

Main-Group Chemistry

Pseudohalogenogermylenes versus Halogenogermylenes: Difference in their Complexation Behavior towards Group 6 Metal Carbonyls

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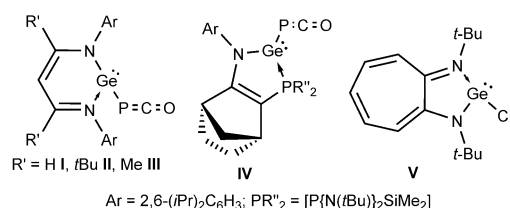
Dedicated to Prof. K. C. Kumara Swamy on the occasion of his 60th birthday

Abstract: Pseudohalogenogermylenes $[(i\text{Bu})_2\text{ATI}]\text{GeY}$ ($\text{Y} = \text{NCO}$ **4**, NCS **5**) show different coordination behavior towards group 6 metal carbonyls in comparison to the corresponding halogenogermylenes $[(i\text{Bu})_2\text{ATI}]\text{GeX}$ ($\text{X} = \text{F}$ **1**, Cl **2**, Br **3**) (ATI = aminotroponimate). The reactions of compounds **4–5** and **1–3** with $\text{cis-}[\text{M}(\text{CO})_4(\text{COD})]$ ($\text{M} = \text{Mo}$, W , COD = cyclooctadiene) gave *trans*-germylene metal complexes $\{[(i\text{Bu})_2\text{ATI}]\text{GeY}\}_2\text{M}(\text{CO})_4$ ($\text{Y} = \text{NCO}$, $\text{M} = \text{Mo}$ **6**, W **11**; $\text{Y} = \text{NCS}$,

$\text{M} = \text{Mo}$ **7**) and *cis*-germylene metal complexes $\{[(i\text{Bu})_2\text{ATI}]\text{GeX}\}_2\text{M}(\text{CO})_4$ ($\text{M} = \text{Mo}$, $\text{X} = \text{F}$ **8**, Cl **9**, Br **10**; $\text{M} = \text{W}$, $\text{X} = \text{Cl}$ **12**), respectively. Theoretical studies on compounds **7** and **9** reveal that donor–acceptor interactions from Mo to Ge atoms are better stabilized in the observed *trans* and *cis* geometries than in the hypothetical *cis* and *trans* structures, respectively.

Introduction

The chemistry of compounds with germanium atoms in low oxidation states has received considerable attention^[1,2] since the isolation of the first germylene $\text{Ge}\{\text{N}(\text{TMS})_2\}$ ($\text{TMS} = \text{SiMe}_3$) by Lappert and co-workers in 1974.^[3] Compounds of the type LGeX ($\text{L} =$ a bidentate monoanionic ligand; $\text{X} = \text{F}$, Cl , Br , I) are generally called halogenogermylenes and among them the chlorogermylenes are well studied and widely used.^[4–7] Apart from these halogenogermylenes, germylenes with other X substituents, such as, H ,^[8] OH ,^[9] NR_2 ,^[10] OR ,^[11] and so forth, have also been synthesized and studied. Although germylenes with different X substituents are known, there is a continuing interest in the synthesis of germylenes with novel X substituents owing to the anticipation of new reactivity/utility. Recently, phosphaketenyl-functionalized germylenes $\text{L}'\text{Ge-P}=\text{C}=\text{O}$ **I–IV** [$\text{L}' = \text{HC}(\text{C}(\text{R}')\text{N}(\text{Ar}))_2$ ($\text{R}' = \text{H}$ **I**,^[12a] $t\text{Bu}$ **II**,^[12a] Me **III**^[12b]); $\text{C}_7\text{H}_8\{\text{N}(\text{Ar})(\text{PR}'_2)\}$ **IV**,^[12c] $\text{PR}'_2 = [\text{P}\{\text{N}(t\text{Bu})\}_2\text{SiMe}_2]$; $\text{Ar} = 2,6\text{-}(i\text{Pr})_2\text{C}_6\text{H}_3]$ were prepared through the reaction of the corre-



Scheme 1. Structure of compounds I–V.

sponding chlorogermylenes $\text{L}'\text{GeCl}$ with sodium phosphoethynolate ($\text{P} \equiv \text{C}-\text{ONa}$) (Scheme 1). These were pursued as precursors for the synthesis of phosphagermyne $\text{L}'\text{Ge} \equiv \text{P}$. We reported cyanogermylene $[t\text{Bu}_2(\text{ATI})\text{GeCN}]$ **V** (ATI = aminotroponimate ligand) through reaction of oxidodigermylene $[(t\text{Bu}_2(\text{ATI})\text{Ge})_2\text{O}]$ with excess TMSCN , and found that it can catalyze the cyanosilylation reaction of aldehydes (Scheme 1).^[13]

In this context, while studying the reactivity of isocyanogermylene $[(i\text{Bu})_2\text{ATI}]\text{GeNCO}$ (**4**) and isothiocyanogermylene $[(i\text{Bu})_2\text{ATI}]\text{GeNCS}$ (**5**) with $\text{cis-}[\text{M}(\text{CO})_4(\text{COD})]$ ($\text{M} = \text{Mo}$, W ; COD = cyclooctadiene), we found that compounds **4–5** show different coordination natures than the corresponding halogenogermylenes $[(i\text{Bu})_2\text{ATI}]\text{GeX}$ ($\text{X} = \text{F}$ **1**, Cl **2**, Br **3**). Compounds **4–5** afford *trans*-germylene metal complexes $\{[(i\text{Bu})_2\text{ATI}]\text{GeY}\}_2\text{M}(\text{CO})_4$ ($\text{Y} = \text{NCO}$, $\text{M} = \text{Mo}$ **6**, W **11**; $\text{Y} = \text{NCS}$, $\text{M} = \text{Mo}$ **7**) and compounds **1–3** result in *cis*-germylene metal complexes $\{[(i\text{Bu})_2\text{ATI}]\text{GeX}\}_2\text{M}(\text{CO})_4$ ($\text{M} = \text{Mo}$, $\text{X} = \text{F}$ **8**, Cl **9**, Br **10**; $\text{M} = \text{W}$, $\text{X} = \text{Cl}$ **12**). DFT studies show that the *trans* geometry in compound **7** is preferred for enhanced donor–acceptor interactions from the Mo to Ge atoms over a *cis* geometry when isothiocyanogermylene **5** is the ligand, and the opposite is true in compound **9** where the ligand is chlorogermylene **2**.

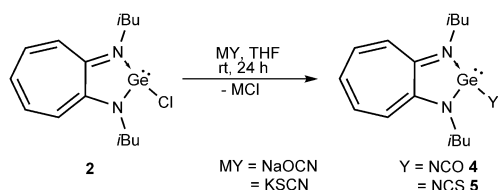
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Results and Discussion

The reactions of chlorogermylene **2** with sodium cyanate and potassium thiocyanate in THF at room temperature for 24 h led to isocyanatogermylene [(*i*Bu)₂ATI]GeNCO (**4**) and isothiocyanatogermylene [(*i*Bu)₂ATI]GeNCS (**5**), respectively. Compounds **4** and **5** were obtained as orange solids in excellent yields of 93% and 95%, respectively (Scheme 2). The formation

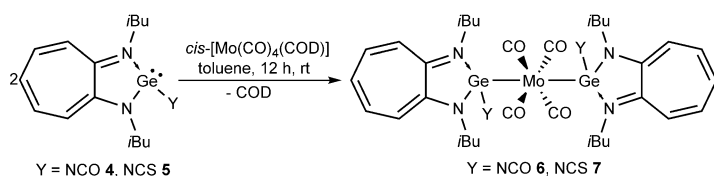


Scheme 2. Synthesis of isocyanatogermylene and isothiocyanatogermylene.

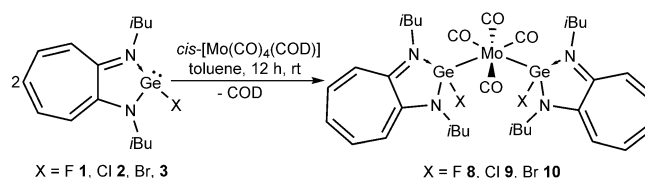
of compounds **4** and **5** reveal the propensity of the germanium atom to bind the nitrogen atom rather than the oxygen atom or the sulfur atom of the pseudohalogen moieties, NCO or NCS, respectively.^[14] Interestingly, apart from germylene diisothiocyanate NHC-Ge(NCS)₂ [(NHC = (MeCN*i*Pr)₂C:)],^[14] there are no well-defined germylens with isocyanate (NCO)/isothiocyanate (NCS) moieties attached to Ge^{II} atoms.

Although various germylens are used as ligands to stabilize transition-metal complexes,^[15] germylens with NCO/NCS substituents have never been tested as ligands. Therefore, to understand the behavior of compounds **4** and **5** as ligands, their reactions with a half equivalent of *cis*-[Mo(CO)₄(COD)]^[21a] were carried out. These reactions in toluene at room temperature afford *trans*-germylene molybdenum complexes **6** and **7** in almost quantitative yields of 97% and 95%, respectively (Scheme 3).

In contrast to this reactivity of pseudohalogenogermylens **4** and **5**, halogenogermylens (X = F **1**, Cl **2**) react with a half equivalent of *cis*-[Mo(CO)₄(COD)] and result in *cis*-germylene molybdenum complexes **8** and **9** as yellow solids in excellent yields of 96% and 95%, respectively (Scheme 4). To analyze if steric effects have any role to play in the *trans* and *cis* preference of compounds **6–7** and **8–9** when pseudohalogeno- and halogenogermylens are ligands, the following experiments were carried out: (a) reaction of two equivalents of bromogermylene [(*i*Bu)₂ATI]GeBr^[10a] **3** (with a heavier halogen atom (Br)

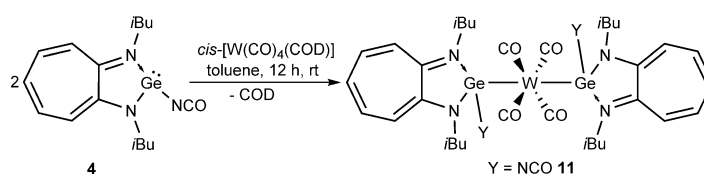


Scheme 3. Reactions of compounds **4** and **5** with *cis*-[Mo(CO)₄(COD)] to afford *trans*-germylene molybdenum complexes **6** and **7**.

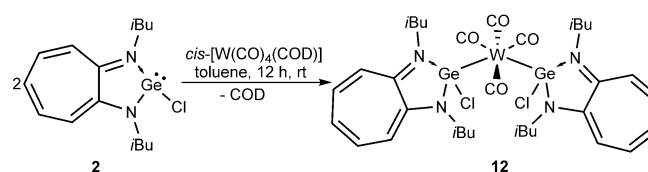


Scheme 4. Reactions of halogenogermylens **1–3** with *cis*-[Mo(CO)₄(COD)] to afford *cis*-germylene molybdenum complexes **8–10**.

than F and Cl atoms) with *cis*-[Mo(CO)₄(COD)] in toluene to get *cis*-germylene molybdenum complex **10** (Scheme 4) as a yellow solid in almost quantitative yield, and (b) reactions of two equivalents of compounds **4** and **2** with *cis*-[W(CO)₄(COD)]^[21b] result in *trans*- and *cis*-germylene tungsten complexes (**11** and **12**; Scheme 5 and Scheme 6) in good yields of 91% and 94%, respectively. As the former and latter reactions resemble the reactions of compounds **1–2** and **4/2**



Scheme 5. Reaction of isocyanatogermylene **4** with *cis*-[W(CO)₄(COD)] to afford *trans*-germylene tungsten complexes **11**.



Scheme 6. Reaction of chlorogermylene **2** with *cis*-[W(CO)₄(COD)] to afford *cis*-germylene tungsten complexes **12**.

with *cis*-[Mo(CO)₄(COD)], respectively, it is understandable that the difference in the reactivity of halogeno- and pseudohalogenogermylens does not depend on steric parameters. Further, as the *cis* product is thermodynamically less stable than the *trans* product, the possibility of converting *cis*-germylene molybdenum complex **9** to the corresponding *trans* product was tested by heating a toluene solution of compound **9** to 90 °C for 12 h. But, there was no conversion to the *trans* product. The same result was achieved when the reaction that afforded compound **9** was carried out at 90 °C. Further, the reaction that afforded compound **9** was carried out in the dark to give the formation of *cis*-germylene molybdenum complex **9** only. However, the irradiation of compound **9** to check its possible conversion to the *trans*-isomer was not performed.

Compounds **4–5** are soluble in common organic solvents such as benzene, toluene, diethyl ether, and tetrahydrofuran. Compounds **6 to 12** are soluble in

tetrahydrofuran, chloroform, and dichloromethane, but, are moderately soluble in benzene and toluene. Compounds 4–5 and 6–12 are stable at room temperature under an inert atmosphere of dry nitrogen or argon. Compounds 4–5 decompose rapidly in chlorinated solvents.

All new compounds (4–12) were characterized by multinuclear NMR (^1H , ^{13}C , and ^{19}F) and IR spectroscopic techniques in the solution and solid states, respectively. In the germylene metal complexes 6–12, almost all the resonances are downfield shifted in comparison to the corresponding resonances seen in their precursors 4–5/1–3. This is due to the donation of electron density by the germanium atoms to the molybdenum/tungsten atoms. In the ^{13}C NMR spectroscopic studies, the anticipated number of signals were seen for compounds 4–12. In compounds 4 and 5, the NCO and NCS resonances are seen at 130.23 and 127.20 ppm, respectively. In compounds 6, 7, and 11, one resonance signal for the carbonyl carbons was observed (211.89, 210.53, and 204.66 ppm, respectively). In compounds 8–10 and 12, two signals owing to carbonyl groups were seen (211.20 and 215.88 ppm 8; 211.47 and 215.62 ppm 9; 211.67 and 215.72 ppm 10; 202.34 and 205.10 ppm 12). These values fall in the range (197–211 ppm) observed for *trans/cis*-germylene metal complexes of the type L_2MCO_4 ($\text{M} = \text{Mo}, \text{W}$).^[16] In the ^{19}F NMR spectrum of compound 8, a singlet resonance at -64.66 ppm was observed. This value is downfield shifted in comparison to that seen for its precursor $[(i\text{Bu})_2\text{ATI}]\text{GeF}^{20}$ (1; -98.91 ppm). In the IR spectra of compounds 4 and 5, strong absorption bands at 2188 and 2030 cm^{-1} are assigned as the asymmetric NCO and NCS stretching vibrations. In the germylene metal complexes 6, 7, and 11, the asymmetric NCO, NCS, and NCO stretching bands appear at slightly higher frequencies of 2217, 2043, and 2212 cm^{-1} in comparison to those of their starting materials (4–5). These assignments are supported by the vibrational frequencies for NCO and NCS groups in Ge^{IV} compounds $\text{Ge}(\text{tm-taa})(\text{NCO})_2$ (2204 cm^{-1}) and $\text{Ge}(\text{tm-taa})(\text{NCS})_2$ (2073 and 2043 cm^{-1}), respectively ($\text{tm-taa} = \text{tetraazacyclotetradecine}$).^[17] In compounds 6, 7, and 11, the ν_{CO} bands at 1910, 1900, and 1881 cm^{-1} reveal a *trans* octahedral geometry with D_{4h} symmetry for these $\text{ML}_2(\text{CO})_4$ type complexes, respectively. The positions of these stretching bands in compounds 6–7 and 11 are comparable to those observed in complexes *trans*- $[\{\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NSiMe}_3\}\text{Ge}(\text{Cl})\}_2\text{Mo}(\text{CO})_4]$ ($\nu_{\text{CO}} = 1903\text{ cm}^{-1}$) and *trans*- $[\{\{\text{Me}_3\text{SiNC}(\text{Ph})\text{NSiMe}_3\}\text{Ge}(\text{Cl})\}_2\text{W}(\text{CO})_4]$ (1894 cm^{-1}), respectively.^[18] Owing to *cis* octahedral geometry having C_{2v} symmetry, four carbonyl stretching bands for compounds 8 (1868, 1893, 1918, and 2011 cm^{-1}), 9 (1876, 1897, 1933, and 2012 cm^{-1}), 10 (1875, 1893, 1925, and 2010 cm^{-1}), and 12 (1869, 1888, 1924, and 2008 cm^{-1}) are seen. These bands in complexes 8–10 and 12 are reminiscent of the situations in molybdenum and tungsten germylene complexes *cis*- $[\text{Py}(\text{CH}_2\text{CPh}_2\text{O})_2\text{Ge}]_2\text{Mo}(\text{CO})_4$ ^[16c] (1897, 1917, 1939, and 2017 cm^{-1}) and *cis*- $[2,6\text{-Py}(\text{CH}_2\text{CPh}_2\text{O})_2\text{Ge}]_2\text{W}(\text{CO})_4$ ^[16c] (1886, 1934, 1944, and 2023 cm^{-1}), respectively.

The molecular structures of compounds 5, 6–9, and 11–12 were further characterized by single-crystal X-ray diffraction studies (see the Supporting Information for details).^[19] Com-

ound 5 crystallized in the monoclinic space group $P2_1/c$ (see Table S1 in the Supporting Information for details). Its molecular structure (Figure 1) shows that it is monomeric and the *iso*-butyl substituents are oriented opposite to the Ge-NCS

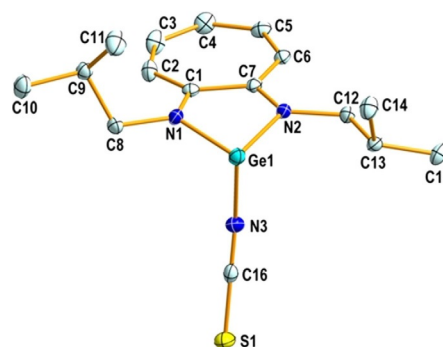


Figure 1. Molecular structure of compound 5. All hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at the 40% probability level. Data collection temperature: 100 K.

moiety. The geometry around the germanium atom is distorted trigonal-pyramidal and the sum of the bond angles around it is 263.52° ; whereas, the corresponding sum in compound 2 is 274.72° .^[20] The distance of the germanium atom in compound 5 from the least-square plane formed by the N1, N2, and N3 atoms is 1.183 \AA . In comparison, in compound 2, the corresponding distance with respect to the least-square plane through the N1, N2, and C1 atoms is 1.155 \AA .^[20] The Ge-N_{NCS} bond ($2.050(2)\text{ \AA}$) is slightly longer than that in $\text{NHC-Ge}(\text{NCS})_2$ ^[14] ($1.983(8)\text{ \AA}$). The average $\text{Ge-N}_{\text{ligand}}$ bond length in compound 5 ($1.946(1)\text{ \AA}$) is comparable to that in chlorogermylene 2 ($1.938(5)\text{ \AA}$).

Trans-germylene metal complexes 6, 7, and 11 crystallized in the monoclinic, triclinic, and monoclinic space groups $P2_1/n$, $P\bar{1}$, and $P2_1/n$, respectively (see Tables S1 and S2 in the Supporting Information for details). In these compounds (6, 7, and 11; Figure S1 in the Supporting Information, and Figures 2 and 3, respectively), germanium atoms adopt distorted tetrahedral geometries and molybdenum/tungsten atoms have distorted octahedral geometries. The two germylenes coordinated to

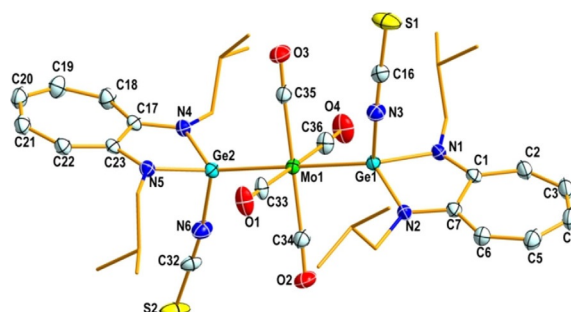


Figure 2. Molecular structure of compound 7. All hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at the 40% probability level. Three independent molecules are present in the asymmetric unit cell; only one molecule is shown here and for further details see the Supporting Information. Data collection temperature: 160 K.

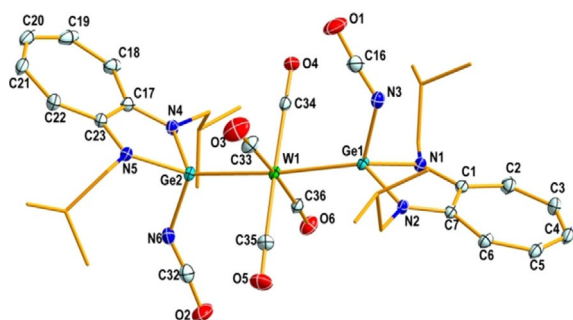


Figure 3. Molecular structure of compound 11. All hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at the 40% probability level. Data collection temperature: 100 K.

the metal atoms are almost *trans* to each other; Ge-M-Ge bond angles in compounds **6**, **7**, and **11** are 171.15(4)°, 179.16(1)°, and 171.28(8)°, respectively (M=Mo **6**, **7**; W **11**).

The average lengths of M–Ge bonds in compounds **6**, **7**, and **11** are 2.510(1) Å, 2.500(3) Å, and 2.501(3) Å, respectively (M=Mo **6**, **7**; W **11**). These are reminiscent of the situation in *trans*-[{{Me₃SiNC(Ph)NSiMe₃}Ge(Cl)}₂Mo(CO)₄]^[18] (2.499(1) Å) and *trans*-[{{Me₃SiNC(Ph)NSiMe₃}Ge(Cl)}₂W(CO)₄]^[18] (2.498(4) Å). The average Ge–N_{NCS} and Ge–N_{ligand} bond lengths in compound **7** (1.961(2) and 1.901(2) Å) are shorter than those in compound **5** (2.050(2) and 1.946(1) Å); this is due to the donation of electron density by germanium atoms to molybdenum atoms.

Compounds **8**, **9**, and **12** (Figure S2 in the Supporting Information, Figure 4, and Figure S3 in the Supporting Information, respectively) crystallized in the monoclinic, triclinic, and monoclinic space groups *Cc*, *P* $\bar{1}$, and *P*₂/*1*/*n*, respectively (see Tables S1 and S2 in the Supporting Information for details). Like in compounds **6**, **7**, and **11**, germanium and molybdenum/tungsten atoms possess distorted tetrahedral and octahedral geometries, respectively. Unlike in compounds **6**, **7**, and **11**, two germylene ligands attached to metal atoms have a *cis* disposition with respect to each other; Ge-M-Ge bond angles in compounds **8**, **9**, and **12** are 90.29(2)°, 94.79(2)°, and 92.61(4)°, respectively (M=Mo **8**, **9**; W **12**).

The average lengths of M–Ge bonds in these *cis*-germylene metal complexes **8**, **9**, and **12** are 2.539(7), 2.570(8), and

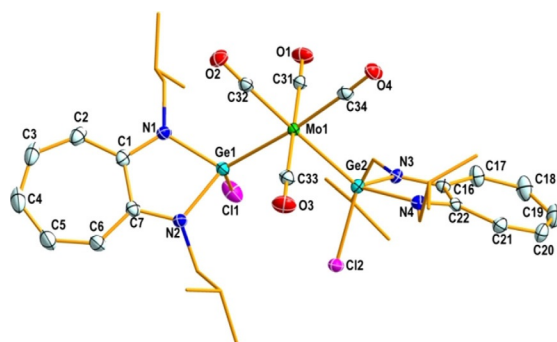
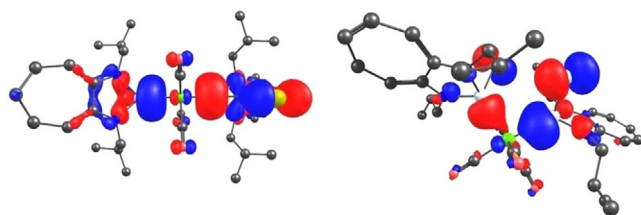


Figure 4. Molecular structure of compound 9. All hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at the 40% probability level. Data collection temperature: 100 K.

2.566(2) Å), respectively (M=Mo **8**, **9**; W **12**). Interestingly, these are longer than the corresponding values in *trans*-germylene metal complexes **6**, **7**, and **11** (see above). As expected, in compounds **8**, **9**, and **12**, the M–C_{CO} bonds *trans* to germylenes [**8** (1.989(4) and 1.990(4) Å), **9** (1.987(4) and 1.997(5) Å), and **12** (1.997(1) and 1.987(1) Å)] are shorter than M–C_{CO} bonds *cis* to germylenes [**8** (2.041(4) and 2.042(4) Å), **9** (2.037(5) and 2.038(5) Å), and **12** (2.057(1) and 2.026(1) Å; M=Mo **8**, **9**; W **12**). The average Ge–N_{ligand} bond lengths in compounds **8** (1.911(3) Å) and **9** (1.906(4) Å), **12** (1.911(9) Å) are shorter than those in germylenes **1** (1.979(1) Å) and **2** (1.938(1) Å), respectively.^[20] Similarly, the average lengths of Ge–X bonds in compounds **8** (X=F; 1.783(3) Å) and **9** (X=Cl; 2.278(1), **12** (X=Cl; 2.292(3) Å) are shorter than those in **1** (1.835(2) Å) and **2** (2.359(5) Å), respectively.^[20] These are due to the donation of electron density by germanium to molybdenum/tungsten atoms.

To understand the *trans* preference of pseudohalogenogermylenes in complexes **6**, **7**, and **11**, and the *cis* preference of halogenogermylenes in complexes **8**, **9**, **10**, and **12** over the *cis* and *trans* orientations, respectively, DFT calculations were carried out by using the Gaussian 09 program on compounds **7**, **9**, model compound **A** (*cis* form of compound **7**), and model compound **B** (*trans* form of compound **9**). For comparison, calculations were done on germylenes **2** and **5** also (see the Supporting Information for details). The frontier molecular orbital analysis on compounds **2** and **5** reveals that the HOMOs (Figures S5a **2** and S5c **5**) in both the compounds have germanium contributions; the wavefunction analysis reveals that the contributions are 13.50% and 19.04%, respectively. The LUMOs in these compounds (Figures S5b **2** and S5d **5**) are formed mainly by the π^* orbitals of the ATI ligand. The natural population analysis (NPA) charges on germanium atoms in compounds/models **2**, **5**, **7**, **9**, **A**, and **B** are 1.08, 1.18, 1.88, 1.67, 1.83, and 1.72, respectively. Higher positive charges in germylene molybdenum complexes (**7**, **9**) and model compounds (**A**, **B**) in comparison to germylenes **2** and **5** indicate a significant electron donation by germanium atoms to molybdenum atoms in germylene molybdenum complexes/model compounds. The Ge–Mo bond in compound **7** is a result of the overlap of the sp^{0.3} hybrid orbital of germanium atom with the sp^{2.33}d^{1.34} hybrid orbital of the molybdenum atom. The same bond in complex **9** is formed between the sp^{0.22} hybrid orbital of the germanium atom and the sp^{3.69}d^{1.72} hybridized orbital of the molybdenum atom. The ionicities (*i*_{Ge–Mo}) of these bonds are almost similar (**7** (0.18) and **9** (0.28)). The contributions from germanium and molybdenum atoms in compound **7** are 59.19% and 40.81%, respectively; the corresponding values in compound **9** are 64.12%, and 35.88%. The molecular orbital analysis confirms the presence of Ge–Mo σ -bonds in these complexes (Figure 5).

The NBO second-order perturbation theory analysis for compound **7** and model compound **A** showed two major donor–acceptor interactions for each compound between the molybdenum and germanium atoms (Figure 6). The donations from the d orbital of molybdenum to the p orbitals of germanium atoms provide an interaction energy of 11.6 kcal mol^{–1} to com-



Compound 7 (HOMO-11)

Compound 9 (HOMO-6)

Figure 5. Molecular orbitals that show the Ge–Mo σ -bonds in compounds 7 and 9.

pound 7 (Figure 6a–b). In the model compound **A**, the same type of donations offer a stabilization energy of 8.1 kcal mol⁻¹ (Figure 6c–d). These data explain why the *trans* arrangement of isothiocyanatogermynes in compound 7 is preferred over their *cis* disposition.

Each of compound 9 and model compound **B**, has four major donor–acceptor interactions from molybdenum to germanium atoms (Figure 7). The interaction between a molybdenum orbital that is predominantly a mixture of d_{xz} and d_{xy} with the $sp^{6.79}$ hybrid orbital of germanium gave a stabilization of 6.36 kcal mol⁻¹ to the Mo–Ge₃ bond in complex 9 (Figure 7a). In all the other three interactions also, the donations arise from the same orbital of molybdenum. The acceptor orbitals and the stabilization energies are: (a) p orbital of Ge₂ and 6.00 kcal mol⁻¹ (Figure 7b), (b) $sp^{6.52}$ hybrid orbitals of Ge₂ and 5.57 kcal mol⁻¹ (Figure 7c), and (c) p orbital of Ge₃ and 4.21 kcal mol⁻¹ (Figure 7d). In model compound **B**, donation

from the d_{yz} orbital of molybdenum to the p orbital of Ge₂ offers a stabilization of 4.36 kcal mol⁻¹ (Figure 7e). The donation from d_{xy} orbital of molybdenum to the $sp^{5.92}$ hybrid orbital of Ge₂ is stabilized by 2.57 kcal mol⁻¹ (Figure 7f). The other two interactions are exactly same as that of the first two interactions, but, the involved orbitals are of Ge₃ instead of Ge₂. Thus, the overall stabilization through donor–acceptor interactions in compound 9 (22.14 kcal mol⁻¹) is higher than that in the model compound **B** (13.86 kcal mol⁻¹). This clearly suggests the formation of *cis*-germylene molybdenum complex 9 over the model compound **B**.

Although the average Mo–Ge bond length in compound 9 is slightly longer (≈ 0.065 Å) than that in compound 7, the NBO Mo–Ge donor–acceptor interactions in compound 9 are stronger than those in compound 7. This may be due to the fact that, although the energy calculations capture the differences observed in the bond lengths, major interactions between the fragments found through NBO analysis has not fully captured all the structural/electronic differences.

Conclusions

We have shown that pseudohalogenogermynes with NCO 4/ NCS 5 moieties react in a different fashion in comparison to halogenogermynes with F 1/Cl 2/Br 3 atoms when reacted with *cis*-[M(CO)₄(COD)] (M=Mo, W). Theoretical studies predict that compounds 4–5 and 1–3 afforded *trans*-germylene metal complexes (M=Mo 6–7, W 11) and *cis*-germylene metal complexes (M=Mo 8–10, W 12) as the donor–acceptor interactions from metal atoms to germanium atoms are better stabilized in

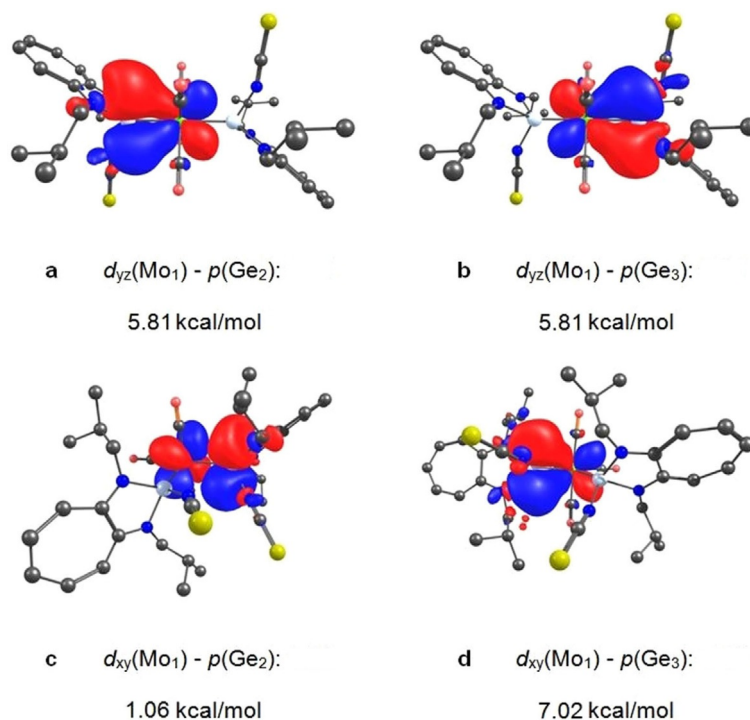


Figure 6. NBO donor–acceptor interactions between molybdenum and germanium atoms in compound 7 (a–b) and model compound **A** (c–d). Interaction threshold was chosen as 1 kcal mol⁻¹.

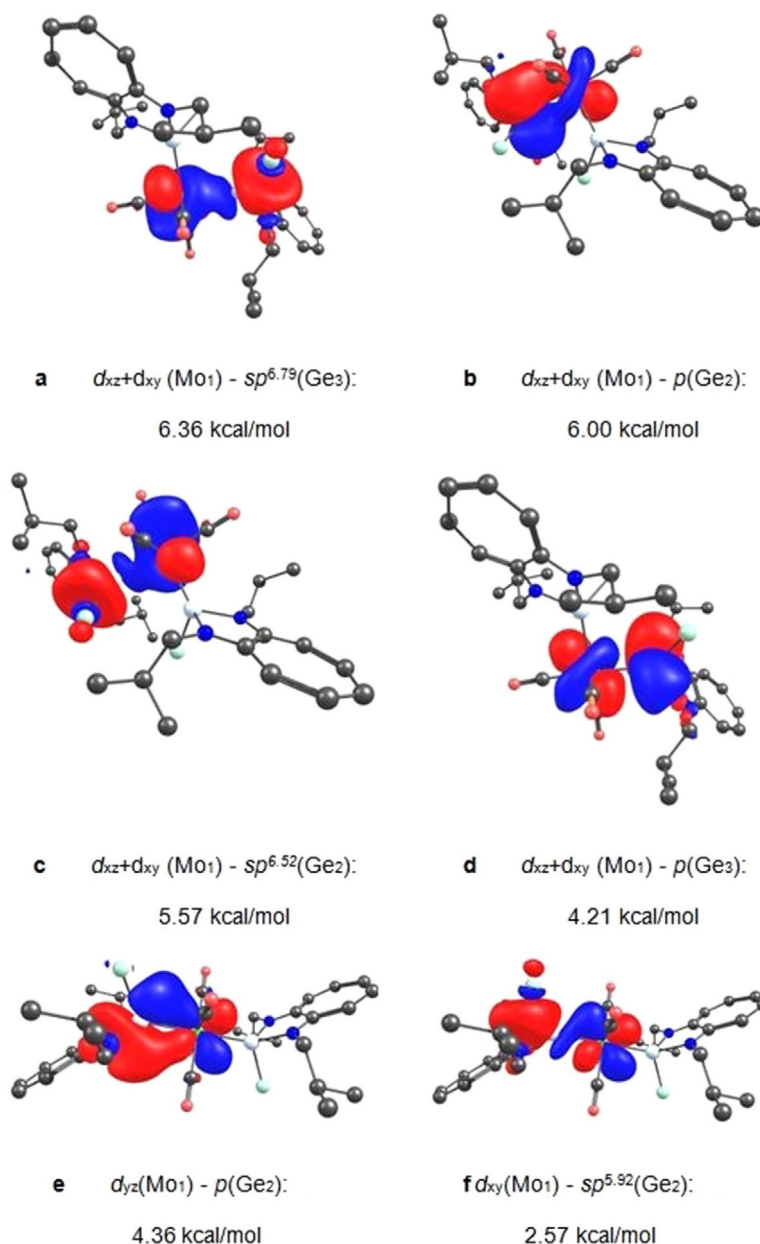


Figure 7. NBO donor–acceptor interactions between molybdenum and germanium atoms in compound **9** (a–d) and model **B** (e–f). Interaction threshold was chosen as 2 kcal mol^{-1} .

these geometries rather than the contrariwise geometries of *cis* and *trans*, respectively.

Experimental Section

All the air and moisture sensitive manipulations were performed under an atmosphere of dry N_2 by using either standard Schlenk or glovebox [GP(Concept)-T2, Jacomex workstation] techniques. Dried solvents were either obtained in the lab through conventional procedures or purchased directly from Aldrich. Compounds [(*i*Bu)₂ATI]GeF (**1**),^[20] [(*i*Bu)₂ATI]GeCl (**2**),^[20] [(*i*Bu)₂ATI]GeBr^[10a] (**3**), *cis*-[Mo(CO)₄(COD)],^[21a] and *cis*-[W(CO)₄(COD)]^[21b] were prepared according to the literature procedures. Potassium thiocyanate

(KSCN), sodium cyanate (NaOCN), cyclooctadiene (C_8H_{12}), $\text{Mo}(\text{CO})_6$, and $\text{W}(\text{CO})_6$ were purchased from Aldrich or Alfa Aesar and used without any further purification. Benzene- d_6 and CDCl_3 for NMR spectroscopic analysis were dried over potassium mirror and molecular sieves (4 Å), respectively, and vacuum-distilled prior to use. Melting points of new compounds were recorded by using Unitech Sales digital melting point apparatus by sealing the samples in glass capillaries and the reported melting points are uncorrected. Elemental analyses were carried out by using a PerkinElmer CHN analyzer. IR spectra were recorded by using an Agilent Resolutions Pro IR spectrophotometer by keeping the samples inside a HARRICK Praying Mantis Ambient Chamber. ^1H and ^{13}C NMR spectra were recorded with a 300 MHz Bruker Topspin NMR spectrometer. The chemical shifts (δ) are reported in ppm and are referenced in-

ternally with respect to the residual solvent (¹H NMR) and solvent (¹³C NMR) resonances.^[22] For ¹⁹F NMR spectroscopic studies, CFCl₃ was used as an external reference.

Synthesis of [(iBu)₂ATI]GeNCO (4)

To a mixture of compound **2** (0.80 g, 2.31 mmol) and excess of sodium cyanate (0.61 g, 9.25 mmol), THF (25 mL) was added and stirred at room temperature for 24 h. Then, it was filtered through a G4 frit with Celite and the solvent from the filtrate was evaporated in vacuo to afford an orange solid. It was washed with hexane (2 mL) and dried in vacuo to afford an analytically pure sample of compound **4** as an orange solid. Yield 0.76 g, 93.0%. M.p.: 65 °C; elemental analysis (%) calcd for C₁₆H₂₃GeN₃O (*M* = 346.01): C 55.54, H 6.70, N 12.14; found: C 55.47, H 6.60, N 12.19; ¹H NMR (300 MHz, C₆D₆): δ = 0.78 (t, ³J_{HH} = 6.9 Hz, 12H, CH(CH₃)₂), 1.93–2.07 (m, 2H, CH(CH₃)₂), 3.04–3.17 (m, 4H, CH₂), 6.23 (t, ³J_{HH} = 9.0 Hz, 1H, CH), 6.30 (d, ³J_{HH} = 10.8 Hz, 2H, CH), 6.72 ppm (t, ³J_{HH} = 10.2 Hz, 2H, CH); ¹³C{¹H} NMR (75 MHz, C₆D₆): δ = 20.94 (CH(CH₃)₂), 21.09 (CH(CH₃)₂), 28.03 (CH(CH₃)₂), 53.94 (CH₂), 115.18 (C₄), 121.94 (C_{2,6}), 130.23 (NCO), 136.73 (C_{3,5}), 161.54 ppm (C_{1,7}); IR (KBr): ν = > = 2188 cm⁻¹ (NCO).

Synthesis of [(iBu)₂ATI]GeNCS (5)

To a mixture of compound **2** (0.75 g, 2.21 mmol) and excess potassium thiocyanate (0.86 g, 8.83 mmol), THF (25 mL) was added and stirred at room temperature for 24 h. Then, it was filtered through a G4 frit with Celite and the solvent from the filtrate was evaporated in vacuo to obtain an orange solid. It was washed with hexane (2 mL) and dried under reduced pressure to get an analytically pure sample of compound **5** as an orange solid. Single crystals of compound **5** suitable for X-ray diffraction studies were grown from its saturated diethyl ether solution at -40 °C. Yield: 0.76 g, 95.0%. M.p.: 69 °C; elemental analysis (%) calcd for C₁₆H₂₃GeN₃S (*M* = 362.08): C 53.07, H 6.40, N 11.61; found: C 52.99, H 6.35, N 11.67; ¹H NMR (300 MHz, C₆D₆): δ = 0.80 (d, ³J_{HH} = 6.0 Hz, 12H, CH(CH₃)₂), 2.00–2.14 (m, 2H, CH(CH₃)₂), 3.24 (d, ³J_{HH} = 6.0 Hz, 4H, CH₂), 6.28 (t, ³J_{HH} = 9.0 Hz, 1H, CH), 6.41 (d, ³J_{HH} = 12.0 Hz, 2H, CH), 6.75 ppm (t, ³J_{HH} = 12.0 Hz, 2H, CH); ¹³C{¹H} NMR (75 MHz, C₆D₆): δ = 20.97 (CH(CH₃)₂), 28.12 (CH(CH₃)₂), 54.04 (CH₂), 115.97 (C₄), 123.48 (C_{2,6}), 127.20 (NCS), 137.12 (C_{3,5}), 161.49 ppm (C_{1,7}); IR (KBr): ν = > = 2030 cm⁻¹ (NCS).

General synthetic route for [(iBu)₂ATI]GeY₂M(CO)₄ complexes (Y = NCO, NCS; M = Mo/W)

To a solution of pseudohalogenogermylene in toluene (10 mL), *cis*-[M(CO)₄(COD)] (M = Mo/W) was added and the resulting solution was stirred overnight at room temperature. After that, the solvent was removed under reduced pressure to get a yellow solid. It was washed with hexane (5 mL) and dried in vacuo to afford an analytically pure sample of the metal complex. Single crystals of the complex suitable for X-ray diffraction studies were grown by slow evaporation of its solution in a mixture of dichloromethane and toluene.

Synthesis of [(iBu)₂ATI]GeNCO₂Mo(CO)₄ (6): Isocyanatogermylene [(iBu)₂ATI]GeNCO **4** (0.50 g, 1.44 mmol) and *cis*-[Mo(CO)₄(COD)] (0.23 g, 0.72 mmol). Yield: 0.63 g, 97.0%. M.p.: 145 °C; elemental analysis (%) calcd for C₃₆H₅₀Ge₂MoN₆O₆ (*M* = 904.04): C 47.83, H 5.57, N 9.30; found: C 47.90, H 5.50, N 9.35; ¹H NMR (300 MHz, CDCl₃): δ = 0.98 (d, ³J_{HH} = 6.0 Hz, 6H, CH(CH₃)₂), 1.04 (d, ³J_{HH} = 6.0 Hz, 6H, CH(CH₃)₂), 2.20–2.31 (m, 2H, CH(CH₃)₂), 3.42 (dd, ³J_{HH} = 9.0, 8.0 Hz, 2H, CH₂), 3.60 (dd, ³J_{HH} = 9.0, 8.0 Hz, 2H, CH₂), 6.77–6.86 (m, 3H, CH), 7.33 ppm (t, ³J_{HH} = 9.0 Hz, 2H, CH); ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 20.82 (CH(CH₃)₂), 21.16 (CH(CH₃)₂), 28.41

(CH(CH₃)₂), 53.15 (CH₂), 115.97 (C₄), 124.06 (C_{2,6}), 137.79 (C_{3,5}), 159.19 (C_{1,7}), 211.89 ppm (CO); IR (KBr): ν = 1910 (CO), 2217 cm⁻¹ (NCO).

Synthesis of [(iBu)₂ATI]GeNCS₂Mo(CO)₄ (7): Isothiocyanatogermylene [(iBu)₂ATI]GeNCS **5** (0.50 g, 1.38 mmol) and *cis*-[Mo(CO)₄(COD)] (0.22 g, 0.70 mmol). Yield: 0.61 g, 95.0%. M.p.: 164 °C; elemental analysis (%) calcd for C₃₆H₅₀Ge₂MoN₆O₄S₂ (*M* = 936.17): C 46.19, H 5.38, N 8.98; found: C 46.12, H 5.30, N 8.90; ¹H NMR (300 MHz, CDCl₃): δ = 1.07 (d, ³J_{HH} = 6.0 Hz, 6H, CH(CH₃)₂), 1.13 (d, ³J_{HH} = 6.0 Hz, 6H, CH(CH₃)₂), 2.33–2.42 (m, 2H, CH(CH₃)₂), 3.62 (dd, ³J_{HH} = 12.0, 9.0 Hz, 2H, CH₂), 3.77 (dd, ³J_{HH} = 6.0, 6.0 Hz, 2H, CH₂), 6.91 (t, ³J_{HH} = 9.0 Hz, 1H, CH), 7.05 (d, ³J_{HH} = 15.0 Hz, 2H, CH), 7.45 ppm (t, ³J_{HH} = 12.0 Hz, 2H, CH); ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 20.81 (CH(CH₃)₂), 21.14 (CH(CH₃)₂), 28.96 (CH(CH₃)₂), 53.39 (CH₂), 116.48 (C₄), 125.18 (C_{2,6}), 138.06 (C_{3,5}), 159.40 (C_{1,7}), 210.53 ppm (CO); IR (KBr): ν = 1900 (CO), 2043 cm⁻¹ (NCS).

General synthetic route for [(iBu)₂ATI]GeX₂M(CO)₄ complexes (X = F, Cl, Br; M = Mo/W)

To a solution of halogenogermylene in toluene (10 mL), *cis*-[M(CO)₄(COD)] (M = Mo/W) was added and the resulting solution was stirred overnight at room temperature. After that, the solvent was removed under reduced pressure to get a yellow solid. It was washed with hexane (5 mL) and dried in vacuo to afford an analytically pure sample of the metal complex. Single crystals of the complex suitable for X-ray diffraction studies were grown by slow evaporation of its solution in a mixture of dichloromethane and toluene.

Synthesis of [(iBu)₂ATI]GeF₂Mo(CO)₄ (8): Fluorogermylene **1** (0.20 g, 0.62 mmol) and *cis*-[Mo(CO)₄(COD)] (0.10 g, 0.33 mmol). Yield: 0.25 g, 96.6%. M.p.: 142 °C; elemental analysis (%) calcd for C₃₄H₄₆F₂Ge₂MoN₄O₄ (*M* = 853.97): C 47.82, H 5.43, N 6.56; found: C 47.74, H 5.50, N 6.49; ¹H NMR (300 MHz, CDCl₃): δ = 0.99 (d, ³J_{HH} = 6.0 Hz, 6H, CH(CH₃)₂), 1.04 (d, ³J_{HH} = 6.0 Hz, 6H, CH(CH₃)₂), 2.19–2.28 (m, 2H, CH(CH₃)₂), 3.54 (dd, ³J_{HH} = 13.2, 5.4 Hz, 2H, CH₂), 3.73 (dd, ³J_{HH} = 14.1, 8.4 Hz, 2H, CH₂), 6.80 (t, ³J_{HH} = 9.0 Hz, 1H, CH), 6.89 (d, ³J_{HH} = 10.8 Hz, 2H, CH), 7.36 ppm (t, ³J_{HH} = 10.5 Hz, 2H, CH); ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 20.97 (CH(CH₃)₂), 21.13 (CH(CH₃)₂), 28.51 (CH(CH₃)₂), 53.37 (CH₂), 115.32 (C₄), 123.96 (C_{2,6}), 137.40 (C_{3,5}), 158.86 (C_{1,7}), 211.20 (CO), 215.88 ppm (CO); ¹⁹F{¹H} NMR (282 MHz, CDCl₃): δ = -64.66 ppm; IR (KBr): ν = 1868, 1893, 1918, 2011 cm⁻¹ (CO).

Synthesis of [(iBu)₂ATI]GeCl₂Mo(CO)₄ (9): Chlorogermylene **2** (0.50 g, 1.47 mmol) and *cis*-[Mo(CO)₄(COD)] (0.23 g, 0.73 mmol). Yield: 0.62 g, 94.8%. M.p.: 140 °C; elemental analysis (%) calcd for C₃₄H₅₀Cl₂Ge₂MoN₄O₄ (*M* = 890.91): C 45.84, H 5.66, N 6.29; found: C 45.80, H 5.69, N 6.35; ¹H NMR (300 MHz, CDCl₃): δ = 1.02 (d, ³J_{HH} = 6.0 Hz, 6H, CH(CH₃)₂), 1.07 (d, ³J_{HH} = 6.0 Hz, 6H, CH(CH₃)₂), 2.40–2.49 (m, 2H, CH(CH₃)₂), 3.61 (dd, ³J_{HH} = 12.0, 6.0 Hz, 2H, CH₂), 3.82 (dd, ³J_{HH} = 6.0, 9.0 Hz, 2H, CH₂), 6.80 (t, ³J_{HH} = 9.0 Hz, 1H, CH), 6.96 (d, ³J_{HH} = 12.0 Hz, 2H, CH), 7.34 ppm (t, ³J_{HH} = 9.0 Hz, 2H, CH); ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 20.96 (CH(CH₃)₂), 21.33 (CH(CH₃)₂), 28.90 (CH(CH₃)₂), 53.05 (CH₂), 116.62 (C₄), 124.58 (C_{2,6}), 137.49 (C_{3,5}), 159.20 (C_{1,7}), 211.47 (CO), 215.62 ppm (CO); IR (KBr): ν = 1876, 1897, 1933, 2012 cm⁻¹ (CO).

Synthesis of [(iBu)₂ATI]GeBr₂Mo(CO)₄ (10): Bromogermylene **3** (0.50 g, 1.30 mmol) and *cis*-[Mo(CO)₄(COD)] (0.20 g, 0.65 mmol). Yield: 0.59 g, 96.0%. M.p.: 152 °C; elemental analysis (%) calcd for C₃₄H₅₀Br₂Ge₂MoN₄O₄ (*M* = 975.78): C 41.85, H 4.75, N 5.74; found: C 41.80, H 4.65, N 5.70; ¹H NMR (300 MHz, CDCl₃): δ = 1.06 (d, ³J_{HH} = 6.0 Hz, 6H, CH(CH₃)₂), 1.10 (d, ³J_{HH} = 6.0 Hz, 6H, CH(CH₃)₂), 2.46–2.55 (m, 2H, CH(CH₃)₂), 3.75 (dd, ³J_{HH} = 13.5, 9.3 Hz, 2H, CH₂), 3.86 (dd, ³J_{HH} = 14.1, 6.9 Hz, 2H, CH₂), 6.90 (t, ³J_{HH} = 9.0 Hz, 1H, CH), 7.09 (d, ³J_{HH} = 12.0 Hz, 2H, CH), 7.42 ppm (t, ³J_{HH} = 9.0 Hz, 2H, CH); ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 20.84 (CH(CH₃)₂), 21.26 (CH(CH₃)₂), 28.83

(CH(CH₃)₂), 52.90 (CH₂), 117.28 (C₄), 125.81 (C_{2,6}), 137.65 (C_{3,5}), 159.32 (C_{1,7}), 211.67 (CO), 215.72 ppm (CO); IR (KBr): ν = 1875, 1893, 1925, 2010 cm⁻¹ (CO).

Synthesis of [(iBu)₂ATI]GeNCO₂W(CO)₄ (11): Isocyanatogermylene **4** (0.50 g, 1.44 mmol) and *cis*-[W(CO)₄(COD)] (0.29 g, 0.72 mmol). Yield: 0.65 g, 91.1%. M.p.: 145 °C; elemental analysis (%) calcd for C₃₆H₅₀Ge₂WN₆O₆ (*M* = 987.91): C 43.77, H 4.69, N 8.51; found: C 43.70, H 4.75, N 8.61; ¹H NMR (300 MHz, CDCl₃): δ = 0.98–1.13 (m, 12H, CH(CH₃)₂), 2.24–2.42 (m, 2H, CH(CH₃)₂), 3.43 (dd, ³J_{HH} = 14.4, 8.7 Hz, 1H, CH₂), 3.56–3.64 (m, 2H, CH₂), 3.70 (dd, ³J_{HH} = 13.8, 7.2 Hz, 1H, CH₂), 6.77–6.89 (m, 2H, CH), 6.97 (d, ³J_{HH} = 11.1 Hz, 1H, CH), 7.31–7.42 ppm (m, 2H, CH); ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 20.64 (CH(CH₃)₂), 20.99 (CH(CH₃)₂), 28.22 (CH(CH₃)₂), 53.07 (CH₂), 115.83 (C₄), 124.67 (C_{2,6}), 137.73 (C_{3,5}), 158.79 (C_{1,7}), 204.66 ppm (CO); IR (KBr): ν = 1881 (CO), 2212 cm⁻¹ (NCO).

Synthesis of [(iBu)₂ATI]GeCl₂W(CO)₄ (12): Chlorogermylene **2** (0.50 g, 1.47 mmol) and *cis*-[W(CO)₄(COD)] (0.30 g, 0.73 mmol). Yield: 0.67 g, 94.0%. M.p.: 140 °C; elemental analysis (%) calcd for C₃₄H₅₀Cl₂Ge₂WN₄O₄ (*M* = 974.78): C 41.89, H 4.76, N 5.75; found: C 41.80, H 4.90, N 5.81; ¹H NMR (300 MHz, CDCl₃): δ = 1.02–1.11 (m, 12H, CH(CH₃)₂), 2.41–2.52 (m, 2H, CH(CH₃)₂), 3.55–3.70 (m, 2H, CH₂), 3.77–3.84 (m, 2H, CH₂), 6.78–6.89 (m, 1H, CH), 6.97 (d, ³J_{HH} = 12.0 Hz, 1H, CH), 7.06 (d, ³J_{HH} = 11.1 Hz, 1H, CH), 7.32–7.44 ppm (m, 2H, CH); ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 20.90 (CH(CH₃)₂), 21.15 (CH(CH₃)₂), 28.72 (CH(CH₃)₂), 52.96 (CH₂), 116.63 (C₄), 124.66 (C_{2,6}), 137.40 (C_{3,5}), 158.75 (C_{1,7}), 202.34 (CO), 205.10 ppm (CO); IR (KBr): ν = 1868, 1888, 1924, 2008 cm⁻¹ (CO).

Structure determination of compounds **5**, **6–9**, and **11–12**

Single-crystal X-ray diffraction data of compounds **5**, **6–8**, (Table S1 in the Supporting Information) and **9**, **11–12** (Table S2 in the Supporting Information) were collected with a Bruker SMART APEX diffractometer equipped with a 3-axis goniometer.^[23] The crystals were covered with a cryoprotectant (Paratone-N) and mounted on a glass capillary. The data were collected under a steady flow of cold dinitrogen by using Mo_{K α} radiation (λ = 0.71073 Å). The data were integrated by using SAINT and an empirical absorption correction was applied by using SADABS.^[24] The structures were solved by direct methods and refined by full-matrix least-squares on *F*² by using either SHELXTL-2014^[25] or SHELXT-2014 incorporated in OLEX2.^[26] In compound **9**, large regions of diffused electron density that could not be modeled (disordered solvents) were removed from the refinement by using the SQUEEZE function in PLATON. All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were fixed according to a riding model and were refined isotropically.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: germanium • heterometallic complexes • main group elements • metallylenes • transition metals

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