

Reversible aryl C–H bond activation in the reaction between $\text{HRu}_3(\text{CO})_{9,10}(\mu\text{-PPh}_2)$ and the diphosphine ligand 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd): X-ray diffraction structures of $\text{H}_2\text{Ru}_3(\text{CO})_7(\text{bpcd})[\mu, \sigma\text{-PPh}(\text{C}_6\text{H}_4)]$ and $\text{Ru}_3(\text{CO})_6(\mu\text{-CO})(\mu\text{-PPh}_2)[\mu, \eta^2, \eta^1\text{-PPhC}=\text{C}(\text{PPh}_2)\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})]$

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Abstract

The reaction between $\text{HRu}_3(\text{CO})_{10}(\mu\text{-PPh}_2)$ (**1**) and the diphosphine ligand 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd) proceeds rapidly in the presence of Me_3NO to furnish $\text{H}_2\text{Ru}_3(\text{CO})_7(\text{bpcd})[\mu, \sigma\text{-PPh}(\text{C}_6\text{H}_4)]$ (**3**). Treatment of the nonacarbonyl cluster $\text{HRu}_3(\text{CO})_9(\mu\text{-PPh}_2)$ (**2**) with bpcd at room temperature affords cluster **3** as the major product in addition to cluster **1**. Thermolysis of cluster **3** in 1,2-dichloroethane yields $\text{Ru}_3(\text{CO})_6(\mu\text{-CO})(\mu\text{-PPh}_2)[\mu, \eta^2, \eta^1\text{-PPhC}=\text{C}(\text{PPh}_2)\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})]$ (**4**) as the major isolable product. The highlights associated with the production of cluster **4** involve the reductive elimination of the orthometalated aryl group with one of the two bridging hydrides in **3** and cleavage of one of the P–Ph bonds of the bpcd ligand, followed by the release of benzene from the transient sigma-bound Ru–Ph group. Both $\text{H}_2\text{Ru}_3(\text{CO})_7(\text{bpcd})[\mu, \sigma\text{-PPh}(\text{C}_6\text{H}_4)]$ and $\text{Ru}_3(\text{CO})_6(\mu\text{-CO})(\mu\text{-PPh}_2)[\mu, \eta^2, \eta^1\text{-PPhC}=\text{C}(\text{PPh}_2)\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})]$ have been isolated and characterized in solution by IR and NMR (^{31}P and ^1H) spectroscopies, in addition to X-ray crystallography. The solid-state structure of $\text{H}_2\text{Ru}_3(\text{CO})_7(\text{bpcd})[\mu, \sigma\text{-PPh}(\text{C}_6\text{H}_4)]$ confirms the presence of an orthometalated μ_2 -phosphido moiety and a chelating bpcd ligand. The crystal structure of cluster **4** consists of a triangular Ru_3 core where one face is capped by the 6e-donor ligand $\mu, \eta^2, \eta^1\text{-PPhC}=\text{C}(\text{PPh}_2)\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})$.

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1. Introduction

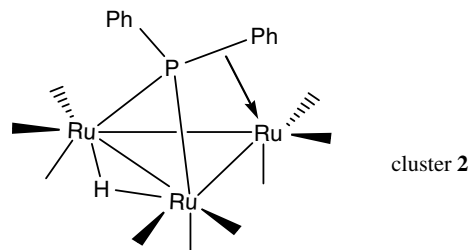
The reactivity of the triruthenium clusters $\text{HRu}_3(\text{CO})_{10}(\mu\text{-PPh}_2)$ (**1**) and $\text{HRu}_3(\text{CO})_9(\mu\text{-PPh}_2)$ (**2**) in ligand substitution reactions and catalytic hydrogenations has been extensively explored [1–5]. The latter clus-

ter, which is readily obtained from the Me_3NO -promoted decarbonylation of $\text{HRu}_3(\text{CO})_{10}(\mu\text{-PPh}_2)$ [6] or by hydrogenation of the acetylide-bridged clusters $\text{Ru}_3(\text{CO})_8(\mu_3\text{-}\eta^2\text{-CCR})(\mu_2\text{-PPh}_2)$ (where $\text{R} = \text{Bu}^t, \text{Pr}^i$) [7], has invoked considerable interest due to its formal unsaturation that is alleviated by coordination of one of the two P–Ph bonds to the non-hydride-bridged Ru center, as shown below [8]. Such an η^2 -coordination of the P–Ph bond is akin to an agostic interaction between a metal and an alkane [9] and may be viewed as an arrested or precursor state for the oxidative cleavage of

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P–Ph bonds at a transition-metal center [10]. The facile addition of a variety of substrates to $\text{HRu}_3(\text{CO})_9(\mu\text{-PPh}_2)$ (**2**) suggests that the P–Ph bond is weakly bound to the ruthenium center and that its dissociation provides a low-energy pathway for the generation of a coordinatively unsaturated site within the cluster [3].



Recently, we have published our results on the ligand substitution behavior of the azavinylidene-bridged cluster $\text{HRu}_3(\text{CO})_{10}(\mu\text{-NCPH}_2)$ with the diphosphine ligands 1,2-bis(dimethylphosphino)ethane (dmpe) and 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd), with the coordination of these ligands giving bridged and chelated diphosphine-substituted clusters, respectively, as depicted in Scheme 1 [11]. $\text{HRu}_3(\text{CO})_{10}(\mu\text{-NCPH}_2)$ is structurally similar to the triruthenium clusters $\text{HRu}_3(\text{CO})_{10}(\mu\text{-PPh}_2)$ (**1**) and $\text{HRu}_3(\text{CO})_9(\mu\text{-PPh}_2)$ (**2**), inasmuch as it possesses a hydride- and pnictogen-bridged ruthenium–ruthenium bond, and this structural similarity, coupled with the absence of reports for the reaction of clusters **1** and **2** with diphosphine ligands,

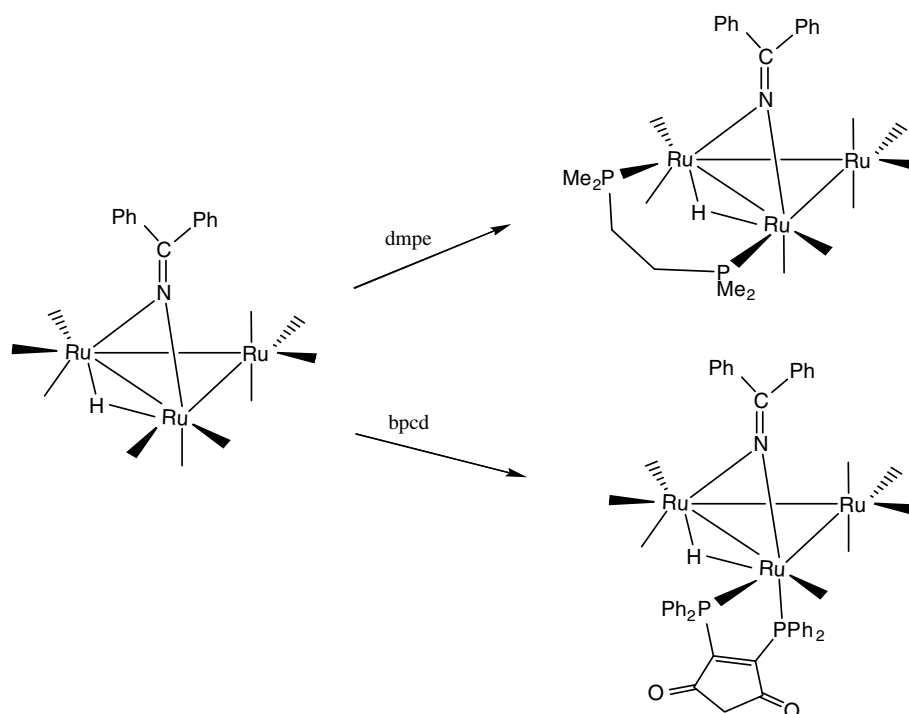
would allow us to test the generality associated with the mode of diphosphine coordination in a given polyhedral motif.

With this rationale for our interest in $\text{HRu}_3(\text{CO})_{10}(\mu\text{-PPh}_2)$ (**1**) and $\text{HRu}_3(\text{CO})_9(\mu\text{-PPh}_2)$ (**2**), we have studied the reaction between clusters **1** and **2** with the diphosphine ligand bpcd [12]. Herein, we present our data on synthesis and structural characterization of the new clusters $\text{H}_2\text{Ru}_3(\text{CO})_7(\text{bpcd})[\mu, \sigma\text{-PPh}(\text{C}_6\text{H}_4)]$ (**3**) and $\text{Ru}_3(\text{CO})_6(\mu\text{-CO})(\mu\text{-PPh}_2)[\mu, \eta^2, \eta^1\text{-PPhC}=\text{C}(\text{PPh}_2)\text{C}(\text{O})\text{-CH}_2\text{C}(\text{O})]$ (**4**). Controlled thermolysis reactions establish cluster **3** as the precursor to cluster **4**. Chelation of the bpcd ligand to the cluster polyhedron is accompanied by an orthometalation of one the aryl groups belonging to the bridging phosphido moiety and this C–H bond activation is reversed upon thermolysis of cluster **3**. The reformation of the $\mu\text{-PPh}_2$ moiety in cluster **4** is accompanied by P–Ph activation of the ancillary bpcd ligand and release of benzene.

2. Experimental

2.1. General methods

The $\text{Ru}_3(\text{CO})_{12}$ and bpcd ligand used in these studies were synthesized from hydrated RuCl_3 and 4,5-dichloro-4-cyclopenten-1,3-dione, respectively, according to known procedures [13,14]. All reaction and NMR solvents were distilled under argon from a suitable



Scheme 1.

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