

Ligand chelation, P–C bond cleavage, and phenyl-group transfer in the reaction between $\text{RCCo}_3(\text{CO})_9$ and 1,8-bis(diphenylphosphino)naphthalene (dppn): Syntheses and X-ray diffraction structures of $\text{PhCCo}_3(\text{CO})_4(\mu\text{-CO})_3(\text{dppn})$ and $\text{PhCCo}_3(\text{CO})_8[\eta^1\text{-PPh(OH)C}_{10}\text{H}_6\text{P(O)Ph}_2]$

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Abstract

The tricobalt cluster $\text{PhCCo}_3(\text{CO})_9$ (**1**) undergoes facile ligand substitution with 1,8-bis(diphenylphosphino)naphthalene (dppn) under thermal and Me_3NO activation to afford the cluster compounds $\text{PhCCo}_3(\text{CO})_8[\text{PPh}_2(1\text{-C}_{10}\text{H}_7)]$ (**2**) and $\text{PhCCo}_3(\text{CO})_4(\mu\text{-CO})_3(\text{dppn})$ (**3**). Whereas thermolysis of dppn with the methylidyne-capped cluster $\text{HCCo}_3(\text{CO})_9$ (**4**) yields only $\text{HCCo}_3(\text{CO})_8[\text{PPh}_2(1\text{-C}_{10}\text{H}_7)]$ (**5**) and $\text{HCCo}_3(\text{CO})_4(\mu\text{-CO})_3(\text{dppn})$ (**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 $\text{PhCCo}_3(\text{CO})_8[\eta^1\text{-PPh(OH)C}_{10}\text{H}_6\text{P(O)Ph}_2]$ (**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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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-à-vis related dppe-substituted complexes [2–5], coordination of dppn to the metal cluster compounds $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$ 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 $\text{Ru}_3(\text{CO})_8(\mu\text{-dppm})(\text{dppn})$,

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which has been isolated in low yield from the thermolysis reaction involving $\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})$ and dppn [6].

Our groups have had a long-term interest in the study of the rigid, unsaturated diphosphine ligands (*Z*)- $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$, 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 $\text{RCCo}_3(\text{CO})_9$ gives the corresponding products $\text{RCCo}_3(\text{CO})_7(\text{P-P})$ (where P–P = diphosphine ligand). In the case of the cluster compound $\text{PhCCo}_3(\text{CO})_7[(\text{Z})\text{-Ph}_2\text{PCH}=\text{CHPPh}_2]$, 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 $\text{PhCCo}_3(\text{CO})_7(\text{bma})$ and $\text{PhCCo}_3(\text{CO})_7(\text{bpcd})$ 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 $\text{Ph}_2\text{P-C}(\text{ring})$ bond, followed by the reductive coupling of the transient $\text{Co-C}(\text{ring})$ moiety and the benzyldiyne capping ligand. Scheme 1 summarizes this chemistry for $\text{PhCCo}_3(\text{CO})_7(\text{bpcd})$.

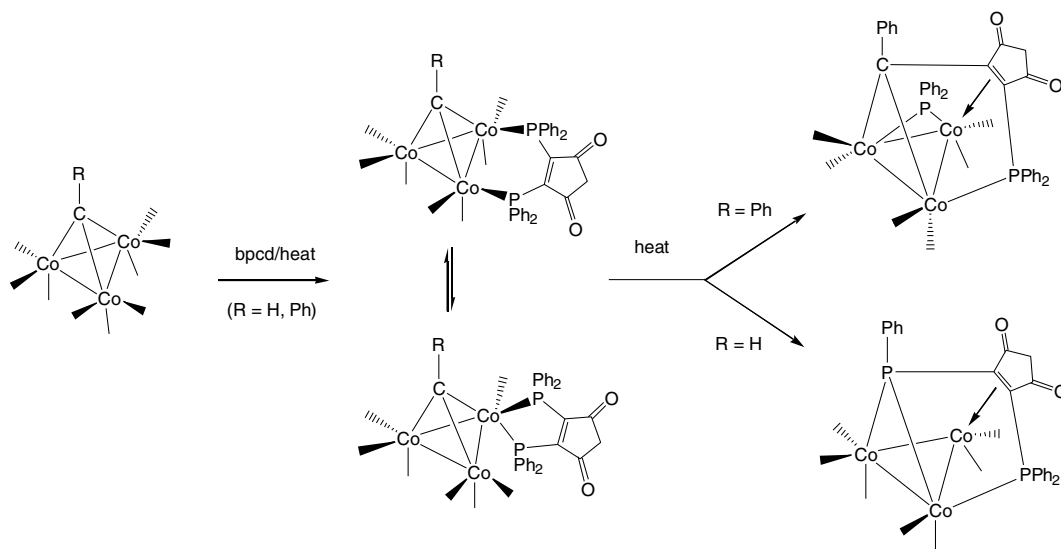
Wishing to extend our substitution studies in the tetrahedrane clusters $\text{RCCo}_3(\text{CO})_9$ with different diphosphine ligands, we have examined the reactivity of dppn with the clusters $\text{PhCCo}_3(\text{CO})_9$ (**1**) and $\text{HCCo}_3(\text{CO})_9$ (**4**). Herein we present our results 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 $\text{PhCCo}_3(\text{CO})_8[\text{PPh}_2(1\text{-C}_{10}\text{H}_7)]$ (**2**), $\text{HCCo}_3(\text{CO})_8[\text{PPh}_2(1\text{-C}_{10}\text{H}_7)]$ (**5**), and $\text{PhCCo}_3(\text{CO})_8[\eta^1\text{-PPh}(\text{OH})\text{C}_{10}\text{H}_6\text{P}(\text{O})\text{Ph}_2]$ (**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 $\text{PhCCo}_3(\text{CO})_9$ and $\text{HCCo}_3(\text{CO})_9$ were prepared from $\text{Co}_2(\text{CO})_8$ [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 $\text{Co}_2(\text{CO})_8$, which was purchased from Strem Chemicals, the other chemicals used in these studies 1,8-diaminonaphthalene, 1-bromonaphthalene, chlorodiphenylphosphine, bromoform, and $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ 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.

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