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含不同取代基的钌-锗化合物的合成及表征

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摘要 钌-锗化合物(PPh$_3$)(X)RuGeCl$_2$ArTrip (X=H, **1**; Cl, **2**; ArTrip=C$_6$H$_3$-2-(η^6-Trip)-6-Trip, Trip=2,4,6-^{i}Pr$_3$-C$_6$H$_3$)与有机试剂如格氏试剂、LiHBEt$_3$以及萘钠反应实现了锗和钌原子上的取代基团的调控. 化合物 **1** 与格氏试剂 EtMgBr 在不同的温度下反应, 分别生成(PPh$_3$)HRuGeBr$_2$ArTrip (**3**)和(PPh$_3$)HRuGeEt$_2$ArTrip (**4**). 化合物 **1** 和 LiHBEt$_3$ 反应也生成化合物 **4**, 在该反应中 LiHBEt$_3$ 作为乙基转移试剂而不是氢化试剂. 此外, 化合物 **1** 与 HBF$_4$ 反应生成离子型化合物[(PPh$_3$)H$_2$RuGeCl$_2$ArTrip][BF$_4$] (**5**). 另外, 利用 Na/naphthalene 还原化合物 **2** 可以得到双羟基化合物(PPh$_3$)HRuGe(OH)$_2$-ArTrip (**6**), 而化合物 **2** 与碘单质的反应历经单碘化, 形成化合物(PPh$_3$)IRuGeCl$_2$ArTrip (**7**). 所有的化合物都经过详细的核磁谱学和 X 射线单晶衍射的表征.
关键词 钌; 锗宾; 取代反应; 结构

Synthesis and Characterization of Ruthenium Germyl Complexes with Various Substituents

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Abstract Reactions of dichlorogermyl ruthenium complexes (PPh$_3$)(X)RuGeCl$_2$ArTrip (X=H, **1**; Cl, **2**; ArTrip=C$_6$H$_3$-2-(η^6-Trip)-6-Trip, Trip=2,4,6-^{i}Pr$_3$-C$_6$H$_3$) with various reagents, including Grignard reagent, LiHBEt$_3$ and Na/naphthalene were investigated, realizing the substituent modulation on Ge and Ru atoms. **1** reacted with EtMgBr forming (PPh$_3$)HRuGeBr$_2$ArTrip (**3**) and (PPh$_3$)HRuGeEt$_2$ArTrip (**4**) depending on the reaction temperature. The reaction of **1** with LiHBEt$_3$ also resulted in the formation of **4**, where LiHBEt$_3$ acted as ethyl transfer reagent instead of hydrogenation reagent. Additionally, **1** reacted with HBF$_4$ afforded ionic product [(PPh$_3$)H$_2$RuGeCl$_2$ArTrip][BF$_4$] (**5**). On the other hand, reduction of **2** with Na/naphthalene produced dihydroxyl complex (PPh$_3$)HRuGe(OH)$_2$ArTrip (**6**), while the reaction with I$_2$ underwent monoiodination on Ru with the formation of (PPh$_3$)IRuGeCl$_2$ArTrip (**7**). All compounds were fully characterized by heteronuclear NMR spectroscopy and single-crystal X-ray diffraction.
Keywords ruthenium; germylene; substitution; structure

1 Introduction

Germylenes, the heavier group 14 carbene analogues, exhibit versatile characters beyond electron donors compared to carbenes.[1] The Ge(II) center contains both an electron pair and an empty p orbital showing amphiphilic capacity, and it is also used as reducing reagent in redox reactions. Therefore, the utilization of germylenes in stabilization of transition metals (TM) has been developing into an active area of research,[1a-1b,1h,1k] among which ruthenium chemistry draws much attention because of the widely catalytic application of ruthenium complexes in organic synthesis.[2] Principally, the bonding modes between Ge(II) and TM are described as either Fischer type or Schrock type.[3] Cabeza and co-workers have successively reported several Fischer-type ruthenium germylene complexes since 2012 (Scheme 1).[4] In 2017, we discussed the coordination mode of *β*-diketiminate germylene with carbonyl ruthenium.[5] These complexes feature triangular bipyramidal or octahedral geometry, in which germylene acts as σ-donor coordinating to Ru center. On the other hand, Tilley *et al.* showed interest in Schrock-type derivatives, which behave somewhat Ru=Ge double bond character and perform unusual reactivity towards small molecules, and half-sandwich ruthenium complexes with germylenes stabilized by bulky terphenyl substituents were synthesized (Scheme

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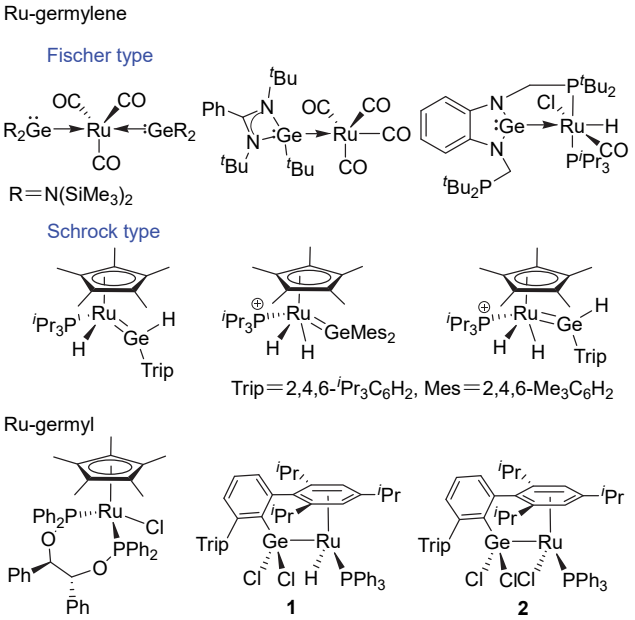
1).[6] In this case, terphenyl substituents provide steric shielding around the tetrel site, and compelling results of terphenyl-stabilized tetrylenes in coordination sphere of transition metals has been obtained based on this strategy.



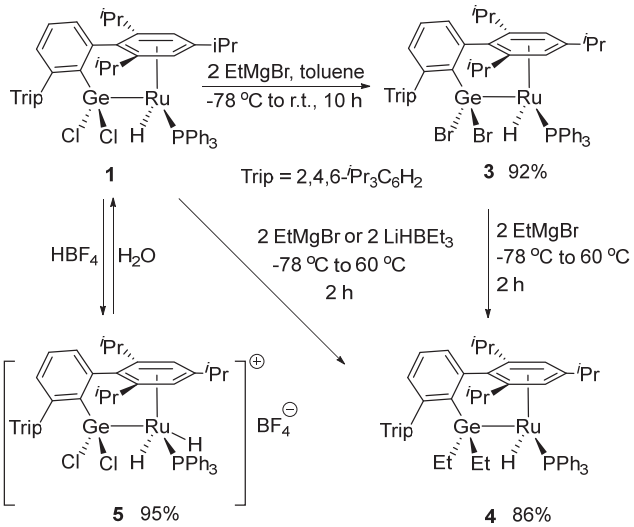
Scheme 1 Selected examples of Ru-germylene and Ru-germyl complexes

Transition-metal germyl complexes are another important eye-catching topic closely related to Ge(II)-TM-complexes and show a reciprocal relationship with Ge(II)-TM complexes, mainly due to their involvement in catalytic transformations with germanium[4c] as well as material chemistry.[7] Generally, the insertion of Ge(II) into TM—X bond is the most versatile process for the synthesis of transition-metal germyl species, especially for the dihalogen species GeX_2. Among the well-studied germyl complexes of transition metals, ruthenium germyl complexes hitherto reported are still scarce.[4c,8] For instance, García-Fontán *et al.* synthesized a half-sandwich ruthenium trichlorogermyl complexes [Ru($GeCl_3$)(η^5-Cp')L] (L=1,2-[bis(diphenyl)phosphanyloxyl)]-1,2-diphenylethane; Cp'=C_5Me_5, C_9H_7).[8g] Recently, we described the synthesis and reactivity of ruthenium germyl complexes **1** and **2** with terphenyl substituent, which represents as the first example of insertion of monochlorogermylene into Ru—Cl bond (Scheme 1), and some transition-metal (Ru and Os) germyl complexes were obtained by reacting TM-germyl complexes with versatile ligands.[8f]

Then we are interested in substituent modulation of Ru-germyl complexes. The environment of metal atoms can be further regulated by substituent modification, and the halogen atoms binding to Ge and Ru provide versatile possibilities of reaction. Herein we report on the reactivity of **1** and **2** with common reagents like organometallic nucleophile (EtMgBr), electrophile (HBF_4), reductant (Na/$C_{10}H_8$), and iodine, and novel ruthenium germyl complexes with different substituents on both Ge and Ru atoms are discussed in detail.

2 Results and discussion

The reaction of **1** with EtMgBr at low temperature afforded (PPh_3)HRuGeBr_2ArTrip (**3**) in 92% yield, which contradicted the general reaction pathway of Grignard reagent (Scheme **2**). This may be due to the higher bonding energy of Mg—Cl bond compared to Mg—Br bond. According to the Hard-Soft-Acid-Base theory, Mg^{2+} is a harder acid than Ge^{4+}, while Br^- is a softer base than Cl^-, therefore Grignard reagent represents a bromine source followed by Br-Cl metathesis reaction, which is similar to previous reports.[9c] In contrast, when carrying out the reaction at 60 ºC, the derivative with ethyl substituents (PPh_3)HRuGeEt_2ArTrip (**4**) were obtained in high yield as expected (Scheme **2**). Compound **3** could also convert to **4** in the presence of **1** equiv. of EtMgBr at 60 ºC. However, the reaction of **1** with LiBr aiming to form **3** failed even at elevated temperature. Compounds **3** and **4** are air and moisture sensitive, and exhibit good solubility in toluene and THF, while are moderately soluble in *n*-hexane. In consideration of the wide application of germylene hydride,[9] the reaction of **1** with $LiHBEt_3$ was carried out to substitute Cl with H atom, since $LiHBEt_3$ is a powerful reducing agent supplying H atom substituent. Interestingly, the reaction underwent unusual pathway forming **4**, instead of the routine product (PPh_3)HRuGeH_2ArTrip (Scheme 2). Similar reactivity of $LiHBEt_3$ was reported in handful examples.[5,10] In addition, we expected the formation of Ge=Ru double bond by the elimination of HCl. Thus, reaction of **1** with Li$N(SiMe_3)_2$ was done, but unfortunately, only led to intractable mixture after several attempts.



Scheme 2 Synthesis of **3**～**5**

After then we turned our eyes to Ru center. In view of the H binding to Ru, we explored the reaction of **1** with HBF_4, which led to the oxidative addition on Ru rather than elimination of H_2 yielding **5** in 95% yield. Even though the formation of H_2 is a thermodynamically favora-

ble process, but slow kinetics inhibits the reaction. Compound **5** could convert back to **1** in the presence of trace amount of H_2O. Furthermore, **1** reacted with $AgBF_4$ forming unidentified mixture at ambient temperature, indicating the varied reactivity of two metal centers.

All these compounds were fully spectroscopically characterized. In the ^1H NMR spectra, the characteristic resonances of terphenyl ligand, for instance, septets and doublets assigned to the isopropyl groups, and two singlets assigned to C_6H_2 group, are clearly displayed. The signal of Ru—H is observed at δ −9.62 (**3**), −11.00 (**4**) and −9.31 (**5**), respectively. The ^1H NMR spectrum of **4** shows the resonances of ethyl substituents at δ 0.07, 1.03 and 0.86, indicating relatively restricted rotation of Ru—Ge bond. In the ^{31}P NMR spectra, the signals of **3** (δ 56.4) and **4** (δ 56.8) corresponding to PPh_3 ligand are close to that of the starting material **1** (δ 56.9),[8f] while the peak of **5** is shifted to higher field as δ 52.2. This is reasonable because the cationic character of metal center in **5** decreases the electron density around P atom. In addition, the ^{19}F NMR spectrum of **5** shows one signal at δ −160.8, approximately to previous reports on ionic species with BF_4 anions.

The crystals of **3** and **4** suitable for X-ray diffraction were grown from *n*-hexane and toluene/*n*-hexane solution, respectively, while that of **5** was obtained by layering diethyl ether on top of saturated dichloromethane solution.[11] Compound **3** crystallizes in the monoclinic space group $P2_1/c$ (Figure 1), while **4** and **5** crystallize in the monoclinic space group $P2_1/n$ and $P2_1$, respectively (Figure 2). In the molecular structures of **3** and **4**, the Ge atom is four coordinates adopting into a distorted tetrahedral geometry, while the Ru atom is binding to H, Ge and PPh_3 ligands, and capped by a Trip group in a η^6 fashion, which exhibits a three-legs piano-stool geometry. The Ru—Ge bond length in **3** is 2.3930(8) Å, which is close to that of **1** (2.3918(8) Å), but shorter compared to that of **4** (2.4488(7) Å). This may be attributed to the electronic difference between halogen and alkyl substituents. All three Ru—Ge

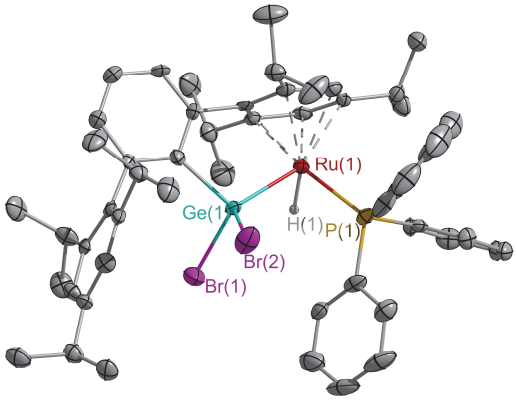


Figure 1 Molecular structure of **3** with thermal ellipsoids at 30% probability level
All hydrogen atoms are omitted for clarity.

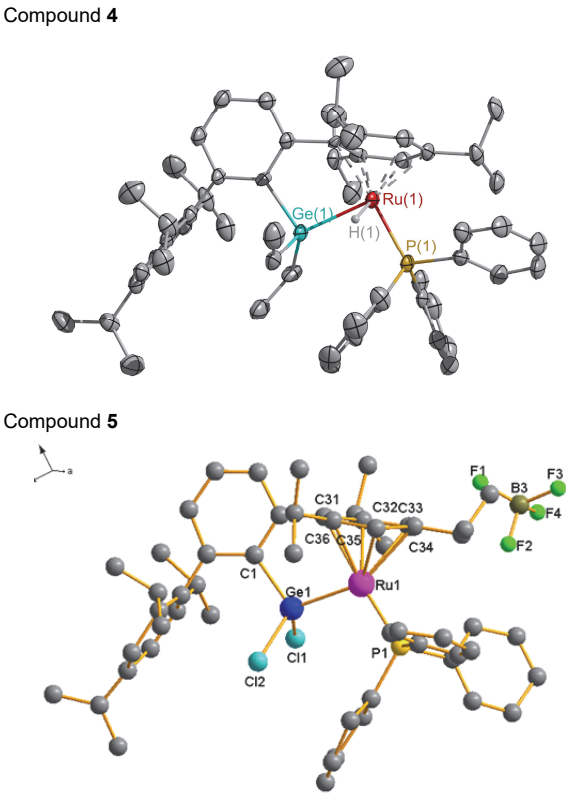


Figure 2 Molecular structures of **4** and **5** with thermal ellipsoids at 30% probability level
All hydrogen atoms are omitted for clarity.

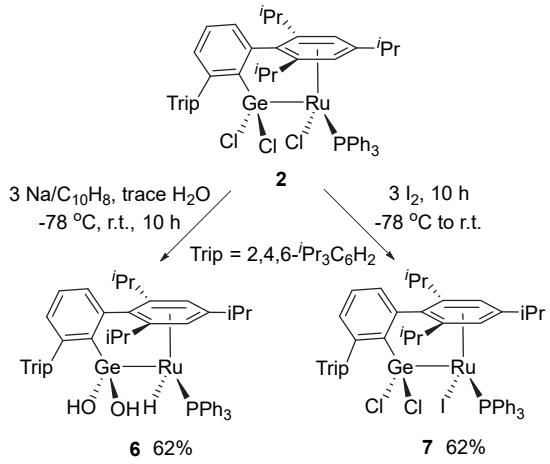
bonds in **1**, **3** and **4** are comparable with those observed in reported ruthenium germyl complexes such as (η^5-Cp)Ru(GeH$_3$)(PPh$_3$)[P(OMe$_3$)] (2.4421(9) Å),[8b] RuCl(GeMe$_3$)(CO)(PPh$_3$)$_3$ (2.4455(4) Å)[8i] and [Ru(GeCl$_3$)(η^5-Cp')L] (Cp' = C$_5$Me$_5$) (2.3975(7) Å).[8g] The Ru—C distances within Ru and the Trip phenyl ring fall in the range of 2.215(6)～2.316(6) Å. The Ru—P bond lengths of **3** (2.3087(17) Å) and **4** (2.2704(13) Å) are similar to those in PPh$_3$-coordinated ruthenium complexes.[8b,8f,8i] Compound **4** shows the sharpest C—Ge—Ru angle of 100.85(13)° compared to those of **1**～**3**, which is reasonable due to the steric bulk of ethyl group than halogen atoms (Table 1).

Starting from **2** with chlorine substituents on both Ge and Ru atoms, we explored the reduction with strong reductants in order to form Ge=Ru complex. Unfortunately, **2** didn't react with potassium and KC_8 at ambient temperature, while heating led to so far unidentified mixtures. In contrast, the treatment with Na/$C_{10}H_8$ in a 1∶3 molar ratio afforded a dihydroxyl ruthenium compound (PPh$_3$)HRuGe(OH)$_2$ArTrip (**6**) in high yield (Scheme 3). Compound **6** seems a hydrolytic product due to the presence of trace amount of H_2O, therefore we added additional water after the reaction and **6** was obtained as expected. However, although anhydrous solvent dried with sodium was used in the reaction, no double-bonded complexes were isolated successfully after several attempts. Moreover, reacting **2** with I_2 in 1∶3 molar ratio yielded **7**, which underwent a monoiodination process with the substituent exchange on

Table 1 Selected bond lengths (Å) and angles (°) of **1**～**4**, **6** and **7**

Compd.	**1**[8f]	**2**[8f]	**3**	**4**	**6**	**7**
Ru—Ge	2.391(8)	2.433(5)	2.393(0)	2.448(8)	2.396(6)	2.401(1)
Ru—P	2.299(2)	2.359(5)	2.308(1)	2.270(4)	2.281(2)	2.340(3)
Ge—C	1.997(3)	1.984(3)	2.005(6)	2.043(4)	1.994(9)	1.992(1)
Ge—Ru—P	95.66(3)	94.04(3)	97.32(5)	94.73(4)	92.82(6)	95.96(8)
C—Ge—Ru	105.96(1)	106.64(8)	106.74(2)	100.85(1)	103.8(2)	104.9(3)

Ru atom (Scheme 3).



Scheme 3 Synthesis of **6** and **7**

The possible reaction mechanism for the synthesis of compound **6** has been proposed. Since water is the only source for hydrogen atom, it must be involved in this reaction. Ruthenium-germene compounds are not moisture stable, which can react with H_2O affording ruthenium-germane compounds.[6] Therefore, we predict that the Ru-germanium complex was reduced by sodium metal resulting in the formation of the corresponding Ru-germanium carbene complex. However, due to its poor stability, it further reacted with trace amount of water affording $(PPh_3)RuHGe(OH)ClTrip$ intermediate products, followed by further hydrolysis to produce $(PPh_3)RuHGe(OH)_2Trip$ compound **6**.

In the ^1H NMR spectrum of **6**, the resonance of Ru-H is observed at δ −10.57 with J_{PH} coupling of 40.9 Hz, and the broad peak at δ 3.88 corresponds to $Ge(OH)_2$, which is absolutely high-field shifted compared to that of dinuclear complex [(RGeOH)W(CO)$_5$] (R = 2,6-$(NEt_2)_2C_6H_3$) (δ 5.78).[12] The ^{31}P NMR spectrum of **6** shows the resonance of PPh_3 group at δ 55.9, while the signal of **7** is shifted to δ 33.3 due to the electron withdrawing property of iodine substituent.

The molecular structures of **6** and **7** were further determined by X-ray single crystal diffraction. Compounds **6** and **7** crystallize in the monoclinic space group $P2_1/c$ and $P2_1/n$, respectively. As shown in Figure 3, both compounds have the same geometry as those of **3**～**5**. The Ru—Ge bond lengths of **6** (2.3966(12) Å) and **7** (2.4011(14) Å) fall in the range of those of **1**～**4**. Moreover, the Ru—P distance of **6** (2.281(2) Å) is similar to those of **3** and **4**, while **7** contains longer Ru—P bond (2.340(3) Å). In comparison with **2**, **7** represents wider Ge—Ru—P angle of 95.96(8)°, attributing to the size-difference of H and I atoms, while that of **6** is absolutely smaller.

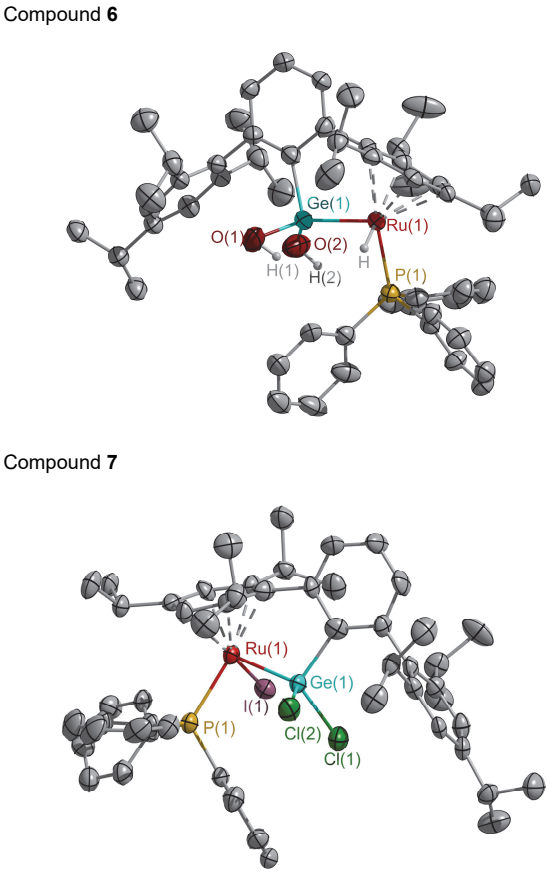


Figure 3 Molecular structures of **6** and **7** with thermal ellipsoids at 30% probability level

All hydrogen atoms and solvent molecule are omitted for clarity.

In comparison with H atom, the I atom is more electronegative, so it can affect the electron distribution on the Ru atom, thereby reducing the electron feedback from the Ru atom to the P atom, thus making the Ru—P bond in **7** is elongated compared to that of **1**, which is due to the higher electronegativity of I than H binding to Ru atom, which decreases the electron back-donation from Ru atom to P atom. In this case, the Ru—P bond in **2** is even longer than those of **1** and **7**.

3 Conclusions

In summary, several novel germyl ruthenium compounds with various substituents were synthesized via unusual reaction process by using common reagents. The reaction of **1** with Grignard reagent EtMgBr afforded (PPh_3)HRuGeBr$_2$ArTrip (**3**) and (PPh_3)HRuGeEt$_2$ArTrip (**4**), respectively, depending on the reaction temperature. In addition, **4** could also be achieved by reacting **1** with $LiHBEt_3$, where $LiHBEt_3$ unusually acts as ethyl transfer reagent instead of hydrogenation reagent. Moreover, anionic compound [(PPh_3)H$_2$RuGeCl$_2$ArTrip][BF_4] (**5**) was obtained in the reaction of **1** with HBF_4. Although the reduction of **1** and **2** is not successful, but the treatment of **2** with Na/naphthalene produced dihydroxyl compound (PPh_3)HRuGe(OH)$_2$ArTrip (**6**). In addition, monoiodination of **2** with I_2 occurs on Ru leading to the formation of **7**.

4 Experimental section

4.1 General procedure

All manipulations were carried out under a dry argon or nitrogen atmosphere by using Schlenk line and/or MBraun glovebox techniques. The toluene, *n*-hexane, and diethyl ether solvents were dried by refluxing with an alloy of sodium/potassium and benzophenone under N_2 prior to use. Dichloromethane was refluxed with calcium hydride before use. The NMR (^{1}H NMR, ^{13}C NMR, ^{31}P NMR, ^{19}F NMR and ^{1}H-^{13}C HSQC) spectra were recorded on Bruker Avance II 400 or 500 MHz spectrometer at 298 K unless otherwise stated. Melting points were measured in a sealed glass tube using Büchi-540 instrument. Elemental analysis was performed on a Thermo Quest Italia SPA EA 1110 instrument. Commercially available reagents were purchased from Aldrich, Acros, or Alfa-Aesar Chemical Co. and used as received. (PPh_3)HRuGeCl$_2$ArTrip (**1**) and (PPh_3)ClRuGeCl$_2$ArTrip (**2**) were prepared according to published procedures.[8f]

4.2 Synthesis of (PPh_3)HRuGeBr$_2$ArTrip (**3**)

To a toluene solution of complex **1** (200 mg, 0.202 mmol) was added dropwise EtMgBr (0.14 mL, 0.424 mmol) at −78 °C. The mixture was stirred for 1 h at −78 °C and then warmed to room temperature and further stirred for 12 h. H_2O (8 μL, 0.424 mmol) was added to quench the reaction. After filtration and removal of all volatiles under vacuum, cooled *n*-hexane (0 °C, 5 mL) was added to the residue with stirring to give a pale yellow solid of **3** with 92% yield, which was collected by filtration, washed with cooled *n*-hexane (0 °C, 5 mL), and dried under vacuum. Single crystals suitable for X-ray diffraction analysis were grown from a concentrated toluene solution of **3** layered with *n*-hexane. ^{1}H NMR (400 MHz, C_6D_6) δ: 7.98～6.94 (m, 20H, C_6H_3, C_6H_2, PPh_3), 5.83 (s, 1H, C_6H_2), 5.06 (s, 1H, C_6H_2), 3.31 (sept, $^3J_{HH}$=6.4 Hz, 1H), 2.98 (sept, $^3J_{HH}$=6.4 Hz, 1H), 2.89 (sept, $^3J_{HH}$=6.4 Hz, 1H), 2.47 (sept, $^3J_{HH}$=6.4 Hz, 1H), 2.34 (sept, $^3J_{HH}$=6.4 Hz, 1H), 1.84 (sept, $^3J_{HH}$=6.4 Hz, 1H, C*H*Me$_2$), 1.79 (d, $^3J_{HH}$=6.4 Hz, 3H), 1.58 (d, $^3J_{HH}$=6.4 Hz, 6H), 1.26 (d, $^3J_{HH}$=6.4 Hz, 6H), 1.20 (d, $^3J_{HH}$=6.4 Hz, 3H), 1.12 (d, $^3J_{HH}$=6.4 Hz, 3H), 1.09 (d, $^3J_{HH}$=6.4 Hz, 3H), 0.86 (d, $^3J_{HH}$=6.4 Hz, 3H), 0.78 (d, $^3J_{HH}$=6.4 Hz, 3H), 0.67 (d, $^3J_{HH}$=6.4 Hz, 6H, CH*Me*$_2$), −9.62 (d, $^2J_{PH}$=41.5 Hz, 1H, Ru-H); ^{31}P NMR (162 MHz, C_6D_6) δ: 56.4 (s, PPh_3); ^{13}C NMR (100 MHz, C_6D_6) δ: 161.5, 148.4, 147.2, 147.1, 147.0, 138.9, 138.4, 136.6, 136.3, 134.0, 133.9, 132.5, 132.4, 31.6, 129.6, 126.0, 120.8, 120.2, 119.2, 116.0, 115.9, 112.1, 108.7, 108.6, 89.4, 82.0 (C_6H_3, C_6H_2, PPh_3), 34.9, 32.0, 31.6, 31.5, 30.3, 29.1, 29.0, 26.9, 26.6 26.2. 25.5, 24.6, 24.4, 24.3, 23.7, 23.5, 23.1, 23.0, 22.4, 21.4 (*CHMe*$_2$). Anal. calcd for $C_{54}H_{65}Br_2GePRu$ C 60.13, H 6.07; found C 59.89, H 6.44.

4.3 Synthesis of (PPh_3)HRuGeEt$_2$ArTrip (**4**)

To a toluene solution of complex **3** (200 mg, 0.185 mmol) was added dropwise EtMgBr (0.13 mL, 0.389 mmol) at −78 °C. The mixture was stirred for 1 h at −78 °C and then slowly warmed to 60 °C and further stirred for 2 h. After filtration and removal of all volatiles under vacuum, cooled *n*-hexane (0 °C, 5 mL) was added to the residue with stirring to give a pale yellow solid of **4** with 86% yield, which was collected by filtration, washed with cooled *n*-hexane (0 °C, 5 mL), and dried under vacuum.

Alternative synthetic procedure: To a toluene solution of complex **1** (200 mg, 0.202 mmol) was added dropwise $LiHBEt_3$ (0.42 mL, 0.424 mmol) at −78 °C. The mixture was stirred for 1 h at −78 °C and then slowly warmed to 60 °C and further stirred for 2 h. After filtration and removal of all volatiles under vacuum, cooled *n*-hexane (0 °C, 5 mL) was added to the residue with stirring to give a pale yellow solid of **4** with 88% yield, which was collected by filtration, washed with cooled *n*-hexane (0 °C, 5 mL), and dried under vacuum. Single crystals suitable for X-ray diffraction analysis were grown from a concentrated toluene solution of **4** layered with *n*-hexane. ^{1}H NMR (500 MHz, C_6D_6) δ: 7.82～6.97 (m, 20H, C_6H_3, C_6H_2, PPh_3), 5.67 (s, 1H, C_6H_2), 5.20 (s, 1H, C_6H_2), 3.02 (sept, $^3J_{HH}$=5.3 Hz, 1H), 2.87 (sept, $^3J_{HH}$=5.3 Hz, 3H), 2.54 (sept, $^3J_{HH}$=5.3 Hz, 1H, C*H*Me$_2$), 1.69 (d, $^3J_{HH}$=5.3 Hz, 3H, CH*Me*$_2$), 1.53 (sept, $^3J_{HH}$=5.3 Hz, 1H, C*H*Me$_2$), 1.49 (d, $^3J_{HH}$=5.3 Hz, 6H), 1.47 (d, $^3J_{HH}$=5.3 Hz, 3H), 1.33 (d, $^3J_{HH}$=5.3 Hz, 3H), 1.26 (d, $^3J_{HH}$=5.3 Hz, 9H), 1.16 (d, $^3J_{HH}$=5.3 Hz, 3H), 1.11 (d, $^3J_{HH}$=5.3 Hz, 3H), 1.07 (d, $^3J_{HH}$=5.3 Hz, 3H, CH*Me*$_2$), 1.03 (t, $^3J_{HH}$=5.4 Hz, 3H, CH$_2$C*H*$_3$), 0.86 (q, $^3J_{HH}$=5.4 Hz, 4H, C*H*$_2$CH$_3$), 0.69 (d, $^3J_{HH}$=5.3 Hz, 3H, CH*Me*$_2$), 0.07 (t, $^3J_{HH}$=5.4 Hz, 3H, CH$_2$C*H*$_3$), −11.00 (d, $^2J_{PH}$=38.1 Hz, 1H, Ru-H); ^{31}P NMR (202 MHz, C_6D_6) δ: 56.8 (s, PPh_3); ^{13}C NMR (125 MHz, C_6D_6) δ: 162.9, 148.1, 147.5, 146.8, 146.7, 144.1, 141.3, 141.0, 140.1, 134.6, 134.5, 131.7, 129.0, 128.3, 128.2, 128.1, 128.0, 127.9, 127.6, 127.4, 126.9, 125.0, 120.5, 120.3, 114.2, 113.6, 108.5, 107.7, 85.0, 80.3 (C_6H_3, C_6H_2, PPh_3), 34.9, 31.9, 31.1, 30.6, 29.8, 29.5, 27.2, 26.7, 26.6, 26.5, 24.6, 24.4, 24.3, 23.6, 23.5, 23.0, 22.4, 22.3, 21.8, 15.8, 14.3, 12.1,

10.4 (CH_2CH_3, $CHMe_2$). Anal. calcd for $C_{58}H_{75}GePRu$ C 71.31, H 7.74; found C 71.15, H 7.93.

4.4 Synthesis of [(PPh_3)(H)$_2$RuGeCl$_2$ArTrip][BF_4] (**5**)

To a dichloromethane solution of complex **1** (200 mg, 0.202 mmol) was added dropwise HBF_4•Et_2O (31 μL, 0.202 mmol) at room temperature, and the solution formed grey precipitate after stirring for 1 h. After filtration and removal of all volatiles under vacuum, cooled Et_2O (0 °C, 5 mL) was added to the residue to give a gray solid of **5** with 95% yield, which was collected by filtration, complex **5** washed with cooled Et_2O (0 °C, 5 mL), and dried under vacuum. Single crystals suitable for X-ray diffraction analysis were grown from a concentrated dichloromethane solution of **5** layered with Et_2O at −20 °C. ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 7.75～7.43 (m, 18H, C_6H_3, PPh_3), 7.00 (s, 2H, C_6H_2), 6.24 (s, 2H, C_6H_2), 2.91 (sept, $^3J_{HH}$=6.6 Hz, 1H), 2.44 (sept, $^3J_{HH}$=6.6 Hz, 4H, C*H*Me$_2$), 1.53 (d, $^3J_{HH}$=6.6 Hz, 6H, CH*Me*$_2$), 1.45 (sept, $^3J_{HH}$=6.6 Hz, 1H, C*H*Me$_2$), 1.35 (d, $^3J_{HH}$=6.6 Hz, 6H), 1.26 (d, $^3J_{HH}$=6.6 Hz, 6H), 1.21 (d, $^3J_{HH}$=6.6 Hz, 6H), 0.95 (d, $^3J_{HH}$=6.6 Hz, 6H), 0.88 (t, $^3J_{HH}$=6.6 Hz, 6H, CH*Me*$_2$), −9.31 (d, $^2J_{PH}$=22.8 Hz, 2H, Ru-H); ^{31}P NMR (202 MHz, CD_2Cl_2) δ: 52.2 (s, PPh_3); ^{19}F NMR (376 MHz, CD_2Cl_2) δ: −160.8 (s, BF_4); ^{13}C NMR (125 MHz, CD_2Cl_2) δ: 159.5, 149.5, 149.4, 148.2, 148.0, 147.4, 147.2, 147.0, 139.9, 139.6, 135.3, 134.8, 134.5, 134.3, 134.1, 133.5, 133.4, 132.7, 132.3, 132.2, 131.6, 131.2, 131.0, 130.5, 129.7, 139.6, 126.0, 125.7, 120.8, 120.6, 93.6 (C_6H_3, C_6H_2, PPh_3), 34.5, 31.6, 31.5, 30.7, 26.3, 25.0, 24.2, 24.1, 22.4, 22.2 (C*H*Me$_2$). Anal. calcd for $C_{54}H_{66}BCl_2F_4GePRu$: C 60.19, H 6.17; found C 60.37, H 6.02.

4.5 Synthesis of (PPh_3)HRuGe(OH)$_2$ArTrip (**6**)

To a toluene solution of complex **2** (200 mg, 0.195 mmol) was added dropwise THF solution of Na/$C_{10}H_8$ (0.605 mmol) at −78 °C. The mixture was stirred for 1 h at −78 °C and 3.1 eqiuv. of H_2O (10 μL, 0.6 mmol) were added, then slowly warmed to room temperature and further stirred for 12 h. After filtration and removal of all volatiles under vacuum, cooled *n*-hexane (0 °C, 5 mL) was added to the residue with stirring to give a pale yellow solid of **6** with 62% yield, which was collected by filtration, washed with cooled *n*-hexane (0 °C, 5 mL), and dried under vacuum. ^{1}H NMR (500 MHz, C_6D_6) δ: 7.94～6.90 (m, 20H, C_6H_3, C_6H_2, PPh_3), 5.90 (s, 1H, C_6H_2), 4.99 (s, 1H, C_6H_2), 3.88 (br, 2H, OH), 3.14 (sept, $^3J_{HH}$=6.7 Hz, 1H), 3.05 (sept, $^3J_{HH}$=6.7 Hz, 1H), 2.79 (sept, $^3J_{HH}$=6.7 Hz, 1H), 2.46 (sept, $^3J_{HH}$=6.7 Hz, 1H), 2.40 (sept, $^3J_{HH}$=6.7 Hz, 1H), 1.97 (sept, $^3J_{HH}$=6.7 Hz, 1H, C*H*Me$_2$), 1.54 (d, $^3J_{HH}$=6.7 Hz, 3H), 1.19 (d, $^3J_{HH}$=6.7 Hz, 18H), 0.91 (m, $^3J_{HH}$=6.7 Hz, 12H), 0.76 (d, $^3J_{HH}$=6.7 Hz, 3H, CH*Me*$_2$), −10.57 (d, $^2J_{PH}$=40.9 Hz, 1H, Ru-H); ^{31}P NMR (202 MHz, C_6D_6) δ: 59.2 (s, PPh_3); ^{13}C NMR (125 MHz, C_6D_6) δ: 166.7, 148.3, 147.7 145.9, 141.1, 140.6, 139.9, 137.7, 135.2, 130.5, 129.0, 126.9, 125.5, 120.6, 120.2, 113.7, 87.1, 81.8 (C_6H_3, C_6H_2, PPh_3), 34.7, 20.2, 26.5, 25.6, 25.3, 24.3, 23.6, 23.3, 22.9, 22.6 (C*H*Me$_2$). Anal. calcd for $C_{54}H_{67}GeO_2PRu$ C 68.07, H 7.09; found C 68.41, H 7.36.

4.6 Synthesis of (PPh_3)IRuGeCl$_2$ArTrip (**7**)

To a toluene solution of **2** (200 mg, 0.195 mmol) was added dropwise THF solution of I_2 (152 mg, 0.598 mmol) at −78 °C. The mixture was stirred for 1 h at −78 °C and then slowly warmed to room temperature and further stirred for 12 h. After filtration, the solution was evaporated under vacuum, and precooled *n*-hexane (0 °C, 5 mL) was added to the residue to give a pale yellow solid of **7** with 65% yield, which was collected by filtration and dried under vacuum. ^{1}H NMR (500 MHz, C_6D_6) δ: 8.10～7.02 (m, 20H, C_6H_3, C_6H_2, PPh_3), 6.10 (s, 1H, C_6H_2), 4.77 (s, 1H, C_6H_2), 3.07～2.98 (m, 3H), 2.88 (sept, $^3J_{HH}$=5.0 Hz, 1H), 2.79 (sept, $^3J_{HH}$=5.0 Hz, 1H), 2.61 (sept, $^3J_{HH}$=5.0 Hz, 1H, C*H*Me$_2$), 1.75 (d, $^3J_{HH}$=10.0 Hz, 3H), 1.56 (d, $^3J_{HH}$ = 10.0 Hz, 3H), 1.50 (d, $^3J_{HH}$ = 5.0 Hz, 3H), 1.29～1.23 (m, 15H), 1.16 (d, $^3J_{HH}$=10.0 Hz, 3H), 0.95 (d, $^3J_{HH}$=5.0 Hz, 3H), 0.85 (d, $^3J_{HH}$=10.0 Hz, 3H), 0.66 (d, $^3J_{HH}$=10.0 Hz, 3H, CH*Me*$_2$); ^{31}P NMR (202 MHz, C_6D_6) δ: 33.3 (s, PPh_3); ^{13}C NMR (125 MHz, C_6D_6) δ: 163.2, 148.2, 147.4, 147.2, 146.6, 136.1, 134.7, 134.6, 132.6, 124.9, 120.2, 114.5, 108.9, 108.8, 101.2, 96.9, 88.4 (C_6H_3, C_6H_2, PPh_3), 34.4, 31.8, 31.4, 31.1, 30.8, 30.3, 29.9, 26.6, 26.4, 26.3, 26.1, 25.9, 24.7, 24.1, 23.9, 23.4, 22.8, 22.2, 21.3, 20.5 (C*H*Me$_2$). Anal. calcd for $C_{54}H_{67}GeCl_2IPRu$: C 57.98, H 6.04; found C 57.71, H 6.17.

Supporting Information ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and 2D NMR spectra of **3**～**7**, crystal data and structure refinement of **3**, **4**, **6**, and **7**, and molecular structures of **3**～**7**. CCDC- 2265581 (**3**), 2265584 (**4**), 2265583 (**6**) and 2265582 (**7**) contain the supplementary crystallographic data. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

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