Mixed Main Group Transition Metal Clusters: Reactions of [Ru$_3$(CO)$_{10}$(μ-dppm)] with Ph$_3$SnH

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ABSTRACT

Novel dppm-ligated ruthenium-tin clusters have been prepared from the reaction of [Ru$_3$(CO)$_{10}$(μ-dppm)] with Ph$_3$SnH. At room temperature and in the presence of Me$_3$NO, [Ru$_3$(CO)$_9$(SnPh$_3$)(μ-dppm)(μ-H)] (1) is produced from the formal loss of CO and Sn-H bond oxidative-addition. Treatment of 1 with a further two equivalents of Ph$_3$SnH (in the presence of Me$_3$NO) gave [Ru$_3$(CO)$_7$(SnPh$_3$)$_2$(μ-SnPh$_2$)(μ-dppm)(μ-H)(μ$_3$-H)] (2) which results from both Sn–H and Sn–C bond scission and contains two different hydride environments (μ and μ$_3$) and a μ-SnPh$_2$ moiety. Cluster 2 has 48 CVE (cluster valence electron) with three formal ruthenium-ruthenium bonds; two of those are very long and fall at the extreme end of distances attributed to ruthenium–ruthenium bonds. Thermolysis of 2 at 66 °C liberates benzene to give [Ru$_3$(CO)$_8$(SnPh$_3$)(μ-SnPh$_2$)(μ$_3$-SnPh$_2$)(μ-dppm)(μ-H)] (3). DFT calculations confirm that the hydride bridges one of the Ru–μ-SnPh$_2$ bonds in 3. The solid-state structures of 2 and 3 have been determined by X-ray crystallography, and the bonding and ligand distribution have been investigated by DFT studies. The geometry-optimized structures are consistent with the solid-state structures.
Keywords: Triruthenium clusters, Triphenyltin activation, Diphosphine ligand, DFT

1. Introduction

Polynuclear metal carbonyl complexes containing tin can serve as precursors to bi- and multi-metallic nanoscale heterogeneous catalysts that exhibit extremely high activity and superior selectivity for certain types of hydrogenation and dehydrogenation reactions when anchored on oxide supports [1-4]. The enhanced catalytic activity extant in such systems is attributed to tin’s ability to modify the electronic properties and particle size distribution of the heterogeneous transition metal catalyst/nanoparticle [4-6]. Consequently, several methods have been developed to incorporate tin into the coordination sphere of polynuclear metal carbonyl complexes. The most widely used method is the oxidative addition of organotin hydrides (Sn-H) to metal cluster complexes as exemplified by the work of Adams [7-9] and Cabeza [10,11]. A second method is the oxidative addition of other (organo)tin-element bonds (Sn-C, Sn-S and Sn-N) to such cluster complexes [12-15]. Recently, Cabeza et al. also shown that stannylenes stabilized by organic amides can be easily incorporated into the coordination sphere of polynuclear metal carbonyl complexes via direct reaction between them [16].

Empirically, the reaction of unsupported metal carbonyl clusters with organotin hydrides or other tin sources is typically accompanied by the formation of lower nuclearity products produced by cluster degradation [9,12]. Since it has been established that the diphosphine bis(diphenylphosphino)methane (dppm) can stabilize the trimetallic core of Group 8 clusters with respect to degradation, we have employed triruthenium and triosmium clusters [M₃(CO)₁₀(µ-dppm)] (M = Ru, Os) to help stabilize the metallic polyhedron from unwanted fragmentation during the incorporation of tin. Stoichiometrically-controlled addition of tin to [M₃(CO)₁₀(µ-dppm)] potentially facilitates the preparation of tin derivatives in a systematic fashion, which in turn allows for reproducible molecular heterogeneity of MₓSnᵧ nanoparticle-derived catalysts. Moreover, important mechanistic insight associated with the early activation steps of the ancillary tin ligands at a trinuclear cluster can be investigated as the catalyst precursor transforms to the alloy catalyst/nanoparticle [13,16,17]. We have previously reported our results from the reactions of [Os₃(CO)₁₀(µ-dppm)] with Ph₃SnH and Ph₃GeH which showed that the dppm ligand successfully prevented cluster fragmentation [13a,18]. Herein we report our findings on related reactions [Ru₃(CO)₁₀(µ-
dpmp)] with Ph₃SnH which gives rise to some novel ruthenium-tin clusters, the structure and bonding of which have been investigated by DFT calculations.

2. Results and discussion

Treatment of [Ru₃(CO)₁₀(µ-dppm)] with excess Ph₃SnH in the presence of Me₃NO at room temperature affords the new clusters [Ru₃(CO)₉(SnPh₃)(µ-dppm)(µ-H)] (1) and [Ru₃(CO)₇(SnPh₃)₂(µ-SnPh₂)(µ-dppm)(µ-H)(µ-H)] (2) in 45 and 24% yield, respectively, after chromatographic separation and workup (Scheme 1). Independent control experiments subsequently revealed that 1 serves as the precursor to 2 when treated with Ph₃SnH under comparable reaction conditions, thus confirming the sequential formation of 1 and then 2 starting from [Ru₃(CO)₁₀(µ-dppm)]. Under no conditions could a product containing two tin atoms (i.e. a Ru:Sn ratio of 3:2) be isolated. Refluxing [Ru₃(CO)₁₀(µ-dppm)] and Ph₃SnH in THF also gave 1 and 2 together with a third product, [Ru₃(CO)₈(SnPh₃)(µ-SnPh₂)(µ-SnPh₂)(µ-SnPh₂)(µ-dppm)(µ-H)] (3), which was isolated in 30% yield. Thermolysis of 1 and 2 in THF in the presence of excess Ph₃SnH also furnished 3 (Scheme 1) and we also confirmed that, while 2 undergoes transformation to 3 when refluxed in THF in the absence of added Ph₃SnH, the reaction is accompanied with extensive decomposition.

Scheme 1. Products isolated from the reaction of [Ru₃(CO)₁₀(µ-dppm)] with Ph₃SnH.
Cluster 1 was characterized by analytical and spectroscopic methods. The FAB mass spectrum shows a molecular ion at \( m/z \) 1291 along with further ions due to the sequential loss of nine carboxyls. The \(^1\)H NMR spectrum displays an upfield doublet at \( \delta -18.32 \) (J \( \text{PH} 31.6 \text{ Hz} \)) for a bridging hydride, the coupling pattern showing that it does not span the dppm-bridged Ru-Ru bond. The spectrum also shows a virtual triplet at \( \delta 4.55 \) (J 10.8 Hz) for the methylene moiety of the dppm ligand, in addition to aryl resonances from \( \delta 7.82 \) - 7.07 ascribed to the dppm and Ph3Sn ligands. The \(^{31}\)P{\(^1\)H} NMR spectrum exhibits two broad singlets at \( \delta 7.9 \) and 6.7 for the dppm ligand instead of two doublets as expected due to the non-symmetrical binding of this ligand. We suggest that the molecule is fluxional in solution at ambient temperatures due to the movement of triphenyltin and hydride ligands (Chart S1 in supplementary information) as observed in related complexes such as \([\text{Os}_3(\text{CO})_9(\text{SnPh}_3)(\mu-dppm)(\mu-H)]\) [13a] and \([\text{Os}_3(\text{CO})_9(\text{SiR}_3)(\mu-dppm)(\mu-H)] (R = \text{Et}, \text{Ph}) [19]\). Most probably for the same reason \(^{119}\)Sn satellites were not observed in the hydride signal at room temperature. In order to arrest this fluxional process we lowered the temperature, but were unable to see the \(^{119}\)Sn satellites even at 213 K (Fig. S10). The two broad singlets observed in the \(^{31}\)P{\(^1\)H} NMR spectrum at room temperature gradually sharpen as the temperature was lowered, but we did not observe the expected splitting even at 213 K (Fig. S12). The IR spectrum of 1 exhibits carbonyl absorptions within the range 2079-1923 cm\(^{-1}\) and the pattern of this spectrum is also quite similar to that observed for \([\text{Os}_3(\text{CO})_9(\text{SnPh}_3)(\mu-dppm)(\mu-H)]\) [13a]. The osmium analogue \([\text{Os}_3(\text{CO})_9(\text{SnPh}_3)(\mu-dppm)(\mu-H)]\) [13a] was structurally characterized which confirmed the disposition of the hydride and Ph3Sn ligands relative to the dppm-tethered Os-Os bond. The large Ph3Sn ligand occupies one of the two equatorial sites at the adjacent ruthenium centre with the hydride located at the sterically least crowded equatorial site \( \text{cis} \) to the Ph3Sn group.

The locus preference for the disposition of the hydride and Ph3Sn ligands relative to the bridging dppm ligand in 1 was investigated by density functional theory (DFT). Two structures were optimized (A and A\(_{\text{alt}}\)), each possessing an edge-bridged hydride and an equatorially situated Ph3Sn ligand that was oriented either \( \text{cis} \) or \( \text{trans} \) to the hydride (Fig. 1). They differ by 2.2 kcal/mol (\( \Delta G \)) in favour of the \( \text{cis} \) isomer A, supporting the anticipated structure for cluster 1. We also computed the natural charges and Wiberg bond index (WBI) for the different Ru-Ru, Ru-Sn, and Ru-H bonds in A (Table 1). The charges on the ruthenium atoms are all negative and range from -1.40 (Ru\(_2\)) to -1.58 (Ru\(_3\)), and the mean
charge for the two phosphorus atoms is 1.34. The computed charges for the tin and hydride ligands are both positive (1.79 and 0.13, respectively). The computed distance of 3.1236 Å for the Ru1-Ru3 bond is 0.18 Å longer than the mean distance for the other two Ru-Ru bonds in A, and this is reflected in the Wiberg bond indices, which serve as a measure of bond strength. The longer hydride-bridged Ru1-Ru3 bond exhibits a Wiberg index that is nearly 60% shorter than the WBIs of other two Ru-Ru bonds. The computed WBIs are consistent with the structure of A and the trends in bond lengths reported by us for related metal clusters [13b,20].

Place Figure 1 and Table 1 Here

The identity of 2 and 3 could not be ascertained from spectroscopic data and accordingly we carried out single crystal X-ray diffraction analyses to establish their molecular architecture. The structure of 2 is depicted in Fig. 2, whose caption also exhibits selected bond lengths and angles. The molecule results from the formal addition of three equivalents of Ph3SnH to the triruthenium centre, followed by further cleavage of a tin-phenyl bond probably extruded as benzene. There are two long and one short ruthenium-ruthenium vectors. The Ru(1)-Ru(2) distance of 2.9439(3) Å is bridged by the dppm ligand and is consistent with a single-bond designation. The Ru(2)-Ru(3) [3.2355(5) Å] and Ru(1)-Ru(3) [3.3992(7) Å] distances are considerably longer than the dppm-bridged metallic edge but do fall within the van der Waals radii for two ruthenium atoms [23]. These are best viewed as weak Ru-Ru single bonds since the cluster has a total electron count of 48 [24]. Examples of polynuclear ruthenium clusters with Ru-Ru bond(s) exceeding 3.10 Å include \[[\eta^6-C_6Me_6)_2Ru_2H_2(CH_2Cl_2)]RuB_{10}H_{18}(OEt)_2\] [25], Ru5Pt5(CO)18(COD)2(μ₃-H)2 [23], \[[Ru3H(pyS)(CO)7]_3\] [24], and \[[AuRu6(μ₃-H)(μ-O:μ-C:η^6-OC₆H₄OMe-4)(CO)16(PPh3)]\] [26].

Place Figure 2 Here

The two Ru-P bond distances in 2 are symmetric [Ru(1)–P(1) 2.3825(7) and Ru(2)–P(2) 2.3996(6) Å] and the seven CO groups exhibit bond distances and angles unremarkable relative to ruthenium clusters containing terminal Ru-CO groups. The diphenyltin ligand asymmetrically bridges the elongated Ru(2)-Ru(3) edge [Ru(2)–Sn(2) 2.6501(2) and Ru(3)–
Sn(2) 2.6926(3) Å, while the two Ph₃Sn ligands are bound to the Ru(1) [Ru(1)–Sn(1) 2.6607(2) Å] and Ru(3) [Ru(3)–Sn(3) 2.6854(3) Å] atoms at an equatorial coordination site. The ruthenium-tin bond distances observed in 2 are similar to those Ru-Sn distances reported in the literature for other structurally characterized Ru₃ and Ru₅ clusters containing an η¹-SnPh₃ ligand(s) [7b,9c,27]. Both hydride ligands were located crystallographically. One spans the dppm-bridged ruthenium-ruthenium edge, while the other is located within the Ru₃ core and is bound to all three ruthenium atoms. The DFT-optimized structure of B reproduces the important structural features found in 2, and the charge data and WBIs are in keeping with the general feature of this cluster. Eq 1 shows the balanced reaction for the conversion of A→B which is highly exergonic by 165.8 kcal/mol. Solution spectroscopic data confirm that the solid-state structure persists in solution. The ¹H NMR spectrum displays two upfield resonances; a triplet at δ -10.21 (JPH 14.6) and a singlet at δ -17.86 assigned to the edge-bridging (µ) and interstitial (µι) hydrides, respectively, in addition to other resonances for the methylene and phenyl protons. The ³¹P{¹H} NMR spectrum shows two equal intensity doublets centered at δ 29.5 and 27.4 (JPP 77 Hz) for the inequivalent PPh₂ moieties of the dppm ligand. Again, the ¹¹⁹Sn satellites were missing in both ¹H NMR and ³¹P{¹H} NMR spectra of 2 even at 213 K (Figs. S13 and S15).

\[
\begin{align*}
A + 2\text{Ph}_3\text{SnH} + 2\text{Me}_3\text{NO} & \rightarrow B + 2\text{CO}_2 + 2\text{Me}_3\text{N} + \text{benzene} \quad \text{Eq 1}
\end{align*}
\]

The molecular structure of 3 is shown in Fig. 3, and the figure caption exhibits selected bond lengths and angles. The Ru(1)-Ru(2) and Ru(2)-Ru(3) bond distances of 3.0136(7) and 3.1724(8) Å, respectively, are on the long side of the ruthenium-ruthenium distances reported for polynuclear ruthenium clusters in the Cambridge Crystallographic Data Centre [28] but are consistent with the designation as Ru-Ru single bonds. The DFT-optimized structure of C (Fig. 1) is in accord with this, the presence of two Ru-Ru bonds being supported by the Wiberg bond indices of 0.33 and 0.27 for the dppm-bridged Ru-Ru bond and the elongated Ru-Ru bond that is tethered by the bridging Ph₂Sn groups, respectively. The Ru(1)···Ru(3) internuclear separation found in the X-ray structure is 5.411 Å which clearly precludes any significant bonding interaction, a feature reflected by the WBI of 0.02 computed for this particular bond (Table 1) and consistent with the total electron count of 50. The triphenyltin ligand [Sn(3)] is equatorially coordinated to the Ru(3) atom and the diphosphine ligand asymmetrically spans Ru(1)-Ru(2) edge [Ru(1)–P(1) 2.376(2) and
The Ph2Sn(2) ligand bridges the long Ru(2)-Ru(3) edge quite symmetrically [Ru(2)-Sn(2) 2.6351(7) and Ru(3)-Sn(2) 2.6518(7) Å], whilst the other Ph2Sn(1) moiety is bound to all three ruthenium atoms through the interior of the expanded metallic polyhedron. Although the Sn(1) is pentacoordinated, it donates two electrons to the cluster core akin to the quadruply bridged PhSn ligands in [Ru4(CO)12(µ4-SnPh)2] [2b,9a], [Ru4(CO)10(µ4-SnPh)2(µ-SnPh2)] [2b], [Ru4(CO)6(µ4-SnPh)2(µ-SnPh2)2] [2b], [Ru4(CO)8(µ4-SnPh)2(µ-SnPh2)4] [2b], [Ru5(CO)11(C6H6)(µ4-SnPh)(µ3-CPh)] [7b] etc. which donates three electrons to the cluster core. Three relatively strong interactions exist between the Sn(1) center and the three ruthenium atoms based on the Wiberg bond indices that range from 0.56 to 0.59. We also computed the free energy change attendant in the conversion of A→C, and Eq 2 shows the balanced reaction that is exergonic by 37.0 kcal/mol.

\[
A + 2\text{Ph}_3\text{SnH} \quad \rightarrow \quad C + \text{CO} + 2(\text{benzene}) \quad \text{Eq 2}
\]

While the hydride ligand was not located in the diffraction structure, it was assumed to span the Ru(1)-Sn(1) edge based on the disposition of the ligands about the cluster polyhedron and the NMR data recorded for the hydride. This premise was subsequently corroborated by DFT calculations that afforded species C as the hydride structure in concert with the solid-state structure. The \(^1\text{H}\) NMR spectrum of 3 shows an upfield doublet of doublets for the lone hydride at δ -7.76 (J\(_{\text{PH}}\) 60.8, 6.8 Hz). The hydride resonance is deshielded slightly relative to those hydride resonances in clusters 1 and 2 reported here and other edge-bridging hydrides in ruthenium clusters whose chemical shifts are typically found from δ -10 to -20. The chemical shift of the hydride in 3 is close to the values reported for the agosticµ-silyl \(\text{Ru}_2(\text{CO})_3(\text{SiTo}_2\text{H})(\mu\text{-dppm})(\mu,\eta^2\text{-HSiTo}_2)\) and µ-silane \(\text{Ru}(\text{CO})_2(\text{SiTo}_2\text{H})_2(\mu\text{-dppm})(\mu,\eta^2\cdot\eta^2\text{-H}_2\text{SiTo}_2)\) complexes [29, 30] that reveal a comparable hydride chemical shift at δ -8.87 and -8.84, respectively. The interaction that exists between the hydride ligand and the Ru2-Sn3 edge in C may be viewed within the context of an agostic-type association based on the Wiberg bond indices of 0.64 (Ru2-H1) and 0.09 (Sn3-H1). The hydride is more strongly bound to the ruthenium centre than the tin center, and this promotes a non-symmetrical bridging interaction of the hydride with the Ru-Sn edge in C. To probe this further, we have recorded and compared the ATR-FTIR spectra of 3 and Ph3SnH. The Ph3SnH shows an absorption at 1838 cm\(^{-1}\) due to a Sn-H stretching vibration in...
its ATR-FTIR spectrum (Fig. S16). Although 3 also displays absorptions around 1850 cm\(^{-1}\) (Fig. S17), we could not assign these absorptions to a Sn-H stretch unambiguously due to the presence of CO ligand stretching in the molecule in this same region. The \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum of 3 exhibits a doublet at \(\delta 41.9\) (\(J_{PP} 68\)) and a triplet at \(\delta 19.8\) (\(J_{PP} 68\)) for the inequivalent PPh\(_2\) moieties of the dppm ligand, the latter resonance also indicates that one of the phosphorus nuclei is coupled with hydride. Akin to 1 and 2, we did not observe \(^{119}\text{Sn}\) satellites in both \(^1\text{H}\) NMR and \(^{31}\text{P}\{^1\text{H}\}\) NMR spectra of 3 even at 213 K (Figs. S18 and S20).

Formation of 3 upon heating 2 results from both cleavage of a Sn-Ph bond (probably extruded as benzene) but also CO addition. As the yield of 3 is relatively low (31\%) then presumably added CO results from degradation of a small amount of cluster 2.

3. Summary and conclusions

The stepwise functionalization of \([\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})]\) by Ph\(_3\)SnH has been demonstrated under Me\(_3\)NO-promoted activation and direct thermolysis. The initial product \([\text{Ru}_3(\text{CO})_9(\text{SnPh}_3)(\mu\text{-dppm})(\mu\text{-H})]\) (1) results from CO loss, coupled with Sn-H bond cleavage. This product reacts with further Ph\(_3\)SnH to give the dihydride cluster \([\text{Ru}_3(\text{CO})_7(\text{SnPh}_3)_2(\mu\text{-SnPh}_2)(\mu\text{-dppm})(\mu\text{-H})(\mu\text{3-H})]\) (2), resulting from the addition of a further two equivalents of Ph\(_3\)SnH and a secondary Sn-Ph bond scission. The cluster contains an edge-bridged hydride and a triply-bridged hydride that lies within the interior of an expanded metallic polyhedron, two of the ruthenium-ruthenium bonds being at the extreme end of distances attributed to ruthenium-ruthenium bonds. The final product, \([\text{Ru}_3(\text{CO})_8(\text{SnPh}_3)(\mu\text{-SnPh}_2)(\mu\text{3-SnPh}_2)(\mu\text{-dppm})(\mu\text{2-H})]\) (3), is obtained upon thermolysis of 2 and is shown to contain two bridging Ph\(_2\)Sn ligands that help maintain the trimetallic framework of the product. Interestingly while it is the thermolysis product of 2 it also has one more CO ligand, thus the thermal rearrangement has led to an increase in the total electron count from 48 to 50, the reverse of the behaviour normally noted in low valent cluster chemistry. The structures of 1-3 have been established by spectroscopic and structural studies, and bonding aspects have been examined by DFT calculations. It is noteworthy that in all new Ru-Sn complexes the triruthenium core is maintained, highlighting once again the stabilising nature of the dppm ligand. A further point of note is our inability to isolate or identify any products with a Ru:Sn ratio of 3:2. These data suggest that the addition of the
second equivalent of Ph$_3$SnH activates the triruthenium centre to further oxidative addition (either Sn-H or Sn-C) and highlights the potential role of tin as a catalytic accelerant. The use of these new clusters as precursors for the stoichiometrically-controlled formation of RuSn nanoparticles and alloy precatalysts is on-going, the results of which will be presented in due course.

4. Experimental

4.1. General remarks

All reactions were carried under an inert atmosphere of nitrogen using standard Schlenk techniques unless otherwise stated. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. All $^1$H and $^{31}$P{$^1$H} NMR spectra were recorded on an Bruker Avance IIIHD (400 MHz) instrument. Solution IR spectra were recorded on a Shimadzu FTIR Prestige 21 spectrophotometer, and ATR-IR spectra were obtained on a Shimadzu IRTracer-100 instrument. Elemental analyses were performed by the Microanalytical Laboratory of Wazed Miah Science Research Centre at Jahangirnagar University. [Ru$_3$(CO)$_{12}$] was purchased from Strem Chemical Inc. and used without further purification. Bis(diphenylphosphino)methane (dppm) and Ph$_3$SnH were purchased from Acros Chemicals Inc. and used as received. [Ru$_3$(CO)$_{10}$($\mu$-dppm)] was prepared according to the published procedures [31]. Products were separated in the air on TLC plates coated with 0.25 mm layer of silica gel (HF$_2$54-type 60, E. Merck, Germany).

4.2. Reaction of [Ru$_3$(CO)$_{10}$($\mu$-dppm)] with Ph$_3$SnH at room temperature

A CH$_2$Cl$_2$ solution (10 mL) of Me$_3$NO (14 mg, 0.19 mmol) was added to a CH$_2$Cl$_2$ solution (20 mL) of [Ru$_3$(CO)$_{10}$($\mu$-dppm)] (50 mg, 0.052 mmol) and Ph$_3$SnH (60 mg, 0.17 mmol) using a pressure equalizing dropping funnel over 15 min. The reaction solution was stirred for 2 h at room temperature, during which time the solution color changed from orange to red. The solution was then filtered through a short silica column (4 cm) to remove excess Me$_3$NO. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with cyclohexane/CH$_2$Cl$_2$ (7:3, v/v) developed two major and two minor bands. The faster moving major band afforded [Ru$_3$(CO)$_7$(SnPh$_3$)$_2$(μ-SnPh$_2$)(μ-dppm)(μ-H)(μ$_3$-H)] (2) (23 mg, 24%) as red crystals while
the slower moving major band gave \([\text{Ru}_3(\text{CO})_9(\text{SnPh}_3)(\mu-\text{dppm})(\mu-\text{H})]\) (1) (30 mg, 45%) as yellow crystals after recrystallization from hexane/\(\text{CH}_2\text{Cl}_2\) at 25 °C. The contents of the remaining minor bands were too small for characterization.

Analytical and spectroscopic data for 1: Anal. Calcd for C_{52}H_{38}O_9P_2RuSn: C, 48.38; H, 2.97. Found: C, 48.85; H, 3.36%. IR (\(\nu\text{CO}, \text{CH}_2\text{Cl}_2\)): 2079w, 2043s, 2005vs, 1983sh, 1942sh, 4.55 (t, J 10.8, 2H), -18.32 (d, J 31.6, 1H). 31P{\(^1\)H} NMR (CD_2Cl_2): 8 7.82 (d, J 7.2, 1H), 6.40 (d, J 7.2, 1H), 7.60-7.07 (m, 33H), 4.55 (t, J 10.8, 2H), -18.32 (d, J 31.6, 1H). 31P{\(^1\)H} NMR (CD_2Cl_2): 8 7.9 (br. s, 1P), 6.7 (br. s, 1P).

FAB-MS: m/z 1291.

Analytical and spectroscopic data for 2: Anal. Calcd for C_{80}H_{64}O_7P_2Ru_3Sn: C, 51.69; H, 3.47. Found: C, 52.05; H, 3.54%. IR (\(\nu\text{CO}, \text{CH}_2\text{Cl}_2\)): 2057m, 2026s, 2014vs, 1970s, 1942m cm\(^{-1}\). 31P{\(^1\)H} NMR (CD_2Cl_2): 8 29.5 (d, J 68, 1P), 27.4 (d, J 68, 1P).

4.3. Reaction of \([\text{Ru}_3(\text{CO})_{10}(\mu-\text{dppm})]\) with \(\text{Ph}_3\text{SnH}\) at 66 °C

A THF solution (30 mL) of \([\text{Ru}_3(\text{CO})_{10}(\mu-\text{dppm})]\) (50 mg, 0.052 mmol) and \(\text{Ph}_3\text{SnH}\) (60 mg, 0.171 mmol) was heated to reflux for 90 min. The solvent was removed under reduced pressure and the residue chromatographically separated by TLC on silica gel. Elution with cyclohexane/\(\text{CH}_2\text{Cl}_2\) (7:3, v/v) developed one major and several minor bands. The major band gave \([\text{Ru}_3(\text{CO})_8(\text{SnPh}_3)(\mu-\text{SnPh}_2)_2(\mu-\text{H})\text{SnPh}_2)(\mu-\text{dppm})]\) (3) (28 mg, 30%) as red crystals after recrystallization from hexane/\(\text{CH}_2\text{Cl}_2\) at 4 °C, while the contents of minor bands were too small for characterization.

Analytical and spectroscopic data for 3: Anal. Calcd for C_{75}H_{58}O_6P_2Ru_3Sn: C, 49.80; H, 3.23. Found: C, 50.33; H, 3.28%. IR (\(\nu\text{CO}, \text{CH}_2\text{Cl}_2\)): 2046w, 2030m, 2015m, 1925sh cm\(^{-1}\). 31P{\(^1\)H} NMR (CD_2Cl_2): 8 41.9 (d, J 68, 1P), 19.8 (t, J 68, 1P).

4.4. Conversion of 1 to 2

To a \(\text{CH}_2\text{Cl}_2\) solution (20 mL) of 1 (10 mg, 0.008 mmol) and \(\text{Ph}_3\text{SnH}\) (6 mg, 0.017 mmol) was added a \(\text{CH}_2\text{Cl}_2\) solution (10 mL) of Me_3NO (2 mg, 0.027 mmol) using a pressure
equalizing dropping funnel. The mixture was stirred at room temperature for 2 h, and the product was isolated by chromatography, as described above, to give 2 (6 mg, 42%).

4.5. Reaction of 1 with Ph₃SnH

A THF solution (20 mL) of 1 (10 mg, 0.008 mmol) and Ph₃SnH (5 mg, 0.014 mmol) was heated to reflux for 2 h. Similar chromatographic separation and workup mentioned above gave 3 (5 mg, 36%).

4.6. Conversion of 2 to 3

A THF solution (15 mL) of 2 (10 mg, 0.0054 mmol) was refluxed for 1 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with cyclohexane/CH₂Cl₂ (7:3, v/v) developed three bands. The first band corresponded to unreacted 2 (3 mg). The second band isolated furnished 3 (3 mg, 31%) while the contents of the other band were too small for complete characterization.

4.7. Crystal structure determination

Single crystals of clusters 2 and 3 suitable for X-ray diffraction analysis were grown by slow diffusion of hexane into a CH₂Cl₂ solution containing each cluster. A suitable single crystal of 2 was mounted on an Agilent Super Nova dual diffractometer (Agilent Technologies Inc., Santa Clara, CA) using a Nylon Loop and the diffraction data were collected at 150(1) K using Cu-Kα radiation (λ = 1.54184). Unit cell determination, data reduction, and absorption corrections were carried out using CrysAlisPro [32]. The structure was solved with the ShelXS [33] structure solution program using Direct Methods and refined by full-matrix least-squares on the basis of F² using SHELXL 2013 [33] within the OLEX2 [34] graphical user interface. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms (except those directly bonded to metals) were included using a riding model. One phenyl substituent on a tin atom [C47-C52] was disordered and refined over two sites with occupancies of 0.65:0.35. Some C-C distances within the minor component of the disordered phenyl group vary significantly from the ideal value of 1.395 Å. A suitable single crystal of 3 was mounted on a Bruker SMART APEX CCD diffractometer using glass fiber and the diffraction data were collected at 150(2) K using Mo-Kα radiation (λ = 0.71073). Data reduction and integration were carried out with SAINT+ and absorption corrections were
applied using the program SADABS [35]. Structures were solved by Direct methods and refined using full-matrix least-squares on $F^2$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in the calculated positions and their thermal parameters linked to those of the atoms to which they were attached (riding model). The SHELXTL PLUS V6.10 program package was used for structure solution and refinement [36]. While PLATON reports solvent accessible voids in 3, the largest residual electron density peak is only 1.062 eÅ$^{-3}$ and we attribute this to poor packing of the many phenyl groups in the structure. This is consistent with the fact that the density of 3 is ca. 0.1 gcm$^{-3}$ less compared to 2. Pertinent crystallographic parameters are given in Table 2.

4.8. Computational Methodology

The DFT calculations were carried out with the Gaussian 09 package of programs [37] using the B3LYP hybrid functional. This functional is comprised of Becke's three-parameter hybrid exchange functional (B3) [38] and the correlation functional of Lee, Yang, and Parr (LYP) [39]. The ruthenium and tin atoms were described with the Stuttgart-Dresden effective core potential and SDD basis set [40], and the 6-31G(d') basis set [41] was employed for the P, O, C, and H atoms.

The reported geometries for A-C were fully optimized, and the analytical Hessian was evaluated at each stationary point to confirm that the geometry was an energy minimum (no negative eigenvalues). Unscaled vibrational frequencies were used to make zero-point and thermal corrections to the electronic energies, and the resulting free energies are reported in kcal/mol relative to the specified standard. The geometry-optimized structures have been drawn with the JIMP2 molecular visualization and manipulation program [42].

Acknowledgments

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CASCaM. We also thank Prof. Michael B. Hall (TAMU) for providing us a copy of his JIMP2 program.

Supplementary data

Electronic supplementary information (ESI) contains IR, NMR, VT NMR spectra and atomic coordinates of DFT-optimized structures. CCDC 1511020 and CCDC 1506077 contain supplementary crystallographic data for 2 and 3 respectively. These data may be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

References


[21] Here we have used a van der Waals radius of 2.07 Å for ruthenium, as taken from the Periodic Table of Elements: Los Alamos National Laboratory (http://periodic.lanl.gov/73).
(c) M.I. Hyder, S.E. Kabir, M.A. Miah, T.A. Siddiquee, G.M.G. Hossain, Polyhedron 24 (2005) 1471-1477;


SMART and SAINT software for CCD diffractometers, version 6.1, Madison, WI (2000).


[42] (a) JIMP2, version 0.091, a free program for the visualization and manipulation of molecules: M.B. Hall, R.F. Fenske, Inorg. Chem. 11 (1972) 768-775; (b) J. Manson, C.E. Webster, M.B. Hall, Texas A&M University, College Station, TX, (2006): http://www.chem.tamu.edu/jimp2/index.html
Table 1
Selected natural charges and Wiberg bond indices for the DFT-optimized species A-C\(^a\)

<table>
<thead>
<tr>
<th>species</th>
<th>Ru(_1)</th>
<th>Ru(_2)</th>
<th>Ru(_3)</th>
<th>P(_1)</th>
<th>P(_2)</th>
<th>Sn(_1)</th>
<th>Sn(_2)</th>
<th>Sn(_3)</th>
<th>H(_1)</th>
<th>H(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-1.52</td>
<td>-1.40</td>
<td>-1.58</td>
<td>1.36</td>
<td>1.31</td>
<td>1.79</td>
<td></td>
<td></td>
<td></td>
<td>0.13</td>
</tr>
<tr>
<td>B</td>
<td>-1.55</td>
<td>-1.52</td>
<td>-1.95</td>
<td>1.30</td>
<td>1.30</td>
<td>1.81</td>
<td>1.83</td>
<td>1.73</td>
<td>0.08</td>
<td>0.10</td>
</tr>
<tr>
<td>C</td>
<td>-1.93</td>
<td>-1.62</td>
<td>-2.16</td>
<td>1.34</td>
<td>1.29</td>
<td>1.82</td>
<td>1.75</td>
<td>1.76</td>
<td>0.11</td>
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</table>

Wiberg bond indices\(^b\)

<table>
<thead>
<tr>
<th>species</th>
<th>Ru(_1)-Ru(_2)</th>
<th>Ru(_2)-Ru(_3)</th>
<th>Ru(_1)-Ru(_3)</th>
<th>Ru(_1)-Sn(_2)</th>
<th>Ru(_2)-Sn(_2)</th>
<th>Ru(_1)-Sn(_3)</th>
<th>Ru(_2)-Sn(_3)</th>
<th>Ru(_1)-H(_2)</th>
<th>Ru(_2)-H(_2)</th>
<th>Sn(_3)-H(_1)</th>
<th>Ru(_1)-H(_1)</th>
<th>Ru(_2)-H(_1)</th>
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<tr>
<td>A</td>
<td>0.37</td>
<td>0.40</td>
<td>0.23</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.42</td>
<td>0.32</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0.22</td>
<td>0.16</td>
<td>0.12</td>
<td>0.62</td>
<td></td>
<td></td>
<td>0.55</td>
<td>0.59</td>
<td>0.25</td>
<td>0.26</td>
<td>0.30</td>
<td>0.43</td>
</tr>
<tr>
<td>C</td>
<td>0.33</td>
<td>0.02</td>
<td>0.27</td>
<td>0.56</td>
<td>0.59</td>
<td>0.58</td>
<td>0.19</td>
<td>0.39</td>
<td></td>
<td>0.09</td>
<td>0.02</td>
<td>0.64</td>
</tr>
</tbody>
</table>

\(^a\)Atom numbers based on the numbering scheme for the different Ru\(_3\) clusters (A-left; B-center; C-right) examined in this study. The depicted Sn and Sn atoms represent Ph\(_3\)Sn and Ph\(_2\)Sn moieties, respectively. \(^b\)The mean WBI for the Ru\(_3\)-Sn\(_1\) vectors is 0.59.
Table 2
Crystallographic and structure refinement data for 2 and 3

<table>
<thead>
<tr>
<th>Compound</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{80}H_{64}O_{7}P_{2}Ru_{3}Sn_{3}</td>
<td>C_{75}H_{58}O_{8}P_{2}Ru_{3}Sn_{3}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1858.53</td>
<td>1808.43</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>150</td>
<td>150(2)</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>1.54184</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P 2 \overline{1}/n$</td>
<td>$P-1$</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>11.83579(7)</td>
<td>11.527(3)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>33.90437(19)</td>
<td>16.216(4)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>17.79811(12)</td>
<td>19.938(5)</td>
</tr>
<tr>
<td>$\alpha$ ($^\circ$)</td>
<td>90</td>
<td>85.646(4)</td>
</tr>
<tr>
<td>$\beta$ ($^\circ$)</td>
<td>90.5029(6)</td>
<td>83.389(4)</td>
</tr>
<tr>
<td>$\gamma$ ($^\circ$)</td>
<td>90</td>
<td>86.554(4)</td>
</tr>
<tr>
<td>Volume (Å$^3$)</td>
<td>7141.84(8)</td>
<td>3686.4(14)</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
<td>2</td>
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<tr>
<td>Density (calculated) (g/cm$^3$)</td>
<td>1.728</td>
<td>1.629</td>
</tr>
<tr>
<td>Absorption coefficient (mm$^{-1}$)</td>
<td>14.082</td>
<td>1.694</td>
</tr>
<tr>
<td>$F(000)$</td>
<td>3648.0</td>
<td>1768</td>
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<tr>
<td>Crystal size (mm$^3$)</td>
<td>$0.17 \times 0.11 \times 0.08$</td>
<td>$0.22 \times 0.18 \times 0.16$</td>
</tr>
<tr>
<td>$2\theta$ range for data collection ($^\circ$)</td>
<td>7.202 to 148.258</td>
<td>4.82 to 56.94</td>
</tr>
<tr>
<td>Index ranges</td>
<td>$-14 \leq h \leq 14$</td>
<td>$-15 \leq h \leq 15$</td>
</tr>
<tr>
<td></td>
<td>$-41 \leq k \leq 42$</td>
<td>$-21 \leq k \leq 21$</td>
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<td></td>
<td>$-22 \leq l \leq 22$</td>
<td>$-25 \leq l \leq 26$</td>
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<tr>
<td>Reflections collected</td>
<td>128435</td>
<td>31011</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>14430 [$R_{int} = 0.0381$]</td>
<td>16520 [$R_{int} = 0.0435$]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>14430 / 0 / 910</td>
<td>16520 / 0 / 820</td>
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<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.121</td>
<td>0.880</td>
</tr>
<tr>
<td>Final $R$ indices [$I&gt;2\sigma(I)$]</td>
<td>$R_1 = 0.0234$, $wR_2 = 0.0513$</td>
<td>$R_1 = 0.0422$, $wR_2 = 0.0855$</td>
</tr>
<tr>
<td>$R$ indices (all data)</td>
<td>$R_1 = 0.0249$, $wR_2 = 0.0520$</td>
<td>$R_1 = 0.0817$, $wR_2 = 0.0917$</td>
</tr>
<tr>
<td>Largest diff. peak and hole (eÅ$^{-3}$)</td>
<td>0.98 and $-0.73$</td>
<td>1.062 and $-0.625$</td>
</tr>
</tbody>
</table>
Fig. 1. DFT-optimized structures for the isomers of $[{\text{Ru}}_3(\text{CO})_9(\text{SnPh}_3)(\mu\text{-dppm})(\mu\text{-H})]$ (A and $\text{A}_{\text{alt}}$), and the clusters $[{\text{Ru}}_3(\text{CO})_7(\text{SnPh}_3)_2(\mu\text{-SnPh}_2)(\mu\text{-dppm})(\mu\text{-H})(\mu_3\text{-H})]$ (B), and $[{\text{Ru}}_3(\text{CO})_8(\text{SnPh}_3)(\mu\text{-SnPh}_2)(\mu_3\text{-SnPh}_2)(\mu\text{-dppm})(\mu\text{-H})]$ (C).
Fig. 2. ORTEP diagram of the molecular structure of $[\text{Ru}_3(\text{CO})_7(\text{SnPh}_3)_2(\mu-\text{SnPh}_2)(\mu-\text{dppm})(\mu-\text{H})(\mu_3-\text{H})]$ (2), showing 50% probability thermal ellipsoids. Hydrogen atoms except those directly bonded to ruthenium are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–Ru(2) 2.9439(3), Ru(2)–Ru(3) 3.2355(5), Ru(1)–Ru(3) 3.3992(7), Ru(1)–Sn(1) 2.6607(2), Ru(2)–Sn(2) 2.6501(2), Ru(3)–Sn(2) 2.6926(3), Ru(3)–Sn(3) 2.6854(3), Ru(1)–P(1) 2.3825(7), Ru(2)–P(2) 2.3996(6), Sn(1)–Ru(1)–Ru(2) 124.686(9), P(1)–Ru(1)–Sn(1) 94.05(2), P(1)–Ru(1)–Ru(2) 90.89(2), P(2)–Ru(2)–Sn(2) 102.91(2), Ru(2)–Sn(2)–Ru(3) 74.537(7), Sn(2)–Ru(3)–Sn(3) 94.045(8), Sn(2)–Ru(2)–Ru(1) 119.208(8).
Fig. 3. ORTEP diagram of the molecular structure of [Ru$_3$(CO)$_8$(SnPh$_3$)(µ-SnPh$_2$)$_2$(µ$_3$-HSnPh$_2$)(µ-dppm)] (3), showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–Ru(2) 3.0136(7), Ru(2)–Ru(3) 3.1724(8), Ru(1)–Sn(1) 3.0640(8), Ru(2)–Sn(1) 2.6284(7), Ru(2)–Sn(1) 2.6284(7), Ru(3)–Sn(1) 2.7953(7), Ru(2)–Sn(2) 2.6351(7), Ru(3)–Sn(2) 2.6518(7), Ru(3)–Sn(3) 2.6570(7), Ru(1)–P(1) 2.376(2), Ru(2)–P(2) 2.312(1), Ru(1)–Sn(1)–Ru(2) 63.39(2), Ru(1)–Sn(1)–Ru(3) 134.84(2), Sn(1)–Ru(1)–Ru(2) 51.25(2), Sn(1)–Ru(2)–Ru(1) 65.38(2), Sn(1)–Ru(2)–Sn(2) 110.08(2), Sn(1)–Ru(3)–Sn(2) 104.70(2), Ru(2)–Sn(1)–Ru(3) 71.50(2), Ru(2)–Sn(2)–Ru(3) 73.72(2), Sn(1)–Ru(3)–Sn(3) 162.68(2), Sn(2)–Ru(3)–Sn(3) 92.60(2), Sn(2)–Ru(2)–Ru(1) 175.06(2), P(1)–Ru(1)–Ru(2) 89.15(4), P(2)–Ru(2)–Sn(2) 95.11(4).
Graphical Abstract

Mixed Main Group Transition Metal Clusters: Reactions of \([\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})]\) with \(\text{Ph}_3\text{SnH}\)

Md. Mehedi Mahabub Khan \(\text{a}\), Shishir Ghosh \(\text{a}\), Graeme Hogarth \(\text{b}\), Derek A. Tocher \(\text{c}\), Michael G. Richmond \(\text{d}\), Shariff E. Kabir \(\text{a, e,}\,\,\,*\), Herbert W. Roesky \(\text{e,}\,\,\,*\)

The structure and bonding of several dppm-ligated ruthenium-tin clusters prepared from the reactions between \([\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})]\) and \(\text{Ph}_3\text{SnH}\) have been examined.