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# Heavier Group 14 Congeners of Metalla-isobenzenes: Access to Metalla-isosilabenzene and Metalla-isogermabenzene by One-Pot Reactions

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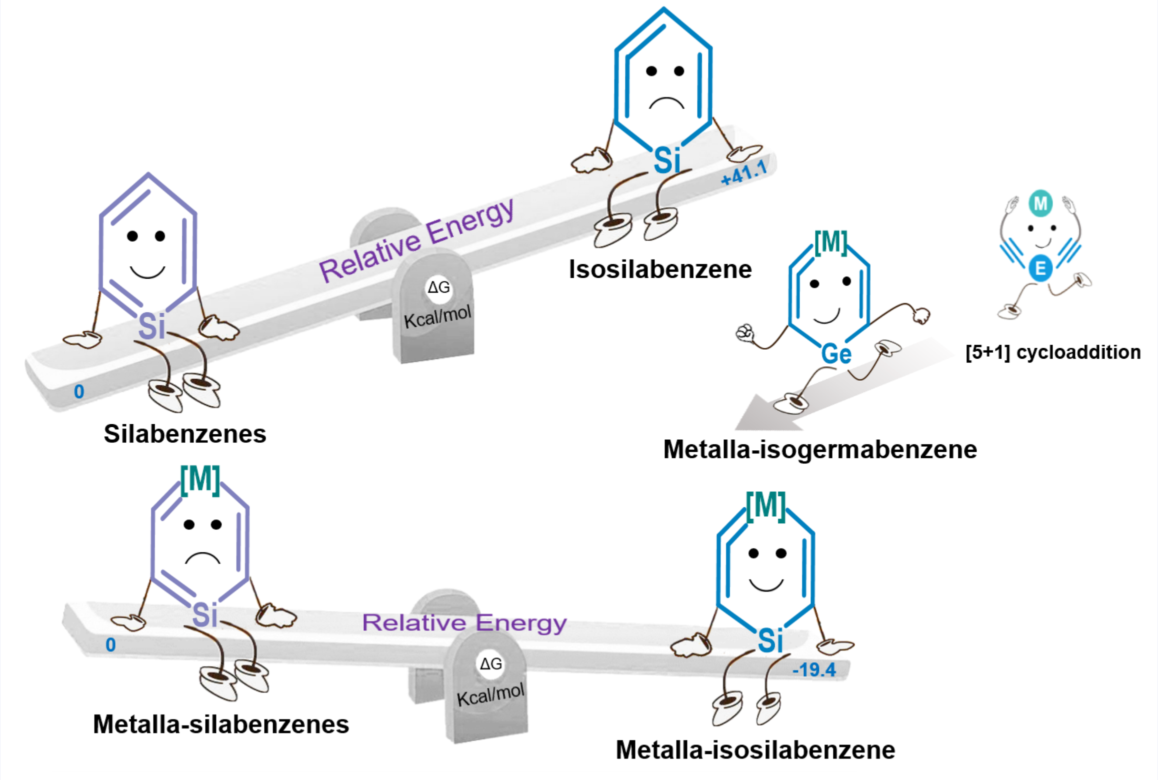
## Keywords

Metalla-isosilabenzene | Metalla-isogermabenzene | Density functional calculations | Cycloaddition | Metallacycles

## Comprehensive Summary



Metalla-isosilabenzenes and metalla-isogermabenzenes have been successfully synthesized by the formal [5+1]-cycloaddition of diethynylsilane or diethynylgermane with simple metal complexes. This is the first example of a heavier Group 14 metalla-isobenzene isomer bearing a cumulative double bond motif within a metallacycle. These novel complexes were fully characterized by NMR spectroscopy and single-crystal X-ray diffraction analysis. The stabilization of the cyclic metal-vinylidene complexes has been analyzed using density functional theory (DFT) calculations. When the metalla-isosilabenzenes bearing Si—H bond were treated with the trityl salt as a hydride scavenger, the formation of silylium cation was observed spectroscopically. Both of metalla-isosilabenzenes and metalla-isogermabenzenes can readily undergo migratory insertion reactions to furnish siloles or germoles.

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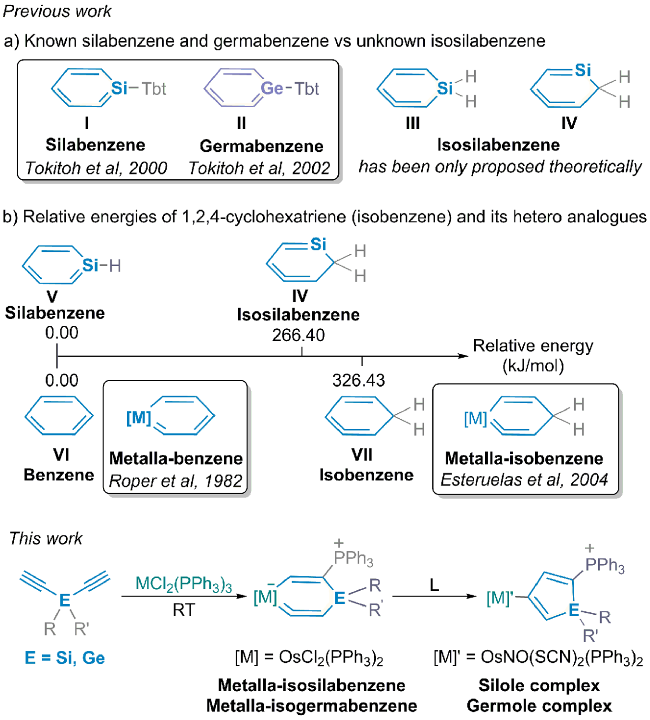
## Background and Originality Content

Incorporation of heteroatoms into the scaffold of cyclic conjugated molecules, especially aromatic hydrocarbons, has attracted significant interest in synthetic and theoretical chemistry.[1] For instance, silabenzenes (**I**) and germabenzenes (**II**),[2] as paradigms of the heavier congeners of carbocyclic aromatic compounds, have been unambiguously achieved (Scheme 1a) and have seen pronounced progress in recent decades.[3] Early calculations predicted two forms of isosilabenzenes (**III**), *i.e.*, 6-hetero-1,2,4-cyclohexatriene (**III**) or 5-hetero-1,2,4-cyclohexatriene (**IV**),[4] which maintain their allene character in their twisted ring geometries. However, although the isomer energy difference between isosilabenzene (**IV**) and silabenzene (**V**) is much smaller than that between isobenzene (**VII**) and benzene (**VI**) (Scheme 1b),[4b] isosilabenzene and its analogues have not been detected or isolated to date. Moreover, the heavier congeners of isosilabenzenes, such as isogermabenzenes, have never been found, to the best of our knowledge.

**Scheme 1** Benzene, isobenzene, metalla-benzene, metalla-isobenzene and their heavier group 14 congeners

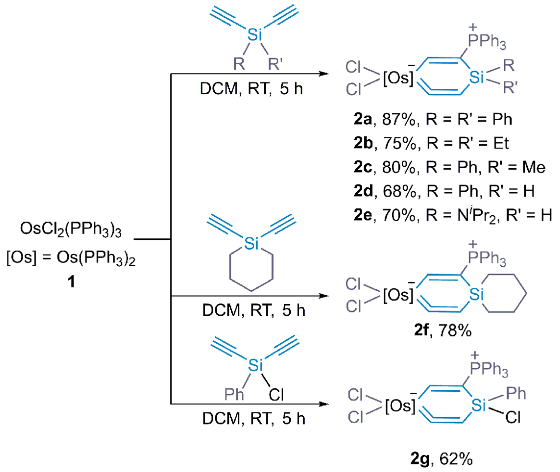


On the other hand, Roper *et al*.[5] have presented a handful of metalla-benzenes in 1982 after the first theoretical prediction by Thorn and Hoffmann in 1979.[6] Over the past years, a variety of transition metal analogs of arenes have garnered considerable attention due to their interesting structural features and properties.[7] As shown in Scheme 1b, the six-membered metallacycle featuring metal vinylidene has been reported by Esteruelas and co-workers, as the first successful attempt to access metal analogs of isobenzene.[8] Indeed, the introducing of transition metals has assisted the isolation of reactive chemical species bearing C$_{sp}$ carbon within rings, such as metalla-benzynes,[9] metalla-pentalynes,[10] and even complexes containing metal vinylidene unit within a five-membered ring.[11] Herein, we report the synthesis of heavier group 14 congeners of metalla-isobenzenes (Scheme 1), namely metalla-isosilabenzene (**2**) and metalla-isogermabenzene (**3**), by formal [5+1]-cycloaddition of diethynylsilane or diethynylgermane with a simple metal complex. The strained heterocycles containing Group 14 elements are thermally stable, and can undergo ligand substitution reactions and easily convert to related siloles or germoles with the aid of nitrosonium reagents. Detailed DFT calculations revealed the stabilization of transition metal and Group 14 atom in strained ring systems and provided information that could lead to the further development of heavy analogs of arenes.

## Results and Discussion

The six-membered metallacycles, especially metallabenzenes, can be synthesized by the [5+1]-cycloaddition of a penta-1,4-diyn-3-ol with low valent transition metal halides.[12] The previous results led us to speculate that diethynylsilane could be an appropriate starting material to incorporate heavy Group 14 elements into metallacycles and produce unprecedented metal analogues of silabenzenes. A variety of aryl, alkyl, alkyl-aryl and amido substituted diethynylsilanes were selected to test this hypothesis by using the one-pot reactions in Scheme 2 as model reactions. Complexes **2a**—**2e** could be readily prepared by reacting complex **1** and the respective diethynylsilane in CH$_2$Cl$_2$ at room temperature (RT) and were isolated in good yield (Scheme 2). The silacycle precursor, 1,1-diethynylsilinane also enabled the synthesis of the respective analogs **2f** in good yield. The room-temperature stable complexes have been structurally characterized by multinuclear NMR spectroscopy and elemental analysis.

**Scheme 2** Synthesis of metalla-isosilabenzene **2** by one-pot reactions of OsCl$_2$(PPh$_3$)$_3$ with (HC≡C)$_2$SiRR'

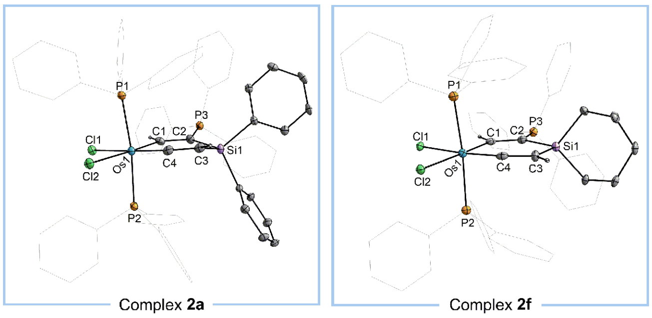


The NMR spectra of complexes **2a**—**2f** were examined (see the Supporting Information (SI) for details). These complexes exhibit two resonances in their $^{31}$P{$^1$H} NMR spectra with an integration ratio of 2 : 1, respectively. This is consistent with the presence of the axial phosphine ligands and the phosphonium substituents of the metallacycle. The characteristic signals in the $^1$H NMR spectra are the doublet signals around $\delta$ 13, which can be assigned to the protons on carbons adjacent to a metal center. The $^{13}$C{$^1$H} NMR spectra of **2** show downfield resonances above $\delta$ 270, suggesting that C$_{sp}$ atoms are bound to the metal. Furthermore, the resonances corresponding to the other carbon atoms of the metallacycles in the complexes **2a**—**2f** have very similar NMR spectroscopic characteristics. For example, complex **2a** displayed the four signals of metallacycle at $\delta$ 228.2 (C1), 94.2 (C2), 74.7 (C3), and 279.1 (C4) in $^{13}$C{$^1$H} NMR spectra with the aid of the $^1$H-$^{13}$C HSQC, $^1$H-$^{13}$C HMBC and $^{13}$C-DEPT-135 spectra, while the corresponding signals of **2f** were observed at $\delta$ 227.1 (C1), 96.2 (C2), 72.0 (C3), and 277.8 (C4). In the $^{29}$Si{$^1$H} NMR spectrum of **2a**, a doublet was observed at $\delta$ −15.81, which suggests that the silicon atom is close to the phosphonium substituent.

Complexes **2a**, **2b**, **2c**, **2e** and **2f** were studied by single-crystal

X-ray diffraction analysis. As shown in Figure 1, the X-ray crystal structure of **2a** clearly showed a twisted six-membered metallacycle, as suggested by the 0.108 Å deviation from the least-squares plane of Os1, Si1 and C1—C4. The distance between Os1 and C4 is only 1.813(3) Å and the bond angle Os1–C4–C3 is 161.9(2)°, which are comparable to those observed previously in cyclic osmium vinylidene complexes.[8] The Si—C bond lengths within the metallacyclic unit in **2a** (Si1—C2 1.906(3) Å, Si1—C3 1.860(3) Å) are obviously longer than those reported for silabenzene,[13] suggesting the $sp^3$ hybridized character of the silicon atom. The structural features of **2f** are very similar to those of **2a**, indicating that the strained metalla-isosilabenzene system could be retained in spiro-fused silacycles where Si is the ring junction.

Having substantiated that formal [5+1]-cycloaddition of diethynylsilane takes place readily with the osmium complex (**1**), we sought to obtain halosilacycle complexes, which could be good precursors capable of producing sila-aromatics by dehalogenation reactions. To this end, the desired chloride complex (**2g**) was generated through combination of chlorodiethynyl(phenyl)silane with the complex **1** (Scheme 2). With the chlorosilacycle (**2g**) in hand, we began our investigations into the aromatization of the metalla-isosilabenzene in the presence of dechlorinative reagents. The cleavage of Si—Cl bond might lead to the formation of silylium cation or other conjugated metallacyclic species. We found that reactions at RT of **2g** with lithium salts, for example, lithium diisopropylamide (LDA), resulted only in the complex mixtures of decomposition products. As shown in Figure 2a, DFT studies demonstrate that the aromatization reaction of **2g** is thermodynamically unfavorable ($\Delta G$ = 47.9 kcal/mol), in sharp contrast to the classical aromatization reaction of chlorosilane **B**



Complex **2a** Complex **2f**

**Figure 1** X-ray crystal structures for **2a** and **2f** drawn at the 50% probability level. Hydrogen atoms and solvent molecules were omitted and phenyl groups in $PPh_3$ ligands are depicted using a wireframe model for clarity. Selected bond lengths [Å] and bond angles for **2a**: Os1—C1 2.044(3), Os1—C4 1.813(3), C1—C2 1.379(4), C3—C4 1.311(4), Si1—C2 1.906(3), Si1—C3 1.860(3); C3–C4–Os1 161.9(2)°, C4–Os1–C1 83.07(12)°, Os1–C1–C2 133.6(2)°, C1–C2–Si1 123.5(2)°, C2–Si1–C3 104.96(12)°, Si1–C3–C4 109.2(2)°. **2f**: Os1—C1 2.029(4), Os1—C4 1.825(4), C1—C2 1.374(5), C3—C4 1.302(5), Si1—C2 1.915(4), Si1—C3 1.857(4); C3–C4–Os1 161.8(3)°, C4–Os1–C1 83.96(15)°, Os1–C1–C2 132.9(3)°, C1–C2–Si1 125.4(3)°, C2–Si1–C3 105.39(16)°, Si1–C3–C4 110.4(3)°.

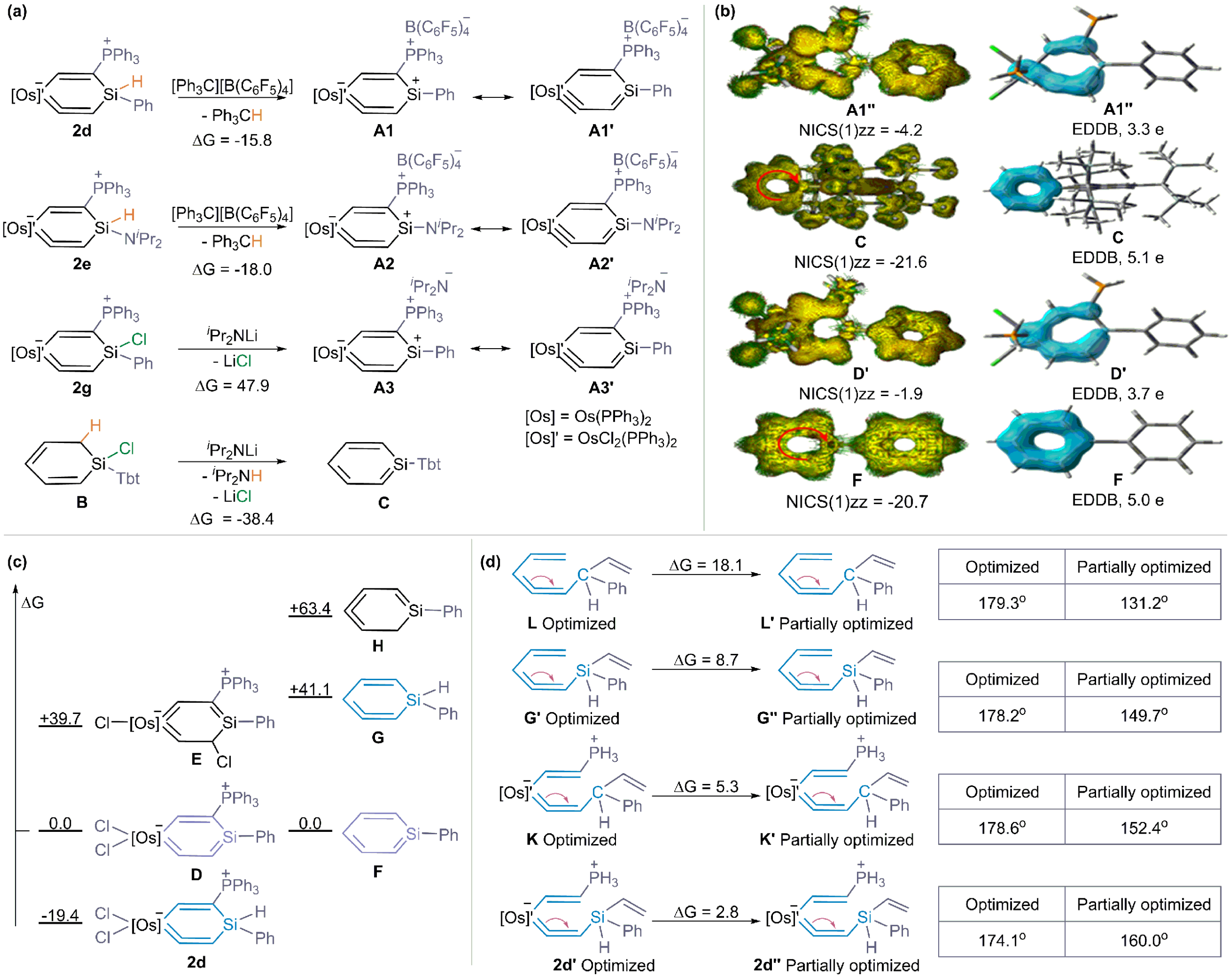


**Figure 2** All DFT calculations were performed at the level of B3LYP/def2-tzvp/PCM(THF)//B3LYP/6-31G* (C, H, O, N, Si, Cl, Li, P, B, F)/SDD (Os). Numerical values are $\Delta G$ (kcal/mol). (a) The calculated aromatization reaction energies of the metallacycle (**2d**), (**2e**), (**2g**) and the silacycle (**B**). (b) AICD plots, $NICS(1)_{zz}$ values and EDDB analysis (In **A1''** and **D'**, the $PPh_3$ are represented as $PH_3$) of **A1''**, **C**, **D'** and **F**. (c) Comparison of energy differences for the silacycle isomers. (d) The calculated strain energies of **2d'**, **G'**, **K** and **L** on the basis of isodesmic reactions.

($\Delta G$ = −38.4 kcal/mol).[14] However, the DFT analysis of the hydride abstraction of **2d** or **2e**, using the established Corey reaction,[15] shows the feasibility of the Si—H bond cleavage ($\Delta G$ = −15.8 or −18.0 kcal/mol). We think the corresponding silylium cation **A1** or **A2** would be stabilized by its metallabenzyne resonance form **A1'** or **A2'**, a heavier Group 14 congeners of metalla-benzynes,[9] due to its aromatic nature. When the in-plane π bonding is excluded, the bonding in metallabenzynes is similar to that of metallabenzenes.[7,9] Computed accessibility of the silylium cation encouraged us to investigate the reactions of **2d** or **2e** with the triphenylmethylium ion (trityl ion, $Ph_3C^+$) in $CD_2Cl_2$, probed by NMR spectroscopy.

Reaction of **2d**/**2e** with $[Ph_3C]^+[B(C_6F_5)_4]^-$ in $CD_2Cl_2$ at RT resulted in an immediate color change from yellow to dark brown. The formation of new products, most likely silylium cation, was evidenced by the absence of characteristic $^1H$ NMR peak of Si–H hydrogen ($\delta$ 5.88). Clearly, stability of the expected silylium cation was found to be much lower than that of **2d**/**2e**, as the reaction performed at RT led to a number of species bearing phosphorus within 5 min (Figure S47). The products fully converted into the final decomposed product $(Ph_3P)_2[B(C_6F_5)_4]_2$ after 3 h in solution based on $^{31}P\{^1H\}$ NMR data. When **2d** was dissolved in $CD_2Cl_2$ in the presence of the trityl ion and cooled to −78 °C in the probe of the spectrometer, the $^1H$ and $^{31}P\{^1H\}$ NMR spectra were recorded. As shown in Figure 3, stacked $^1H$ NMR spectra clearly indicate characteristic resonance for the triphenylmethane detected at $\delta_{1H}$ 5.59 accompanied by the disappearance of Si–H hydrogen at $\delta_{1H}$ 5.80. This is consistent with the occurrence of Si—H bond cleavage and the formation of a silylium cation. As can clearly be seen, a new doublet proton signal at $\delta$ 12.74 ($J_{P\text{-}H}$ = 40.0 Hz) from the metallacycle arises in the $^1H$ NMR spectra of **A1** accompanied by the disappearance of the characteristic H1 signal at $\delta$ 13.72 for **2d**. Additionally, **A1** displays the phosphonium resonance at $\delta_{31P}$ 23.12 in the $^{31}P\{^1H\}$ NMR spectrum, which is more downfield than the corresponding chemical shift in **2d**. This can be attributed to the electron-withdrawing effect of the silylium fragment in **A1**. Evidently, such silylium cations do form by using trityl ion, enabling NMR spectroscopic characterization of a highly unsaturated cyclic silylium for the first time, although it is much less stable than the starting material metalla-isosilabenzene.

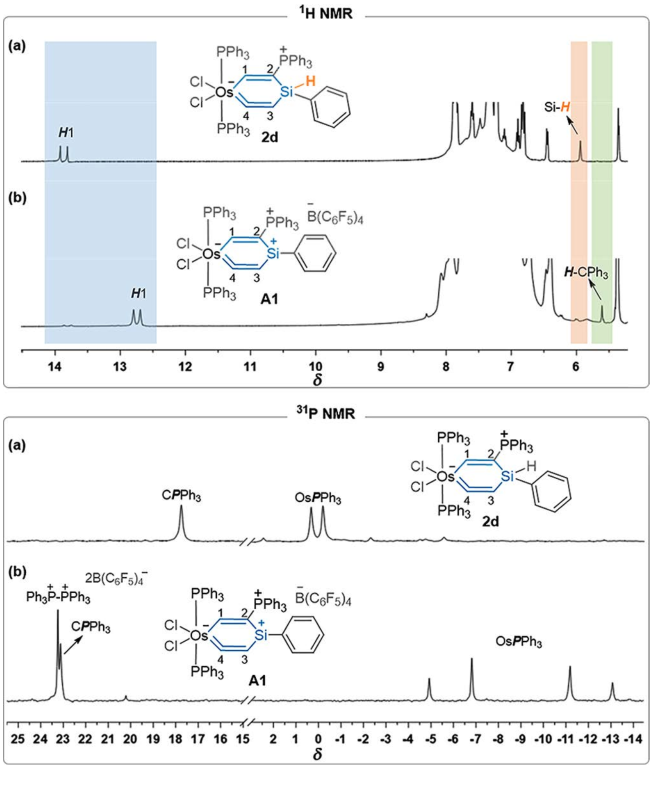


**Figure 3** The silylium cation formation attempts starting from **2d** observed by low-temperature NMR in $CD_2Cl_2$: (a) partial $^1H$ NMR and $^{31}P\{^1H\}$ NMR of **2d** at −78 °C; (b) partial $^1H$ NMR and $^{31}P\{^1H\}$ NMR of the reaction mixture of **2d** and $[Ph_3C]^+[B(C_6F_5)_4]^-$ within 10 min at −78 °C.

We speculate that aromaticity might play an important role in the stability of the conjugated six-membered ring skeletons. In this regard, the aromaticity of six-membered rings was estimated through the nucleus-independent chemical shift (NICS) value,[16] and the visualized electron delocalization is plotted through the anisotropy of the induced current density (AICD),[17] and electron density of delocalized bonds (EDDB).[18] As shown in Figure 2b, the $NICS(1)_{zz}$ value for the silabenzene product (**C**) of the aromatization reaction was much more negative (−21.6) than the value of the silylium cation **A1''** (−4.2), indicating less contribution from a delocalized aromatic resonance form **A1'** when compared to aromatic silabenzene. Furthermore, clearly clockwise current density vectors could be observed in the AICD of silabenzene (**C**), which is in good agreement with the calculated NICS value. In contrast, negative but near zero NICS value corresponds to a discontinuous electron density in the metallacycle of **A1''**. Figure 2b shows that the electron density in metallacycles of **A1''** is interrupted between Si—C, which might be the basis of the non-aromaticity of these rings. We also determined the aromatic index EDDB, which has been demonstrated to be well-suited to evaluation of the aromaticity of organometallics.[19] The striking break of delocalization in **A1''** is also reflected by EDDB calculations. The respective results are given in Figure 2b showing 3.3e for **A1''** vs. 5.1e for **C**; larger EDDB values suggest higher electron delocalization, which are consistent with the findings by NICS and AICD descriptions. The difference in aromaticity between the metalla-silabenzene (**D**) and silabenzene (**F**) is similar to that between the **A1'** and **C**.

In addition, the free energy of all isomers in THF solution at 298 K and 1 atm has been calculated (Figure 2c). The results show that the most stable isomer of metalla-silabenzenes is not the same as that in silabenzene isomers. Thus, the experimentally obtained metalla-isosilabenzene and silabenzene can be interpreted in terms of the relative thermodynamic energies between the corresponding silabenzenes and isosilabenzenes, *i.e.*, **2d** is 19.4 kcal/mol more stable than **D**, but **G** is 41.1 kcal/mol less stable than **F**. Given the aromaticity of silabenzene **F**, it is reasonable for the calculated thermodynamic stability order **F** > **G** > **H**, although it is much difficult for heavier main group atoms to form multiple bonds.[20] The formal replacement of a CH group in conjugated organic molecules by an isolobal transition metal fragment has been shown to bring great changes in the structure, bonding, and reactivity of the organometallic complexes when compared to their organic counterparts.[21] In this regard, we have demonstrated that the introduction of transition metals could thermodynamically stabilize a number of strained ring systems.[22] The increased stability of the metalla-isosilabenzene (**2d'**) could be partly attributed to the strain release induced by the transition metal and silicon atom. The calculated M/C=C=C angles of 160.0° in metalla-isosilabenzene **2d''**, compared to 152.4° in metalla-isobenzene **K'**, 149.7° in isosilabenzene **G''**, and 131.2° in isosilabenzene **L'**, show some evidence of ring strain differences in the rings with cumulative double bonds (Figure 2d). This is clearly reflected in the decreased strain energy of metalla-isosilabenzene (2.8 kcal/mol) with comparison to those of metalla-isobenzene (5.3 kcal/mol), isosilabenzene (8.7 kcal/mol) and isobenzene (18.1 kcal/mol) due to the non-linear distortion of the M=C=C unit. The theoretical results manifest that both of osmium and silicon contribute to the stabilization of the nonlinear cumulative double bonds. Consequently, it is reasonable to conclude that the experimental observation of metalla-isosilabenzene rather than metalla-silabenzene may be mainly due to the near non-aromaticity of metalla-silabenzene and the decreasing of the ring strain on the cumulative double bonds.

Having identified the essential reason for the relatively high stability of metalla-isosilabenzene, we explored the heavier congeners. The use of diethynylgermane in place of diethynylsilane indeed led to metalla-isogermabenzene (**3**), whose synthesis on a gram scale is illustrated in Figure 4a. Complex **3** was characterized by NMR spectroscopy, which exhibited spectral features similar to those of metalla-isosilabenzene (**2**). Addition of silver thiocyanate reagents to **2a** or **3** generated the ligand substitution product (**4** or **5**), respectively (Figure 4b). Both of the structure of **4** and **5** have been confirmed by an X-ray diffraction study (Figure 4c). The structural parameters of the metallacyclic framework are similar to those of **2a**. The M=C=C bond length (Os1—C4 1.842(7) Å, C3—C4 1.297(9) Å for **4**; Os1—C4 1.838(4) Å, C3—C4 1.300(6) Å for **5**) as well as the M=C=C angle of 160.8(6)° (**4**)/162.6(3)° (**5**) is a typical structural feature of a metal-vinylidene moiety within a metallacycle (Figure 4c). The slightly increased M=C=C angle in **5** suggests decreasing ring strain in the order of germacycle < silacycle. It could be noted that both metalla-isosilabenzene (**4**) and metalla-isogermabenzene (**5**) are inert toward air and moisture for at least 2 months at RT, and decomposition was not observed even when heating the solid samples to 80 °C.

Natural bond orbital analysis of metalla-isobenzene and metalla-isosilabenzene at the B3LYP/6-31G* level with Stuttgart-Dresden-Bonn relativistic effective core potentials (SDD) for the Os atom revealed that the Wiberg bond indices[23] (Scheme S5) for the bonds of the M=C=C units are 1.395/1.393 (Os1—C4) and 1.859/1.840 (C4—C3). The resulting NBO charges at $C_\alpha$ and $C_\beta$ of the M=C=C units are shown in the respective schemes (Scheme S6). For metalla-isosilabenzene, the charge with $C_\alpha$ is negative, −0.940 au, and $C_\beta$ slightly positive, +0.186 au; this is consistent with those for the metalla-isobenzene, indicating similar reactivity trend. Meanwhile, the highest occupied molecular orbitals (HOMO) of metalla-isosilabenzenes are very similar, which are mainly located at the M=C=C bonds of the six-membered rings with some contribution from the Cl substituents (Table S5). In literature, metallabenzenes[7b] and metallabenzynes,[24] even metalla-isobenzenes,[8e] can undergo migratory insertion reactions to generate cyclopentadienyl complexes. As shown in Figure 4b, treating the isolated metalla-isosilabenzene (**4**) with an additional equivalent of NOBF$_4$ at RT afforded the complex (**6**), which was unequivocally characterized as a metal silole complex (Figure 4c). Similarly, the germole complex (**7**) was isolated from the reaction between metalla-isogermabenzene (**5**) and stoichiometric amounts of NOBF$_4$. Both siloles and germoles have established reputations as potentially useful synthetic reagents and enjoy promising applications as for example chemical sensors, light emitting diodes and biological probes due to their energetically low-lying LUMOs.[25] The six-membered titana-sila-cyclohexadiene complexes[26] and bora-sila-cyclohexadiene complexes[27] have been proposed as precursors or intermediates for the synthesis of substituted siloles. In view of the less studied synthetic methods for germoles, the conversion of the metalla-isogermabenzene (**5**) to the germole complex (**7**) would be useful in the development of new catalytic transformations of organogermanium compounds.

## Conclusions

In summary, we report the first synthesis of isosilabenzene and isogermabenzene species that possess a metal-vinylidene unit within a six-membered metallacycle through the one-pot reaction of diethynylsilane or diethynylgermane with simple metal complexes.

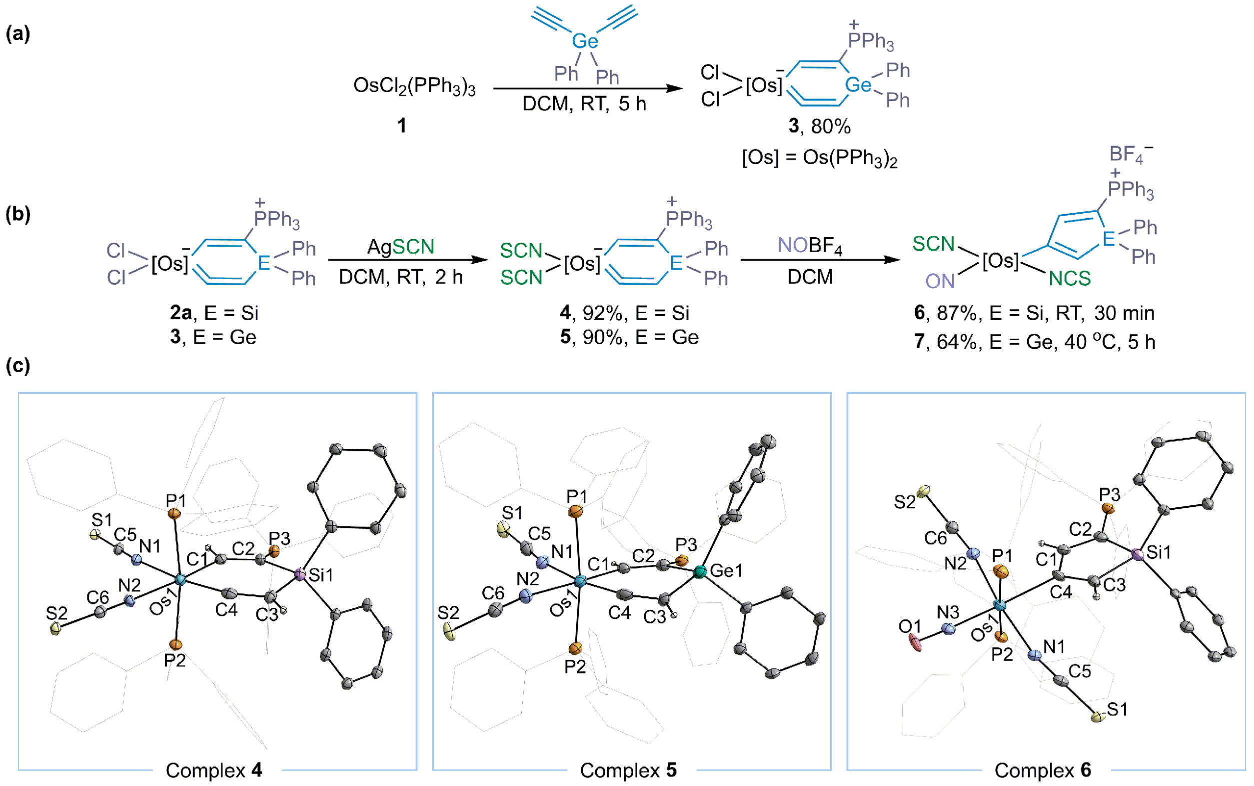


**Figure 4** (a) Synthesis route of metalla-isogermabenzene **3**. (b) Synthesis of complexes **4** and **5**, and their reactions with NOBF$_4$. (c) X-ray crystal structures for **4**, **5** and **6** drawn at the 50% probability level. Hydrogen atoms and solvent molecules were omitted and phenyl groups in PPh$_3$ ligands are depicted using a wireframe model for clarity. Selected bond lengths [Å] and bond angles for **4**: Os1—C1 2.075(6), Os1—C4 1.842(7), C1—C2 1.366(9), C3—C4 1.297(9), Si1—C2 1.911(7), Si1—C3 1.857(7); C3–C4–Os1 160.8(6)˚, C4–Os1–C1 82.9(3)˚, Os1–C1–C2 133.9(5)˚, C1–C2–Si1 124.4(5)˚, C2–Si1–C3 105.4(3)°, Si1–C3–C4 111.9(5)°. **5**: Os1—C1 2.051(3), Os1—C4 1.838(4), C1—C2 1.369(5), C3—C4 1.300(6), Ge1—C2 1.983(4), Ge1—C3 1.952(3); C3–C4–Os1 162.6(3)°, C4–Os1–C1 83.50(14)°, Os1–C1–C2 135.5(3)°, C1–C2–Ge1 122.9(3)°, C2–Ge1–C3 103.46(15)°, Ge1–C3–C4 109.2(3)°. **6**: Os1—C4 2.152(4), C1—C2 1.355(6), Si1—C2 1.897(5), Si1—C3 1.870(4), C3—C4 1.340(6), C1—C4 1.491(6); C3–C4–Os1 124.4(3)°, Os1–C4–C1 121.6(3)°, C3–C4–C1 113.9(4)°, C4–C1–C2 117.9(4)°, C1–C2–Si1 107.1(3)°, C2–Si1–C3 90.2(2)°, Si1–C3–C4 110.8(3)°.

The isolation of metalla-isosilabenzenes rather than fully conjugated metalla-silabenzenes is consistent with the computational analysis showing that the metalla-silabenzene is predicted to be less stable than the metalla-isosilabenzene isomers by 19.4 kcal/mol. The labile silylium cation, which can be viewed as the resonance form of metalla-silabenzyne, was observed spectroscopically by the hydride abstraction of metalla-isosilabenzene. However, DFT calculations have demonstrated the lack of aromaticity of the fully conjugated metallacycles, *i.e*., metalla-silabenzene or metalla-silabenzyne. In addition, the smaller calculated energy difference hints the strain-release influence of transition metal and Group 14 atom in the rings bearing cumulative double bonds. These novel transition-metal-involving isosilabenzenes and isogermabenzenes, together with their facile conversion to siloles and germoles, would provide new insights for the rational design of future catalytic systems to efficiently access conjugated heterocycles with Group 14 elements.

## Experimental

Experimental procedures and characterization data are available in Supporting Information.

## Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.202400016.

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