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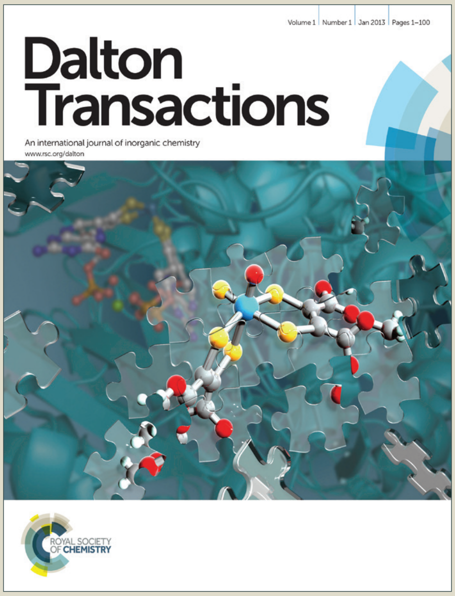

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rationalizes the presence of a single type of Cp* ligand indicating high symmetry. The presence of Cp* ligand has also been supported by ^{13}C NMR.

In order to confirm the spectroscopic assignments and to determine the solid state structure of **2**, the X-ray structure analysis was undertaken (Fig. 1).[§] The crystal structure of **2** corresponds to a highly symmetric adamantanoid core consisting of germanium and oxygen atoms. Each of the Ge atoms lies at the vertex of a tetrahedron with the oxygen at the edges forming a Ge_4O_6 framework. The Ge–O bond length (1.793(5) Å) of the six membered rings in **2** is slightly longer than those of normal six membered ring structures, $(Ph_2GeO)_3$ [Ge–O = 1.769(4) Å][17] and $(^tBu_2GeO)_3$ [Ge–O = 1.781(1) Å][17b] however, comparable with that of adamantanoid oxotellurido- germanate $[Ge_4O_6Te_4]^-$ anion.[13] The Ge–Ru bond length of 2.4004(11) Å is very close to that of **1**.[18]

Another interesting feature of **2** is the presence of an *exo*-{Cp*Ru(CO)$_2$} fragment which is attached to Ge via Ru atom. This *exo*-fragment provides one electron towards each of the germanium centre making all valence electrons of germanium atom available for bonding. [19] A similar description has also been given by Housecraft for a Ru_4B core in boride cluster $[H_2Ru_5(CO)_{13}Cp^*BH_2]$.[19a] Note that there are reports available for other group 14 compounds[20] as well as metal oxides, such as As_4O_6[21], Bi_4O_6[22], $V_4O_6^-$ and Ti-V bimetallic oxides[23] that exhibit adamantane like structure. The main group metal-oxo clusters are less explored compared to their transition metal counterparts except the adamantane-type M_4O_6 clusters of aluminium and gallium,[24] indium,[25] tin,[26] and antimony[27]. To the best of our knowledge, there is only one such framework is known with Ge_4O_6 core having Te attachement.[13]

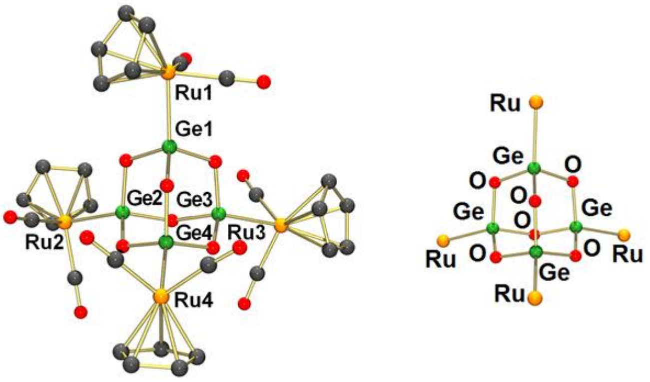

Fig. 1 Molecular structure of **2**, (Right view: adamantane core). All methyl groups on each Cp* carbon atom were omitted for clarity. Selected bond lengths (Å) and angels (°): O9−Ge2 1.787(5), O10−Ge3 1.797(5), O11−Ge4 1.790(5), O11−Ge3 1.793(5), Ge1−Ru1 2.3960(11), Ge2−Ru2 2.4042(11), Ge4−Ru4 2.4021(11); O13−Ge1−O9 104.2(2), O9−Ge1−Ru1 112.40(17), O9−Ge2−Ru2 113.72(16), O14−Ge2−Ru2 113.66(17).

The spectroscopic data of **2** are fully in accord with the solid-state X-ray structure, and no evidence of fluxional behavior is observed. The IR spectrum shows the terminal CO stretching frequencies appeared at 2009 and 1956 cm^{-1}. An intense band, appeared at 769 cm^{-1}, corresponds to Ge–O stretching mode.

The molecular packing of **2** is stabilized by intermolecular interactions and van der Waals forces between the hydrogen atoms. As shown in Fig. S2 (ESI†), the intermolecular hydrogen bonding interactions have been found between one of the oxygen atoms of carbonyl group in *exo*-{Cp*Ru(CO)$_2$} fragment with the Cp* unit [C9–H9a···O5 0.961 Å, 2.587 Å, 3.299 (131°)] and toluene [C49–H49c···O7 0.959 Å, 2.669 Å, 3.494 (144°)]. The Cp* moiety (C13···C22) has also C–H···π interaction with toluene (C56···C62) through one of the methyl groups. Normal distance between the methyl hydrogen (H21C) and the mean plane of the toluene molecule is 2.891 Å that is comparable to the standard values of 2.8–2.9 Å.

Further, in an attempt to generate heavier group 16 analogues of **2**, we performed the reaction of **1** with K in THF followed by reaction with chalcogen powders (S and Se) at room temperature. Unfortunately, all our attempts to produce $[(Cp^*Ru(CO)_2Ge)_4(\mu\text{-}E)_6]$ (E = S, Se) were unsuccessful. The failure to isolate the S and Se analogues of **2**, led us to examine the apparent stability of them ($\mathbf{2^s}$ and $\mathbf{2^{se}}$; S and Se analogues of **2** respectively).[28] The calculated HOMO-LUMO gap and vertical ionization potential clearly indicate that as one changes the chalcogen atom from O to S or Se (Table S1, ESI†) the apparent stability increase in the order $\mathbf{2^{Se}}<\mathbf{2^{S}}<\mathbf{2}$. These results have also been corroborated with the calculated natural charges on Ge (q_{Ge}) and chalcogen atoms (q_E).[29] The electron density of chalcogen is donated exclusively to the Ge centre, which is evidenced of an increase in natural valence population in Ge and a decrease in chalcogen atoms. A similar result has also been identified from the electrostatic potential analysis (Fig S7, ESI†). Therefore, based on the above calculations it is reasonable to assume that the S or Se analogues of **2** are indeed synthetically challenging targets.

The pathway of the formation of **2** is intriguing, thus in order to get some insight into the formation of **2** from **1**, density functional theory (DFT) calculations were carried out. Our calculations proposed three intermediates; germylene **(A)**, germyne **B**, and cyclotetragermane **C**, prior to the formation of **2** (Scheme S1, ESI†). The formation of ruthenocene $[Cp^*_2Ru]$ during the first step of the reaction provides evidence of the source of “extra” CO ligand in **2**.[30] Treatment of **1** with K metal yields intermediate **A**, which might have converted to *trans*-bent germyne **B** taking two CO from the reaction mixture and satisfies the 18 electron count around Ru. The calculated Ge-Ge distance of 2.277 Å in **B** is comparable to those observed in (Bbt)GeΞGe(Bbt)) (2.2060(7) and 2.2260(7) Å; Bbt = 2,6-bis[bis (trimethylsilyl)methyl]-4-[tris-(trimethylsilyl)methyl] phenyl)[32], $[L^2Ge\Xi Ge^2]$[33] (L^2 = N(Ar^2)(Si*i*Pr_3), Ar^2 = 2,6-[C(H)Ph_2]$_2$-4-*i*Pr C_6H_2) (2.3568(3) Å) and 2,6-$Dipp_2H_3C_6Ge\Xi GeC_6H_3$-2,6-$Dipp_2$ (2.2850 Å) (Dipp C_6H_3-2,6-iPr_2).[4] The existence of the multiple bonding in **B** was further supported by MO and NBO analysis (Fig S8 and S9, ESI†). The intermediate **C** might have generated through the dimerization of **B**, which finally on reaction with oxygen yielded **2**. The calculated ΔG values show that the formation of **A**, **B** and **C** are reasonably exothermic. However the formation of **2** following the reaction of **C** with O_2 is highly favorable (Scheme S2, ESI†)

Germanium dioxide is used as an optical material in wide angle lenses and in optical microscope objective lenses due to its refractive index and optical dispersion properties. Further, studies show that doping of germoxane increases the refractive index of siloxane polymer.[8d] Encouraged by these results; we were also interested to study the refractive index of **2**. The refractive index value for **2**, measured using refractometer instrument, was found to be 1.48.

In order to get an insight into the redox properties of **2**, we performed the electrochemical studies. The cyclic voltammograms, shown in Fig. S10 (ESI†), exhibits two anodic waves (Ep_a), 1.23 V and 1.70 V vs SCE. The anodic wave at 1.70 V does not have its counterpart in the cathodic wave. This may be assigned to one electron oxidation process for Ru-centre that shows that **2** is electrochemically inactive. A similar irreversible behavior has also been observed for $[Cp^*_2FeRu(C_8H_8)]$,[34] which is electrochemically inactive and decomposes upon electrochemical oxidation.

In conclusion, this work describes the synthesis and structural characterisation of the first tetrametallagermoxane. The title compound contains an adamantanoid Ge_4O_6 framework, in which an *exo*-Cp*Ru(CO)$_2$ fragment attached to all four germanium atoms. Compound **2** is believed to be generated through some key unstable intermediates, such as germylene and digermyne.

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Notes and references

Synthesis of **2**: A solution of $[Cp^*RuCO(GeCl_2)]_2$, **1** (0.175 g, 0.21 mmol) in 15 mL of THF was added to the K metal (0.035 g, 0.92 mmol). The reaction mixture was stirred for 48 h in glove box. During this time the colour of the solution changed from yellow to brownish yellow and full consumption of K metal was observed. The flask was sealed with rubber septum, moved out of glove box and O_2 was purged for 10 min at room temperature. The solvent was evaporated under high vacuum and the residue was dissolved in toluene, filtered using Celite yielded a pale yellow **2** (0.234 g, 70%). Recrystallization from a toluene/hexane mixture gave pale yellow crystals. Mp: 235 °C (dec). ^{1}H NMR (400 MHz, toluene-d_8): δ = 1.76 (s, 60 H, Cp*); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 9.6, (C_5Me_5), = 98.1, (C_5Me$_5$), 198.2 (C=O). IR (CH_2Cl_2) v/cm^{-1}: 2009, 1956 (CO), 769 (Ge–O). MS (ESI): m/z calcd for $C_{48}H_{60}Ge_4O_{14}Ru_4$, 1555.82; found: 1556 $[M]^+$

§ X-ray Structure Determination: The crystal data of **2** was collected and integrated using a Bruker Axs kappa apex2 CCD diffractometer, with graphite monochromatic MoKa (λ = 0.71073) radiation at 296 K. The structures were solved by heavy atom methods using SHELXS-97 or SIR 92 and refined using SHELXL-97.[35] Crystal data for **2** at 296 K: molecular formula $C_{62}H_{76}Ge_4O_{14}Ru_4$, mol wt 1739.86, monoclinic, space group $C2/c$, a= 24.8437(10) Å, b = 23.3689(9) Å, c = 23.9666(9) Å, β = 102.763(2)°, V = 13570.5(9) Å^3, Z = 8, ρ_{calcd} = 1.703 g·cm^{-3}, μ = 2.670 mm^{-1}, GOF = 1.055, F(000) = 6912, R_1 = 0.0439, wR_2 = 0.1052, 32484 independent reflections [2θ≤50°] and 742 parameters.

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28 See supporting information for full computational details.

29 For Ge the positive charge decreases and for chalcogen the negative charge decreases in the order O<S<Se (**2**: q_{Ge} = 1.936, q_E = -1.150; **2^S**: q_{Ge} = 0.953, q_E = -0.556; **2^{Se}**: q_{Ge} = 0.705, q_E = -0.393).

30 Addition of K metal to a THF solution of $(Cp^*(CO)_2RuGeCl_2)_2$ in glove box generated a brown solution. The ^{1}H NMR of this brown solution shows the presence of ruthenocene[31] and no traces of **2** observed, even after three days. However, when the brown solution was bubbled with O_2 for 10 min it led to the formation of germoxane, **2** in 70% yield.

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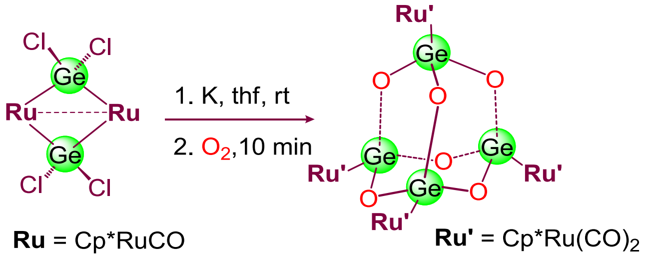
All metallagermoxane with an adamantanoid cage structure: $[(Cp^*Ru(CO)_2Ge)_4(\mu\text{-}O)_6]$ ($Cp^* = \eta^5\text{-}C_5Me_5$)

K. Bakthavachalam, K. Yuvaraj, Bijan Mondal, Rini Prakash and Sundargopal Ghosh*

The first tetrametallagermoxane $[(Cp^*Ru(CO)_2Ge)_4(\mu\text{-}O)_6]$, with an adamantanoid cage structure has been synthesized and structurally characterized with an exo-$\{Cp^*Ru(CO)_2\}$ fragment in each germanium atom.



Keywords: metallagermoxane, germanium, cage structure, ruthenium and adamantane