

Ligand substitution in the tetrahedrane clusters $\text{RCCo}_2\text{Mo}(\eta^5\text{-indenyl})(\text{CO})_8$ 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 $\text{HCCo}_2\text{Mo}(\eta^5\text{-indenyl})(\text{CO})_6(\mu\text{-bpcd})$ and $\text{CoMo}(\eta^5\text{-indenyl})(\mu\text{-CPh})(\text{CO})_2(\mu\text{-bpcd})\text{Cl}$

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Abstract

The ligand substitution behavior of the tetrahedrane clusters $\text{RCCo}_2\text{Mo}(\eta^5\text{-indenyl})(\text{CO})_8$ [$\text{R} = \text{H}$ (**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_2Cl_2 , 1,2-dichloroethane, or toluene affords the bpcd-bridged cluster $\text{HCCo}_2\text{Mo}(\eta^5\text{-indenyl})(\text{CO})_6(\mu\text{-bpcd})$ (**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_2Cl_2 or 1,2-dichloroethane furnishes the thermally unstable mixed-metal cluster $\text{Co}_2\text{MoCp}(\eta^5\text{-indenyl})(\text{CO})_5[\mu_2, \eta^2, \eta^1\text{-C(Ph)C=C(PPh}_2\text{)C(O)CH}_2\text{C(O)}](\mu\text{-PPh}_2)$ (**4**) and the carbyne-bridged dinuclear compound $\text{CoMo}(\eta^5\text{-indenyl})(\mu\text{-CPh})(\text{CO})_2(\mu\text{-bpcd})\text{Cl}$ (**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_2Mo 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 π 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 $\text{PhCCo}_2\text{Mo}(\eta^5\text{-Cp})(\text{CO})_8$.

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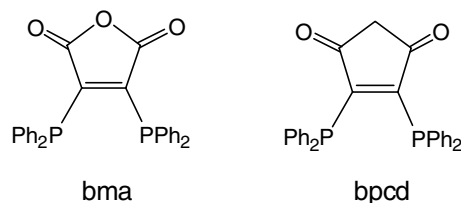
1. Introduction

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

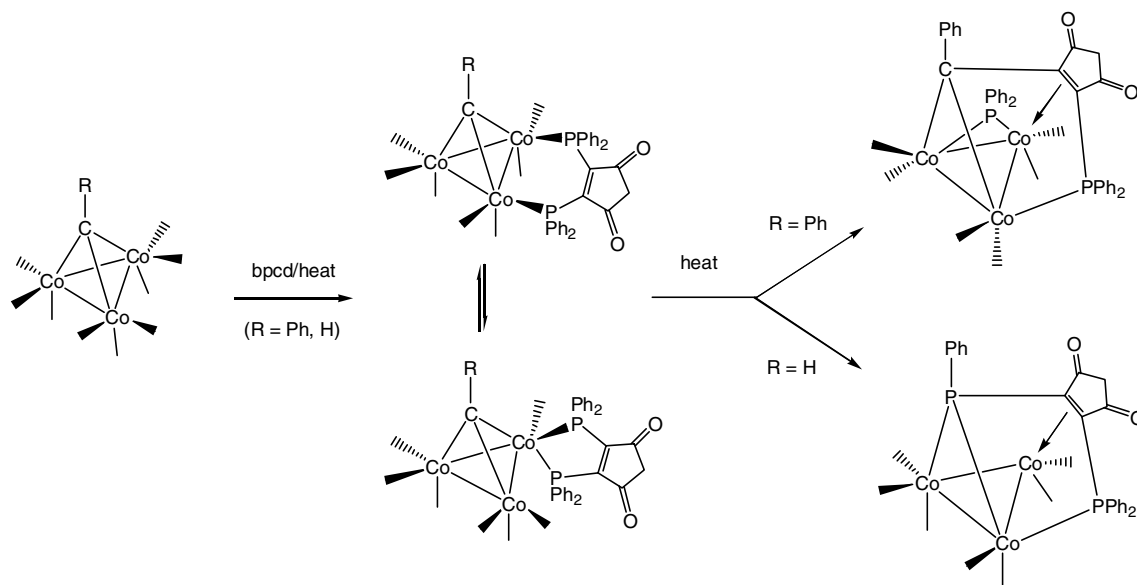
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(bma) and 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd) for the last several years. While the substitution chemistry exhibited by the two diphosphine ligands with the $\text{RCCO}_3(\text{CO})_9$ clusters is identical, the bma-substituted 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 $\text{RCCO}_3(\text{CO})_9$ to give the corresponding diphosphine-substituted clusters $\text{RCCO}_3(\text{CO})_7(\text{P-P})$ [1–5]. The $\text{RCCO}_3(\text{CO})_7(\text{P-P})$ 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 $\text{RCCO}_3(\text{CO})_7(\text{P-P})$ 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 $\text{PhCCO}_3(\text{CO})_7(\text{bpcd})$ and $\text{HCCO}_3(\text{CO})_7(\text{bpcd})$, where the benzylidene-containing cluster $\text{Co}_3(\text{CO})_6[\mu_2, \eta^2, \eta^1\text{-C(Ph)C=C(PPh}_2\text{)C(O)CH}_2\text{C(O)}](\mu_2\text{-PPh}_2)$ and the phosphido-bridged cluster $\text{Co}_3(\text{CO})_7[\mu_2, \eta^2, \eta^1\text{-P(Ph)C=C(PPh}_2\text{)C(O)CH}_2\text{C(O)}]$ are formed, respectively [3,4]. The former cluster arises from an oxidative cleavage of one of the $\text{Ph}_2\text{P-C(dione)}$ bonds, followed by the reductive coupling of the μ_3 -benzylidene 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 $\text{RCCO}_2\text{NiCp(CO)}_6$ ($\text{R} = \text{H, Ph}$) and $\text{PhCCO}_2\text{MoCp(CO)}_8$ [6–9]. Thermolysis of the Co_2Mo cluster with bma leads to the sequential formation of the mono- and bis-phosphido-bridged clusters $\text{Co}_2\text{MoCp(CO)}_5[\mu_2, \eta^2, \eta^1\text{-C(Ph)C=C(PPh}_2\text{)C(O)OC(O)}](\mu_2\text{-PPh}_2)$ and $\text{Co}_2\text{MoCp(CO)}_4[\eta^3, \eta^1, \eta^1\text{-C(Ph)C=CC(O)OC(O)}](\mu_2\text{-PPh}_2)_2$, respectively, as shown in Scheme 2. Of interest to us and unlike the tricobalt clusters, the expected diphosphine-bridged cluster $\text{PhCCO}_2\text{MoCp(CO)}_6(\text{bma})$ was not observed during the thermolysis reaction, suggesting that the putative $\text{PhCCO}_2\text{MoCp(CO)}_6(\text{bma})$ cluster undergoes facile CO loss, followed by rapid P-C bond cleavage and reductive coupling of the $\mu_3\text{-CPh}$ group with the $\text{Co-C(maleic anhydride)}$ moiety. The second P-C bond cleavage experienced by $\text{Co}_2\text{MoCp(CO)}_5[\mu_2, \eta^2, \eta^1\text{-C(Ph)C=C(PPh}_2\text{)C(O)OC(O)}](\mu_2\text{-PPh}_2)$ 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



Scheme 1.

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