging P–P ligand. Other than **2**, the only other clusters containing a chelating diphosphine ligand that have been structurally characterized are $\text{PhCCo}_3(\text{CO})_7(\text{P–P})$ (where P–P = bma, bpcd) and $\text{PhCCo}_3(\text{CO})_5(\text{dmpe})_2$, all of which have been prepared by our groups [1,3,21]. Moreover, cluster **2** is unique because the seven ancillary carbonyl groups are all terminal in nature, with the bpcd ligand bound to the Co(1) center at both equatorial sites. The diphosphine ligand in benzylidyne-capped clusters $\text{PhCCo}_3(\text{CO})_7(\text{bpcd})$ and $\text{PhCCo}_3(\text{CO})_7(\text{bma})$ is coordinated at axial and equatorial sites and is accompanied by three μ_2 -CO groups (see Eq. 1) [22], each of which spans a Co–Co bond in solution at low temperatures and the solid state of recrystallized samples.

Samples of **2** were observed to decompose over the course of weeks at room temperature, as initially assessed by TLC analysis. Gently heating solutions of **2** at temperatures <50 °C led to the complete destruction of **2** and the formation of a new cluster whose IR spectrum supported the formation of a new bpcd-substituted cluster. Since the decarbonylation of the acyl clusters $\text{RC}(\text{O})\text{CCo}_3(\text{CO})_9$ (where R = various aromatic groups) has been shown to furnish the corresponding $\text{RCCo}_3(\text{CO})_9$ clusters [23], it seemed reasonable that decarbonylation of the formyl moiety could yield the methylidyne-capped cluster $\text{HCCo}_3(\text{CO})_7(\text{bpcd})$ (**4**). Our premise was subsequently confirmed by the independent synthesis of **4** from the reaction of bpcd with $\text{HCCo}_3(\text{CO})_9$ (**3**). Treatment of cluster **3** with bpcd in the presence of Me_3NO afforded cluster **4** as a temperature- and oxygen-sensitive black solid in low yields after chromatographic purification at –78 °C. The direct thermolysis of **3** and bpcd also produced small amounts of **4** and the phosphido-bridged cluster $\text{Co}_3(\text{CO})_7[\mu_2, \eta^2, \eta^1\text{-P}(\text{Ph})\text{C}=\text{C}(\text{PPh}_2)\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})]$ (**5**), along with extensive decomposition. Scheme 2 outlines the relationship between clusters **2**, **4**, and **5**.

Cluster **4** was characterized in solution by the usual solution methods and X-ray diffraction analysis. The IR spectrum of **4** mirrors that of cluster **2** in the terminal carbonyl region with two strong $\nu(\text{CO})$ bands at 2063 and 2008 cm^{-1} , whose ca. 11 cm^{-1} shift to lower frequency is consistent with the presence of a hydrogen versus an electron-withdrawing formyl capping group. The two dione carbonyl stretches in **4** are unaffected by the nature of the capping carbonyl moiety and appear at 1748 (w) and 1717 (m) cm^{-1} . ^1H NMR resonances recorded at δ 3.29 (s), 7.35–7.49 (m), and 10.99 (s) for the methylene, aromatic, and methylidyne hydrogens are in full agreement with the structure of **4**. A single, broad ^{31}P NMR resonance at δ 51 was recorded at room temperature in THF. This resonance sharpened slightly as the temperature was lowered and split into two new resonances at δ 65.57 and 41.20 at 187 K that are assigned to the chelating (58%) and bridging (42%) isomers analogous to the isomeric behavior found with cluster **2**.

The thermal ellipsoid plot of cluster **4** shown in Fig. 1 (right-hand side) confirms the coordination of the bpcd ligand across the Co(1)–Co(2) vector. The Co–Co bonds in **4** are highly asymmetric in length, ranging from 2.4720(4) Å [Co(1)–Co(2)] to 2.4937(4) Å [Co(1)–Co(3)] and exhibiting a mean distance of 2.4831 Å. The internuclear P(1)–P(2) distance of 3.493(1) Å is only slightly longer than the corresponding internuclear distance found in the chelating bpcd ligand in cluster **2** and indicates that the bridging coordination mode observed here exerts no adverse perturbation on the cluster core. The observation of a bridging bpcd ligand in the solid-state structure of **4** is of interest as the benzylidyne-capped cluster $\text{PhCCo}_3(\text{CO})_7(\text{bpcd})$ displays a chelating diphosphine ligand [3]. The adoption of a bridging bpcd ligand in cluster **4** may be attributed, in part, to the smaller methylidyne capping ligand (HC) vis-à-vis $\text{PhCCo}_3(\text{CO})_7(\text{bpcd})$; however, we also note that the crystallization thermodynamics, electronic effects from the capping ligand, and the participation of the ancillary carbonyls in the redistribution of electron density about the molecular polyhedron may also influence the outcome of the recrystallization. Clearly additional examples of $\text{RCCo}_3(\text{CO})_7(\text{bpcd})$ clusters bearing different RC capping groups are required before any gross



Scheme 2.

generalizations can be made concerning the preferred solid-state structure in this genre of cluster. The seven CO groups in **4** are all linear, and the alkene bond in the bpcd that is defined by the C(4) and C(5) atoms exhibits a distance of 1.357(3) Å.

3.2. Activation of clusters **2** and **4** and molecular structure of the phosphido-bridged cluster $\text{Co}_3(\text{CO})_7[\mu_2, \eta^2, \eta^1\text{-P(Ph)C=C(PPh}_2\text{)C(O)CH}_2\text{C(O)}]$ (**5**)

Heating samples of cluster **2** led to the loss of the formyl carbonyl group and formation of methylidyne cluster **4** and the concomitant formation of an additional product that was later identified as $\text{Co}_3(\text{CO})_7[\mu_2, \eta^2, \eta^1\text{-P(Ph)C=C(PPh}_2\text{)C(O)CH}_2\text{C(O)}]$ (**5**). That **4** serves as the direct precursor for **5** was independently verified from thermolysis reactions using **4** as a starting material. Two strong terminal $\nu(\text{CO})$ bands at 2072 and 2028 cm^{-1} were recorded for **5**, along with two moderately intense dione carbonyl groups at 1712 and 1686 cm^{-1} . The observed low energy shift of ca. 35 cm^{-1} in the latter two carbonyl stretching bands supports the coordination of the dione ring to the cluster frame through the carbon–carbon π bond [24]. Unequivocal proof for the activation of the bpcd ligand was seen in the ^{31}P NMR spectrum of **5**, where two singlets at δ 171.58 and 23.25 that are readily ascribed to a bridging phosphido group and phosphine moiety, respectively [25]. Examination of the same sample by ^1H NMR spectroscopy shed no information on the nature of the organic derived by-product(s) derived from the activation of the methylidyne-capping group and P–Ph bond due to extensive broadening of the ^1H resonances by trace amounts of paramagnetic Co(II) species. The solution spectroscopic data for isolated **5** closely match those data reported by us for the related tricobalt cluster $\text{Co}_3(\text{CO})_7[\mu_2, \eta^2, \eta^1\text{-P(Ph)C=C(PPh}_2\text{)C(O)OC(O)}]$, which has been isolated as one of four products from the thermolysis of $\text{Co}_4(\text{CO})_9(\text{mesitylene})$ and bma [26].

The X-ray structure of **5** is shown in Fig. 2. Cluster **5** possesses 48-electrons and the structure consists of a triangular array of cobalt atoms, where the mean Co–Co bond distance of 2.561 Å is in good agreement with those distances found in other tricobalt clusters and $\text{Co}_3(\text{CO})_7[\mu_2, \eta^2, \eta^1\text{-P(Ph)C=C(PPh}_2\text{)C(O)OC(O)}]$. The presence of the seven-electron face-capping $\mu_2, \eta^2, \eta^1\text{-P(Ph)C=C(PPh}_2\text{)C(O)CH}_2\text{C(O)}$ moiety confirms the loss of one of the phenyl groups belonging to the bpcd ligand and the methylidyne capping CH group. The fate of these moieties has not been ascertained but the formation of the transient carbene species “PhCH” from the phenyl and methylidyne cap would not be unreasonable, which could subsequently dimerize to give stilbene [27]. Coordination of the C(1)–C(5) bond to Co(3) leads to a ca. 0.07 Å elongation relative to the free π bond found in clusters **2** and **4**, a fact that reaffirms the Duncanson–Dewar–Chatt bonding model between an alkene and a transition metal [28]. The remain-

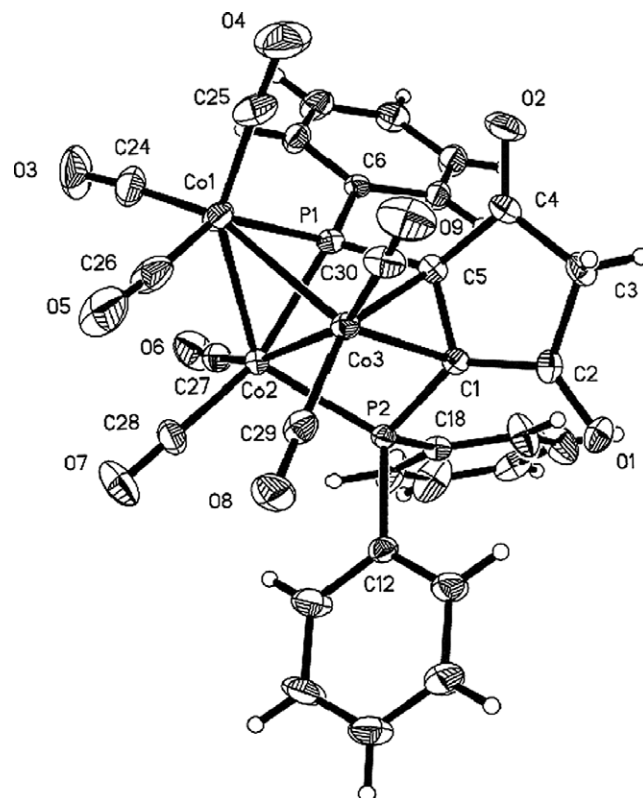


Fig. 2. Thermal ellipsoid plot of $\text{Co}_3(\text{CO})_7[\mu_2, \eta^2, \eta^1\text{-P(Ph)C=C(PPh}_2\text{)C(O)CH}_2\text{C(O)}]$ (**5**) showing the thermal ellipsoids at the 50% probability level.

ing bond distances and angles are unexceptional and require no comment.

4. Conclusions

The reaction between the formyl-capped cluster $\text{HC(O)CCo}_3(\text{CO})_9$ and the rigid diphosphine ligand bpcd yields the substituted cluster $\text{HC(O)CCo}_3(\text{CO})_7(\text{bpcd})$, which is shown to undergo facile decarbonylation upon heating to give the methylidyne-capped cluster $\text{HCCo}_3(\text{CO})_7(\text{bpcd})$, followed by the loss of the capping HC moiety and one phenyl ligand from the bpcd ligand to furnish the phosphido-bridged cluster $\text{Co}_3(\text{CO})_7[\mu_2, \eta^2, \eta^1\text{-P(Ph)C=C(PPh}_2\text{)C(O)CH}_2\text{C(O)}]$. The fluxional behavior of the ancillary bpcd ligand in the former two clusters has been verified by VT ^{31}P NMR spectroscopy, and the molecular structures of all three cluster products have been established by X-ray crystallography. The stability and course of cluster/diphosphine ligand activation in different $\text{RCCo}_3(\text{CO})_7(\text{P-P})$ clusters will be investigated as a function of the RC capping moiety.

5. Supporting information available

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 277904 for **2**; 277905 for **4**; and 277906

for **5**. Copies of these data may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK [fax: +44 1223 336 033; email: deposit@ccdc.ac.uk or <http://www.ccdc.cam.ac.uk>.

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