Transmetallation vs adduct Diverse reactivity of N,O-ketiminato germylene with [Cp*MCl2]2 (M = Rh or Ir; Cp* = η5-C5Me5) and MCl5 (M = Nb and Ta)

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Transmetallation vs Adduct: Diverse Reactivity of N,O-ketiminato germylene with $[Cp^*MCl_2]_2$ (M = Rh or Ir; Cp* = η^5-C_5Me_5) and MCl_5 (M = Nb and Ta)

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Abstract:

The reactions of the germylenes, [(Dipp)NCMeCHCORGeCl] (**1a**: R = Me, **1b**: R = Ph) with $[Ir_2Cl_2(\mu\text{-}Cl)_2(\eta^5\text{-}Cp^*)_2]$ led to the formation of the adducts $[(Dipp)NCMeCHCORGeClIrCl_2Cp^*]$ (**3a**: R = Me and **3b**: R = Ph).On the other hand, $[Rh_2Cl_2(\mu\text{-}Cl)_2(\eta^5\text{-}Cp^*)_2]$ does not react with the germylenes (**1a** and **1b**). When the reactions of **1a** and **1b** are carried out with $[Cp^*TaCl_4]$, the reaction led to decomposition. The reaction of **1a** or **1b** with $TaCl_5$ yielded the transmetallated products $[(Dipp)NCMeCHCORTaCl_4]$ (**4a**: R = Me, **4b**: R = Ph) with the extrusion of $GeCl_2$. Our theoretical studies show that for, the insertion of $TaCl_5$ to **1a** and the formation of **4a** with concomitant elimination of $GeCl_2$ is energetically favourable. Extrusion of $SnCl_2$ is also observed

when the corresponding stannylene, [(Dipp)NCMeCHCOMeSnCl] was reacted with $TaCl_5$. All these compounds have been characterized by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis and the constitution of compounds **1b**, **3b,** and **4a** were confirmed by single-crystal X-ray crystallography.

1. Introduction

The chemistry of the heavier analogues of carbenes has been expanded from synthetic curiosity towards application in synthesis.[1] Heavier carbene analogues are utilized as donor ligands in low-valent main group species[2] as well as in transition metal complexes.[3] The synthesis of heavier analogues of carbenes would not have been possible without the proper choice of ligands. By occupying larger areas of the metal coordination sphere and physically blocking decomposition routes, sterically bulky ligands have often been used to improve the kinetic stability of carbenes and their heavier congeners. The most extensively used monoanionic and bidentate ligands in low-valent group 14 chemistry possessing nitrogen donors with bulky substituents are the *β*-diketiminate ligands, popularly known as "nacnac". Many variations of the nacnac ligand with respect to the group attached to the nitrogens, have been reported with an extensive series of metal complexes synthesized using these ligands.[4] Iconic examples of low-valent main group compounds stabilized through the latter ligand system include LAl(I),[5] LMg(I)-Mg(I)L,[6] LGe(II)H[7] (L=HC{C(Me)N(Ar)}$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$ or 2,4,6-Me$_3$C$_6$H$_2$), L'E(II) (L' = HC{C(=CH$_2$)(C-Me)(NAr)$_2$}, E = Si and Ge).[8] Compared to *β*-diketiminates, the class of *β*-ketoiminate ligands has not earned much interest due to the reduction of sterics around the metal center. In this context, we have recently prepared two new germylenes using N,O ketiminato ligands of compositions (Dipp)NCMeCHCOMeGeCl (**1a**) and (Dipp)NCMeCHCOMeGeN(SiMe$_3$)$_2$ (**2a**).[9] We have further shown that the germylene amide (**2a**) undergoes deprotonation from the backbone methyl upon reacting with [$M_2Cl_2(\mu\text{-}Cl)_2(\eta^5\text{-}Cp^*)_2$] (M = Rh and Ir), leading to the formation of a cyclometallated product (Scheme 1).[9] In this study, we have replaced one of the backbone methyl groups with a phenyl moiety and prepared a new germylene, (Dipp)NCMeCHCOPhGeCl (**1b**). The reaction of **1b** with LiN(TMS)$_2$ led to the formation of a metathetical product, (Dipp)NCMeCHCOPhGeN(TMS)$_2$

(**2b**) in quantitative yield. Subsequently, we sought to compare the reactions of **1a**, **1b, 2b** with previously reported **2a**. At the outset, the reactions of **1a**, **1b, 2b** with rhodium and iridium precursors have three possible outcomes: (a) aliphatic C–H bond activation and subsequent cyclometallation (b) aromatic C–H bond activation and subsequent cyclometallation and (c) stable adduct formation. We have observed that **1a** and **1b** does not undergo deprotonation reaction with the Ir precursor, but forms adducts. The analogous reactions with **2b** led to undefined product. The reactions of **1a** and **1b** with $TaCl_5$ led to theformation of ketoiminato Ta complexes, [(Dipp)NCMeCHCORTaCl_4] R = Me (**4a**) and R = Ph (**4b**) with the extrusion of $GeCl_2$. Our results are reported herein.

(Scheme 1 near here)

2. Results and discussion

*2.1. Synthesis and characterizations of germylenes, **1b**-**2b***

The phenyl substituted N,O-ketoimine ligand was synthesized by the literature method.[10] The reaction of 1-phenyl butane-1, 3-dione with 2,6-diisopropylaniline in toluene with a catalytic amount of *p*-toluene sulfonic acid led to the formation of the ligand.[10] The phenyl substituted chlorogermylene (Dipp)NCMeCHCOPhGeCl (**1b**) was synthesized from the reaction of $GeCl_2$·dioxane with one equivalent of potassium salt of ketoimine ligand in THF (Scheme 2). **1b** was purified by crystallization and isolated as pale-yellow crystals in good yield. The ^{1}H NMR spectrum of **1b** shows a single resonance peak for the γ-proton at δ 6.06 ppm and the corresponding ^{13}C NMR appears at δ 99.59 ppm. Two septets appear at δ 3.58 and 2.79 ppm. Further, the solid-state structural analysis of **1b** was carried out using single-crystal X-ray diffraction.

(Scheme 2 near here)

As shown in Fig. 1, the germanium center in **1b** adopts a distorted trigonal pyramidal geometry, in which the three-coordinated germanium is surrounded by one nitrogen, one oxygen, and one chlorine atom. There is a lone pair of electrons on the germanium center. This feature has been observed in various chlorogermylene complexes, such as [HC{C(Me)}$_2$N(Dipp)O]GeCl,[9] [HC{C(Me)N(Dipp)}$_2$]GeCl,[11] [PhC{N(*t*Bu)}$_2$]GeCl,[12] [*t*BuC{N(Dipp)}$_2$]GeCl,[13] and [(*t*Bu)$_2$ATI]GeCl (ATI = Aminotroponiminate).[14] The Ge1-Cl1 (2.2960(7) Å), Ge1-O1 (1.8864(14) Å), and Ge1-N1 (2.0106(16)Å) bond distances of the six-membered {C_3NGeO} ring of **1b** are almost identical with that of the reported N,O-ketoiminate-chlorogermylene complex [HC{C(Me)}$_2$N(Dipp)O]GeCl [Ge1–Cl12.306(3) Å, Ge1-O1 1.902(5) Å, and Ge1-N1 2.011(5) Å]. The O1-Ge1-N1 bond angle of 90.39(6)^o is slightly higher than the reported (Dipp)NCMeCHCOMeGeCl [O1-Ge1-N1 90.0(2)^o].[9]

(Fig. 1 near here)

As shown in Scheme 2, the reaction of **1b** with [LiN(SiMe$_3$)$_2$] led to the formation of the metathesis product, [(Dipp)NCMeCHCOPhGeN(SiMe$_3$)$_2$], **2b**. **2b** was characterized by ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR spectrum of **2b** displayed a single resonance peak for the γ-proton at δ 5.43 ppm and the corresponding ^{13}C NMR appears at δ 95.82 ppm which is shifted to the higher field region compared to its parent germylene chloride and a single resonance at δ 0.22 ppm for the N(SiMe$_3$)$_2$ group, which indicates the replacement of the chlorine atom by the amide group *via* salt elimination.

*2.2. Reactivity of chlorogermylenes (**1a-1b**) with [Ir$_2$Cl$_2$(μ-Cl)$_2$(η^5-Cp*)$_2$]*

Recently, we have reported that the reaction of a germylene amide [(Dipp)NCMeCHCOMeGeN(SiMe$_3$)$_2$] (**2a**) with [Rh$_2$Cl$_2$(μ-Cl)$_2$(η^5-Cp*)$_2$] and [Ir$_2$Cl$_2$(μ-Cl)$_2$(η^5-Cp*)$_2$] dimers led to the formation of cyclometallated Rh(III) and Ir(III) complexes *via* deprotonation from the C–H bond of the germylene ligand.[9] In order to expand this chemistry further, we have probed the reactivity of **2b** with [Rh$_2$Cl$_2$(μ-Cl)$_2$(η^5-Cp*)$_2$] as well as [Ir$_2$Cl$_2$(μ-Cl)$_2$(η^5-Cp*)$_2$] dimers. Unfortunately, the reactions led to unidentified products and we were unable to isolate them.

The reaction of $[Ir_2Cl_2(\mu\text{-}Cl)_2(\eta^5\text{-}Cp^*)_2]$ with **1a** and **1b** gave rise to the formation of germylene adducts, $[(Dipp)NCMeCHCOMeGeClIrCl_2Cp^*]$ (**3a**) and $[(Dipp)NCMeCHCOPhGeClIrCl_2Cp^*]$ (**3b**), respectively (Scheme 3). We have also studied the reactivity of **1a-b** with the Rh dimer, but unfortunately the germylenes do not react with the Rh-dimer.

(Scheme 3 near here)

Both complexes were characterized by ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectra of **3a** and **3b** displayed a septet around δ 3.6 ppm for the isopropyl methine protons and one singlet resonance peak was observed nearly at δ 1.5 ppm for the Cp* proton. It can be noted here that four doublets appear for each **3a** and **3b**, indicating the overlapping of two septets into one. Additionally, the constitution of complex **3b** was confirmed by single crystal X-ray diffraction studies. The ORTEP diagram for **3b** is shown in Fig. 2. The Ge-Ir bond length of 2.3726(10)Å is slightly shorter as compared to $[IrCl(\eta^4\text{-cod})\{Ge(PhC\text{-}(N\textit{t}Bu)_2)\}$ amidinate (2.4203(3) Å).[15] To the best of our knowledge this is the first example of N,O-chelated germanium adduct with a transition metal.

(Fig.2 near here)

*2.3. Reactivity of chlorogermylenes (**1a-1b**) with $TaCl_5$*

As an extension to this chemistry, we have enthusiastically started the reactivity of the germylenes (**1a-b**) with $[Cp^*TaCl_4]$. Unfortunately, the reactions of **1a** or **1b** with $[Cp^*TaCl_4]$ led to the immediate formation of a black solution indicating the leaching of the metal. However, when $TaCl_5$ was used as the metal precursor, it led to a color change from pale yellow to deep orange indicating the formation of a new product (Scheme 4, (a)). The product was crystallized from toluene at -30.0 °C and was isolated as deep orange colored needle shaped crystals. The single-crystal X-ray diffraction analysis revealed the formation of an unexpected transmetallated product $[(Dipp)NCMeCHCOMeTaCl_4]$ (**4a**) instead of the adduct analogous to **3a** and **3b**. The reaction of **1a-1b** with $NbCl_5$, we were not able to get any clean product.

(Scheme 4 near here)

The molecular structure and selected bond parameters are shown in Fig. 3. The unit cell contains two analogous but independent molecules in the asymmetric unit, which was crystallized in the monoclinic $P2_1/c$ space group. **4a** exhibits slightly distorted octahedral geometry around the Ta center that is bound to four chlorine atoms, one nitrogen atom, and one oxygen atom. The four Ta-Cl bond distances are almost equal (~2.32 Å) and the O1-Ta1-N1 bond angle of 80.04(8)^o is considerably smaller than a regular octahedral bond angle of 90^o. The Ta atom in **4a** lies ~0.16 Å above the six-membered C_3NTaO ring.

(Fig.3 near here)

The ^1H NMR spectrum of **4a** displays a single septet corresponding to the isopropyl methine proton instead of showing two septets for the isopropyl methine in **1a**. This spectral evidence corroborates the formation of the new complex.

A significant amount of transmetallation chemistry has been reported in the literature. It can be divided into three types: i) a transition metal replaced by a main group element or vice versa,[16] ii) a main group element replaced by a main group element,[17] and iii) the transition metal replaced by a transition metal.[18] The formation of **4a** from **1a** falls into the first category of transmetallation. One of the interesting facets of the reaction is the extrusion of $GeCl_2$. Filippou and coworkers proposed that the reaction of $CpMo(CO)_3GeCl_2H$ with PMe_3 gave trans-$CpMo(CO)_2(PMe_3)GeCl_2H$ and the mechanism of this ligand exchange reaction involves $GeCl_2$ extrusion.[19] Recently, Roesler reported a similar mechanism for the formation of a Ni(0) germylene complex. The complex was prepared from a germylenium cation with $Ni(cod)_2$, which involved Ni–Ge transmetalation, followed by coordination of the extruded $GeCl_2$ moiety to Ni[16c] Unlike these cases, Ta metal is stabilized in an octahedral environment; hence, it is not possible for $GeCl_2$ to coordinate the metal centre easily.

To prove the formation of the complex (**4a**) by the extrusion of $GeCl_2$ during the reaction, we have performed the NMR tube reaction between N,O-ketoiminate-chlorogermylene and $TaCl_5$ in C_6D_6. This showed a clear and complete conversion of **1a** into **4a** within 10 min (Fig. S15). Under similar condition, compound [(Dipp)NCMeCHCOPhTaCl_4] (**4b**) was prepared from **1b** and was confirmed by the ^{1}H and ^{13}C NMR spectroscopic studies. To check the generality of this reaction, we have carried out the same reaction with analogous N,O-ketoiminate stannylene chloride (**B**), [HC{C(Me)}$_2$N(Dipp)O]SnCl[20] which also led to the formation of **4a**. Complex **4a** could be alternatively synthesized from the reaction mixture of the ketoiminate lithium salt (**A**) with $TaCl_5$ at room temperature (Scheme 4, (b)).

2.4. Computational details.

Full quantum chemical calculations were done with density functional theory (DFT) at the dispersion and solvent corrected PBE/TZVP level of theory mainly to understand the mechanism(s) of the reactions occurring in the presence of Ir and $TaCl_5$ complexes. The experimental results indicated that the reaction between species **1a** and the tantalum complex led to the transmetallated product, but in case of the iridium dimer, only adduct formation was observed.

(Scheme 5 near here)

The DFT calculations showed that the adducts, which are formed between the reaction of [$Ir_2Cl_2(\mu\text{-}Cl)_2(\eta^5\text{-}Cp^*)_2$] or $TaCl_5$ with **1a**, are cyclic germylene intermediates (**3a** and **4a'**), which are thermodynamically feasible by -14.1 kcal/mol and-3.6 kcal/mol respectively (Scheme 5). However, the next step, that is, insertion of Ir between the nitrogen and the oxygen and the elimination of $GeCl_2$, was calculated to be thermodynamically unfavourable, by 45.8 kcal/mol. This, however, is not the case for **4a'**, in which the insertion and the elimination of $GeCl_2$ is favourable by -4.4 kcal/mol. The reason why the transmetallated tantalum complex **4a** is stable and the complex **3a'** is observed to be unstable has been established by DFT studies. The DFT studies that we have conducted do not represent a comprehensive mechanism, as that would entail expensive transition state calculations that are beyond the scope of the current work. However, the computational studies do provide support to the experimental observations by providing insight into the thermodynamics of the different reactions investigated. The cyclopentadienyl ring, attached to Ir in **3a'**, is found to slip from an η^5- to an η^3-coordination mode. This loss of hapticity of the Cp ring in **3a'** may be due to the steric constraints induced by the formation of a six-membered heterocyclic ring structure. It is to be noted that there is no loss of hapticity in the complex **3a**: the formation of **3a'** thus involves a loss of hapticity, and would therefore be thermodynamically disfavoured. The DFT optimized three dimensional structures of **3a'** and **4a** are shown in Fig. 4. As shown in Fig. 4, the central metal in complex **4a** is in an octahedral configuration. This may be due to the fact that the smaller chloride ligands face no difficulties adjusting to the steric demands introduced by the formation of the six-membered heterocyclic ring.

(Fig.4 near here)

3. Conclusion

In summary, we have made a phenyl substituted N, O-ketoiminate germylene chloride, **1b** and a germylene amide, **2b**. Treatment of germylene chlorides (**1a** and **1b**) with $[Ir_2Cl_2(\mu\text{-}Cl)_2(\eta^5\text{-}Cp^*)_2]$ led to the formation of adducts, **3a** and **3b**, whereas $TaCl_5$ yielded transmetallated products **4a** and **4b** with the extrusion of $GeCl_2$. However, the reactions of **1a** and **1b** with $[Rh_2Cl_2(\mu\text{-}Cl)_2(\eta^5\text{-}Cp^*)_2]$ and $[Cp^*TaCl_4]$ were unsuccessful. The results show that the replacement of one of the backbone methyl groups with a phenyl moiety offered a different reactivity pattern. Computational studies were performed to elucidate the diverse reactivity shown by **1a** and in that connection, theoretical studies show that for the formation of **4a** the insertion of $TaCl_5$ to **1a** and elimination of $GeCl_2$ is energetically favourable.

4. Experimental details

4.1. General procedures and instrumentation

All experiments and manipulations were conducted under dry oxygen-free argon using standard Schlenk line techniques or in an Mbraun inert atmosphere dry box containing an atmosphere of purified argon. Acetyl acetone, $GeCl_2$·dioxane, calcium hydride, $TaCl_5$ and potassium hydride were purchased from Aldrich and used as received. All other starting materials were purchased from commercial sources and used without further purification. All solvents were dried by standard methods (hexane, toluene and THF from Na/benzophenone ketyl radical) and freshly distilled prior to use. $CDCl_3$ used for NMR spectral measurements was dried over calcium hydride overnight, distilled and stored in a glovebox. C_6D_6 was dried over sodium metal. ^1H and ^{13}C spectra were recorded on a Bruker 400 MHz instrument. Elemental analyses were performed using a Thermo scientific FLASH 2000 Organic Elemental Analyzer. The NMR signals are reported relative to the residual solvent peaks (^1H: $CDCl_3$:7.26 ppm; ^{13}C: 77.1 ppm and ^1H: C_6D_6: 7.16 ppm;^{13}C: 128.06 ppm). The following abbreviations are used in connection with NMR; s = singlet; d = doublet; t = triplet; q = quartet; dd = doublet of doublets; sept = septet and m = multiples.

4.2. Synthesis of compounds

*4.2.1. Synthesis of [(Dipp)NCMeCHCOPhGeCl] (**1b**)*

To a stirred solution of potassium hydride (0.054 g, 1.370 mmol) in THF (10 mL) was added *α*-phenyl-ketimine ligand (0.400 g, 1.246 mmol) in THF (10mL) at -78 °C. The reaction mixture was warmed to room temperature and stirred for 6 h. The reaction mixture was again brought to -78 °C, and a solution of $GeCl_2$.dioxane (0.288 g, 1.246 mmol) dissolved in THF (10 mL) was added slowly using cannula and the mixture was stirred overnight at room temperature. The solvent was removed under high vacuum, the residue was dissolved in hexane and filtered through celite, and the filtrate was concentrated under reduced pressure and kept at -30 °C to afford pale yellow crystals of **1b**. Yield: 0.485 g (91%). ^1H NMR (400 MHz, C_6D_6): δ = 7.90 (d, J = 7.9 Hz, 2H), 7.15-7.07 (m, 4H), 6.99-6.97 (t, 2H), 6.06 (s, 1H), 3.58 (sept, J = 6.8 Hz, 1H), 2.79 (sept, J = 6.9 Hz, 1H), 1.50 (s, 3H), 1.41 (d, J = 6.6 Hz, 3H), 1.14 (d, J = 6.9 Hz, 3H), 1.09 (d, J = 6.8 Hz, 3H), 0.87 ppm (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, C_6D_6): δ = 172.16, 171.02, 144.84, 143.84, 138.34, 137.44, 131.69, 127.92, 125.44, 124.63, 99.59, 29.23, 28.58, 26.91, 24.79, 24.27, 24.13, 23.35 ppm. Anal. Calcd for $C_{22}H_{26}ClGeNO$: C, 61.66; H, 6.12; N, 3.27. Found: C, 61.62; H, 6.10; N, 3.24.

*4.2.2. Synthesis of [(Dipp)NCMeCHCOPhGeN(SiMe$_3$)$_2$] (**2b**)*

A 50 mL Schlenk flask was charged with **1b** (0.450 g, 1.048 mmol) and $LiN(SiMe_3)_2$ (0.184, 1.101 mmol) in 20 mL dry THF. The suspension was stirred at room temperature for 24 h. The volatiles were removed under high vacuum and the residue was dissolved in hexane and filtered through celite, and the filtrate was removed under reduced pressure to afford an orange solid of **2b**. Yield: 0.540 g (93%). ^{1}H NMR (500 MHz, C_6D_6): δ = 7.79–7.77 (m, 2H), 7.06-7.02 (m, 6H), 5.43 (s, 1H), 3.28 (sept, J = 6.9 Hz, 1H), 3.14 (sept, J = 6.8 Hz, 1H), 1.35 (s, 3H), 1.33 (d, J = 7.0 Hz, 3H), 1.30 (d, J = 6.7 Hz, 3H), 0.96 (d, J = 6.8 Hz, 3H), 0.91 (d, J = 6.8 Hz, 3H), 0.22 ppm (s, 18H). ^{13}C NMR (101 MHz, C_6D_6): δ = 171.48, 171.16, 143.28, 142.98, 139.71, 138.35, 131.03, 127.67, 125.35, 124.56, 95.82, 29.40, 28.34, 25.33, 24.96, 24.86, 24.19, 6.08 ppm. Anal. Calcd for $C_{28}H_{44}GeN_2OSi_2$: C, 60.76; H, 8.01; N, 5.06. Found: C, 60.78; H, 8.02; N, 5.03.

4.2.3. Synthesis of [(Dipp)NCMeCHCOMeGeClIrCl$_2$Cp] (**3a**)*

One equivalent of germylene chloride (**1a**) (0.040 g, 0.108 mmol) and 0.5 equivalents of Ir dimer (0.043 g, 0.054 mmol) are taken in a small vial (15 mL size) inside the glove box. Toluene (4 mL) was added into the mixture of solids at room temperature and stirred for 3 h, during which the color of the solution changed from a pale yellow to a reddish orange. The solvent was removed under high vacuum and the residue was washed with *n*-hexane to obtain the orange color solid, **3a**. Yield: 0.068 g (82%); ^{1}H NMR (400 MHz, C_6D_6): δ =7.20-7.09 (m, 3H), 5.15 (s, 1H), 3.55 (sept, 2H), 1.73 (s, 3H), 1.68 (d, J = 6.4 Hz, 3H), 1.54 (d, 6.8 Hz, 3H), 1.49 (s, 15H), 1.33 (s, 3H), 1.16(d, J = 6.8 Hz, 3H), 0.92 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, C_6D_6): δ = 181.64, 176.85, 145.29, 143.80, 139.45, 129.31, 127.97, 125.42, 124.65, 103.55, 91.14, 29.31, 28.68, 25.79, 25.59, 25.22, 24.99, 24.32, 24.15, 22.72, 22.64, 8.96 ppm. Anal. Calcd for $C_{27}H_{39}Cl_3GeIrNO$: C, 42.40; H, 5.14; N, 1.83. Found: C, 42.43; H, 5.19; N, 1.82.

4.2.4. Synthesis of [(Dipp)NCMeCHCOPhGeClIrCl$_2$Cp] (**3b**)*

One equivalent of germylene chloride (**1b**) (0.030 g, 0.069 mmol) and 0.5 equivalents of Ir dimer (0.028 g, 0.034 mmol) are taken in a small vial (15 mL size) inside the glove box. Toluene (4 mL) was added into the mixture of solids at room temperature and stirred for 3 h, during which the color of the solution changed from a pale yellow to a reddish orange. The solvent was removed under high vacuum. The residue was dissolved in hexane, filtered through celite, and kept at room temperature, which afforded reddish orange color crystals of **3b** after two days. Yield: 0.051 g (89%); ^{1}H NMR (400 MHz, C_6D_6): δ = 7.99-7.96 (m, 2H), 7.20-7.11 (m, 6H), 6.12 (s, 1H), 3.63 (sept, 2H), 1.67 (d, J = 6.4 Hz, 3H), 1.57 (d, 3H), 1.53 (s, 3H), 1.51 (s, 15H), 1.20 (d, J = 6.8 Hz, 3H), 0.85 ppm (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, C_6D_6): δ = 177.51, 174.28, 145.45, 143.89, 139.70, 135.67, 132.68, 129.47, 129.06, 127.92, 125.56, 124.85, 100.53, 91.21, 29.48, 28.82, 25.99, 25.50, 25.19, 25.06, 24.37, 9.18 ppm. Anal. Calcd for $C_{32}H_{41}Cl_3GeIrNO$: C, 46.48; H, 5.00; N, 1.69. Found: C, 46.49; H, 5.03; N, 1.67.

*4.2.5. Synthesis of [(Dipp)NCMeCHCOMeTaCl$_4$] (**4a**)*

Equimolar mixture of germylene chloride (**1a**) (0.060 g, 0.163 mmol) and $TaCl_5$ (0.058 g, 0.163 mmol) are taken in a 25 mL Schlenk flask inside the glove box. Toluene (4 mL) was added into the mixture of solids at room temperature and stirred for 1 h, during which the color of the solution changed from a pale yellow to a reddish orange solution. The solution was filtered through celite, and kept at -30 °C to afford orange color crystals of **4a**. Yield: 0.080 g (85%); ^{1}H NMR (500 MHz, C_6D_6): δ = 7.07-7.02 (m, 3H), 4.87 (s, 1H), 3.14 (sept, 2H), 1.43 (d, J = 6.5 Hz, 6H), 1.30 (s, 3H), 1.28 (s, 3H), 0.90 ppm (d, J = 6.5 Hz, 6H). ^{13}C NMR (101 MHz, C_6D_6): δ =175.88, 170.06, 146.62, 142.07, 124.95, 113.57, 28.42, 27.01, 25.34, 24.98, 21.26 ppm. Anal. Calcd for $C_{17}H_{24}Cl_4NOTa$: C, 35.14; H, 4.16; N, 2.41. Found: C, 35.14; H, 4.15; N, 2.40.

*4.2.6. Synthesis of [(Dipp)NCMeCHCOPhTaCl$_4$] (**4b**)*

Equimolar mixture of phenyl substituted germylene chloride (**1b**) (0.055 g, 0.128 mmol) and $TaCl_5$ (0.045 g, 0.128 mmol) are taken in a 25 mL Schlenk flask inside the glove box. Toluene (4 mL) was added into the mixture of solids at room temperature and stirred for 1 h, during which the color of the solution changed from a pale yellow to a reddish orange solution. The solution was filtered through celite, and dried to afford orange color solid of **4b**. Yield: 0.067 g (82%); ^{1}H NMR (500 MHz, C_6D_6): δ = 7.63 (m, 2H), 7.15-7.01 (m, 4H), 6.95-6.92 (m, 2H), 5.82 (s, 1H), 3.21 (sept, 2H), 1.44 (t, 9H), 0.93 ppm (d, J = 7 Hz, 6H). ^{13}C NMR (101 MHz, C_6D_6): δ =176.86, 165.69, 142.42, 132.95, 132.13, 129.43, 127.71, 125.34, 110.23, 28.79, 27.78, 25.72, 25.28 ppm. Anal. Calcd for $C_{22}H_{26}Cl_4NOTa$: C, 41.08; H, 4.07; N, 2.18. Found: C, 41.01; H, 4.06; N, 2.21.

4.4. X-ray crystal structure determinations

The crystal data for **1b**, **3b** and **4a** were collected and integrated using a Bruker APEXII AXS diffractometer, equipped with a CCD detector, using Mo Kα radiation (λ = 0.71073 Å) at 150(2) K. The structures were solved by heavy atom methods using SHELXS-97 or SIR92 and refined using SHELXL-2014.[21]

Crystal data for **1b**

CCDC No. 1894681, $C_{22}H_{26}GeNOCl$, M. Wt. 428.52, orthorhombic, Space group = $P2_12_12_1$, a = 10.932(2) Å, b = 12.110(2) Å, c = 15.926(2) Å, α = 90°, β = 90°, γ= 90°, V = 2108.6(3) $Å^3$, Z =4, ρcalc= 1.3498 mg/m^3, μ = 1.590 mm-1, F(000) = 889.5, R_1 = 0.0276, wR_2 = 0.0617, Independent reflections = 4842 [R_{int} = 0.0415, R_{sigma} = 0.0409], Goodness-of-fit on F^2 = 1.029.

Crystal data for **3b**

CCDC No. 1894682, $C_{38}H_{45}NOCl_3GeIr$, M.Wt. 902.89, monoclinic, Space group = $P2_1/c$, a = 19.5641(15) Å, b = 12.4425(9) Å, c = 16.6456(10) Å, α = 90°, β = 109.604(4)°, γ= 90°, V = 3817.1(5) $Å^3$, Z =4, ρcalc= 1.571 mg/m^3, μ = 4.509mm -1, F(000) = 1792.0, R_1 = 0.0462, wR_2 =0.0963, Independent reflections = 6150 [R_{int} = 0.0780, R_{sigma} = 0.0842], Goodness-of-fit on F^2 = 1.047.

Crystal data for **4a**

CCDC No. 1894683, $C_{17}H_{24}Cl_4TaON$, M.Wt. 581.14, monoclinic, Space group = $P2_1/c$, a = 14.5412(12) Å, b = 13.3067(11) Å, c = 21.616(2) Å, α = 90°, β = 95.151(3)°, γ= 90°, V = 4165.7(6) $Å^3$, Z =8, ρcalc= 1.8531 mg/m^3, μ = 5.795 mm-1, F(000) = 2256.9, R_1 = 0.0218, wR_2 = 0.0501, Independent reflections = 9592 [R_{int} = 0.0366, R_{sigma} = 0.0290], Goodness-of-fit on F^2 = 1.029.

Conflict of interest

There are no conflicts to declare.

Acknowledgements

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Author Information

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org

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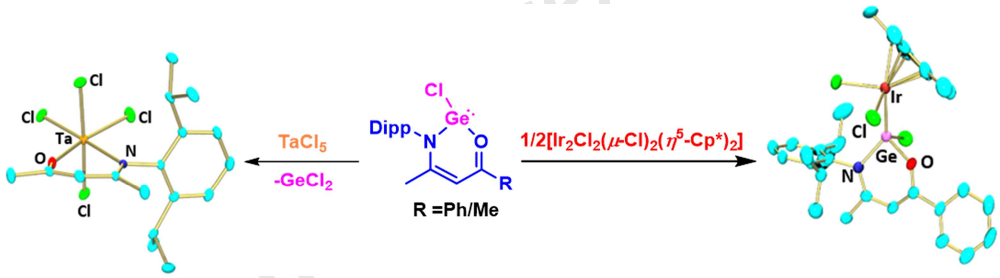
Table of Content

The reactions of the germylene chlorides with $[Ir_2Cl_2(\mu\text{-}Cl)_2(\eta^5\text{-}Cp^*)_2]$ led to adduct formation (see picture right). On the other hand, $TaCl_5$ led to the formation of transmetallated product with the extrusion of $GeCl_2$ (see picture left).



Scheme 1 Our previous work on the synthesis of cyclometallated complexes.

Scheme 2 Synthesis of germylenes and their reactivity.

Fig. 1 Single-crystal X-ray structure of **1b**. All the hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°] for **1b**: Ge1-N1 2.0106(16), Ge1-Cl1 2.2960(7), Ge1-O1 1.8864(14); O1-Ge1-N1 90.39(6), N1-Ge1-Cl1 94.39(5), O1-Ge1-Cl1 94.73(5).

Scheme 3 Synthesis of complexes **3a** and **3b**

Fig. 2 Single-crystal X-ray structure of **3b**. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°] for **3b**: Ge1-N1 1.936(7), Ge1-Cl1 2.232(3), Ge1-O1 1.839(6), Ge1-Ir1 2.3726(10), Ir1-Cl2 2.405(3), Ir1-Cl3 2.385(2); O1-Ge1-N1 94.3(3), N1-Ge1-Cl1 96.6(2), N1-Ge1-Ir1 131.8(2), Cl1-Ir1-Cl3 89.80(10), O1-Ge1-Cl1 94.55(19), O1-Ge1-Ir1 110.53(18).

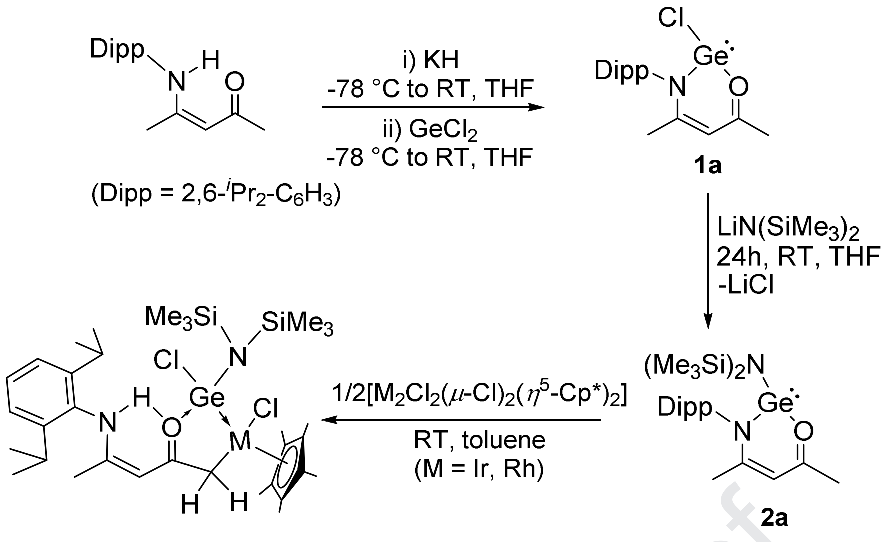
Scheme 4 (a): Transmetallation from N, O-ketoiminate germylenes; (b) transmetallation from stannylenechloride and from ketoiminate lithium salt.

Fig.3 Single-crystal X-ray structure of **4a**. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°] for **4a**: Ta1-N1 2.265(2), Ta1-O1 1.9040(19), Ta1-Cl1 2.3382(7), Ta1-Cl2 2.3473(7), Ta1-Cl3 2.3236(6), Ta1-Cl4 2.3125(8), O1-Ta1-N1 80.04(8), O1-Ta1-Cl1 94.97(6), O1-Ta1-Cl3 168.45(6), Cl4-Ta1-Cl2 178.73(3), N1-Ta1-Cl3 88.49(6), O1-Ta1-Cl1 94.97(6), N1-Ta1-Cl1 174.16(5).

Scheme 5 Transmetallation reaction mechanism for the iridium and tantalum complexes with germylene **1a**, calculated at the PBE/TZVP level of theory with DFT. ΔG represents the Gibbs free energy of the reaction.

Fig.4 The DFT optimized structures of **3a'** and **4a**. The color scheme is as follows: carbon: black, oxygen: red, nitrogen: blue, chlorine: green, hydrogen: grey, tantalum: violet and iridium: yellow.

Scheme 1



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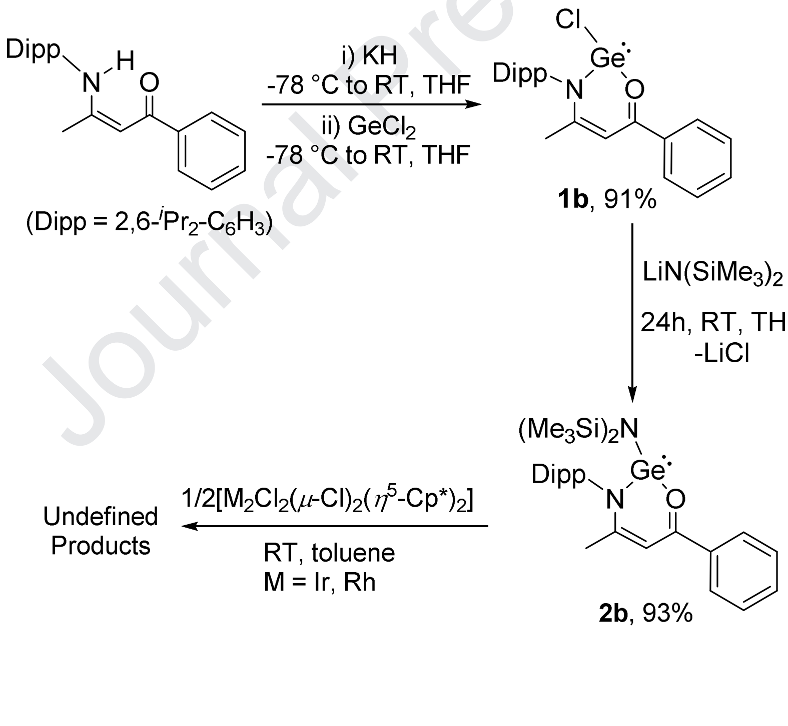

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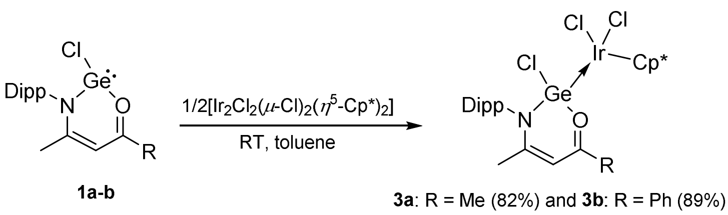

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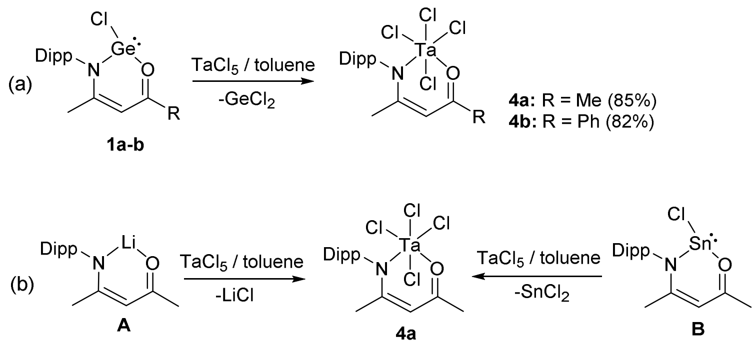

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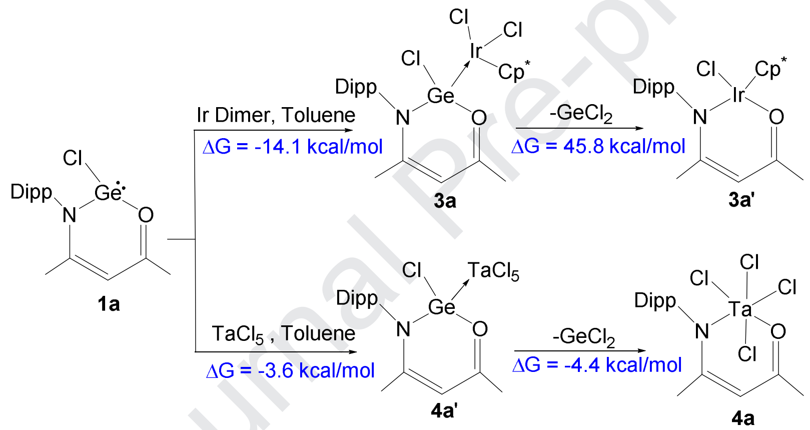


Fig. 1

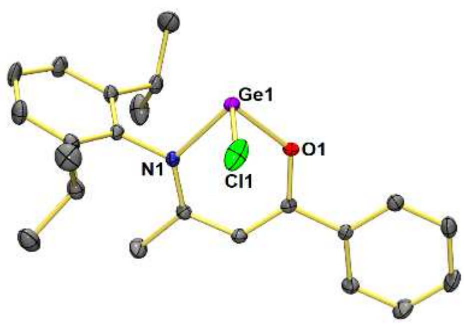


Fig. 2

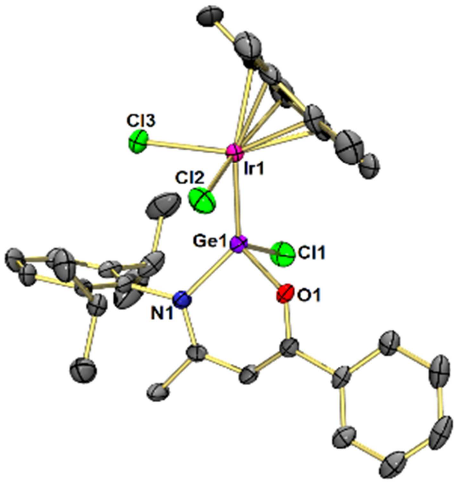


Fig. 3

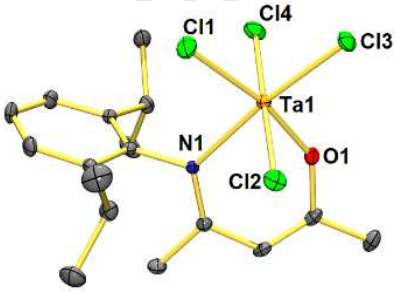
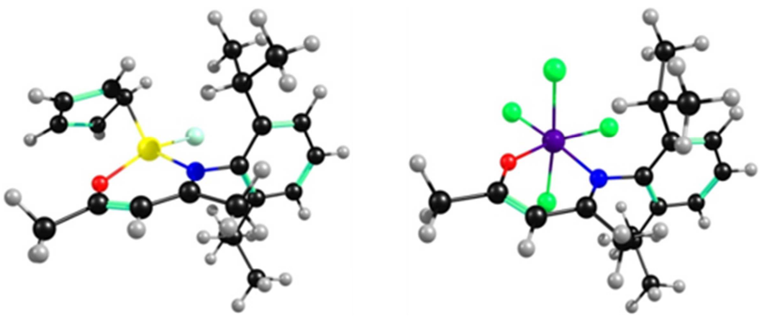


Fig. 4



3a'

4a

Highlights:

- This manuscript reports the first example of N,O-chelated germanium adduct with a transition metal.
- We have reported the synthesis of transmetallated Ta-complex using ketiminate-germylene chlorides and stannylene chlorides.
- The formation of transmatallated and adduct products were established by DFT analysis.

Conflict of interest

There are no conflicts to declare.