# Ligand substitution in the tetrahedrane clusters RCCo$_2$Mo($\eta^5$-indenyl)(CO)$_8$ with 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd): Influence of the carbyne and indenyl ligands on the stability of the substitution products and X-ray diffraction structures of HCCo$_2$Mo($\eta^5$-indenyl)(CO)$_6$($\mu$-bpcd) and CoMo($\eta^5$-indenyl)($\mu$-CPh)(CO)$_2$($\mu$-bpcd)Cl

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## Abstract

The ligand substitution behavior of the tetrahedrane clusters RCCo$_2$Mo($\eta^5$-indenyl)(CO)$_8$ [R = H (**1**); Ph (**3**)] with the diphosphine ligand 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd) has been investigated. Thermolysis of cluster **1** with bpcd in CH$_2$Cl$_2$, 1,2-dichloroethane, or toluene affords the bpcd-bridged cluster HCCo$_2$Mo($\eta^5$-indenyl)(CO)$_6$($\mu$-bpcd) (**2**) as the initial product. Cluster **2** is unstable and undergoes decomposition upon prolonged heating. Unlike cluster **1**, heating the benzylidyne-capped cluster **3** with bpcd in either CH$_2$Cl$_2$ or 1,2-dichloroethane furnishes the thermally unstable mixed-metal cluster Co$_2$MoCp($\eta^5$-indenyl)(CO)$_5$[$\mu_2$,$\eta^2$,$\eta^1$-C(Ph)C═C(PPh$_2$)C(O)CH$_2$C(O)]($\mu$-PPh$_2$) (**4**) and the carbyne-bridged dinuclear compound CoMo($\eta^5$-indenyl)($\mu$-CPh)(CO)$_2$($\mu$-bpcd)Cl (**5**) as the principal reaction products. Thermolysis of **3** with added bpcd in toluene gives **4** as the sole observed product. Compounds **2**, **4**, and **5** have been fully characterized in solution, and the solid-state structures of **2** and **5** have been established by X-ray crystallography. The structure of **2** consists of a triangular Co$_2$Mo core that is capped by the methylidyne group and that contains a bpcd ligand that bridges the two cobalt centers. The X-ray structure of **5** provides support for the partial fragmentation of the original cluster through the loss of a cobalt vertex and the abstraction of a chlorine atom from the chlorinated solvent. The presence of a bridging carbyne moiety that spans the Co–Mo vector and a bpcd ligand that is chelated to the cobalt center by the two phosphine groups and attached to the molybdenum center by the alkene $\pi$ bond of the dione ring are confirmed. The reactivity differences exhibited by clusters **1** and **3** are discussed, and these data are briefly contrasted with that of the cyclopentadienyl counterpart PhCCo$_2$Mo($\eta^5$-Cp)(CO)$_8$.

## 1. Introduction

Our groups have been actively studying the ligand substitution chemistry of the homometallic tetrahedrane clusters RCCo$_3$(CO)$_9$ with the redox-active diphosphine ligands 2,3-bis(diphenylphosphino)maleic anhydride

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(bma) and 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd) for the last several years. While the substitution chemistry exhibited by the two diphosphine ligands with the $RCCo_3(CO)_9$ clusters is identical, the bma-substituted derivatives tend to be more difficult to purify by column chromatography due to the support-promoted hydrolysis of the anhydride moiety. Accordingly, we have begun to devote a greater amount of our attention to the examination of the chemistry associated with the bpcd ligand. These particular ligands, whose structures are depicted below, react with $RCCo_3(CO)_9$ to give the corresponding diphosphine-substituted clusters $RCCo_3(CO)_7(P–P)$ [1–5]. The $RCCo_3(CO)_7(P–P)$ clusters are of interest as they display dynamic, non-dissociative chelate-to-bridge diphosphine isomerization about the cluster polyhedron and facile cluster/diphosphine activation at ambient temperatures. With respect to the latter reactivity, we have found two decomposition manifolds for the $RCCo_3(CO)_7(P–P)$ clusters that are influenced by the nature of the capping carbyne group. Scheme 1 illustrates the two cluster/diphosphine activation reactions for the bpcd-substituted clusters $PhCCo_3(CO)_7(bpcd)$ and $HCCo_3(CO)_7(bpcd)$, where the benzylidene-containing cluster $Co_3(CO)_6$-$[\mu_2,\eta^2,\eta^1-C(Ph)C=C(PPh_2)C(O)CH_2C(O)](\mu_2-PPh_2)$ and the phosphido-bridged cluster $Co_3(CO)_7[\mu_2,\eta^2,\eta^1-P(Ph)C=C(PPh_2)C(O)CH_2C(O)]$ are formed, respectively [3,4]. The former cluster arises from an oxidative cleavage of one of the $Ph_2P–C(dione)$ bonds, followed by the reductive coupling of the $\mu_3$-benzylidyne group with the transient Co–C(dione) moiety, with the latter tricobalt cluster deriving from the loss of one of the phenyl groups from the bpcd ligand and the original methylidyne capping group.
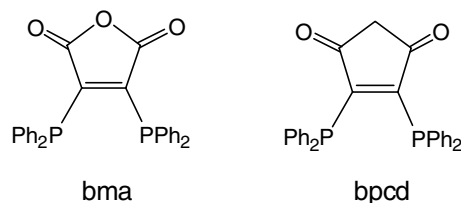
Recently we have published our results on the reaction of the ligands bma and bpcd with the mixed-metal tetrahedrane clusters $RCCo_2NiCp(CO)_6$ (R = H, Ph) and $PhCCo_2MoCp(CO)_8$ [6–9]. Thermolysis of the $Co_2Mo$ cluster with bma leads to the sequential formation of the mono- and bis-phosphido-bridged clusters $Co_2MoCp$-$(CO)_5[\mu_2,\eta^2,\eta^1-C(Ph)C=C(PPh_2)C(O)OC(O)](\mu_2-PPh_2)$ and $Co_2MoCp(CO)_4[\eta^3,\eta^1,\eta^1-C(Ph)C=CC(O)OC(O)](\mu_2-PPh_2)_2$, respectively, as shown in Scheme 2. Of interest to us and unlike the tricobalt clusters, the expected diphosphine-bridged cluster $PhCCo_2MoCp(CO)_6(bma)$ was not observed during the thermolysis reaction, suggesting that the putative $PhCCo_2MoCp(CO)_6(bma)$ cluster undergoes facile CO loss, followed by rapid P–C bond cleavage and reductive coupling of the $\mu_3$-CPh group with the Co–C(maleic anhydride) moiety. The second P–C bond cleavage experienced by $Co_2MoCp(CO)_5[\mu_2,\eta^2,\eta^1-C(Ph)$-$C=C(PPh_2)C(O)OC(O)](\mu_2-PPh_2)$ occurs competitively with that of the first activation step. This represents the first example of a diphosphine ligand that undergoes a double P–C bond activation in this genre of cluster. That the nature of the diphosphine ligand contributes to the observed reactivity in these tetrahedrane clusters is underscored by the synthesis and isolation of the related clusters containing the archetypal diphosphine ligand



bma                    bpcd
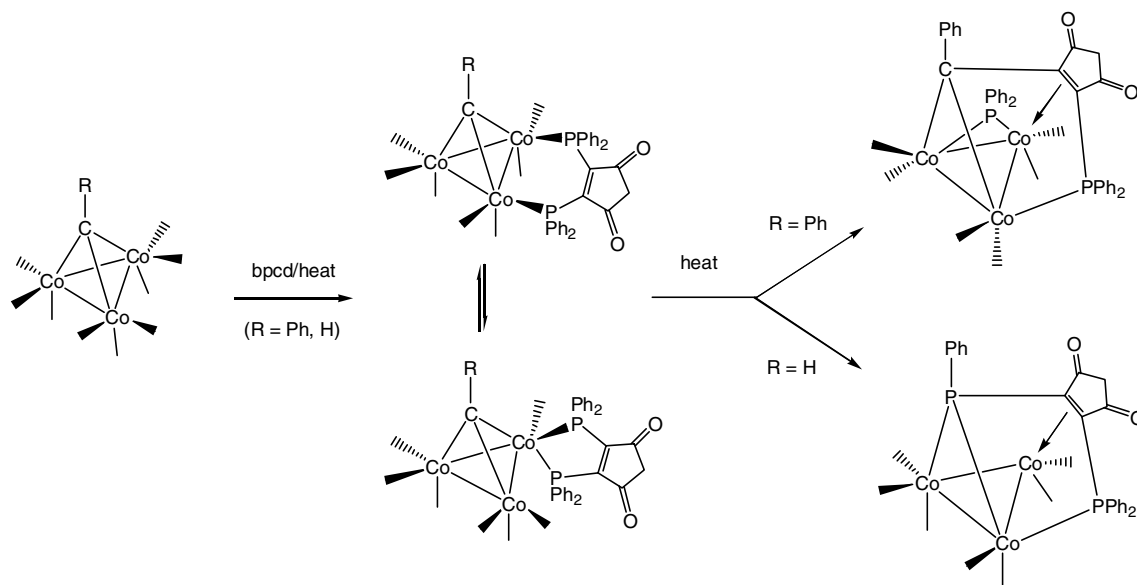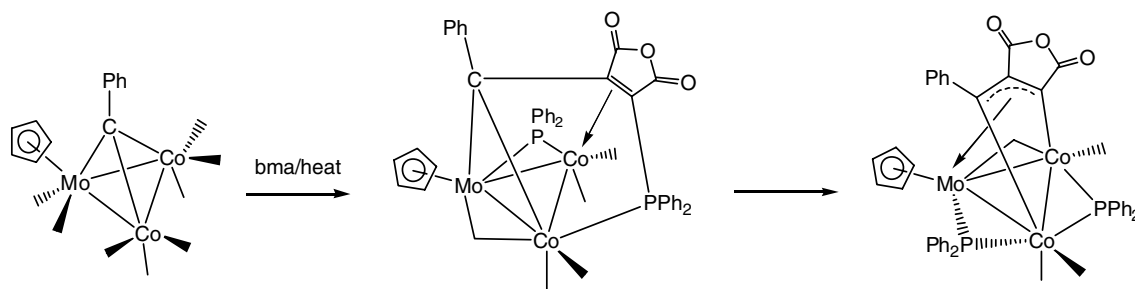


Scheme 1.

Scheme 2.

(Z)-Ph$_2$PCH=CHPPh$_2$. Here the structurally similar clusters RCCo$_3$(CO)$_7$[(Z)-Ph$_2$PCH=CHPPh$_2$] [10] and PhCCo$_2$MoCp(CO)$_6$[(Z)-Ph$_2$PCH=CHPPh$_2$] [11] have been shown to be stable under conditions comparable to those used to promote the transformations illustrated in Schemes 1 and 2.

Given the rich and unexpected reaction chemistry in the thermolysis of PhCCo$_2$MoCp(CO)$_8$ with bma, we wished to next probe the effect, if any, that the ancillary cyclopentadienyl and the carbyne ligands have on the substitution reaction. Fortunately for us the syntheses for the mixed-metal clusters RCCo$_2$Mo($\eta^5$-indenyl)(CO)$_8$ [R = H (1); Ph (3)] have recently been published [12], allowing us to extend our ligand substitution studies to clusters 1 and 3. Herein we report our results on the thermolysis reaction between the ligand bpcd and clusters 1 and 3. The resulting products HCCo$_2$Mo($\eta^5$-indenyl)(CO)$_6$($\mu$-bpcd) (2), Co$_2$-MoCp($\eta^5$-indenyl)(CO)$_5$[$\mu_2$,$\eta^2$,$\eta^1$C(Ph)C=C(PPh$_2$)C(O)-CH$_2$C(O)]($\mu$-PPh$_2$) (4), and CoMo($\eta^5$-indenyl)($\mu$-CPh)-(CO)$_2$($\mu$-bpcd)Cl (5) have been isolated and fully characterized in solution by IR and NMR spectroscopies and by X-ray crystallography in the case of compounds 2 and 5. The reactivity differences between PhCCo$_2$MoCp(CO)$_8$ and the corresponding indenyl-substituted clusters 1 and 3 are discussed.

## 2. Experimental

### 2.1. General methods

The starting clusters HCCo$_2$Mo($\eta^5$-indenyl)(CO)$_8$ and PhCCo$_2$Mo($\eta^5$-indenyl)(CO)$_8$ were synthesized from [($\eta^5$-indenyl)Mo(CO)$_3$][K] and the tricobalt clusters HCCCo$_3$(CO)$_9$ and PhCCo$_3$(CO)$_9$, respectively [12]. The latter tricobalt clusters were synthesized from Co$_2$(CO)$_8$ (Strem Chemical Co.) [13], while the bpcd ligand was prepared from 4,5-dichloro-4-cyclopenten-1,3-dione and Ph$_2$PSiMe$_3$ [14,15]. All reaction and NMR solvents were distilled under argon from a suitable drying agent and stored in Schlenk storage vessels [16]. 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

$^{31}$P NMR spectra were recorded on a Varian 300-VXR spectrometer at 121 MHz. The $^{31}$P NMR data were acquired in the proton-decoupled mode and are reported relative to external H$_3$PO$_4$, taken to have $\delta = 0$.

### 2.2. Thermolysis of HCCo$_2$Mo($\eta^5$-indenyl)(CO)$_8$ (1) in the presence of bpcd

To a 100-mL Schlenk vessel under argon was added 0.10 g (0.21 mmol) of HCCo$_2$Mo($\eta^5$-indenyl)(CO)$_8$, followed by 30 mL of CH$_2$Cl$_2$ and then 96 mg (0.21 mmol) of bpcd. The vessel was next sealed and heated at 55 °C in a thermostated circulating bath. The progress of the reaction was monitored by TLC, which confirmed the complete consumption of the starting cluster after 2 h and the formation of a single green spot ($R_f = 0.60$ in CH$_2$Cl$_2$) corresponding to HCCo$_2$Mo($\eta^5$-indenyl)(CO)$_6$(bpcd) (2). After the solvent was removed under vacuum, cluster 2 was isolated by column chromatography over silica gel using CH$_2$Cl$_2$/hexane (3:2) as the eluent. The analytical sample and single crystals of 2 suitable for X-ray diffraction analysis were grown from a CH$_2$Cl$_2$ solution containing 2 that was layered with hexane and placed in the refrigerator at 0 °C. Yield of 2: 83% (0.17 g). IR (CH$_2$Cl$_2$): $\nu$(CO) 2023 (s), 1990 (vs), 1967 (m), 1901 (m), 1747 (w, sym dione), 1716 (s, antisym dione) cm$^{-1}$. $^{31}$P NMR (CDCl$_3$; 298 K): $\delta$ 29.70 (br, s). Anal. Calc. (found) for C$_{45}$H$_{30}$Co$_2$-MoO$_8$P$_2 \cdot$ 1/4CH$_2$Cl$_2$: C, 54.46 (54.62); H 3.06 (3.66).

### 2.3. Thermolysis of PhCCo$_2$Mo($\eta^5$-indenyl)(CO)$_8$ (3) in the presence of bpcd

#### 2.3.1. CH$_2$Cl$_2$ solvent

To 0.10 g (0.18 mmol) of PhCCo$_2$Mo($\eta^5$-indenyl)(CO)$_8$ in a medium-sized Schlenk tube was added 84 mg (0.18 mmol) of bpcd and then 30 mL of CH$_2$Cl$_2$, after which the vessel was sealed and heated at 55 °C in a thermostated bath. TLC examination (in CH$_2$Cl$_2$) of the reaction solution after 2 h revealed the presence of green ($R_f = 0.70$) and orange ($R_f = 0.10$) spots belonging to the trinuclear cluster Co$_2$MoCp($\eta^5$-indenyl)(CO)$_5$[$\mu_2$,$\eta^2$,$\eta^1$-C(Ph)C=C(PPh$_2$)C(O)CH$_2$C(O)]($\mu$-PPh$_2$) (4) and the carbyne-bridged compound CoMo($\eta^5$-indenyl)-

($\mu$-CPh)(CO)$_2$($\mu$-bpcd)Cl (**5**), respectively, in addition to unreacted **3** and bpcd. Heating was continued until the two starting materials were completely consumed (ca. 6 h), at which time the solution was allowed to cool and the reaction solvent removed under vacuum. The reaction products were next separated by column chromatography over silica gel using CH$_2$Cl$_2$/hexane (3:2) as the eluent for cluster **4**, after which changing the eluent to CH$_2$Cl$_2$/ethyl acetate (9:1) furnished compound **5**. Since repeated attempts to secure a suitable microanalysis on **4** were unsuccessful due do its thermal instability, the full characterization of cluster **4** was limited to solution methods. Recrystallization of **5** from EtOAc and benzene afforded the sample of **5** that was used in the combustion analysis. Yield of **4**: 39% (70 mg). IR (CH$_2$Cl$_2$): $\nu$(CO) 2045 (s), 2023 (vs), 2007 (m), 1991 (m), 1793 (m, $\mu_2$-CO), 1711 (m, sym dione), 1683 (s, antisym dione) cm$^{-1}$. $^{31}$P NMR (CDCl$_3$; 298 K): $\delta$ 188.19 (b, s, phosphido), 28.60 (b, s, phosphine). Yield of **5**: 37% (60 mg). IR (CH$_2$Cl$_2$): $\nu$(CO) 2023 (vs), 1977 (vs), 1709 (s, sym dione), 1676 (s, antisym dione) cm$^{-1}$. $^{31}$P NMR (CDCl$_3$; 298 K): $\delta$ 54.08 (d, $^2J_{P-P} = 20$ Hz), 35.30 (d, $^2J_{P-P} = 20$ Hz). Anal. Calc. (found) for C$_{47}$H$_{34}$ClCoMoO$_4$P$_2 \cdot$ EtOAc $\cdot$ 1/2C$_6$H$_6$: C, 62.43 (62.57); H 4.34 (5.08).

### 2.3.2. Toluene solvent

This reaction was carried out exactly as described above using CH$_2$Cl$_2$, except with toluene as the solvent. Heating a toluene solution containing cluster **3** and an equimolar amount of bpcd proceeds to completion at 55 °C over the course of ca. 8 h. Monitoring the reaction solution revealed cluster **4** as the only product and extensive decomposition based on the material that remained at the origin of the TLC plate. Cluster **4** was isolated as described above and found to exhibit identical spectroscopic properties as the material prepared in CH$_2$Cl$_2$ solvent.

### 2.4. X-ray crystallographic data

Crystals of compounds and **2** and **5**, both of which were obtained as the CH$_2$Cl$_2$ solvate, suitable for X-ray analysis were grown from CH$_2$Cl$_2$ containing each compound 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 **2** $\cdot$ CH$_2$Cl$_2$ and **5** $\cdot$ CH$_2$Cl$_2$. 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 [17], and the structures were solved and refined using the SHELXTL program package [18]. The molecular structure of **2** $\cdot$ **CH$_2$Cl$_2$** was checked by using PLATON [19], 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.

Table 1
X-ray crystallographic data and processing parameters for the compounds **2** $\cdot$ CH$_2$Cl$_2$ and **5** $\cdot$ CH$_2$Cl$_2$

| Compound | **2** $\cdot$ CH$_2$Cl$_2$ | **5** $\cdot$ CH$_2$Cl$_2$ |
|---|---|---|
| CCDC entry number | 613422 | 613421 |
| Space group | Triclinic, $P\bar{1}$ | Monoclinic, $P2(1)/c$ |
| $a$ (Å) | 12.054(4) | 18.837(2) |
| $b$ (Å) | 12.955(4) | 12.328(1) |
| $c$ (Å) | 15.245(5) | 18.193(2) |
| $\alpha$ (°) | 104.367(6) | |
| $\beta$ (°) | 108.782(6) | 100.471(2) |
| $\gamma$ (°) | 96.692(6) | |
| $V$ (Å$^3$) | 2133(1) | 4154.5(8) |
| Molecular formula | C$_{45}$H$_{30}$Co$_2$MoO$_8$P$_2 \cdot$ CH$_2$Cl$_2$ | C$_{47}$H$_{34}$ClCoMoO$_4$P$_2 \cdot$ CH$_2$Cl$_2$ |
| Formula weight | 1059.36 | 999.93 |
| Formula units per cell ($Z$) | 2 | 4 |
| $D_{calcd}$ (Mg/m$^3$) | 1.650 | 1.599 |
| $\lambda$ (Mo K$\alpha$) (Å) | 0.71073 | 0.71073 |
| Absorption coefficient (mm$^{-1}$) | 1.313 | 1.018 |
| Maximum/minimum transmission | 0.8284/0.6218 | 0.7966/0.6944 |
| Total reflections | 17523 | 33229 |
| Independent reflections | 9349 | 8981 |
| Data/restraints/parameters | 9349/0/533 | 8981/0/532 |
| $R$ | 0.0546 | 0.0674 |
| $R_w$ | 0.1127 | 0.0705 |
| Goodness-of-fit on $F^2$ | 0.963 | 0.920 |
| 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$^3$) | 1.074, −1.024 | 0.914, −0.871 |

In the case of compound **5** $\cdot$ CH$_2$Cl$_2$, the small, amorphous looking crystal (0.15 × 0.06 × 0.05 mm$^3$) that was selected yielded good diffraction spots. The unit cell dimensions appeared to be monoclinic, but after processing with SAINT the axes were rearranged and XPREP suggested a triclinic space group. Attempts to solve the structure in the monoclinic space group $P2(1)/c$ were not successful. The structure for **5** $\cdot$ CH$_2$Cl$_2$ was solved in $P\bar{1}$ with two independent molecules per cell and refined to $R = 0.044$ with the thermal parameters of two atoms not refining satisfactorily. PLATON indicated that the structure should be monoclinic with the space group $P2(1)/c$. The PLATON transformation was applied and the structure refined to $R = 0.0674$ with satisfactory thermal parameters and the largest residual peak being 0.914 e/Å$^3$. The application of SADABS and face-indexed absorption corrections did not significantly change $R$, $R_{merge}$, or the thermal parameters.

### 3. Results and discussion

### 3.1. Synthesis and molecular structure of HCCo$_2$Mo($\eta^5$-indenyl)(CO)$_6$(bpcd) (**2**)

The methylidyne-capped cluster HCCo$_2$Mo($\eta^5$-indenyl)(CO)$_8$ (**1**) reacts cleanly and rapidly with bpcd in

Table 2
Selected bond distances (Å) and angles (°) for the compounds **2** · CH$_2$Cl$_2$
and **5** · CH$_2$Cl$_2$[a]

**Compound 2 · CH$_2$Cl$_2$**

*Bond distances*

| | | | |
|---|---|---|---|
| Co(1)–Mo(1) | 2.749(1) | Co(2)–Mo(1) | 2.7568(9) |
| Co(1)–Co(2) | 2.522(1) | Mo(1)–C(30) | 2.444(4) |
| Mo(1)–C(35) | 2.429(5) | Mo(1)–C(36) | 2.331(4) |
| Mo(1)–C(37) | 2.325(5) | Mo(1)–C(38) | 2.331(4) |
| Mo(1)–C(43) | 1.953(5) | Mo(1)–C(44) | 1.952(5) |
| Mo(1)–C(45) | 2.080(5) | Co(1)–P(2) | 2.198(2) |
| Co(2)–P(1) | 2.201(1) | Co(1)–C(39) | 1.752(5) |
| Co(1)–C(40) | 1.806(5) | Co(1)–C(45) | 1.881(5) |
| Co(2)–C(41) | 1.767(5) | Co(2)–C(41) | 1.803(5) |
| Co(2)–C(45) | 1.874(4) | C(1)–C(5) | 1.355(6) |
| C(1)–C(2) | 1.508(6) | C(2)–C(3) | 1.507(7) |
| C(3)–C(4) | 1.514(7) | C(4)–C(5) | 1.503(6) |

*Bond angles*

| | | | |
|---|---|---|---|
| P(2)–Co(1)–Co(2) | 103.92(4) | P(2)–Co(1)–Mo(1) | 154.85(4) |
| P(1)–Co(2)–Co(1) | 101.66(4) | P(1)–Co(2)–Mo(1) | 144.18(4) |
| C(1)–P(1)–Co(2) | 115.3(1) | C(5)–P(2)–Co(1) | 118.5(2) |
| C(39)–Co(1)–C(45) | 102.7(2) | C(40)–Co(1)–C(45) | 139.8(2) |
| C(45)–Co(1)–P(2) | 105.9(2) | C(42)–Co(2)–C(45) | 105.2(2) |
| C(41)–Co(2)–C(45) | 144.2(2) | C(45)–Co(2)–P(1) | 96.0(2) |
| C(44)–Mo(1)–C(45) | 110.7(2) | C(43)–Mo(1)–C(45) | 111.5(2) |
| O(3)–C(39)–Co(1) | 177.6(5) | O(4)–C(40)–Co(1) | 176.9(5) |
| O(5)–C(41)–Co(2) | 179.0(5) | O(6)–C(42)–Co(2) | 177.1(5) |
| O(7)–C(43)–Mo(1) | 171.4(5) | O(8)–C(44)–Mo(1) | 171.8(4) |

**Compound 5 · CH$_2$Cl$_2$**

*Bond distances*

| | | | |
|---|---|---|---|
| Mo(1)–Co(1) | 2.789(1) | Mo(1)–Cl(1) | 2.446(2) |
| Mo(1)–C(1) | 2.249(6) | Mo(1)–C(2) | 2.230(6) |
| Mo(1)–C(30) | 2.617(7) | Mo(1)–C(31) | 2.381(6) |
| Mo(1)–C(32) | 2.331(6) | Mo(1)–C(33) | 2.336(6) |
| Mo(1)–C(34) | 2.573(6) | Mo(1)–C(39) | 1.856(6) |
| Co(1)–P(1) | 2.219(2) | Co(1)–P(2) | 2.217(2) |
| Co(1)–C(39) | 1.974(6) | Co(1)–C(46) | 1.763(7) |
| Co(1)–C(47) | 1.746(7) | C(1)–C(2) | 1.497(8) |
| C(1)–C(5) | 1.508(8) | C(2)–C(3) | 1.472(8) |
| C(3)–C(4) | 1.512(8) | C(4)–C(5) | 1.514(8) |

*Bond angles*

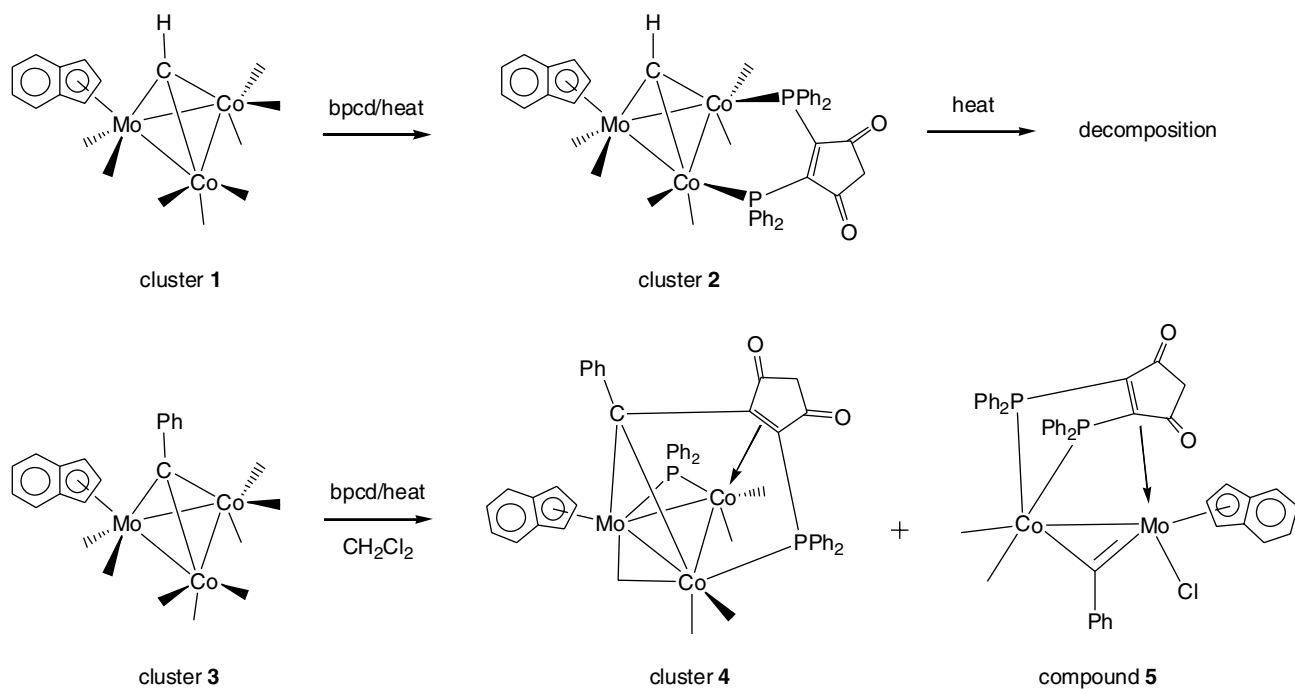| | | | |
|---|---|---|---|
| C(2)–Mo(1)–C(1) | 39.1(2) | C(39)–Mo(1)–Cl(1) | 98.1(2) |
| C(2)–Mo(1)–Cl(1) | 83.4(2) | C(1)–Mo(1)–Cl(1) | 114.3(2) |
| Cl(1)–Mo(1)–Co(1) | 129.68(5) | C(47)–Co(1)–C(46) | 94.4(3) |
| C(47)–Co(1)–C(39) | 87.6(3) | C(46)–Co(1)–C(39) | 118.7(3) |
| C(47)–Co(1)–P(2) | 97.6(2) | C(46)–Co(1)–P(2) | 119.7(2) |
| C(39)–Co(1)–P(2) | 120.7(2) | C(47)–Co(1)–P(1) | 168.2(2) |
| C(46)–Co(1)–P(1) | 93.5(2) | C(39)–Co(1)–P(1) | 80.9(2) |
| P(2)–Co(1)–P(1) | 86.10(7) | C(47)–Co(1)–Mo(1) | 94.6(2) |
| C(46)–Co(1)–Mo(1) | 157.8(2) | P(2)–Co(1)–Mo(1) | 79.12(5) |
| P(1)–Co(1)–Mo(1) | 75.01(5) | C(40)–C(39)–Mo(1) | 141.1(4) |
| C(40)–C(39)–Co(1) | 124.4(4) | Mo(1)–C(39)–Co(1) | 93.4(3) |
| O(3)–C(46)–Co(1) | 179.0(6) | O(4)–C(47)–Co(1) | 176.5(6) |

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.
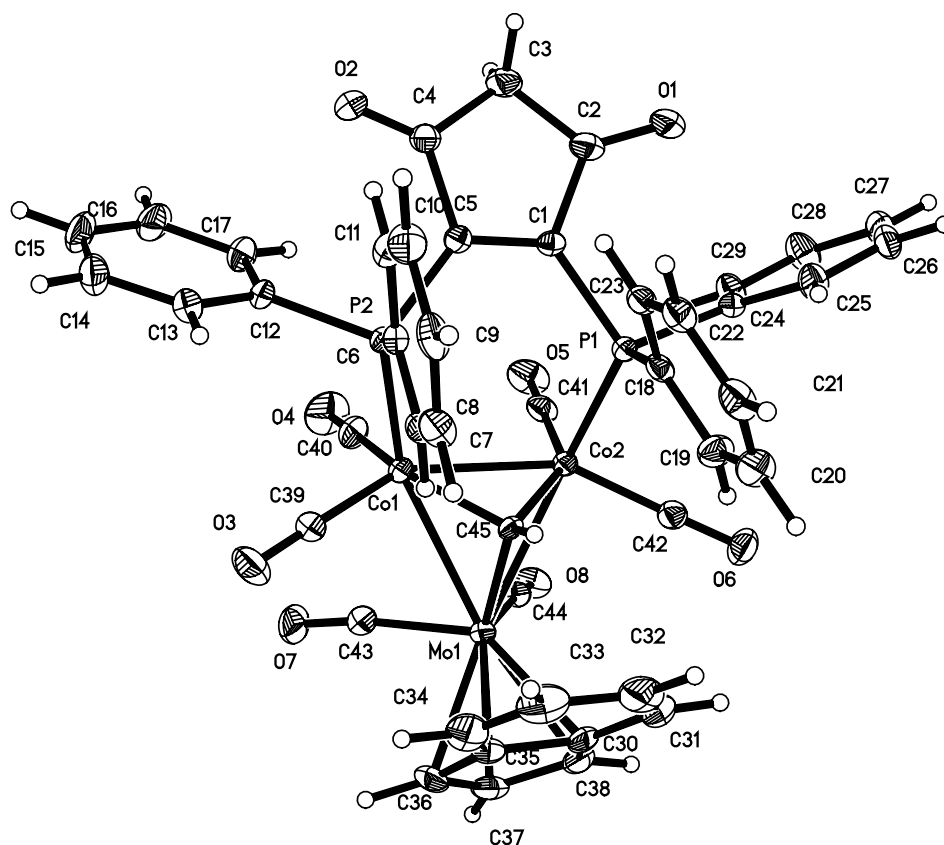
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sis reactions were carried out in 1,2-dichloroethane (DCE) or toluene solvents. Cluster **2** was isolated by column chromatography and characterized by spectroscopic methods, X-ray crystallography, and elemental analysis. **2** appears to is stable in the solid state for a period of months, with solutions of **2** that have been exposed to the atmosphere exhibiting noticeable decomposition after several hours. The top portion of Scheme 3 depicts the reaction that affords cluster **2**.

The IR spectrum of HCCo$_2$Mo($\eta^5$-indenyl)(CO)$_6$(bpcd) in CH$_2$Cl$_2$ shows four terminal carbonyl stretching bands at 2023 (s), 1990 (vs), 1967 (m) and 1901 (m) cm$^{-1}$, and a pair of lower frequency carbonyl bands at 1747 (w) and 1716 (s) cm$^{-1}$. These latter two bands are readily assignable to the vibrationally coupled C=O groups of the dione ring [20]. The $^{31}$P NMR spectrum of **2** displays a single $^{31}$P resonance at $\delta$ 29.70 that is consistent with the presence of a bridging bpcd and in agreement with those chemical shifts reported by us in other bpcd-bridged clusters [3,4,21]. Unfortunately the $^{31}$P NMR data do allow us to unequivocally assign the metal–metal bond that is bridged by the bpcd ligand in cluster **2**.

The coordination mode adopted by the bpcd ligand in cluster **2** was established by X-ray crystallography. The thermal ellipsoid plot of cluster **2** · CH$_2$Cl$_2$ shown in Fig. 1 confirms that the diphosphine ligand bridges the two cobalt centers through the formal replacement of two basal CO groups in the parent cluster **1**. Cluster **2** contains 48-valence electrons and represents the first structurally characterized phosphine-substituted cluster derived from **1**. The dihedral angle formed by the metallic plane and the plane coincident with the indenyl ring is 86.40(4)°, and the indenyl ligand displays a *syn* or proximal disposition relative to the capping methylidyne ligand. The two ancillary phenyl groups defined by the atoms C(6)–C(11) and C(18)–C(23) exhibit a pseudo axial disposition relative to the cyclohexane-like boat conformation that is defined by the atoms P(1)–C(1)–C(5)–P(2)–Co(1)–Co(2). It is important to note that these same two phenyl rings are oriented *syn* to the $\mu_3$-CH moiety, which in turn leads to a sterically shielded methylidyne ligand. This adoption of mutually *cis* or *syn* phenyl and indenyl groups relative to the carbyne cap moiety accounts nicely for our failure to observe the analogous bpcd-bridged cluster based on **3** (vide infra). The Co(1)–Mo(1) [2.749(1) Å], Co(2)–Mo(1) [2.7568(9) Å], and Co(1)–Co(2) [2.522(1) Å] bond distances parallel those distances found in other Co$_2$Mo clusters [11,12,22,23]. The five Mo–C bond distances associated with the indenyl ring are unexceptional with those distances reported for the parent cluster **3** and other related indenyl-substituted molybdenum compounds [24]. The six CO groups in **2** are all linear, ranging from 171.4(5)° [O(7)–C(43)–Mo(1)] to 179.0(5)° [O(5)–C(41)–Co(2)]. The remaining bond distances and angles in cluster **2** · CH$_2$Cl$_2$ are unremarkable and require no comment.

CH$_2$Cl$_2$ at 55 °C to furnish the bpcd-substituted cluster HCCo$_2$Mo($\eta^5$-indenyl)(CO)$_6$(bpcd) (**2**) as the sole observable product. No reaction was observed when cluster **1** and bpcd were stirred at room temperature, and cluster **2** was also obtained as the exclusive product when the thermoly-

Scheme 3.



Fig. 1. Thermal ellipsoid plot of HCCo$_2$Mo($\eta^5$-indenyl)(CO)$_6$(bpcd) (2 · CH$_2$Cl$_2$) showing the thermal ellipsoids at the 50% probability level.

*3.2. Reaction of bpcd with PhCCo₂Mo(η⁵-indenyl)(CO)₈ (3) and X-ray structure of CoMo(η⁵-indenyl)(μ-CPh)- (CO)₂(μ-bpcd)Cl (5)*

Unlike the thermolysis reaction between the methylidyne-capped cluster **1** and bpcd that proceeds by the facile loss of two CO groups and formation of the bpcd-bridged cluster **2**, the benzylidyne-capped derivative **3** reacts with bpcd in $CH_2Cl_2$ under analogous conditions to furnish two products, as assessed by TLC analysis. Identical reaction products were observed when DCE was employed as the reaction solvent. The reaction between cluster **3** and bpcd is noticeably slower than the corresponding reaction involving cluster **1** given the fact that, under analogous conditions, the time for the complete consumption of **3** and bpcd was 2–3 times longer than that for **1** and bpcd. The two products from the reaction of **3** with bpcd were subsequently isolated by column chromatography over silica gel. Here a green spot corresponding to **4** was isolated by using $CH_2Cl_2$/hexane (3:2) as the eluent and a slower moving orange spot for **5** was obtained when the polarity of the mobile phase was increased by using a mixture of $CH_2Cl_2$/ethyl acetate (9:1). Both new compounds were fully characterized in solution by IR and ³¹P NMR spectroscopies and X-ray crystallography. The bottom portion of Scheme 3 illustrates the reaction between cluster **3** and bpcd in $CH_2Cl_2$ solvent.

Due to its thermal instability, cluster **4** was characterized in solution by IR and ³¹P NMR spectroscopies and not by combustion analysis. The IR spectrum for **4** exhibits terminal *v*(CO) bands at 2045 (s), 2023 (vs), 2007 (m), 1991 (m) cm⁻¹, along with a bridging CO group at 1793 (m) cm⁻¹. These frequencies and the spectral pattern are very different from that of the bpcd-bridged cluster **2** and the related cluster PhCCo₂MoCp(CO)₆[(Z)-Ph₂PCH=CHPPh₂] [11], immediately ruling out a bpcd-bridged cluster based on **3**. The IR spectrum of **4** does, however, display a close resemblance to the phosphido-bridged cluster Co₂MoCp-(CO)₅[μ₂,η²,η¹-C(Ph)C=C(PPh₂)C(O)OC(O)](μ₂-PPh₂) [9]. The two carbonyl groups belonging to the dione moiety exhibit medium intensity bands at 1711 and 1683 cm⁻¹, which are pairwise shifted by ca. 35 cm⁻¹ to lower energy due to π coordination of the alkene bond of the done moiety to one of the cobalt atoms [25]. The ³¹P NMR spectrum revealed two broad singlets at δ 188.19 and 28.60 that are ascribed to the bridging phosphido and a phosphine groups, respectively. The recorded ³¹P chemical shifts for cluster **4** compare favorably to the reported ³¹P NMR data for the corresponding cyclopentadienyl-substituted phosphido-bridged cluster Co₂MoCp(CO)₅[μ₂,η²,η¹-C(Ph)C=C(PPh₂)C(O)OC(O)](μ₂-PPh₂) that displays two ³¹P singlets at δ 179.59 (μ₂-PPh₂) and 21.29 (phosphine) [9]. In an attempt to unequivocally establish the identity of cluster **4**, we resorted to X-ray crystallography. Unfortunately, publication-quality X-ray crystals of **4** could not be obtained despite repeated attempts to grow crystals of **4** in a variety of solvents and under different conditions. However, we were able to grow one poor quality crystal that afforded a structure consistent with the proposed identity for cluster **4**. The structural composition of **4** is similar in terms of its ligand binding with that of the cyclopentadienyl relative Co₂MoCp(CO)₅[μ₂,η²,η¹-C(Ph)C=C (PPh₂)C(O)OC(O)](μ₂-PPh₂) [9,26]. Finally, cluster **4** is thermally sensitive, decomposing slowly at room temperature under argon over the course of several days. The observed decomposition of cluster **4** stands in contrast to that of the phosphido-bridged cluster Co₂MoCp(CO)₅-[μ₂,η²,η¹-C(Ph)C=C(PPh₂)C(O)OC(O)](μ₂-PPh₂), which transforms into the bis(phosphido) cluster Co₂MoCp-(CO)₄[η³,η¹,η¹-C(Ph)C=CC(O)OC(O)](μ₂-PPh₂)₂ on gentle heating.

The IR spectrum of compound **5** displayed two terminal carbonyl stretching bands at 2023 (vs) and 1977 (vs) cm⁻¹, along with two lower frequency *v*(CO) bands at 1709 (s) and 1676 (s) cm⁻¹ belonging to the symmetric and antisymmetric dione C=O stretches, respectively [20]. In comparison to the IR data recorded for clusters **2** and **4**, the spectral simplicity exhibited by **5** provided the first evidence for the fragmentation of the Co₂Mo core. The ³¹P NMR spectrum of **5** exhibits a pair of inequivalent doublets at δ 54.08 and 35.30 that are in keeping with an intact chelating bpcd ligand [27]. The molecular structure for **5** was determined by X-ray diffraction analysis. The thermal ellipsoid plot of **5** · $CH_2Cl_2$ is shown in Fig. 2. The structure of compound **5** · $CH_2Cl_2$ is best described as an electronically saturated dimer that possesses 34-valence electrons. The structural highlights associated with **5** · $CH_2Cl_2$ include: (1) a bpcd ligand that functions as a six-electron donor that is chelated to the cobalt center by the two phosphine moieties and π bound through the C=C bond of the dione ring to the molybdenum center, and (2) the presence of a bridging benzylidyne moiety that spans the Co–Mo vector. A check of the Cambridge Structural Database reveals that **5** represents the first crystallographically characterized benzylidyne-bridged CoMo dinuclear compound. The Co(1)–Mo(1) bond distance of 2.789(1) Å agrees well with those Co–Mo distances in simple ligand-bridged dinuclear compounds [28] and CoMo polynuclear clusters [9,11,22,21,29]. The Co(1)–C(39) and Mo(1)–C(39) bond distances of 1.974(6) and 1.856(6) Å, respectively, and the 93.4(3)° for the Co(1)–C(39)–Mo(1) atoms are consistent with bridging of the Co–Mo bond by the benzylidyne moiety. The P(1)–Co(1)–P(2) bond angle of 86.10(7)° and the C(1)–C(2) bond length of 1.497(8) Å are in good agreement with those values found in related bpcd-substituted compounds prepared by us [25a,25b]. The Mo–C bond distances associated with the indenyl ring are unexceptional with respect to the parent cluster **3** [12], as are the remaining bond distances and angles.

The confirmation of a chlorine group in the solid-state structure of **5** is of interest because the chlorine must originate from the $CH_2Cl_2$ solvent. The thermolysis reaction between cluster **3** and bpcd was also studied with DCE as a solvent. Heating a DCE solution containing **3** and
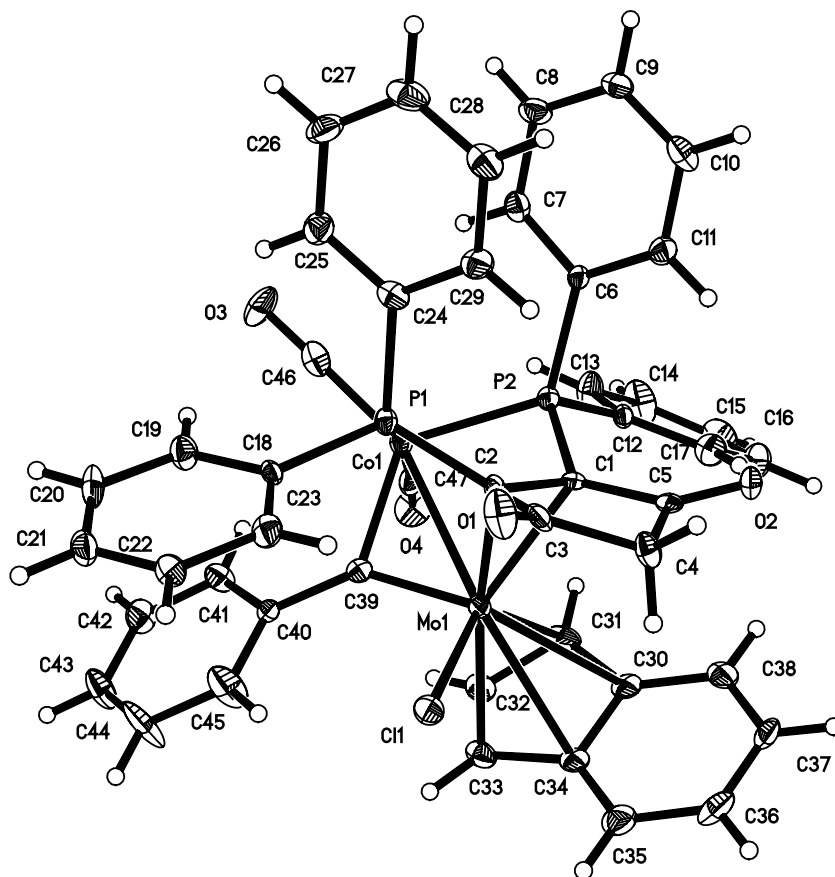
Fig. 2. Thermal ellipsoid plot of CoMo($\eta^5$-indenyl)($\mu$-CPh)(CO)$_2$($\mu$-bpcd)Cl (5 · CH$_2$Cl$_2$) showing the thermal ellipsoids at the 50% probability level.

bpcd at 55 °C afforded a 1:1 mixture of cluster **4** and compound **5**. Carrying the same thermolysis out in toluene furnished only cluster **4**, along with considerable decomposition, as assessed by TLC analysis. While not observed, a plausible intermediate en route to compound **5** is the molybdenum-centered radical shown below, which could afford compound **5** through the abstraction of a chlorine atom from the solvents CH$_2$Cl$_2$ and DCE.
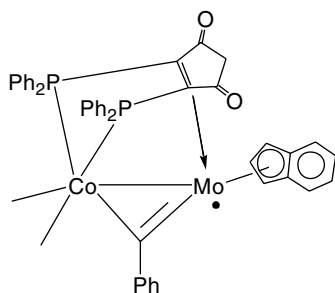


### 4. Conclusions

The reaction between the methylidyne-capped cluster HCCo$_2$Mo($\eta^5$-indenyl)(CO)$_8$ (**1**) and bpcd gives the cluster HCCo$_2$Mo($\eta^5$-indenyl)(CO)$_6$($\mu$-bpcd) (**2**) in high yield. X-ray diffraction analysis has confirmed the bridging coordination mode adopted by the ancillary bpcd ligand across the Co–Co bond in **2**. Heating the corresponding benzylidyne-capped cluster PhCCo$_2$Mo($\eta^5$-indenyl)(CO)$_8$ (**3**) with bpcd in either CH$_2$Cl$_2$ or DCE solvent affords the thermally unstable cluster Co$_2$MoCp($\eta^5$-indenyl)-(CO)$_5$[$\mu_2$,$\eta^2$,$\eta^1$-C(Ph)C=C(PPh$_2$)C(O)CH$_2$C(O)]($\mu$-PPh$_2$) (**4**) and the carbyne-bridged compound CoMo($\eta^5$-indenyl)($\mu$-CPh)(CO)$_2$($\mu$-bpcd)Cl (**5**). Unlike the reaction between cluster **1** and bpcd, no evidence for the formation of the bpcd-bridged cluster PhCCo$_2$Mo($\eta^5$-indenyl)(CO)$_6$($\mu$-bpcd) was found. Since PhCCo$_2$Mo($\eta^5$-indenyl)(CO)$_6$($\mu$-bpcd) is the logical precursor to cluster **4**, this suggests that the bpcd-bridged cluster is unstable and decomposes, in part, to furnish cluster **4**. The identities of compounds **4** and **5** have been determined by solution spectroscopic methods and X-ray diffraction analyses.

**Appendix A. Supplementary data**

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 613422 for **2 · CH$_2$Cl$_2$** and 613421 for **5 · CH$_2$Cl$_2$**. Copies of these data may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 366 033, e-mail: deposit@ccdc.ac.uk or on the web www: http://www.ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.08.095.

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