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Reactivity studies on aminotroponiminatogermylene stabilized ruthenium(II) complexes

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Dedicated to Prof. V. Chandrasekhar on the occasion of his 60th birthday

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ABSTRACT

Aminotroponiminatogermylene stabilized ruthenium(II) complexes and reactivity studies on *N*-heterocyclic germylene stabilized ruthenium(II) complexes were not known. Therefore, this work reports the synthesis of aminotroponiminatogermylene stabilized ruthenium(II) complexes [L_1Ge(X){$RuCl_2$(Y)}] (L_1 = (*i*-Bu)$_2$ATI; (ATI = aminotroponiminate), X = Cl **1**, NC_4H_4 **2**, Y = η^6-*p*-cymene), and the reactivity studies on complex **2**. *N*-pyrrolylgermylene stabilized ruthenium(II) complex **2** reacts with H_2O and $SnCl_2$ to afford hydroxygermylene stabilized ruthenium(II) complex [L_1Ge(OH){$RuCl_2$(Y)}] (**3**) and a bimetallic complex [L_1Ge(NC_4H_4){Ru($SnCl_3$)Cl(Y)}] (**4**), respectively. The chlorogermylene analogue [L_1GeCl{Ru($SnCl_3$)Cl(Y)}] (**5**) of complex **4** is also isolated by reacting complex **4** with chlorotrimethylsilane.

1. Introduction

N-heterocyclic carbene (NHC) stabilized ruthenium(II) complexes find immense applications as catalysts in reduction, oxidation, and olefin metathesis reactions [1–7]. This attraction has motivated the synthesis of ruthenium(II) complexes stabilized through heavier analogs, such as, *N*-heterocyclic silylenes (NHSis) and *N*-heterocyclic germylenes (NHGes) [8–15]. With respect to NHGes, Cabeza and co-workers have synthesized amidinatogermylene and PGeP pincer-type diphosphane-germylene stabilized ruthenium(II) complexes [$RuCl_2$(Y){Ge(*t*-Bu_2bzam)*t*-Bu}] (**I**) and [RuHCl(CO){k^2Ge,*P*-Ge(NCH_2P*t*-Bu_2)$_2C_6H_4$}(P*i*-Pr_3)] (**II**) (*t*-Bu_2bzam = *N*,*N*′-bis(*tert*-butyl)benzamidinate), respectively (Chart 1) [15a-b]. The complex **I** has been used as a homogeneous catalyst for the (a) transfer hydrogenation of cyclohexanone with isopropyl alcohol and (b) *N*-alkylation of aniline using benzyl alcohol [15a]. Apart from these complexes, there are *non*-NHGe stabilized ruthenium complexes, such as [(SiP^{Ph}_3)Ru(H)($GePh_2$)] ([SiP^{Ph}_3] = tris(2-(diphenylphosphino)phenyl)silyl) (**III**), [Cp*(*i*-Pr_2MeP)(H)Ru=Ge(H)(Trip)] (Trip = 2,4,6-*i*-$Pr_3C_6H_2$) (**IV**), [RuH_2(=$GePh_2$)(η^2-H_2)(PCy_3)$_2$] (**V**), and *trans*-[$RuCl_2$(CHPh){Ge(*t*-Bu_2bzam)*t*-Bu}$_2$] (**VI**)/*cis*-[$RuCl_2$(CHPh){Ge(*t*-Bu_2bzam)CH_2SiMe_3}$_2$] (**VII**), which were reported by the groups of Peters, Tilley, Grellier/Sabo-Etienne, and Cabeza, respectively (Chart 1) [15c-f]. Further, the synthesis and reactivity of *non*-NHGe stabilized cationic ruthenium complexes [Cp*(*i*-Pr_3P)$(H)_2$Ru = $GeMes_2$][OTf] (Mes = 2,4,6-$Me_3C_6H_2$) (**VIII**), and [Cp*(*i*-Pr_3P)$(H)_2$Ru=Ge(H)(Trip)][B(C_6F_5)$_4$] (**IX**) were shown by Tilley and co-workers [15g]. It should also be mentioned here that there are various examples of amidinatogermylene stabilized Ru(0) complexes, which are mainly reported by the group of Cabeza [16a-e]. A few examples of these complexes (**X-XI**) are shown in Chart 1 along with other such examples (**XII-XIII**) reported by the groups of Zhu/Wen using β-diketiminatogermylene [16f]. These brief deliberations reveal that though a variety of germylene stabilized ruthenium complexes are reported, the following lacunas, such as (a) absence of an aminotroponiminatogermylene stabilized Ru(II) complexes, and (b) no reactivity study on NHGe stabilized Ru(II) complexes, still exist [17]. Aminotroponiminate (ATI) ligands are *N*-heterocyclic ligands with 10π−electrons, and they have been very much useful in the stabilization of various transition metal and main group element complexes [17k]. ATI ligands with Me and *i*-Pr

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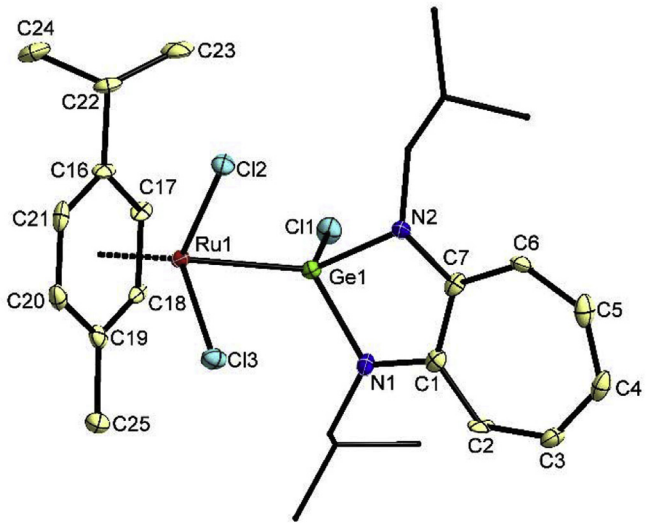


Fig. 1. Molecular structure of complex **1**.* Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and a solvent molecule (toluene) are omitted for clarity. Data collection temperature: 298 K. Selected bond lengths (Å) and bond angles (°): *Molecule 1* Ge1-Ru1 2.411(1), Ge1-N1 1.909(6), Ge1-N2 1.901(6), Ge1-Cl1 2.257(2), Ru1−Cl2 2.415(2), Ru1−Cl3 2.416(2); N1-Ge1-N2 84.7(2), Cl1-Ge1-Ru1 113.09(6), Ge1-Ru1-Cl2 87.78(5), Ge1-Ru1-Cl3 84.92(5), Cl2−Ru1−Cl3 88.92(6). *Molecule 2* Ge2-Ru2 2.406(1), Ge2-N3 1.902(5), Ge2-N4 1.889(5), Ge2-Cl4 2.227(2), Ru2−Cl5 2.413(2), Ru2−Cl6 2.411(2); N3-Ge2-N4 83.4(2), Cl4-Ge2-Ru2 116.96(6), Ge2-Ru2-Cl5 80.92(5), Ge2-Ru2-Cl6 88.88(5), Cl5−Ru2−Cl6 87.04(7). (*The asymmetric unit cell contains two crystallographically independent molecules; one of them is shown here).

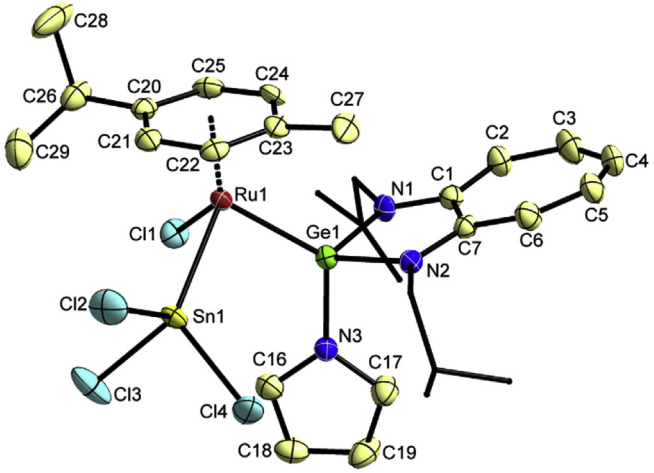


Fig. 2. Molecular structure of complex **4**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Data collection temperature: 298 K. Selected bond lengths (Å) and bond angles (°): Ge1-Ru1 2.398(8), Ge1-N1 1.903(4), Ge1-N2 1.902(4), Ge1-N3 1.892(4), Ru1−Cl1 2.408(1), Ru1−Sn1 2.573(8), Sn1−Cl2 2.375(2), Sn1−Cl3 2.356(2), Sn1−Cl4 2.374(2); N1-Ge1-N2 83.6(2), N3-Ge1-Ru1 122.4(1), Ge1-Ru1-Cl1 84.69(4), Ge1-Ru1-Sn1 90.43(2), Cl1−Ru1−Sn1 88.00(4).

substituents on the nitrogen atoms were used by Dias and co-workers for the isolation of the first examples of amino-troponiminatogermylenes in 1997.[18e] Using these germylenes they have contributed to the germylene chemistry [17a,18] and isolated the germylene stabilized silver complexes, such as [HB(3,5-$(CF_3)_2Pz)_3$]AgGe(X′)[(Y′)$_2$ATI] (Y′ = Me, X′ = Cl; Y′ = *n*-Pr, X′ = Cl, N_3; HB(3,5-$(CF_3)_2Pz)_3$ = hydrotris(3,5-bis(trifluoromethyl)pyrazolyl) borate) [18f,i,j]. We started to develop the chemistry of germylenes stabilized by ATI ligands with bulky *t*-Bu and *i*-Bu groups on the nitrogen atoms from 2008, and have synthesized germylene stabilized chromium, molybdenum, tungsten, platinum, copper, silver, gold, and zinc complexes [19a-i]. Owing to our enduring interest in the study of the germylene stabilized metal complexes and to address the aforementioned issues especially with respect to germylene stabilized Ru(II) complexes (vide supra), we report here the isolation of the first examples of aminotroponiminatogermylene stabilized Ru(II) complexes and their reactivity. Accordingly, NHGe stabilized Ru(II) complexes [L_1Ge(X){$RuCl_2$(Y)}] (L_1 = (*i*-Bu)$_2$ATI; Y = η^6-*p*-cymene; X = Cl **1**; NC_4H_4 **2**) are synthesized and reactions of complex **2** towards water, $SnCl_2$, and chlorotrimethylsilane (TMSCl) are shown. The reactivity studies have afforded further examples of NHGe stabilized Ru(II) complexes, such as hydroxygermylene stabilized Ru(II) complex [L_1Ge(OH){$RuCl_2$(Y)}] (**3**), and bimetallic complex [L_1Ge(NC_4H_4){RuCl($SnCl_3$)(Y)}] (**4**).

2. Results and discussion

Reactions of two equivalents of aminotroponiminatogermylenes [L_1GeX] (L_1 = (*i*-Bu)$_2$ATI; X = Cl **a**, NC_4H_4 **b**) [19b-c] with an equivalent of [$RuCl_2$(Y)]$_2$ in toluene at room temperature for 12 h afforded aminotroponiminatogermylene stabilized Ru(II) complexes **1** and **2** with 98% and 95% yields, respectively (Scheme 1) (Y = η^6-*p*-cymene).

To study the reactivity of *N*-heterocyclic germylene stabilized Ru(II) complexes (with Ge(II)→Ru(II) bond), reactions of complex **2** with water and $SnCl_2$ were tested. The reaction of complex **2** with water affected the Ge-$N_{pyrrole}$ bond and produced hydroxygermylene stabilized ruthenium complex [L_1Ge(OH){$RuCl_2$(Y)}] (**3**) in about 90% yield (Scheme 2). Complexes **1**–**3** are soluble in polar organic solvents, such as tetrahydrofuran, chloroform, and dichloromethane.

In contrast, the reaction of complex **2** with $SnCl_2$ resulted in a bimetallic complex [L_1Ge(NC_4H_4){RuCl($SnCl_3$)(Y)}] (**4**) quantitatively (Scheme 3). Here, the insertion of $SnCl_2$ into the Ru−Cl bond has occurred. Though Ge→Ru bond in compound **2** also seems to be an active bond, it is not affected during the reactivity. This may be due the high σ-donating nature of the germylene ligand that might have strengthened the Ge→Ru bond [19j]. Complex **4** is soluble in chlorinated solvents, such as chloroform and dichloromethane.

Reactions of complexes **2** and **4** with chlorotrimethylsilane afforded complex **1** (Scheme 4) and another bimetallic complex **5** in quantitative yields (Scheme 5), respectively. The latter complex is the chlorine analogue of bimetallic complex **4**. Encouraged by the reactivity of compound **2**, the reaction of compound **1** was carried out with water (under the same reaction conditions) to get compound **1** as the product. This reveals that compound **1** is not reacting with water. Further, it is understandable that compound **1** is stable in water containing THF for atleast 6 h. In the reaction of complex **1** with chlorotrimethylsilane, compound **1** was again obtained as the product. On the basis of this, whether complex **1** is reacting or not cannot be ascertained, as either of the scenarios would lead to the same result. The solubility of complex **5** is poorer in comparison to other complexes **1**–**4**. The (a) successful isolations of complexes **3**–**4** and **5** starting from complexes **2** and **4**, respectively, and (b) ability to convert complex **2** to complex **1**, were possible due to the intactness of the Ge(II)→Ru(II) bond during these reactions. This illustrates the robustness of the Ge(II)→Ru(II) bond in these germylene stabilized Ru(II) complexes.

Complexes **1**–**5** were characterized in solution through NMR spectroscopic studies and the important details are provided here. In complex **3**, the hydroxyl proton resonates as a singlet at 3.27 ppm (in $CDCl_3$). The hydroxyl proton in compounds with (OH)Ge(II)→M moiety (M = a metal), such as [$C_6H_3(CH_2NEt_2)_2$Ge(OH)($W(CO)_5$)][20a] and [HC{(CMe)(2,6-*i*-$Pr_2C_6H_3N$)}$_2$Ge(OH)($Fe(CO)_4$)][20c] appears at

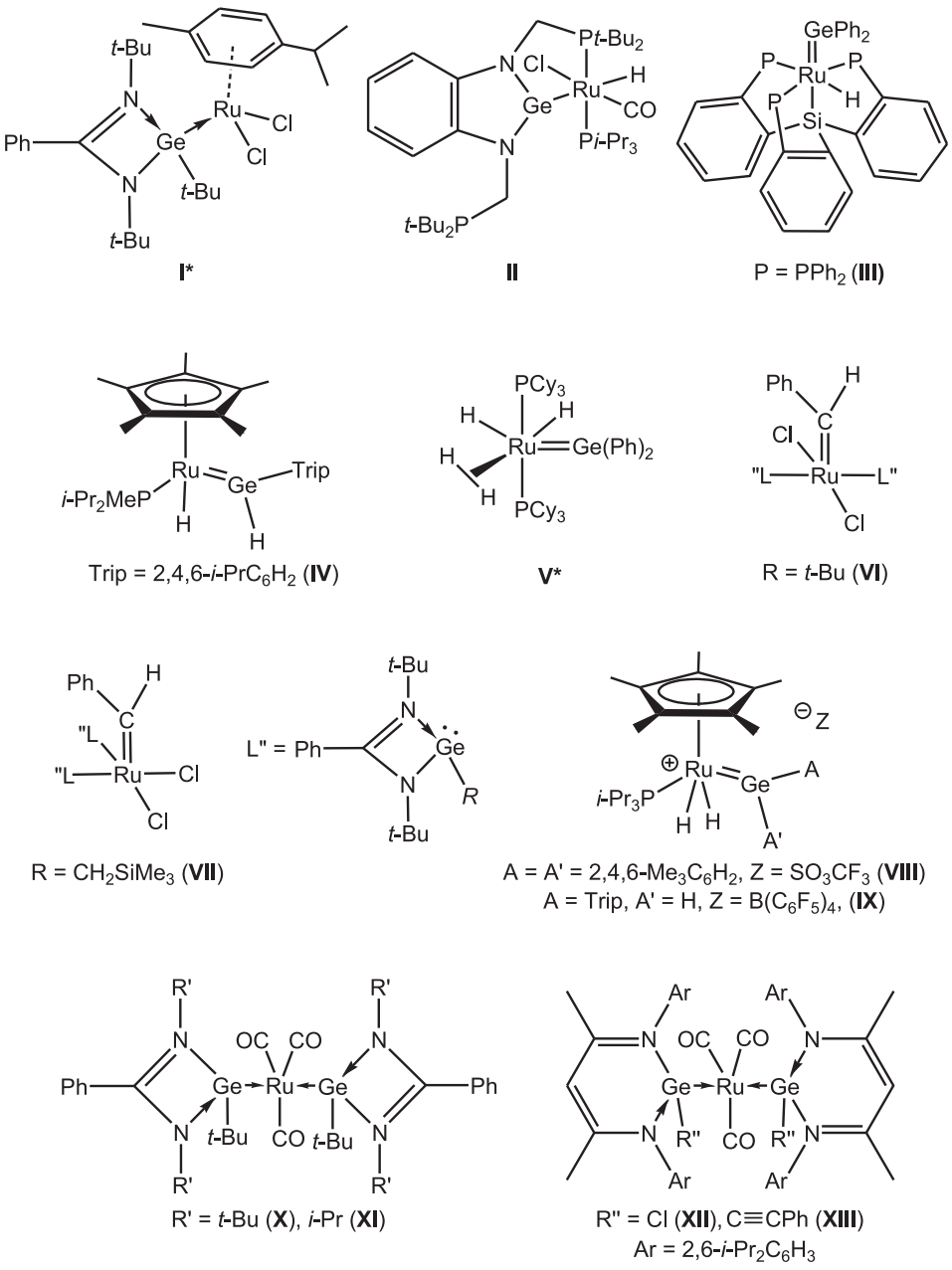
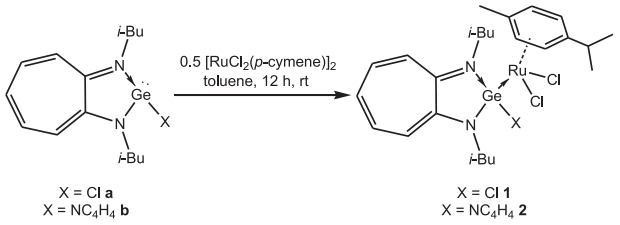
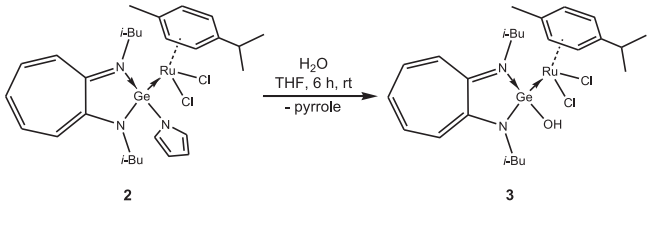


Chart 1. Examples of ruthenium complexes stabilized through germylenes. *Used as a catalyst.

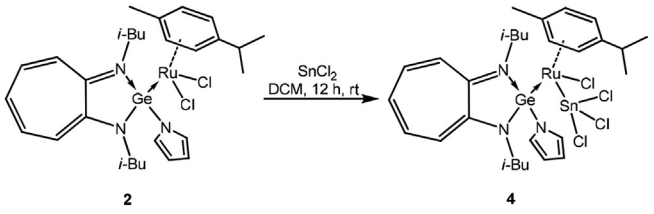


Scheme 1. Synthesis of aminotroponiminatogermylene stabilized Ru(II) complexes **1** and **2**.

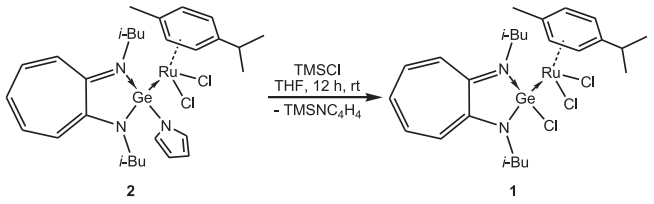


Scheme 2. Reaction of *N*-pyrrolylgermylene stabilized Ru(II) complex **2** with water to afford hydroxygermylene stabilized Ru(II) complex **3**.

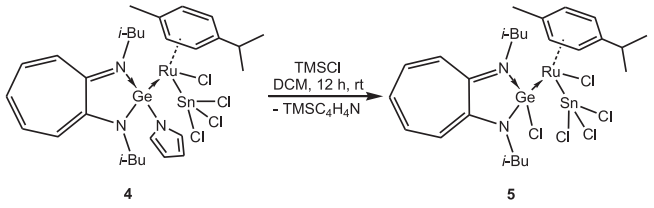
5.78 (in C_6D_6) and 4.24 (in THF-d_8) ppm, respectively [20]. As the (a) spectra of these hydroxygermylene stabilized complexes are recorded in different solvents, and (b) hydroxygermylenes are stabilized through different ligands and coordinated to different metal centers, a direct comparison of these hydroxyl proton resonances with that of complex **3** may not be conceivable. In the ^{13}C



Scheme 3. Reaction of complex **2** with $SnCl_2$ to afford bimetallic complex **4**.



Scheme 4. Reaction of complex **2** with chlorotrimethylsilane to afford complex **1**.



Scheme 5. Reaction of complex **4** with chlorotrimethylsilane to afford bimetallic complex **5**.

NMR spectra of complexes **1**, **3**, and **4**, anticipated numbers of signals were observed. In complex **2**, due to the overlapping of a seven-membered ring carbon signal with a pyrrolyl carbon signal, sixteen resonances were observed instead of seventeen signals. In complex **5**, only thirteen out of the fifteen anticipated signals were observed (even after a huge number of scans) due to its poor solubility. In the ^{119}Sn NMR spectrum of compound **4**, a resonance at −153.18 ppm ($CDCl_3$) revealed the presence of $SnCl_3$ moiety. The tin resonances in the phosphine and stannylene stabilized ruthenium complexes with Ru−$SnCl_3$ moiety, such as [$(PPh_3)Ru(SnCl_3)Cl(C_6H_6)$][21a] (**XIV**) and [$(L_2SnCl)Ru(SnCl_3)Cl(Y)$][21b] (**XV**) were observed at −205.8 (in C_3D_6O) and −191.2 (in $CDCl_3$) ppm, respectively (L_2 = 2-(CH_2NEt_2)-4,6-(*t*-Bu)$_2C_6H_2$). The tin chemical shift of compound **4** is almost comparable to the corresponding value seen in complexes **XIV-XV**, and offers support for the tetracoordinate nature of the tin atom in compound **4**. Due to the poor solubility of compound **5**, no signal was obtained in the ^{119}Sn NMR spectrum of this compound.

3. Molecular structures of compounds 1-5

Complexes **1**–**5** were characterized in the solid state through single crystal X-ray diffraction studies [see Table S1 in the Supporting Information (SI)]. Complex **1** crystallized in the triclinic space group $P\bar{1}$ (Fig. 1) and the germanium atom is tetracoordinate with two nitrogen, one chlorine, and one ruthenium atom. The Ge→Ru bond distances (2.406(1) and 2.411(1) Å) are almost comparable to that in complex **I** (2.434(5) Å) (due to the close resemblance complex **1** with complex **I**), but are longer than those in the germylene ruthenium complexes **III** (2.358 Å) [15c] and **IV** (2.282(6) Å) [15d] (because of the formal double bond between Ge and Ru atoms in complexes **III-IV**). The Ge−Cl bond distances (2.257(2) and 2.227(2) Å) are shorter than that in compound **a** (2.360(5) Å) [19b]. Further, the Ge−N bond distances (1.889(5), 1.902(5), 1.901(6), and 1.909(6) Å) are also shorter than the corresponding bond distances in complex **a** (1.933(1) and 1.943(1) Å). These effects are due to the donation of electron density by the germanium atom to the ruthenium atom. The Ru−Cl bond distances (2.415(2), 2.416(2) Å, 2.413(2), and 2.411(2) Å) are by and large comparable to those in complex **I** (2.408(1) and 2.407(1) Å). Complexes **2**, **3**, **4**, and **5** crystallized in the monoclinic space groups $P2_1/n$, $P2_1/c$, $P2_1/n$, and $P2_1/c$, respectively. Their structures are shown in Fig. S1 (complex **2**), S2 (complex **3**), S3 (complex **5**), and Fig. 2 (complex **4**).

The Ge−O bond distance (1.788(2) Å) in complex **3** is shorter than those in hydroxygermylene stabilized metal complexes [HC{(CMe)(2,6-*i*-$Pr_2C_6H_3N$)}$_2$GeOH(Fe(CO)$_4$)] (1.840(2) Å) and [HC{(CMe)(2,6-*i*-$Pr_2C_6H_3N$)}$_2$GeOH(MnCp(CO)$_2$)] (1.816(2) Å) [20c]. But, it is comparable to that in [$C_6H_3(CH_2NEt_2)_2$GeOH(W(CO)$_5$)] (1.787(2) Å) [20a]. Offering an explain to this trend may be demanding as several variables are involved. The Ru−Sn bond length in complexes **4** (2.573(8) Å) and **5** (2.566(1) Å) are comparable to the corresponding value in complexes [$(PPh_3)Ru(SnCl_3)Cl(Y)$] (2.5830(9) Å) [21a] and **XV** (2.5738(3) Å) [21b].

In complex **5**, the Ge−Cl (2.230(3) Å) bond distance is shorter than that in chlorogermylene **a** (2.360(5) Å), and this due to the σ-donation by the Ge(II) atom to the Ru(II) atom.

4. Conclusion

In summary, the first examples of amino-troponiminatogermylene stabilized Ru(II) complexes are reported. Also, the first reactivity of *N*-heterocyclic germylene stabilized Ru(II) complexes are shown through the reactions of complex **2** with water, $SnCl_2$, and TMSCl; these reactions afforded hydroxygermylene stabilized Ru(II) complex **3**, bimetallic complex **4**, and chlorogermylene stabilized Ru(II) complex **1**, respectively. In these reactions, substitution and insertion occurs at the germanium and Ru−Cl bond without agitating the Ge(II)−Ru(II) bond, respectively. Further, the reaction of complex **4** with TMSCl offered another bimetallic complex **5**.

5. Experimental section

Manipulations that involve air- and moisture-sensitive complexes were performed under an inert atmosphere of dry dinitrogen using either standard Schlenk or glovebox [Jacomex (GP Concept)-T2 work station] techniques [22]. $SnCl_2$ and [$RuCl_2$(*p*-cymene)]$_2$ were purchased from Alfa Aesar. Chlorotrimethylsilane was obtained from Spectrochem Chemicals Pvt. Ltd. Germylenes **a** and **b** were prepared according to literature procedures [19b-c]. Elemental analyses were carried out on a Perkin-Elmer CHN analyzer. Multinuclear NMR spectroscopic studies were performed using a 300/400 MHz Bruker Topspin NMR spectrometer; $CDCl_3/CD_2Cl_2$ was used as a solvent. The chemical shifts δ are reported in ppm and are referenced internally with respect to the residual solvent (^{1}H NMR) and solvent (^{13}C NMR) resonances [23]. For ^{119}Sn NMR spectroscopic studies, $(CH_3)_4Sn$ was used as an external reference. The melting points of compounds **1**–**5** are not reported as they did not melt up to 200 °C.

6. Synthesis of [L_1Ge(Cl)$RuCl_2$(Y)] (1)

To a solution of compound **a** (0.20 g, 0.58 mmol) in toluene (10 mL), [$RuCl_2$(*p*-cymene)]$_2$ (0.180 g, 0.29 mmol) was added and stirred for 12 h. All the volatiles were then removed under reduced

pressure to get a solid product. This solid was washed with hexane (3 × 5 mL) and the resultant residue was dried under vacuum to afford an analytically pure sample of complex **1** as a brown solid. Crystals of complex **1** suitable for single crystal X-ray diffraction studies were grown by the slow evaporation of solvents from its solution in a mixture of toluene and dichloromethane at room temperature. Yield: 0.37 g, 98%. Anal. Calcd for $C_{25}H_{37}Cl_3GeN_2Ru$ ($M = 645.64$): C, 46.51; H, 5.78; N, 4.34. Found: C, 46.65; H, 5.83; N, 4.31. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.00 (d, $^3J_{HH} = 6.0$ Hz, 6H, CH(CH_3)$_2$), 1.09 (d, $^3J_{HH} = 6.0$ Hz, 6H, CH(CH_3)$_2$), 1.30 (d, $^3J_{HH} = 6.9$ Hz, 6H, CH(CH_3)$_2$), 2.17 (s, 3H, CH_3), 2.35–2.44 (m, 2H, CH(CH$_3$)$_2$), 2.93–3.02 (m, 1H, CH(CH$_3$)$_2$) 3.49 (dd, $^3J_{HH} = 14.7$, 8.4 Hz, 2H, CH_2), 3.91 (dd, $^3J_{HH} = 14.7$, 6.9 Hz, 2H, CH_2), 5.58 (d, 2H, $^3J_{HH} = 6.0$ Hz C$_6H_4$), 5.65 (d, $^3J_{HH} = 6.0$ Hz, 2H, C$_6H_4$), 6.81 (t, $^3J_{HH} = 9.3$ Hz, 1H, CH), 6.99 (d, $^3J_{HH} = 11.4$ Hz, 2H, CH), 7.32 (t, $^3J_{HH} = 10.2$ Hz, 2H, CH). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 18.49 (*C*H(CH$_3$)$_2$), 21.21(CH(*C*H$_3$)$_2$), 21.63 (CH(*C*H$_3$)$_2$), 22.32 (CH(*C*H$_3$)$_2$), 29.23 (*C*H(CH$_3$)$_2$), 30.56 (*C*H$_3$), 55.03 (*C*H$_2$), 86.41 (Ar–*C*), 86.79 (Ar–*C*), 95.89 (Ar–*C*), 104.69 (Ar–*C*), 116.99 (Ar–*C*), 125.73 (Ar–*C*), 137.71 (Ar–*C*), 158.79 (Ar–*C*).

7. Synthesis [L_1Ge(C_4H_4N)RuCl$_2$(Y)] (2)

To a solution of compound **b** (0.30 g, 0.81 mmol) in toluene (15 mL), [RuCl$_2$(*p*-cymene)]$_2$ (0.248 g, 0.40 mmol) was added and the resultant mixture was stirred for 12 h. All the volatiles were then removed under reduced pressure to get a solid product. This solid was washed with hexane (3 × 5 mL) and dried under vacuum to obtain an analytically pure sample of complex **2** as a reddish brown solid. Crystals of complex **2** suitable for single crystal X-ray diffraction studies were grown by the slow evaporation of the solvent from its solution in tetrahydrofuran at room temperature. Yield: 0.52 g, 95%. Anal. Calcd for $C_{29}H_{41}Cl_2GeN_3Ru$ ($M = 676.27$): C, 51.50; H, 6.11; N, 6.21. Found: C, 51.42; H, 6.15; N, 6.16. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.73 (d, $^3J_{HH} = 6.6$ Hz, 6H, CH(CH_3)$_2$), 0.85 (d, $^3J_{HH} = 6.9$ Hz, 6H, CH(CH_3)$_2$), 1.28 (d, $^3J_{HH} = 6.9$ Hz, 6H, CH(CH_3)$_2$), 1.74–1.83 (m, 2H, CH(CH$_3$)$_2$), 2.07 (s, 3H, CH_3), 2.90–2.95 (m, 1H, CH(CH$_3$)$_2$) 3.43 (dd, $^3J_{HH} = 13.8$, 7.8 Hz, 2H, CH_2), 3.88 (dd, $^3J_{HH} = 13.8$, 6.3 Hz, 2H, CH_2), 5.35 (d, 2H, $^3J_{HH} = 6.0$ Hz C$_6H_4$), 5.52 (d, $^3J_{HH} = 6.0$ Hz, 2H, C$_6H_4$), 6.11 (t, $^3J_{HH} = 2.1$ Hz, 2H, C$_4H_4$N), 6.79–6.84 (m, 3H, C$_4H_4$N, CH), 7.00 (d, $^3J_{HH} = 11.4$ Hz, 2H, CH), 7.35 (t, $^3J_{HH} = 9.6$ Hz, 2H, CH). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 18.80 (*C*H(CH$_3$)$_2$), 20.93 (CH(*C*H$_3$)$_2$), 21.43 (CH(*C*H$_3$)$_2$), 22.51 (CH(*C*H$_3$)$_2$), 28.96 (*C*H(CH$_3$)$_2$), 30.68 (*C*H$_3$), 54.73 (*C*H$_2$), 84.02 (Ar–*C*), 85.08 (Ar–*C*), 95.16 (Ar–*C*), 108.87 (Ar–*C*), 109.40 (Ar–*C*), 116.11 (Ar–*C*), 124.52 (Ar–*C*), 137.86 (Ar–*C*), 159.34 (Ar–*C*).

8. Reaction of complex 1 with water

To a solution of complex **1** (0.40 g, 0.59 mmol) in tetrahydrofuran (15 mL), an excess of water (0.1 mL) was added and the resultant mixture was stirred for 6 h at room temperature. Then, all the volatiles were removed under reduced pressure to obtain a brown solid. Its ^{1}H NMR spectrum revealed that it was the unreacted complex **1**.

9. Reaction of complex 1 with chlorotrimethylsilane

To a solution of complex **1** (0.20 g, 0.29 mmol) in tetrahydrofuran, chlorotrimethylsilane (0.037 g, 0.32 mmol) was added and the reaction mixture was stirred overnight. All the volatiles were then removed under reduced pressure to get a brown solid. Analysis of this solid through ^{1}H NMR spectroscopy revealed that it was complex **1**.

10. Conversion of complex 2 to 1

To a solution of complex **2** (0.20 g, 0.29 mmol) in tetrahydrofuran, chlorotrimethylsilane (0.035 g, 0.32 mmol) was added and the resulting mixture was stirred overnight. All the volatiles were then removed under reduced pressure to afford a brown solid. It was washed with hexane and dried to obtain an analytically pure sample of complex **1** quantitatively (0.18 g, 98%).

11. Synthesis of [L_1Ge(OH)RuCl$_2$(Y)] (3)

To a solution of complex **2** (0.40 g, 0.59 mmol) in tetrahydrofuran (15 mL), an excess of water (0.1 mL) was added and the resultant mixture was stirred for 6 h. All the volatiles were then removed under reduced pressure to get a brown solid. It was washed with hexane (5 mL) and dried under reduced pressure to afford an analytically pure sample of complex **3**. Crystals of complex **3** suitable for single crystal X-ray diffraction studies were grown by the slow evaporation of solvent from its solution in tetrahydrofuran at room temperature. Yield: 0.33 g, 90%. Anal. Calcd for $C_{25}H_{38}Cl_2GeN_2ORu$ ($M = 627.19$): C, 47.87; H, 6.11; N, 4.47. Found: C, 47.95; H, 5.87; N, 4.61. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.01 (d, $^3J_{HH} = 6.6$ Hz, 6H, CH(CH_3)$_2$), 1.07 (d, $^3J_{HH} = 6.9$ Hz, 6H, CH(CH_3)$_2$), 1.23 (d, $^3J_{HH} = 6.9$ Hz, 6H, CH(CH_3)$_2$), 1.99 (s, 3H, CH_3), 2.23–2.32 (m, 2H, CH(CH$_3$)$_2$), 2.71–2.76 (m, 1H, CH(CH$_3$)$_2$), 3.27 (s, 1H, OH), 3.54 (dd, $^3J_{HH} = 13.5$, 6.0 Hz, 2H, CH_2), 3.73 (dd, $^3J_{HH} = 13.2$, 8.1 Hz, 2H, CH_2), 5.13 (d, 2H, $^3J_{HH} = 5.7$ Hz C$_6H_4$), 5.33 (d, $^3J_{HH} = 5.7$ Hz, 2H, C$_6H_4$), 6.81 (t, $^3J_{HH} = 9.3$ Hz, 2H, CH), 6.96 (d, $^3J_{HH} = 11.1$ Hz, 2H, CH)), 7.37 (t, $^3J_{HH} = 10.2$ Hz, 2H, CH). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 18.87 (*C*H(CH$_3$)$_2$), 21.33 (CH(*C*H$_3$)$_2$), 22.53 (CH(*C*H$_3$)$_2$), 28.50 (*C*H(CH$_3$)$_2$), 30.97 (*C*H$_3$), 54.26 (*C*H$_2$), 83.89 (Ar–*C*), 84.19 (Ar–*C*), 95.65 (Ar–*C*), 107.46 (Ar–*C*), 115.42 (Ar–*C*), 124.11 (Ar–*C*), 137.85 (Ar–*C*), 158.24 (Ar–*C*).

12. Synthesis of [L_1Ge(C_4H_4N)RuCl($SnCl_3$)(Y)] (4)

To a solution of complex **2** (0.50 g, 0.73 mmol) in dichloromethane (20 mL), $SnCl_2$ (0.14 g, 0.73 mmol) was added and the resultant mixture was stirred for 12 h. All the volatiles were then removed under reduced pressure to obtain a yellow solid. It was washed with hexane (5 mL) and dried under reduced pressure to produce an analytically pure sample of complex **4**. Single crystals suitable for X-ray diffraction studies were grown by the slow evaporation of solvent from its dichloromethane solution at room temperature. Yield: 0.63 g, 98%. Anal. Calcd for $C_{29}H_{41}Cl_4GeN_3RuSn$ ($M = 865.88$): C, 40.23; H, 4.77; N, 4.85. Found: C, 40.29; H, 4.83; N, 4.84. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.52 (d, $^3J_{HH} = 6.3$ Hz, 3H, CH_3), 0.69 (d, $^3J_{HH} = 6.3$ Hz, 3H, CH_3), 0.89 (d, $^3J_{HH} = 6.6$ Hz, 3H, CH_3), 1.04 (d, $^3J_{HH} = 6.3$ Hz, 3H, CH_3), 1.28 (d, $^3J_{HH} = 6.9$ Hz, 3H, CH_3), 1.36 (d, $^3J_{HH} = 6.6$ Hz, 3H, CH_3), 1.94–1.99 (m, 1H, CH(CH$_3$)$_2$), 2.11 (s, 3H, CH_3)) 2.94–3.00 (m, 1H, CH(CH$_3$)$_2$), 3.39–3.59 (m, 4H, CH_2), 3.92–3.99 (m, 1H, CH(CH$_3$)$_2$), 5.63 (d, 1H, $^3J_{HH} = 6.3$ Hz C$_6H_4$), 5.77 (d, 1H, $^3J_{HH} = 6.0$ Hz C$_6H_4$), 5.88 (d, 1H, $^3J_{HH} = 6.3$ Hz C$_6H_4$), 6.11 (d, 1H, $^3J_{HH} = 6.3$ Hz C$_6H_4$) 6.23–6.25 (m, 2H, C$_4H_4$N), 6.85–6.95 (m, 3H, C$_4H_4$N, CH), 7.06 (t, $^3J_{HH} = 11.2$ Hz, 2H, CH), 7.43 (t, $^3J_{HH} = 11.2$ Hz, 2H, CH). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 18.84, 20.82, 21.27, 21.69, 22.61, 29.84, 30.33, 31.00, 57.52, 83.22 (Ar–*C*), 83.97 (Ar–*C*), 97.44 (Ar–*C*), 104.74 (Ar–*C*), 116.91 (Ar–*C*), 124.29 (Ar–*C*), 136.64 (Ar–*C*), 160.99 (Ar–*C*). ^{119}Sn{ [1] H} NMR (149 MHz, $CDCl_3$): δ −153.18 ppm.

13. Synthesis of [L_1Ge(Cl)RuCl($SnCl_3$)(Y)] (5)

To a solution of complex **4** (0.25 g, 0.28 mmol) in dichloromethane (15 mL), an excess of chlorotrimethylsilane (0.1 mL) was

added and the resultant mixture was stirred for 12 h. All the volatiles were then removed under reduced pressure to get a light yellow solid which was washed with hexane (5 mL). The resultant residue was dried under vacuum to afford an analytically pure sample of complex **5**. Crystals suitable for single crystal X-ray diffraction studies were grown by the slow evaporation of solvent from its solution in dichloromethane at room temperature. Yield: 0.23 g, 95%. Anal. Calcd for $C_{25}H_{37}Cl_5GeN_2RuSn$ ($M = 835.25$): C, 35.95; H, 4.46; N, 3.35. Found: C, 36.01; H, 4.50; N, 3.39. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.05 (d, $^3J_{HH} = 6.0$ Hz, 6H, CH(CH_3)$_2$), 1.11 (d, $^3J_{HH} = 6.0$ Hz, 6H, CH(CH_3)$_2$), 1.36 (d, $^3J_{HH} = 6.0$ Hz, 6H, CH(CH_3)$_2$), 2.34–2.43 (m, 2H, CH(CH$_3$)$_2$), 2.59 (s, 3H, CH_3), 3.28–3.37 (m, 1H, CH(CH$_3$)$_2$), 3.55 (dd, $^3J_{HH} = 10.0$, 6.0 Hz, 2H, CH_2), 3.71 (dd, $^3J_{HH} = 10.0$, 6.0 Hz, 2H, CH_2), 5.98 (d, 2H, $^3J_{HH} = 6.0$ Hz C$_6H_4$), 6.16 (d, 2H, $^3J_{HH} = 6.0$ Hz C$_6H_4$), 7.06–7.14 (m, 3H, CH), 7.58 (t, $^3J_{HH} = 9.0$ Hz, 2H, CH). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 20.53, 21.04, 23.44, 28.11, 53.67, 54.03, 54.39, 77.49 (Ar–*C*), 88.91 (Ar–*C*)89.56 (Ar–*C*), 119.00 (Ar–*C*), 138.52 (Ar–*C*), 157.90 (Ar–*C*).

14. Structure determination of compounds 1-5

Single crystals of complexes **1**–**5** were coated with a cryoprotectant and mounted on a glass fiber. Data were collected at 298 K using a Bruker SMART APEX CCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) [24]. Data integration was performed using the SAINT program. Empirical absorption correction was applied using the SADABS program [25]. The structures were solved by direct methods and refined by full matrix least-squares on F [2] using SHELXTL software [26]. All the non-hydrogen atoms were refined anisotropically, and the positions of hydrogen atoms were fixed according to a riding model. Important crystallographic data are summarized in Table S1 (see Supporting Information).

Author contributions

All the experimental work was carried out by D. Y. and D. Singh. Further, they also wrote the manuscript. D. Sarkar helped D. Y. in carrying out the experimental studies. S. S. and M. K. S. did the crystallographic studies. The manuscript was corrected by S. N.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.02.006.

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