



Reactions of $\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})$ with Ph_3GeH : Ge–H and Ge–C bond cleavage in Ph_3GeH at triruthenium clusters



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ABSTRACT

The activation of Ph_3GeH at the dppm-bridged cluster $\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})$ [dppm = bis(diphenylphosphino)methane] has been investigated. $\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})$ reacts with Ph_3GeH at room temperature in the presence of Me_3NO to give the new cluster products $\text{Ru}_3(\text{CO})_9(\mu\text{-GePh}_3)(\mu\text{-dppm})(\mu\text{-H})$ (**1**) and $\text{Ru}_3(\text{CO})_8(\text{GePh}_3)_2(\mu\text{-dppm})(\mu\text{-H})_2$ (**2**) via successive oxidation-addition of two Ge–H bonds. Refluxing **1** in THF furnishes the diruthenium complex $\text{Ru}_2(\text{CO})_6(\mu\text{-GePh}_2)(\mu\text{-dppm})$ (**3**) as the major product (44%), in addition to $\text{Ru}_3(\text{CO})_7(\mu\text{-CO})(\text{GePh}_3)\{\mu_3\text{-PhPCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4\}(\mu\text{-H})$ (**4**) and the known cluster $\text{Ru}_3(\text{CO})_9(\mu\text{-H})(\mu_3\text{-Ph}_2\text{PCH}_2\text{PPh})$ (**5**) in 7 and 8% yields, respectively. Heating samples of cluster **2** also afforded **3** as the major product together with a small amount of $\text{Ru}_3(\text{CO})_7(\text{GePh}_3)(\mu\text{-OH})(\mu\text{-dppm})(\mu\text{-H})_2$ (**6**). DFT calculations establish the stability of the different possible isomers for clusters **1**, **2**, and **6**, in addition to providing insight into the mechanism for hydride fluxionality in **2**. All new compounds have been characterized by analytical and spectroscopic methods, and the molecular structures of **1**, **3**, and **6** have been established by single-crystal X-ray diffraction analyses.

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1. Introduction

Both germanium [1] and tin [2,3] are employed with transition metals from Group 8–10 to create composite alloy systems for catalytic reforming processes. The resulting heterogeneous nanoparticle catalysts may be prepared by the deposition of a metal cluster containing a Group 14 ligand on an oxide support, yielding systems that exhibit high activity and selectivity for certain types of hydrogenation and dehydrogenation reactions [4]. We have been investigating the synthesis and structure of metal carbonyl complexes containing organogermanium and organotin ligands that can be used as precursors in the synthesis of such nanoscale catalysts during the last few years [5–8]. Ruthenium combined with the Group 14 elements, such as germanium or tin, continues to

dominate the attention of different research groups with interest in catalysis [9–11]. Notwithstanding the existing literature on transition metal complexes containing Group 14 elements as ligands [12–14], well-defined examples of triruthenium clusters with an ancillary germanium ligand(s) remain scarce [15–20]. The first example of a triruthenium compound containing an organogermanium moiety e.g. $[(\text{Me}_2\text{Ge})\text{Ru}(\text{CO})_3]_3$, was reported by Howard and Woodward in 1971 from the thermolysis of $(\text{Me}_3\text{Ge})_2\text{Ru}(\text{CO})_4$, which in turn was synthesized from the reaction of $\text{Ru}_3(\text{CO})_{12}$ with Me_3GeH [15]. Since that initial report, the related ruthenium-germanium compounds $[(\mu_3\text{-Ge}\{\text{Ru}(\text{CO})_2(\eta^5\text{-C}_5\text{Me}_4\text{H})\})]_2\text{Ru}_3(\text{CO})_9$ and $\text{Ru}_3\{\mu\text{-Ge}(\text{NCH}_2\text{CMe}_3)_2\text{C}_6\text{H}_4\}_3(\text{CO})_9$ have been isolated from the thermolysis reaction of $\text{Ru}_3(\text{CO})_{12}$ with $\text{C}_5\text{Me}_4\text{HMe}_2\text{GeGeMe}_2\text{C}_5\text{Me}_4\text{H}$ and 1,3-bis(neo-pentyl)-2-germabenzimidazol-2-ylidene, respectively [16,17]. The former cluster exhibits a trigonal-bipyramidal Ge_2Ru_3 polyhedral frame while the latter cluster reveals a triangular Ru_3 core where each metallic edge is bridged by a germylene moiety.

Studies have shown that the incorporation of organogermanium/organotin moieties into the coordination sphere of a

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metal carbonyl cluster by oxidative addition of the corresponding hydrides R_3EH (where $E = Ge, Sn$; $R = \text{alkyl, aryl}$) remains a convenient and widely used method for the synthesis of new Group 14-substituted metal clusters [6,7,21–24]. Recently, we reported the preparation of new Os_3Sn_x and Os_3Ge_x clusters from the reactions of $Os_3(CO)_{10}(\mu\text{-dppm})$ and the related ligand-activated cluster $Os_3(CO)_8[\mu_3\text{-Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4](\mu\text{-H})$ with Ph_3SnH [6] and Ph_3GeH [7]. This work reinforces the view that cluster degradation, which is frequently observed during the reaction between metal carbonyl clusters and organotin/organogermanium hydrides or other tin/germanium sources, may be significantly inhibited by the presence of a bridging dppm ligand that can impart additional stabilization to the metallic polyhedron by the ability to hold contiguous metal centers together. Accordingly, we have examined the functionalization of $Ru_3(CO)_{10}(\mu\text{-dppm})$ with Ph_3GeH as a route to new Ru_3Ge_x clusters that can serve as precursors for alloy and nanoparticle catalysts. Herein we report on our results of the synthesis and characterization of new germanium-containing $Ru_3(\mu\text{-dppm})$ clusters.

2. Results and discussion

2.1. Reaction of $Ru_3(CO)_{10}(\mu\text{-dppm})$ with Ph_3GeH through Ge–H bond activation

The Me_3NO -initiated reaction between $Ru_3(CO)_{10}(\mu\text{-dppm})$ and Ph_3GeH at room temperature gives $Ru_3(CO)_9(GePh_3)(\mu\text{-dppm})(\mu\text{-H})$ (**1**) and $Ru_3(CO)_8(GePh_3)_2(\mu\text{-dppm})(\mu\text{-H})_2$ (**2**) in 31 and 19% yield, respectively, after chromatographic separation and recrystallization (Scheme 1). In a separate experiment, **1** was shown to react with Ph_3GeH under similar reaction conditions to afford **2**, thus confirming the sequential formation of **1** and **2** through an oxidative-addition process of the Ge–H bond of the germanium reagent. Both Ru_3 products are new and they have been characterized by analytical and spectroscopic methods, and the molecular structure of **1** was determined by single crystal X-ray diffraction analysis.

An ORTEP diagram of the molecular structure of **1** is depicted in Fig. 1, and selected bond distances and angles are presented in the figure caption. The molecule contains a triruthenium core with three formal Ru–Ru single bonds [Ru(1)–Ru(2) 2.8441(3), Ru(2)–Ru(3) 2.8813(3) and Ru(1)–Ru(3) 3.0148(3) Å] that exhibit a mean distance of 2.9134 Å. Nine terminal carbonyl groups are noted, of which three are equally distributed at each ruthenium center. The dppm and hydride ligands bridge adjacent metallic edges, and the Ph_3Ge moiety is situated *syn* to the hydride at the phosphine-free ruthenium center. The hydride ligand was located from a Fourier map and found to bridge the longest of the three ruthenium–ruthenium edges defined by the Ru(1)–Ru(3) distance. The triphenylgermanium ligand is coordinated to Ru(1), occupying an equatorial site as expected, and the Ru(1)–Ge(1) bond distance of 2.5054(3) Å is comparable to the terminally coordinated $GeMe_3$ ligands in $C_8H_6[(CO)_2Ru(GeMe_3)]_2$ (mean 2.487 Å) [25]. The gross structural features of **1** are similar to those displayed in the related trimetallic clusters $[Ru_3(CO)_9(SiPh_3)(\mu\text{-dppm})(\mu\text{-H})]$ [26] and

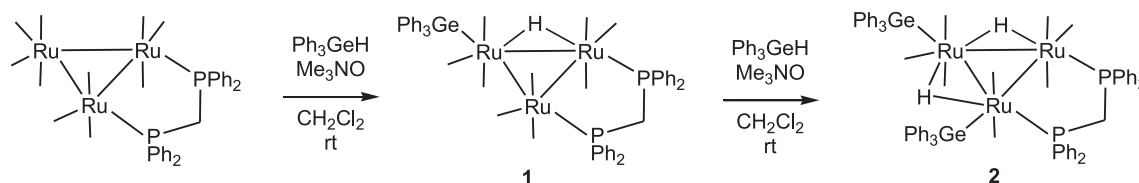
$[Os_3(CO)_9(GePh_3)(\mu\text{-dppm})(\mu\text{-H})]$ [7] reported by us. The solution spectroscopic data for **1** indicate that the solid-state structure persists in solution. The 1H NMR spectrum displays an upfield doublet at -18.25 ppm (J 30.0 Hz) due to the bridging hydride and a virtual triplet at 4.43 ppm (J 10.0 Hz), integrating for two protons, that is attributed to the methylene protons of the dppm ligand. The aryl hydrogens appear as three sets of multiplets from 7.26 to 7.54 ppm. The two ^{31}P doublets centered at 9.0 and 7.3 ppm (J_{PP} 52.0 Hz) in the $^{31}P\{^1H\}$ NMR spectrum are consistent with the non-equivalent phosphorus atoms of the dppm ligand.

The preferred disposition of the Ph_3Ge ligand relative to the edge-bridging hydride was examined by electronic structure calculations. Here we optimized the structure of **1** (**A1**) and the corresponding stereoisomer where the Ph_3Ge ligand is situated at the alternative equatorial site distal to the hydride (**A2**). These structures are depicted in Fig. 2 and **A1** is computed to be 3.8 kcal/mol (ΔG) more stable than **A2**. This locus preference for the ancillary Ph_3Ge ligand follows that recently computed by us for the corresponding Ph_3Sn derivative $[Ru_3(CO)_9(SnPh_3)(\mu\text{-dppm})(\mu\text{-H})]$ [27], whose stereoisomers differ in energy by 2.2 kcal/mol in favor of the *syn* disposed Ph_3Sn and hydride groups.

Attempts to grow single crystals of cluster **2** for X-ray diffraction analysis were met with failure, yielding either amorphous or highly disordered crystalline material. Therefore, **2** was characterized by a combination of analytical and spectroscopic methods. The IR spectrum of **2** exhibits six carbonyl absorptions over the wave number range 2061 to 1971 cm^{-1} , indicating that all of the carbonyl groups are terminally bound in the cluster. The FAB mass spectrum displays a molecular ion at m/z 1522 in addition to fragment ions due to sequential loss of seven carbonyls, all of which are consistent with the formulated structure in Scheme 1.

The 1H and ^{31}P NMR data recorded for **2** provide evidence for hydride fluxionality at room temperature. The 1H NMR spectrum revealed a pair of broad hydride resonances and the ^{31}P NMR spectrum exhibited similar behavior, making an unequivocal structural and spectral assignment problematic. Spectral clarity was achieved when **2** was examined by VT NMR over the temperature range 298–233 K, and these data are shown in Figs. 3 and 4. Lowering the temperature to 233 K led to a sharpening of the hydride and the phosphine resonances in their respective spectra as the limiting spectrum is reached. The observation of inequivalent hydride doublets and distinct ^{31}P doublets at 233 K rules out a structure that contains an edge-bridging hydride at the dppm-ligated Ru–Ru edge as an energy minimum. While the structure of **2** is consistent with that depicted in Scheme 1, alternative structures may be reconciled with the limiting NMR data and cannot be eliminated from consideration at this juncture.

The fluxional behavior displayed by **2** likely originates from a rapid hydride movement between adjacent Ru–Ru bonds or a turnstile-type rotation that promotes an exchange of the $GePh_3$ ligand between the two equatorial sites at the $Ru(CO)_3(GePh_3)$ moiety. The dynamic NMR properties in related triphenylsilane-substituted clusters have been attributed to a variant of the latter exchange process [28]. Scheme 2 illustrates the possible exchange mechanisms.



Scheme 1. Reaction of $Ru_3(CO)_{10}(\mu\text{-dppm})$ with Ph_3GeH .

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