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# Ligand chelation, P–C bond cleavage, and phenyl-group transfer in the reaction between $RCCo_3(CO)_9$ and 1,8-bis(diphenylphosphino)naphthalene (dppn): Syntheses and X-ray diffraction structures of $PhCCo_3(CO)_4(\mu\text{-}CO)_3(dppn)$ and $PhCCo_3(CO)_8[\eta^1\text{-}PPh(OH)C_{10}H_6P(O)Ph_2]$

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## Abstract

The tricobalt cluster $PhCCo_3(CO)_9$ (**1**) undergoes facile ligand substitution with 1,8-bis(diphenylphosphino)naphthalene (dppn) under thermal and $Me_3NO$ activation to afford the cluster compounds $PhCCo_3(CO)_8[PPh_2(1\text{-}C_{10}H_7)]$ (**2**) and $PhCCo_3(CO)_4(\mu\text{-}CO)_3(dppn)$ (**3**). Whereas thermolysis of dppn with the methylidyne-capped cluster $HCCo_3(CO)_9$ (**4**) yields only $HCCo_3(CO)_8[PPh_2(1\text{-}C_{10}H_7)]$ (**5**) and $HCCo_3(CO)_4(\mu\text{-}CO)_3(dppn)$ (**6**) as isolable products, the reaction between **4** and dppn in the presence of $Me_3NO$ furnishes the latter two clusters in addition to the phenyl-capped cluster $PhCCo_3(CO)_8[\eta^1\text{-}PPh(OH)C_{10}H_6P(O)Ph_2]$ (**7**). The clusters **2** and **5** represent simple substitution products based on the ligand diphenyl(1-naphthyl)phosphine, while clusters **3** and **6** each possess a chelating dppn ligand and three bridging CO groups in the solid state. Oxidation of the two phosphine moieties by $Me_3NO$ and transfer of one of the phenyl groups from the dppn ligand to the methylidyne carbon moiety in cluster **4** produces the thermally unstable cluster **7**. These clusters have been characterized in solution by IR and $^{31}P$ NMR spectroscopies, and the solid-state structures of **3** and **7** established by X-ray crystallography.
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*Keywords:* Tricobalt clusters; Ligand substitution; Diphosphine ligand; P–C bond cleavage; Phenyl-group transfer

## 1. Introduction

The synthesis of the diphosphine ligand 1,8-bis(diphenylphosphino)naphthalene (dppn) was first reported in 1993 [1], but unlike the well-known and thoroughly studied diphosphine ligands 1,1-bis(diphenylphosphino)methane (dppm) and 1,2-bis(diphenylphosphino)ethane (dppe), the coordination chemistry associated with the dppn ligand has received relatively little attention. Early expectations for dppn as a ligand were high due to the transannular properties extant from the *peri*-disposed phosphorus atoms associated with the naphthalene platform and new compounds exhibiting novel physical properties were anticipated. While the reported mononuclear complexes possessing a dppn ligand have not provided unusual properties vis-á-vis related dppe-substituted complexes [2–5], coordination of dppn to the metal cluster compounds $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ is accompanied by facile degradation of the diphosphine ligand via C–H and P–C bond cleavages [6,7]. The only known cluster structure containing an intact dppn ligand is $Ru_3(CO)_8(\mu\text{-}dppm)(dppn)$,

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which has been isolated in low yield from the thermolysis reaction involving $Ru_3(CO)_{10}(\mu\text{-dppm})$ and dppn [6].

Our groups have had a long-term interest in the study of the rigid, unsaturated diphosphine ligands $(Z)$-$Ph_2PCH$ $=CHPPh_2$, 2,3-bis(diphenylphosphino)maleic anhydride (bma) and 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd) with numerous metal cluster compounds [8]. Reaction of these ligands with the tricobalt clusters $RCCo_3(CO)_9$ gives the corresponding products $RCCo_3$-$(CO)_7(P–P)$ (where P–P = diphosphine ligand). In the case of the cluster compound $PhCCo_3(CO)_7[(Z)$-$Ph_2PCH=CHPPh_2]$, the diphosphine ligand functions as a bridging ligand that stabilizes the cluster against fragmentation relative to the bma- and bpcd-substituted derivatives. Moreover, the cluster compounds $PhCCo_3(CO)_7(bma)$ and $PhCCo_3(CO)_7(bpcd)$ display reversible chelate-to-bridge fluxionality of the diphosphine ligand at ambient temperature, in addition to exhibiting facile cluster/ligand activation that involves the cleavage of a $Ph_2P–C(ring)$ bond, followed by the reductive coupling of the transient Co–C(ring) moiety and the benzylidyne capping ligand. Scheme 1 summarizes this chemistry for $PhCCo_3(CO)_7(bpcd)$.

Wishing to extend our substitution studies in the tetrahedrane clusters $RCCo_3(CO)_9$ with different diphosphine ligands, we have examined the reactivity of dppn with the clusters $PhCCo_3(CO)_9$ (**1**) and $HCCo_3(CO)_9$ (**4**). Herein we present our results on the thermolysis and $Me_3NO$-activated reactions of clusters **1** and **4** in the presence of dppn to afford the dppn-chelated clusters **3** and **6** as the major products. The minor products isolated from these reactions include $PhCCo_3(CO)_8[PPh_2(1\text{-}C_{10}H_7)]$ (**2**), $HCCo_3(CO)_8[PPh_2(1\text{-}C_{10}H_7)]$ (**5**), and $PhCCo_3(CO)_8[\eta^1\text{-}PPh(OH)C_{10}H_6P(O)Ph_2]$ (**7**), all of which provide evidence for the fragmentation of the dppn during the course of the reaction.

## 2. Experimental

### 2.1. General methods

The starting clusters $PhCCCo_3(CO)_9$ and $HCCo_3(CO)_9$ were prepared from $Co_2(CO)_8$ [9], while the ligand dppn was synthesized by employing either 1,8-dibromonaphthalene or 1-bromonaphthalene as starting materials according to the published procedures [1,10,11]. The 1-naphthyldiphenylphosphine ligand used in the independent preparation of clusters **2** and **5** was synthesized from 1-bromonaphthalene and chlorodiphenylphosphine [12]. With the exception of $Co_2(CO)_8$, which was purchased from Strem Chemicals, the other chemicals used in these studies 1,8-diaminonaphthalene, 1-bromonaphthalene, chlorodiphenylphosphine, bromoform, and $Me_3NO \cdot 2H_2O$ were all obtained from Aldrich Chemical Co. The latter reagent was dried by azeotropic distillation from benzene, after which it was stored under argon. All reaction and NMR solvents were distilled under argon from a suitable drying agent and stored in Schlenk storage vessels [13]. All preparative chromatographic separations were done by column chromatography under atmospheric conditions without any special precautions. The combustion analyses were performed by Atlantic Microlab, Norcross, GA. The reported ESI-APCI (positive ionization mode) and FAB mass spectral data of cluster **7** were recorded at the UC San Diego Mass Spectrometry Center, with 3-nitrobenzyl alcohol employed as the sample matrix in the acquisition of the FAB mass spectrum.

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 $^{31}P$ NMR spectra were recorded on a Varian 300-VXR
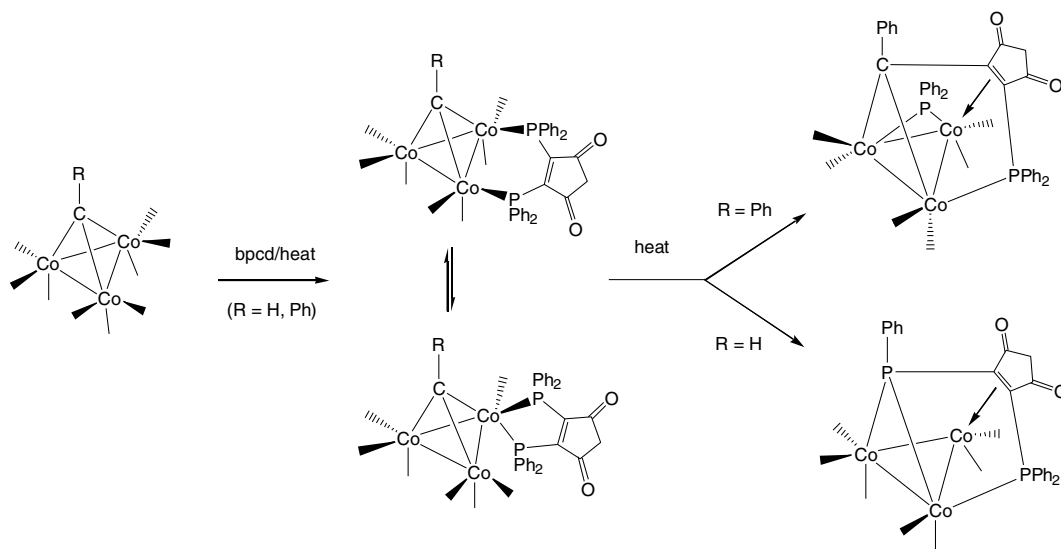


Scheme 1.

spectrometer at 121 MHz. 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. Thermolysis of $PhCCo_3(CO)_9$ (1) with dppn

50 mg (0.096 mmol) of $PhCCo_3(CO)_9$ and 52 mg (0.10 mmol) of dppn were charged to a small Schlenk tube, followed by 20 mL of 1,2-dichloroethane (DCE) via syringe. The vessel was sealed and the reaction solution heated overnight at 50 °C. TLC examination of the cooled reaction solution using a 1:4 mixture of $CH_2Cl_2$/hexane revealed the presence of two new spots belonging to clusters 2 ($R_f = 0.70$) and 3 ($R_f = 0.55$), along with some unreacted cluster 1. The solvent was removed under vacuum and the residue subsequently purified by column chromatography over silica gel using the aforementioned solvent system. Both product clusters were recrystallized from $CH_2Cl_2$ and hexane. Cluster 2: 7.5 mg (10% yield). IR ($CH_2Cl_2$): $v$(CO) 2078 (s), 2042 (vs), 2021 (vs) cm$^{-1}$. $^{31}$P NMR (CDCl$_3$): $\delta$ 31.80. Cluster 3: 32 mg (35% yield). IR ($CH_2Cl_2$): $v$(CO) 2052 (s), 2017 (vs), 1988 (vs), 1862 (m), 1827 (m) cm$^{-1}$. $^{31}$P NMR (CDCl$_3$): $\delta$ 40.18 (s), 35.12 (s), 30.54 (s). Anal. Calc. (found) for $C_{48}H_{31}Co_3O_7P_2 \cdot CH_2Cl_2$: C, 56.40 (56.28); H, 3.19 (3.46).

## 2.3. $Me_3NO$ activation of $PhCCo_3(CO)_9$ (1) in the presence of dppn

To a 250-mL Schlenk flask under argon flush was added 0.10 g (0.19 mmol) of $PhCCo_3(CO)_9$, 0.11 g (0.21 mmol) of dppn, and 20 mL of $CH_2Cl_2$. Stirring was initiated and 31 mg (0.41 mmol) of $Me_3NO$ was next added in one portion to the reaction and stirring continued for 1 h, after which the progress of the reaction was checked by TLC analysis. The presence of clusters 2 and 3 were confirmed and then isolated as described above. Yield of cluster 2: 23 mg (15%). Yield of cluster 3: 74 mg (40%).

## 2.4. Thermolysis of $HCCo_3(CO)_9$ (4) with dppn

The thermolysis reaction was carried similarly as that described for cluster 1. Here 50 mg (0.11 mmol) of $HCCo_3(CO)_9$, 61 mg (0.12 mmol) of dppn, and 20 mL of $CH_2Cl_2$ were employed. The reaction was heated at 45 °C overnight, allowed to cool to room temperature, and then examined by TLC analysis using $CH_2Cl_2$/hexane (1:3). The presence of the monophosphine-substituted cluster 5 ($R_f = 0.75$) and the dppn-chelated cluster 6 ($R_f = 0.55$) were the sole observed products. These clusters were isolated by column chromatography over silica gel and recrystallized from $CH_2Cl_2$ and benzene. Yield of 5: 10% (8.5 mg). IR ($CH_2Cl_2$): $v$(CO) 2081 (s), 2038 (vs), 2022 (vs) cm$^{-1}$. $^{31}$P NMR (CDCl$_3$): $\delta$ 44.50. Yield of 6: 30% yield (31 mg). IR ($CH_2Cl_2$): $v$(CO) 2055 (s), 2021 (vs), 1993 (vs), 1858 (m), 1824 (m) cm$^{-1}$. $^{31}$P NMR (CDCl$_3$): $\delta$ 44.80 (s), 35.00 (s), 30.05 (s). Anal. Calc. (found) for

$C_{48}H_{31}Co_3O_7P_2 \cdot CH_2Cl_2 \cdot 1/2C_6H_6$: C, 54.84 (54.95); H, 3.40 (3.94).

## 2.5. $Me_3NO$ activation of $HCCo_3(CO)_9$ (4) in the presence of dppn

To a Schlenk tube was added 0.10 g (0.22 mmol) of cluster 4, 0.12 g (0.24 mmol) of dppn, and 36 mg (0.47 mmol) of $Me_3NO$, after which 20 mL of $CH_2Cl_2$ was syringed into the flask. The reaction was stirred for 1 h at room temperature and then examined by TLC using $CH_2Cl_2$/hexane (1:3), which revealed the presence of two spots corresponding to clusters 5 and 6 along with a slower moving spot ($R_f = 0.30$) attributed to cluster 7. These products were subsequently isolated by careful chromatography. Yield of 5: 10% (17 mg). Yield of 6: 35% (70 mg). Yield of 7: 10% (21 mg). IR ($CH_2Cl_2$): $v$(CO) 2075 (s), 2032 (vs), 2018 (vs), 2010 (sh) cm$^{-1}$. $^{31}$P NMR (CDCl$_3$): $\delta$ 130.49 (s), 39.62 (s). FAB-MS ($m/z$): 743 [7]$^+$. ESI-APCI MS (m/z): 958.95 [7+H$_2$O+H]$^+$ and 974.96 [7+MeOH+H]$^+$.

## 2.6. X-ray crystallographic data

Crystals of clusters 3 and 7 suitable for X-ray diffraction analysis were grown from a $CH_2Cl_2$ solution containing each cluster that had been layered with hexane. Tables 1 and 2 provide the X-ray data and processing parameters and selected bond distances and angles, respectively, for compounds 3 and 7. The reported X-ray data were col-

Table 1
X-ray crystallographic data and processing parameters for the clusters 3 and 7

| Compound | 3 | 7 |
|---|---|---|
| CCDC entry no. | 619643 | 619644 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ | $P2_1/c$ |
| $a$ (Å) | 11.296(1) | 8.990(1) |
| $b$ (Å) | 19.146(3) | 35.591(5) |
| $c$ (Å) | 19.345(3) | 12.928(2) |
| $\beta$ (°) | 102.384(2) | 103.182(3) |
| $V$ (Å$^3$) | 4086.5(9) | 4028(1) |
| Molecular formula | $C_{48}H_{31}Co_3O_7P_2$ | $C_{43}H_{27}Co_3O_{10}P_2$ |
| Formula weight | 958.46 | 942.38 |
| Formula units per cell ($Z$) | 4 | 4 |
| $D_{calc}$ (Mg/m$^3$) | 1.558 | 1.554 |
| $\lambda$ (Mo K$\alpha$) (Å) | 0.71073 | 0.71073 |
| Absorption coefficient (mm$^{-1}$) | 1.336 | 1.359 |
| Maximum/minimum transmission | 0.5150/0.4161 | 0.8462/0.7258 |
| Total reflections | 34270 | 24042 |
| Independent reflections | 9507 | 5767 |
| Data/restraint/parameters | 9507/0/541 | 5767/0/528 |
| $R$ | 0.0475 | 0.0406 |
| $R_w$ | 0.0870 | 0.0749 |
| GOF on $F^2$ | 0.870 | 0.889 |
| Weights | $[0.04F^2 + (\sigma F)^2]^{-1}$ | $[0.04F^2 + (\sigma F)^2]^{-1}$ |
| Absorption correction | Empirical | Empirical |
| Largest difference in peak and hole (e/Å$^3$) | 0.561 and $-0.349$ | 0.419 and $-0.335$ |

Table 2
Selected bond distances (Å) and angles (°) for clusters **3** and **7**

*Cluster 3*
*Bond distances*

| | | | |
|---|---|---|---|
| Co(1)–Co(2) | 2.5308(6) | Co(1)–Co(3) | 2.5202(6) |
| Co(2)–Co(3) | 2.3989(6) | P(1)···P(2) | 3.112(1) |
| Co(1)–P(2) | 2.1998(9) | Co(1)–P(1) | 2.2544(9) |
| Co(1)–C(41) | 1.960(3) | Co(2)–C(41) | 1.915(3) |
| Co(3)–C(41) | 1.950(3) | Co(1)–C(42) | 1.826(3) |
| Co(1)–C(43) | 1.912(3) | Co(2)–C(43) | 2.029(3) |
| Co(2)–C(46) | 2.022(3) | Co(3)–C(42) | 2.197(3) |
| Co(3)–C(46) | 1.901(3) | | |

*Bond angles*

| | | | |
|---|---|---|---|
| P(2)–Co(1)–P(1) | 88.62(3) | P(2)–Co(1)–C(41) | 101.47(9) |
| P(1)–Co(1)–C(41) | 169.82(9) | P(2)–Co(1)–Co(3) | 144.63(3) |
| P(1)–Co(1)–Co(3) | 120.43(3) | P(2)–Co(1)–Co(2) | 123.80(3) |
| P(1)–Co(1)–Co(2) | 126.31(3) | O(1)–C(42)–Co(1) | 156.7(3) |
| O(1)–C(42)–Co(3) | 126.0(2) | Co(1)–C(42)–Co(3) | 77.0(1) |
| O(2)–C(43)–Co(1) | 149.2(3) | O(2)–C(43)–Co(2) | 130.9(2) |
| Co(1)–C(43)–Co(2) | 79.9(2) | O(5)–C(46)–Co(3) | 145.6(3) |
| O(5)–C(46)–Co(2) | 139.0(3) | Co(2)–C(46)–Co(3) | 75.3(1) |

*Cluster 7*
*Bond distances*

| | | | |
|---|---|---|---|
| Co(1)–Co(2) | 2.474(1) | Co(1)–Co(3) | 2.473(1) |
| Co(2)–Co(3) | 2.478(1) | Co(1)–P(1) | 2.221(2) |
| P(1)···P(2) | 3.771(3) | O(1)···O(2) | 2.481(5) |
| Co(1)–C(29) | 1.917(5) | Co(2)–C(29) | 1.901(5) |
| Co(3)–C(29) | 1.936(5) | P(1)–O(1) | 1.592(4) |
| P(1)–C(1) | 1.849(5) | P(1)–C(23) | 1.816(5) |
| P(2)–O(2) | 1.499(4) | P(2)–C(9) | 1.836(6) |
| P(2)–C(11) | 1.802(6) | P(2)–C(17) | 1.818(6) |
| O(1)–H(1) | 1.10(7) | H(1)···O(2) | 1.39(7) |

*Bond angles*

| | | | |
|---|---|---|---|
| P(1)–Co(1)–Co(3) | 158.30(6) | P(1)–Co(1)–Co(3) | 98.23(5) |
| O(1)–P(1)–Co(1) | 109.4(2) | C(23)–P(1)–Co(1) | 108.2(2) |
| C(1)–P(1)–Co(1) | 118.3(2) | O(2)–P(2)–C(11) | 113.4(2) |
| O(2)–P(2)–C(17) | 107.2(3) | O(2)–P(2)–C(9) | 116.3(2) |
| O(1)–H(1)···O(2) | 175(7) | | |

lected 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 [14], and the structures were solved and refined using the SHELXTL program package [15]. The molecular structures for both cluster compounds were checked using PLATON [16], 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. The hydrogen atom H(1) in **7** was located in a difference map, and it was allowed to refine isotropically.

## 3. Results and discussion

### 3.1. Reaction of PhCCo$_3$(CO)$_9$ with dppn and molecular structure of 3

The benzylidyne-capped cluster PhCCo$_3$(CO)$_9$ (**1**) reacts with the diphosphine ligand dppn readily at 50 °C in 1,2-dichloroethane to afford PhCCo$_3$(CO)$_8$[PPh$_2$(1-C$_{10}$H$_7$)] (**2**) and PhCCo$_3$(CO)$_4$(μ-CO)$_3$(dppn) (**3**) as the principal

cluster products, as confirmed by TLC analysis of the reaction solution. The same product distribution was also observed when cluster **1** and dppn were allowed to react in the presence of the oxidative-decarbonylation reagent Me$_3$NO. Both methods of cluster activation afforded a black solid that remained at the origin of the TLC plate and whose identity is attributed to some type of cluster-related decomposition product(s). The characterization of this origin material was not pursued since it remained irreversibly bound to the chromatographic support under all conditions. Both **2** and **3** were subsequently isolated by column chromatography and characterized in solution by IR and $^{31}$P NMR spectroscopies, and the solid-state structure of the latter product determined by X-ray diffraction analysis. Both products appear to be stable in the solid state for a period of months, with solutions of both clusters that have been exposed to the atmosphere exhibiting noticeable decomposition after several hours. Eq. (1) depicts the two products isolated from the reaction between cluster **1** and dppn
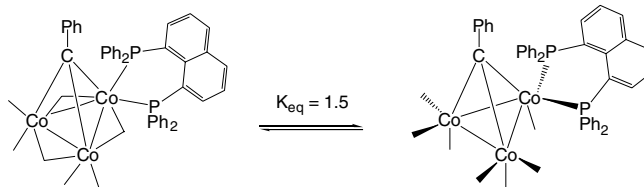


cluster **1**
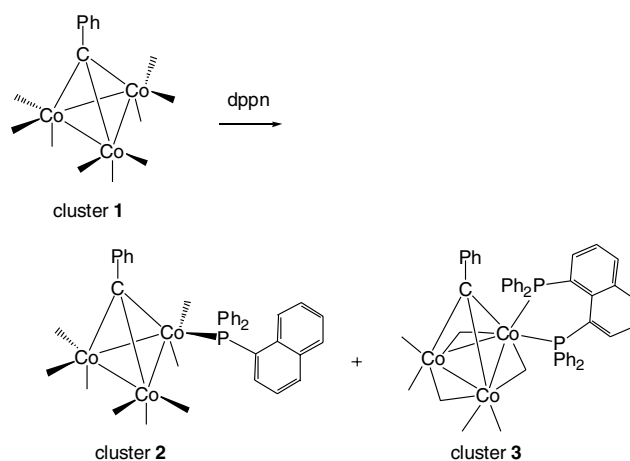
cluster **2** + cluster **3**

(1)

The IR spectrum of **2** in CH$_2$Cl$_2$ displays the signature pattern of a monosubstituted RCCo$_3$(CO)$_8$P cluster (where P = phosphine ligand) based on terminal $v$(CO) bands 2078 (s), 2042 (vs), and 2021 (vs) cm$^{-1}$ [17], while the broad singlet observed at $\delta$ 31.80 in the $^{31}$P NMR spectrum of **2** agrees nicely with the $^{31}$P chemical data reported for other RCCo$_3$(CO)$_8$P clusters [17c]. Given the facile fragmentation and activation of the dppn ligand reported during the thermolysis with the cluster compounds M$_3$(CO)$_{12}$ (where M = Ru, Os) by Bruce and co-workers [6,7], two logical possibilities existed for cluster **2**. Here the dppn ligand could undergo a formal transformation to the monodentate phosphine ligands PPh$_3$ or PPh$_2$(1-naphthyl) [18]. Control experiments between the parent cluster **1** and the ligands PPh$_3$ and PPh$_2$(1-naphthyl) were carried out and the corresponding PhCCo$_3$(CO)$_8$P clusters isolated and characterized by IR and $^{31}$P spectroscopies and TLC analyses. The IR data for **2** in hexane best matched that of independently prepared PhCCo$_3$(CO)$_8$[PPh$_2$(1-naphthyl)], also recorded in hexane. The small but observable frequency differences in the

high-energy $v(CO)$ band in these clusters serve as a very sensitive indicator as to the amount and nature of the ancillary phosphine ligand associated with the cluster [19]. Moreover, TLC analysis (eluent: $CH_2Cl_2$/hexane 1:4) revealed that of the two independently prepared clusters $PhCCo_3$-$(CO)_8(PPh_3)$ and $PhCCo_3(CO)_8[PPh_2(1-naphthyl)]$, the former cluster exhibited a slightly larger $R_f$ value (0.72) in comparison to $PhCCo_3(CO)_8[PPh_2(1-naphthyl)]$, whose $R_f$ value (0.70) exactly matched that of cluster **2** isolated from the reaction. That the ancillary phosphine ligand in **2** derives from diphenyl(1-naphthyl)phosphine and not $PPh_3$ is in good agreement with those data reported by Bruce and co-workers for the formation of $Os_3(CO)_{11}[PPh_2(1-naphthyl)]$ from dppn and $Os_3(CO)_{12}$ [7].

The IR spectrum for **3** exhibited prominent terminal carbonyl stretching bands at 2052 (s), 2017 (vs), and 1988 (vs) $cm^{-1}$, along with bridging $v(CO)$ bands at 1862 (m) and 1827 (m) $cm^{-1}$. The room temperature $^{31}P$ NMR spectrum displayed three singlets at $\delta$ 40.18, 35.12, and 30.54 that may be ascribed to the two dppn chelating isomers shown to the right. Here the latter two high-field singlets are assigned to the inequivalent phosphine groups in the triply bridged $\mu_2$-CO isomer on the left-hand side of the equilibrium. The more intense $^{31}P$ resonance at $\delta$ 40.18 is consistent with the all terminal carbonyl isomer of $PhCCo(CO)_7(dppn)$ that contains an equatorially disposed dppn ligand. Integration of these resonances yields a $K_{eq}$ value of ca. 1.5 in favor of the all-terminal carbonyl isomer [20,21]. Another possibility for the all-terminal carbonyl isomer of $PhCCo(CO)_7(dppn)$ involves a dppn ligand that is chelated to a single cobalt atom at the axial and one of the two equatorial sites (not shown). In this particular isomer one expects two different $^{31}P$ resonances in the absence of a rapid rocking motion that would equilibrate the two phosphine moieties, giving rise to a weighted-average $^{31}P$ resonance. Examples of homo- and heterometallic tetrahedrane clusters exhibiting such diphosphine-ligand fluxionality have been published by our groups [22].

The thermal ellipsoid plot shown in the left-hand side of Fig. 1 confirms the chelation of the dppn ligand to the cluster polyhedron in **3**, along with the presence of three $\mu_2$-CO groups. Cluster **3** contains 48-valence electrons and may be considered electron precise [23]. The triangular array of cobalt atoms is best described by an isosceles triangle, where the two longer, pairwise equivalent Co(1)–Co(3) and Co(1)–Co(2) bonds display a mean length of 2.526(5) Å, with the Co(2)–Co(3) vector of 2.3989(6) Å shorter by ca. 0.13 Å. The observed Co–Co bond-length trends in cluster **3** are in keeping with a dppn-induced perturbation that manifests itself in the elongation of the metal–metal bonds associated with the cobalt atom tethered to the chelating dppn ligand. These Co–Co bond distances are well within the range of those distances reported for the parent cluster **1** and related $RCCo_3(CO)_{9-n}P_n$ clusters [24]. The Co(1)–P(1) [2.2544(9) Å] and Co(1)–P(2) [2.1998(9) Å] distances and 88.62(3)° bite angle exhibited by the P(1)–Co(1)–P(2) atoms are in excellent agreement with those values reported in $Ru_3(CO)_8(\mu-dppm)(dppn)$, which represents the only other structurally characterized cluster containing an intact chelating dppn ligand.[6] The three bridging CO groups exhibit highly asymmetric Co–C bond distances, ranging from 1.826(3) Å [Co(1)–C(42)] to 2.029(3) Å [Co(2)–C(43)] but well within the boundaries found for those distances in other carbonyl-bridged derivatives [17a,19,25]. The remaining distances and angles are unremarkable and require no comment.
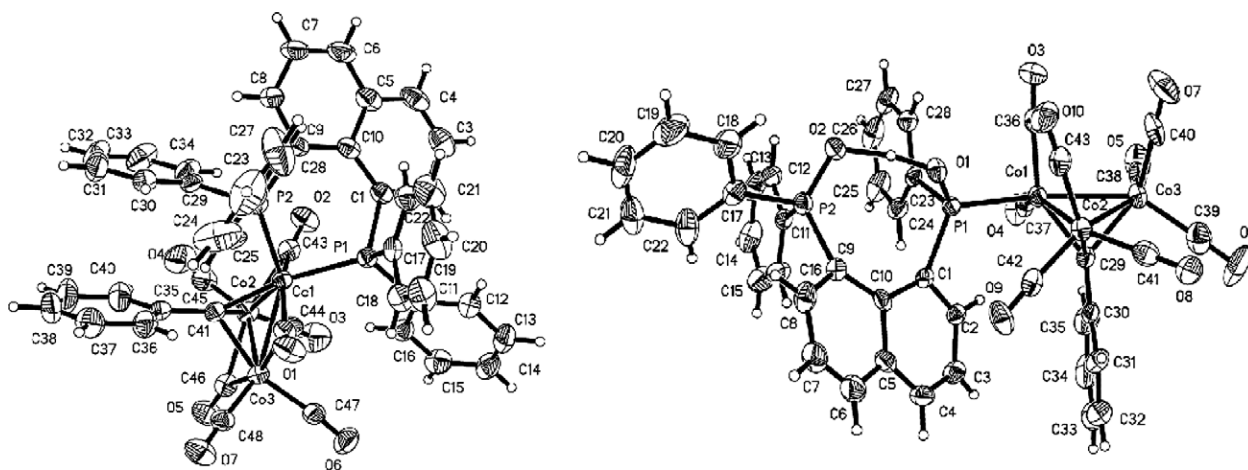


Fig. 1. Thermal ellipsoid plots of the tricobalt clusters **3** (left) and **7** (right) showing the thermal ellipsoids at the 50% probability level.

## 3.2. Thermolysis of HCCo₃(CO)₉ with dppn and formation of clusters 5 and 6

Thermolysis of HCCo₃(CO)₉ (**4**) with a slight excess of dppn at 45 °C leads to CO displacement and formation the clusters HCCo₃(CO)₈[PPh₂(1-C₁₀H₇)] (**5**) and HCCo₃-(CO)₄(μ-CO)₃(dppn) (**6**) in yields comparable to those found in the reactions between cluster **1** and dppn. Both new products were isolated and spectroscopically characterized in solution and by comparison to an independently prepared sample in the case of cluster **5** (vide supra for **2**). The IR spectral data for the methylidyne-capped clusters **5** and **6** parallel those data already described for the benzylidyne-substituted derivatives **2** and **3**, with only a slight exception found in the $^{31}$P NMR spectrum of the dppn-chelated cluster **6**. Here three $^{31}$P resonances were observed at $\delta$ 44.80 (s), 35.00 (s), and 30.05 (s), with the all-terminal carbonyl isomer of HCCo₃(CO)₇(dppn) ($\delta$ 44.80) present in solution as the major species (ca. 95%). Subtle steric effects involving the capping carbyne R group and the ancillary dppn ligand are presumably at play and control the amount of the all-terminal carbonyl isomer in solution. The preparation of other derivatives are planned in order to more fully probe the effect of the R-capping group on the isomeric equilibrium in RCCo₃(CO)₇(dppn).

## 3.3. Reaction of HCCo₃(CO)₉ with dppn using Me₃NO and molecular structure of 7

Treatment of cluster **4** and a slight excess of dppn with Me₃NO led to an immediate reaction and the formation of three products when the reaction solution was monitored by TLC using CH₂Cl₂/hexane (1:3). The two faster moving spots were readily assigned to clusters **5** and **6**, while the slower moving compound **7** ($R_f = 0.30$) represented a compound not observed in the thermolysis reaction of **4** and dppn. All products were separated by column chromatography over silica gel, after which **7** was appropriately characterized in solution by IR and $^{31}$P NMR spectroscopies, mass spectrometry, and X-ray diffraction analysis. **7** was isolated in low yield as an air-sensitive solid having limited thermal stability.

The IR spectrum of compound **7** displayed terminal carbonyl stretching bands at 2075 (s), 2032 (vs), 2018 (vs), and 2010 (sh) cm⁻¹, signaling the presence of a monosubstituted RCCo₃(CO)₈P cluster. The possibility of HCCo₃-(CO)₈($\eta^1$-dppn) representing **7** was immediately eliminated from contention based on $^{31}$P NMR spectroscopy and mass spectrometry. The $^{31}$P NMR spectrum of **7** exhibited a pair of inequivalent singlets $\delta$ 130.49 and 39.62 that indicated the presence of distinctly different phosphine moieties from the coordination of an activated dppn ligand. Both FAB and ESI mass spectral data for **7** revealed parent peaks whose mass was in excess of the simple $\eta^1$-dppn derivative. The unequivocal molecular structure for **7** was determined by X-ray diffraction analysis. The thermal ellipsoid plot of **7** is shown in Fig. 1 (right-hand side). The

structural highlights associated with **7** include (1) the replacement of the carbyne hydrogen atom in **4** by a phenyl group from the dppn ligand and (2) oxidation of the phosphine groups of the dppn ligand to hydroxyl phosphine and phosphine oxide moieties, as shown in the below picture of cluster **7** [26,27].
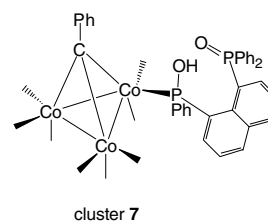


cluster **7**

The mean Co–Co bond distance of 2.475(2) Å in **7** is unremarkable compared to those distances reported in the nonacarbonyl clusters RCCo₃(CO)₉ and simple-substituted Co₃ derivatives [19,24,25]. The coordination of the two-electron hydroxyl phosphine moiety P(1) to the cluster core is supported by conventional electron-counting rules, similarity of the IR spectrum of **7** relative to other RCCo₃(CO)₈P clusters [17], and an observed Co(1)–P(1) bond length of 2.221(2) Å, all of which support the existence of a cobalt–phosphorus single bond [28]. The P(1)–O(1) [1.592(4) Å] and P(2)–O(2) [1.499(4) Å] distances are in accord with P–O and P=O bond character, respectively, and those distances found in other oxidized phosphine compounds [29]. The H(1) atom is covalently bound to O(1) based on a 1.10(7) Å bond length found for the O(1)–H(1) vector and is hydrogen bonded, albeit asymmetrically, to O(2) based on the 1.39(7) Å bond distance found for the H(1)···O(2) atoms. This intramolecular hydrogen bond is essential linear, displaying a bond angle of 175(7)° for the O(1)–H(1)···O(2) linkage [30]. The remaining distances and angles in **7** are unremarkable.

## 3.4. Reactivity studies using clusters 3 and 6

The thermal stability of the dppn-chelated clusters **3** and **6** was next explored given our interest on the decomposition pathways attendant in clusters containing a diphosphine ligand [8,20,31]. Heating solutions of **3** in CH₂Cl₂ or toluene overnight at 55 °C lead to the decomposition of the starting cluster, as assessed by TLC analysis. Here the formation of a black colored material that was irreversibly bound at the origin of the TLC plate was found. Monitoring the same reaction by IR spectroscopy revealed only a slow loss of the carbonyl bands associated with **3**. Thermolysis of cluster **6** under identical conditions affords two new compounds when monitored by TLC. However, attempts to isolate these highly air- and thermally-sensitive products for more thorough characterization were met with very limited success. We were able to record the $^{31}$P NMR spectrum before decomposition intervened and

found two sets of $^{31}$P resonances at $\delta$ 35.30 and 35.73 and $\delta$ 74.57 and 75.25 that are ascribed to phosphine and phosphido moieties, respectively [32]. While the nature of the phosphido moieties cannot be absolutely ascertained at this juncture, cleavage of P–Ph and P–C(naphthyl) bonds in the dppn ligand is fully consistent with the dppn-degradation manifolds promoted by the group 8 clusters $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ [6,7].

## 4. Conclusions

The reaction of the tricobalt clusters $PhCCo_3(CO)_9$ (**1**) and $HCCo_3(CO)_9$ (**4**) with the diphosphine ligand dppn has been investigated. Evidence is presented for both the facile fragmentation of the dppn ligand (clusters **2**, **5**, and **7**) and chelation of the ligand to the cluster frame (clusters **3** and **6**). In the case of cluster **7**, it is clear that the detrimental oxidation of the dppn ligand by $Me_3NO$ and transfer of one of the phenyl groups from the dppn ligand to the cluster complicate and lower the yields of the substitution reaction. Our data on the reactivity of dppn with clusters **1** and **4** are in agreement with those observations of Bruce and co-workers and underscore the inability of the dppn ligand to serve as a stabilizing ligand for multimetallic polyhedra vis-á-vis diphosphine ligands such as dppe and $(Z)$-$Ph_2PCH{=}CHPPh_2$.

## 5. Supplementary material

CCDC 619643 and 619644 contain the supplementary crystallographic data for **3** and **7**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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