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CO substitution in $H_4Ru_4(CO)_{12}$ by the diphosphine ligands 1,2-bis(diphenylphosphino)benzene (dppbz) and 1,8-bis(diphenylphosphino)naphthalene (dppn): X-ray diffraction structures of the diphosphine-chelated clusters 1,1-$H_4Ru_4(CO)_{10}$(dppbz) and 1,1-$H_4Ru_4(CO)_{10}$(dppn)

Vladimir N. Nesterov [a,*], William H. Watson [b,*], Srikanth Kandala [c], Michael G. Richmond [c,*]

[a] *Department of Chemistry, New Mexico Highlands University, Las Vegas, NM 87701, United States*
[b] *Department of Chemistry, Texas Christian University, Fort Worth, TX 76129, United States*
[c] *Department of Chemistry, University of North Texas, Denton, TX 76203, United States*

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Abstract

The reaction of the diphosphine ligands 1,2-bis(diphenylphosphino)benzene (dppbz) and 1,8-bis(diphenylphosphino)naphthalene (dppn) with the hydride-bridged cluster $H_4Ru_4(CO)_{12}$ (**1**) has been investigated under thermal and Me_3NO activation conditions. Both activation methods furnish the diphosphine-substituted clusters 1,1-$H_4Ru_4(CO)_{10}$(P–P) (where P–P = dppbz, dppn) as the sole isolable products. The chelating coordination mode adopted by the ancillary diphosphine ligands has been confirmed by NMR spectroscopies and X-ray crystallography. The stability of the new clusters 1,1-$H_4Ru_4(CO)_{10}$(dppbz) and 1,1-$H_4Ru_4(CO)_{10}$(dppn) has been examined, and both clusters have been found to be stable at elevated temperatures in toluene and extended near-UV photolysis.

Keywords: Diphosphine ligands; Ligand substitution; Ruthenium clusters

1. Introduction

The substitution chemistry and reactivity study of ruthenium clusters containing diphosphine ligands have continued to occupy the attention and efforts of our research groups [1]. While many different types of diphosphine ligands exist, we have had a particular interest in unsaturated diphosphines that possess a rigid carbon backbone. Here the ancillary π system associated with the unsaturated ligand platform has been shown to trigger cluster fragmentation in a manner unparalleled to that of the corresponding saturated ligand counterparts. One of the first examples demonstrating this aspect of enhanced lability comes from the reaction of $Ru_3(CO)_{12}$ with (Z)-$Ph_2PCH{=}CHPPh_2$. The initially formed cluster 1, 1-$Ru_3(CO)_{10}$[(Z)-$Ph_2PCH{=}CHPPh_2$], which contains a chelating diphosphine ligand, is unstable and transforms into the donor–acceptor diruthenium compound $Ru_2(CO)_6$[(Z)-$Ph_2PCH{=}CHPPh_2$] on mild heating [2,3]. Accompanying this reaction is the release of $Ru(CO)_4$ that subsequently trimerizes to afford $Ru_3(CO)_{12}$. Another example of unprecedented reactivity between a metal cluster and an unsaturated diphosphine ligand involves the reaction of the hexaruthenium cluster $Ru_6(\mu_6\text{-}C)(CO)_{17}$

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[*] Corresponding authors. Tel.: +1 505 454 3464 (V.N. Nesterov); tel.: +1 817 257 7195 (W.H. Watson); tel.: +1 940 565 3548; fax: +1 940 565 4318 (M.G. Richmond).

E-mail addresses: vnesterov@nmhu.edu (V.N. Nesterov), w.watson@tcu.edu (W.H. Watson), cobalt@unt.edu (M.G. Richmond).

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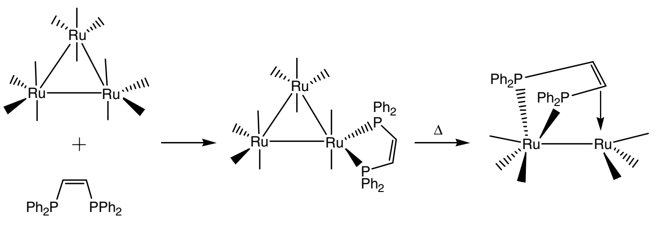
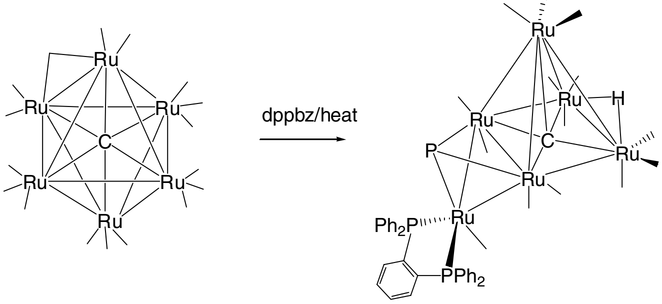
with dppbz. It is believed that the chelation of the dppbz ligand to $Ru_6(\mu_6\text{-}C)(CO)_{17}$ leads to a polyhedral expansion of the ruthenium core, coupled with the scavenging of phosphorus and hydrogen atoms from an additional dppbz ligand to furnish the edge-bridged cluster $HRu_6(\mu_5\text{-}C)(\mu_3\text{-}P)(CO)_{14}$(dppbz) [4]. These novel reactions are depicted in Eqs. (1) and (2).

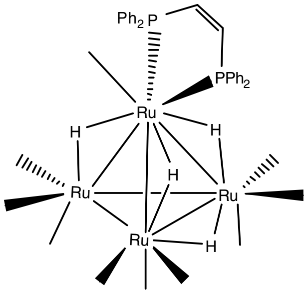


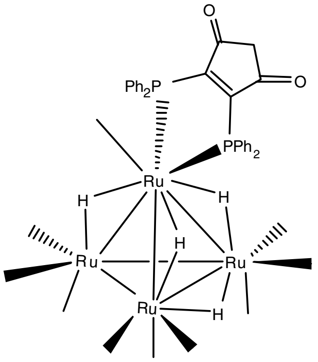
(1)



(2)

The reaction between the ruthenium cluster $Ru_3(CO)_{12}$ and myriad diphosphine ligands has been thoroughly explored over the last three decades [5]. The formal replacement of two carbonyl groups by the diphosphine ligand affords the corresponding cluster $Ru_3(CO)_{10}$(P–P), where the diphosphine ligand (P–P) may be coordinated to the cluster frame across adjacent ruthenium centers (bridging) or at a single metal center (chelating). Numerous examples exist for both P–P ligand coordination modes. The study of $Ru_3(CO)_{10}$(P–P) clusters has provided valuable insight into the stability of diphosphine ligands (P–P) relative to deleterious ligand decomposition through P–C bond cleavage, C–H bond ortho metalation, and cyclometalation pathways [6]. The observed degradation of phosphine ligands at well-defined metal complexes provides crucial evidence that debunks the innocent or spectator status of such ligands [7]. In comparison, the reactivity of diphosphine ligands with the hydride-bridged cluster $H_4Ru_4(CO)_{12}$ (**1**) has received scant attention vis-a-vis $Ru_3(CO)_{12}$. Other than our recent report on the synthesis and structural characterization of 1,1-$H_4Ru_4(CO)_{10}$[(*Z*)-$Ph_2PCH{=}CHPPh_2$] and 1,1-$H_4Ru_4(CO)_{10}$(bpcd), whose structures are shown below, there exist no other examples for the reaction of $H_4Ru_4(CO)_{12}$ with rigid, unsaturated diphosphine ligands [8,9]. The diphosphine ligands (*Z*)-$Ph_2PCH{=}CHPPh_2$ and bpcd react with cluster **1** to give the diphosphine-chelated clusters without any sign of the corresponding diphosphine-bridged species.





Wishing to establish the generality of ligand chelation at cluster **1** with other unsaturated diphosphine ligands, we have investigated the thermal and Me_3NO oxidative-decarbonylation activation of cluster **1** in the presence of the ligands 1,2-bis(diphenylphosphino)-benzene (dppbz) and 1,8-bis(diphenylphosphino)naphthalene (dppn). The course of these substitution reactions has been established through NMR spectroscopies and X-ray crystallographic analyses of the cluster compounds $H_4Ru_4(CO)_{10}$(dppbz) (**2**) and $H_4Ru_4(CO)_{10}$(dppn) (**3**). The thermal and photochemical stability of both product clusters have been investigated, with the results discussed relative to other diphosphine-substituted ruthenium clusters.

2. Experimental

2.1. General

The starting hydride cluster $H_4Ru_4(CO)_{12}$ (**1**) was prepared from $Ru_3(CO)_{12}$ and H_2 according to the published procedure [10], with the $Ru_3(CO)_{12}$ synthesized from hydrated $RuCl_3$ and CO using a 1l Parr Series 4000 rocking autoclave [11]. The dppn ligand was prepared from 1-bromonaphthalene and Ph_2PCl [12]. The chemicals 1-bromonaphthalene, dppbz, and $Me_3NO \cdot nH_2O$ were purchased from Aldrich Chemical Co. The $Me_3NO \cdot nH_2O$ was dried by azeotropic distillation from benzene and the anhydrous Me_3NO was stored in a Schlenk tube under argon. All reaction, IR, and NMR solvents were of reagent grade and were distilled from a suitable drying agent and stored in Schlenk vessels equipped with Teflon stopcocks [13]. The combustion analyses were performed by Atlantic Microlab, Norcross, GA.

The IR spectral data were recorded on a Nicolet 20 SXB FT-IR spectrometer in sealed 0.1 mm NaCl cells, while the ^1H NMR (200 MHz) and ^{31}P NMR (121 MHz) spectra were recorded on Varian Gemini-200 and 300-VXR spectrometers, respectively. The ^{31}P NMR spectra were collected in the proton-decoupled mode with the reported chemical shifts referenced to external H_3PO_4 (85%), taken to have $\delta = 0$.