

Regiospecific and sequential P–C bond activation/cluster transformations in the reaction of $\text{PhCCO}_2\text{MoCp}(\text{CO})_8$ with the diphosphine ligands 2,3-bis(diphenylphosphino)maleic anhydride (bma) and 3,4-bis(diphenylphosphino)-5-methoxy-2(5H)-furanone (bmf)

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Abstract

Thermolysis of the mixed-metal cluster $\text{PhCCO}_2\text{MoCp}(\text{CO})_8$ (**1**) with the diphosphine ligand 2,3-bis(diphenylphosphino)maleic anhydride (bma) in CH_2Cl_2 leads to the sequential formation of the phosphido-bridged cluster $\text{Co}_2\text{MoCp}(\text{CO})_5[\mu_2, \eta^2, \eta^1\text{-C}(\text{Ph})\text{C}=\text{C}(\text{PPh}_2)\text{C}(\text{O})\text{OC}(\text{O})](\mu\text{-PPh}_2)$ (**3**) and the bis(phosphido)-bridged cluster $\text{Co}_2\text{MoCp}(\text{CO})_4[\eta^3, \eta^1, \eta^1\text{-C}(\text{Ph})\text{C}=\text{C}(\text{O})\text{OC}(\text{O})](\mu\text{-PPh}_2)_2$ (**4**). **3** and **4** have been isolated and characterized in solution by IR and NMR (^1H , ^{13}C , and ^{31}P) spectroscopies, and the solid-state structures have been established by X-ray diffraction analyses. Both clusters contain 48e- and exhibit triangular Co_2Mo cores. The structure of **3** reveals the presence of a phosphido moiety that bridges the Co–Co vector and a six-electron $\mu_2, \eta^2, \eta^1\text{-C}(\text{Ph})\text{C}=\text{C}(\text{PPh}_2)\text{C}(\text{O})\text{OC}(\text{O})$ ligand that caps one of the Co_2Mo faces. The X-ray structure of **4** confirms that the five-electron $\eta^3, \eta^1, \eta^1\text{-C}(\text{Ph})\text{C}=\text{C}(\text{O})\text{OC}(\text{O})$ ligand is σ -bound to the two cobalt centers in an η^1 fashion and π -coordinated to the molybdenum center through a traditional η^3 -allylic interaction. The reaction between $\text{PhCCO}_2\text{MoCp}(\text{CO})_8$ and the chiral diphosphine ligand 3,4-bis(diphenylphosphino)-5-methoxy-2(5H)-furanone (bmf) proceeds similarly, furnishing the phosphido-bridged cluster $\text{Co}_2\text{MoCp}(\text{CO})_5[\mu_2, \eta^2, \eta^1\text{-C}(\text{Ph})\text{C}=\text{C}(\text{PPh}_2)\text{C}(\text{O})\text{OCH}(\text{OMe})](\mu\text{-PPh}_2)$ (**6**), followed by conversion to $\text{Co}_2\text{MoCp}(\text{CO})_4[\eta^3, \eta^1, \eta^1\text{-C}(\text{Ph})\text{C}=\text{C}(\text{O})\text{OCH}(\text{OMe})](\mu\text{-PPh}_2)_2$ (**7**). The identities of clusters **6** and **7** have been ascertained by solution spectroscopic methods and X-ray crystallography. The overall molecular structure of cluster **6** is similar to that of cluster **3**, except that the P–C(furanone ring) bond cleavage occurs with high regioselectivity and high diastereoselectivity. The cleavage of the remaining P–C(furanone ring) bond in cluster **6** gives rise to the bis(phosphido)-bridged cluster **7**, whose structure is discussed relative to its bma-derived analogue **4**. The diastereoselectivity that accompanies the formation of **6** and **7** is discussed relative to steric effects within the Co_2Mo polyhedron. The cyclic voltammetric properties of cluster **3** have been examined, with three well-defined one-electron processes for the 0/+1, 0/–1, –1/–2 redox couples found. The composition of the HOMO and LUMO in **3** was established by extended Hückel MO calculations, with the data discussed relative to the parent tetrahedrane cluster **1**.

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Keywords: Mixed-metal clusters; Ligand substitution; P–C bond cleavage; Chiral clusters

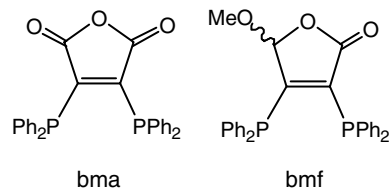
1. Introduction

The reaction of the diphosphine ligands 2,3-bis(diphenylphosphino)maleic anhydride (bma) and 3,4-bis(diphenylphosphino)-5-methoxy-2(5H)-furanone (bmf) with the tetrahedrane clusters $\text{RCCO}_3(\text{CO})_9$ (R = Ph, Fc) and

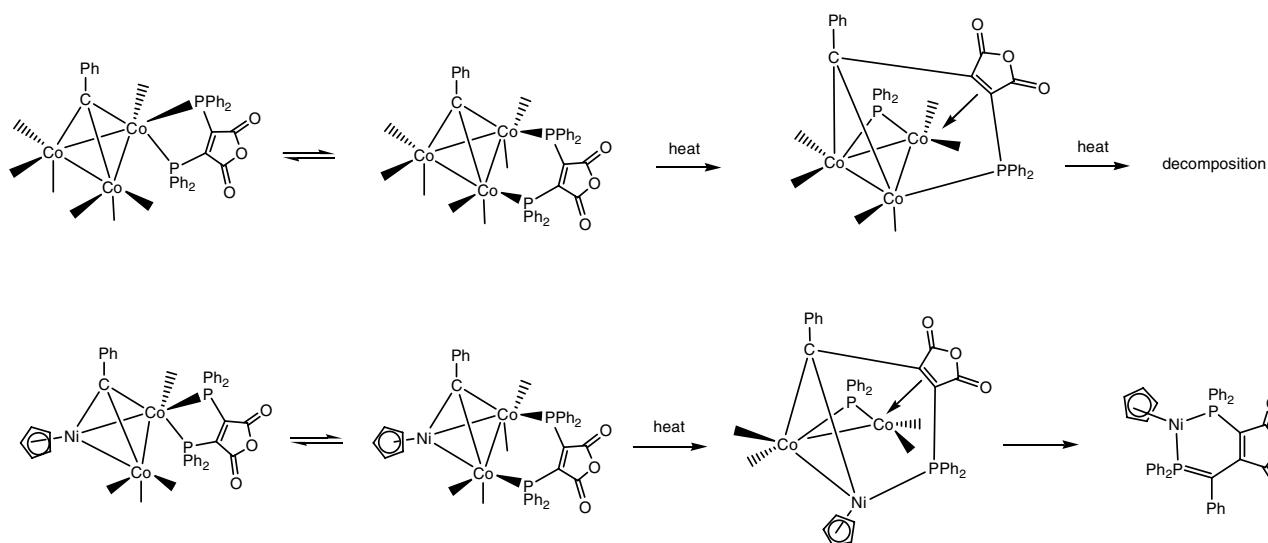
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$\text{RCCo}_2\text{NiCp}(\text{CO})_6$ ($\text{R} = \text{Ph}, \text{H}$) has been actively investigated by our groups the last several years [1–4]. The structures of these rigid diphosphine ligands are shown to the right. Coordination of the these diphosphine ligands at each type of cluster affords the corresponding substituted products $\text{RCCo}_3(\text{CO})_7(\text{P-P})$ and $\text{RCCo}_2\text{NiCp}(\text{CO})_4(\text{P-P})$. The electron-withdrawing carbonyl groups on the maleic anhydride (bma) and furanone (bmf) rings promote the degradation of the $\text{RCCo}_3(\text{CO})_7(\text{P-P})$ and $\text{RCCo}_2\text{NiCp}(\text{CO})_4(\text{P-P})$ clusters, with the oxidative cleavage of one P–C ligand bond serving as a point of entry for the observed diphosphine/cluster activation. The course and outcome of these reactions depend on several variables, one of which is the metallic composition of the cluster, as shown in Scheme 1 for the phenyl-capped clusters $\text{PhCCo}_3(\text{CO})_7(\text{bma})$ and $\text{PhCCo}_2\text{NiCp}(\text{CO})_4(\text{bma})$. Thermolysis of the bma-substituted Co_3 and Co_2Ni clusters furnishes the structurally different phosphido-bridged clusters $\text{Co}_3(\text{CO})_6[\mu_2, \eta^2, \eta^1\text{-C}(\text{Ph})\text{C}=\text{C}(\text{PPh}_2)\text{C}(\text{O})\text{OC}(\text{O})](\mu\text{-PPh}_2)$ and $\text{Co}_2\text{NiCp}(\text{CO})_4[\mu_2, \eta^2, \eta^1\text{-C}(\text{Ph})\text{C}=\text{C}(\text{PPh}_2)\text{C}(\text{O})\text{OC}(\text{O})](\mu\text{-PPh}_2)$. Both phosphido-bridged clusters are thermally sensitive; the former homometallic cluster undergoes gross decomposition when heated at temperatures $>80^\circ\text{C}$ while the latter Co_2Ni cluster furnishes the mononuclear nickel compound $\text{CpNi}[\text{PPh}_2\text{C}(\text{H})\text{C}=\text{C}(\text{PPh}_2)\text{C}(\text{O})\text{OC}(\text{O})]$. Definitive proof for the enhanced diphosphine ligand reactivity in $\text{PhCCo}_3(\text{CO})_7(\text{bma})$ and $\text{PhCCo}_2\text{NiCp}(\text{CO})_4(\text{bma})$ derives from the synthesis of the related clusters containing the archetypal diphosphine ligand (*Z*)- $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$. The structurally similar $\text{PhCCo}_3(\text{CO})_7[(\text{Z})\text{-Ph}_2\text{PCH}=\text{CHPPh}_2]$ [5] and $\text{PhCCo}_2\text{NiCp}(\text{CO})_4[(\text{Z})\text{-Ph}_2\text{PCH}=\text{CHPPh}_2]$ [6] clusters have been shown to be stable under conditions comparable to those used to promote the transformations illustrated in Scheme 1.



The synthesis and reactivity of the chiral clusters $\text{HCCo}_2\text{NiCp}(\text{CO})_4(\text{bmf})$ and $\text{PhCCo}_2\text{NiCp}(\text{CO})_4(\text{bmf})$ have recently been described by us [4]. Both bmf-substituted clusters exist as a ca. 70:30 mixture of diastereomers in solution and are obtained in good yield from thermolysis of the $\text{RCCo}_2\text{NiCp}(\text{CO})_6$ in the presence of added bmf ligand. Here the bridging bmf ligand is equatorially disposed across the Co–Co bond in each product, as deduced by NMR analyses. The important role played by the capping R-group in controlling the chemistry exhibited by these bmf-substituted clusters was verified during routine thermolysis studies of $\text{HCCo}_2\text{NiCp}(\text{CO})_4(\text{bmf})$ and $\text{PhCCo}_2\text{NiCp}(\text{CO})_4(\text{bmf})$. Whereas heating $\text{PhCCo}_2\text{NiCp}(\text{CO})_4(\text{bmf})$ at 83°C leads to cluster decomposition, the latter methylidyne cluster undergoes a regiospecific cleavage of one of the two distinct P–C(furanone) bonds, followed by diastereoselective formation of the phosphido-bridged cluster $\text{Co}_2\text{NiCp}(\text{CO})_4[\mu_2, \eta^2, \eta^1\text{-C}(\text{H})\text{C}=\text{C}(\text{PPh}_2)\text{C}(\text{O})\text{OCH}(\text{OMe})](\mu\text{-PPh}_2)$. This transformation is depicted in Eq. (1). Of interest to us was the oxidative P–C bond cleavage of the least basic phosphine moiety at the C-4 atom of the furanone ring [7]. The release or slippage of one of the phosphine moieties from a bidentate coordinated bmf ligand is believed to promote the observed P–C bond cleavage at the cluster. The selective dissociation of the less strongly bound phosphine moiety, followed by its subse-



Scheme 1.

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