

## Short Note

# (*N,N'*-Di-*tert*-butyl-S-phenylsulfinimidamido- $\kappa N, \kappa N'$ )-chlorogermanium- $\kappa Ge$ -chloro( $\eta^2, \eta^2$ -cycloocta-1,5-diene)rhodium

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**Abstract:** The title complex  $[(\text{PhS}(t\text{BuN})_2)(\text{Cl})\text{Ge} \rightarrow \text{RhCl}(\text{cod})]$  (**2**) was synthesized by the reaction of three-coordinated chlorogermylene,  $[\text{PhS}(t\text{BuN})_2]\text{GeCl}$  (**1**), supported by a diimidosulfinate ligand with a half equivalent of  $[\text{RhCl}(\text{cod})]_2$  in benzene. The molecular structure of **2** was determined by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopies and single-crystal X-ray diffraction (SCXRD) analysis. The electronic property of germylene **1** was assessed by determining the Tolman electronic parameter of the corresponding *cis*-dicarbonyl Rh(I) complex,  $[(\text{PhS}(t\text{BuN})_2)(\text{Cl})\text{Ge} \rightarrow \text{RhCl}(\text{CO})_2]$  (**3**), that was prepared by the treatment of **2** with carbon monoxide.

**Keywords:** rhodium; germylene; diimidosulfinate; single-crystal X-ray diffraction analysis

## 1. Introduction

In recent years, the utilization of more substantial carbene congeners, commonly known as tetrylenes, as ligands in transition metal chemistry has experienced significant growth [1–10]. This heightened interest has been propelled by the amphiphilic property of tetrylenes, enabling them to function as both Lewis base and acid, as well as their enhanced electron-donating capacity, surpassing that of most phosphines and *N*-heterocyclic carbenes (NHCs) [11–13]. Indeed, certain tetrylene-transition metal complexes have demonstrated their efficacy as catalysts for homogeneous transformations [14–24]. Furthermore, theoretical calculations support that germylenes can potentially serve as an ancillary ligand for transition metal catalysts compared to common NHC and phosphine ligands [25].

We have been conducting research on the synthesis and properties of a series of three-coordinated tetrylenes supported by iminophosphonamide  $[\text{Ph}_2\text{P}(\text{RN})_2]^-$  ( $\text{R} = t\text{Bu}$ , 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) [26–32] and diimidosulfinate  $[\text{PhS}(\text{RN})_2]^-$  ( $\text{R} = t\text{Bu}$ , SiMe<sub>3</sub>) [33] ligands, which are isoelectronic ligands of amidinate  $[\text{R}'\text{C}(\text{RN})_2]^-$ . In particular, we demonstrated that iminophosphonamido silylenes and germylenes not only display strong electron-donating properties surpassing those of NHCs but also exhibit diverse reactivities, including unique coordination behavior [32]. In our ongoing investigation into three-coordinated tetrylenes, we present the synthesis and structure of the germylene-Rh(I) complex  $[(\text{PhS}(t\text{BuN})_2)(\text{Cl})\text{Ge} \rightarrow \text{RhCl}(\text{cod})]$  ( $\text{cod} = 1,5\text{-cyclooctadiene}$ ), in which the germylene fragment is supported by a diimidosulfinate ligand, as well as its reactivity toward carbon monoxide.

## 2. Results and Discussion

The treatment of  $[\text{PhS}(t\text{BuN})_2]\text{GeCl}$  **1** [33] with a half equivalent of  $[\text{RhCl}(\text{cod})]_2$  in benzene gave the corresponding germylene-Rh(I) complex  $[(\text{PhS}(t\text{BuN})_2)(\text{Cl})\text{Ge} \rightarrow \text{RhCl}(\text{cod})]$  **2** as an orange powder in a 66% yield (Scheme 1). In the  $^1\text{H}$  NMR spectrum of **2**, a singlet signal due to *tert*-butyl groups was observed at 1.34 ppm. Four non-equivalent signals assigned to methylene protons in the cod ligand were found at 1.70–1.78, 2.12, and 2.24 ppm. Two alkenyl



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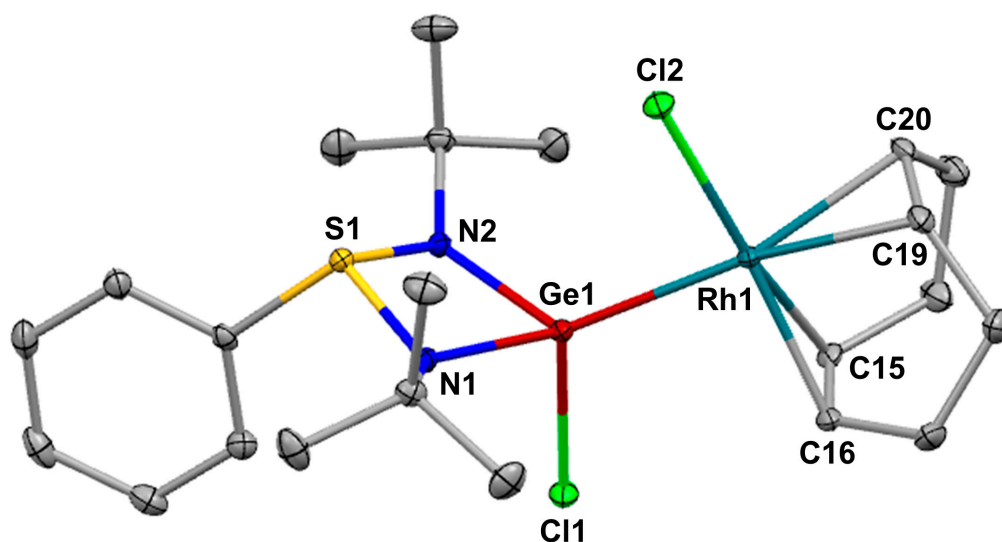


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protons in the cod ligand appeared at 4.23 and 5.62 ppm as a broad signal. Single crystals of **2** suitable for X-ray diffraction analysis were obtained from a saturated benzene solution at room temperature. The ORTEP of **2** is illustrated in Figure 1, and selected bond lengths and bond angles are provided in Table 1. Complex **2** crystallizes in the triclinic space group *P*-1 with a benzene molecule per unit cell. As depicted in Figure 1, the central rhodium atom, to which the germanium atom is coordinated, and the phenyl group on the sulfur atom are oriented in opposite directions relative to the four-membered ring GeN<sub>2</sub>S skeleton. The rhodium atom exhibits a distorted planar square geometry. The Ge–Rh bond length [2.3924(4) Å] of **2**, which lies within the range of previously reported germylene-Rh(I) complexes [2.3366(9)–2.4499(8) Å] [34–39]. The Ge–Cl bond length [2.2620(6) Å] of **2** is somewhat shorter than that of the starting **1** [2.3498(19) Å] [33]. This shortening of the bond length can be attributed to the coordination of the lone-pair electron on the germanium atom to the rhodium atom, leading to a decrease in electron density on the germanium atom that is a factor to the elongation of the Ge–Cl bond in **1** due to the electronic repulsive interaction between both atoms. The average Rh–C distance (2.204 Å) to the carbon atom (C19, C20) positioned *trans* to the germanium atom is longer than the distance to the cis-oriented carbon atoms (2.126 Å), indicating the strong trans influence of the germylene ligand.



**Scheme 1.** Synthesis of  $[\{\text{PhS}(\text{tBuN})_2\}(\text{Cl})\text{Ge} \rightarrow \text{RhCl(cod)}] \text{2}$ .

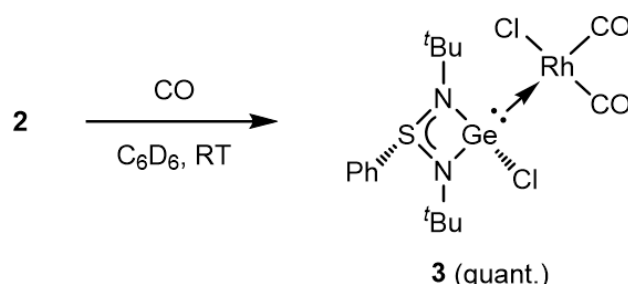


**Figure 1.** ORTEP of **2** with thermal ellipsoids at 50% probability. All hydrogen atoms and a molecule of benzene in the unit cell are omitted for clarity.

**Table 1.** Selected bond lengths [Å] and bond angles [°].

Bond Lengths	[Å]	Bond Angles	[°]
Ge1–Rh1	2.3924(4)	Ge1–Rh1–Cl2	88.829(18)
Ge1–Cl1	2.2620(6)	Rh1–Ge1–Cl1	114.36(2)
Ge1–N1	1.9290(19)	Rh1–Ge1–N1	132.77(6)
Ge1–N2	1.925(2)	Rh1–Ge1–N2	125.71(6)
Rh1–Cl2	2.3631(6)	Cl1–Ge1–N1	99.59(6)
Rh1–C15	2.134(2)	Cl1–Ge1–N2	101.15(6)
Rh1–C16	2.118(2)		
Rh1–C19	2.213(2)		
Rh1–C20	2.194(2)		

To assess the electron-donating property of germylene ligand **1** using Tolman's electronic parameter [40,41], we next conducted the synthesis of the corresponding *cis*-dicarbonyl Rh(I) complex,  $[\{\text{PhS}(t\text{BuN})_2\}(\text{Cl})\text{Ge}:\rightarrow\text{RhCl}(\text{CO})_2]$  (**3**). Treatment of **2** with carbon monoxide (1 atm) in  $\text{C}_6\text{D}_6$  resulted in the quantitative formation of **3** (Scheme 2). In the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3**, the carbonyl carbons resonated at 185.8 ppm as a broad signal, which is comparable to that of the germylene-Rh(I) complex bearing an iminophosphonamide ligand,  $[\{\text{Ph}_2\text{P}(t\text{BuN})_2\}(\text{Cl})\text{Ge}:\rightarrow\text{RhCl}(\text{CO})_2]$  (183.1 ppm) [32]. In the IR spectrum of **3**, two absorptions due to carbonyl stretching vibration were observed at 2005 and 2069  $\text{cm}^{-1}$ . Comparing the average carbonyl stretching frequency (2037  $\text{cm}^{-1}$ ) with that of the corresponding rhodium complexes bearing common *N*-heterocyclic carbenes (NHCs) or cyclic (alkyl)(amino) carbenes (cAACs), the donor intensity of germylene **1** is relatively high, falling between NHCs (2046–2051  $\text{cm}^{-1}$ ) and cAACs (2031–2036  $\text{cm}^{-1}$ ).

**Scheme 2.** Synthesis of  $[\{\text{PhS}(t\text{BuN})_2\}(\text{Cl})\text{Ge}:\rightarrow\text{RhCl}(\text{CO})_2]$  **3**.

### 3. Materials and Methods

#### 3.1. General Considerations

Unless otherwise noted, all experiments were carried out under an argon atmosphere using standard Schlenk-line techniques or a glovebox (UNICO Ltd., Ibaraki, Japan).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Bruker Avance-500 (500 MHz for  $^1\text{H}$ ) and Bruker Avance-400 (101 MHz for  $^{13}\text{C}$ ) spectrometers (Bruker, Kanagawa, Japan) using  $\text{C}_6\text{D}_6$  as the solvent at room temperature. IR spectrum was recorded on a TENSOR II (Bruker, Kanagawa, Japan). All melting points were determined on a Mel-Temp capillary tube apparatus and were uncorrected. Elemental analyses were conducted at the Molecular Analysis and Life Science Center of Saitama University. All solvents were dried over 4A molecular sieves or potassium mirrors before use. All materials were obtained from commercial suppliers and used without further purification except **1** that was prepared according to the corresponding literature procedure [33].

#### 3.2. Synthesis of $[\{\text{PhS}(t\text{BuN})_2\}(\text{Cl})\text{Ge}:\rightarrow\text{RhCl}(\text{cod})]$ **2**

In a Schlenck tube, germylene **1** (52.1 mg, 0.14 mmol) and  $[\text{Rh}(\text{cod})\text{Cl}]_2$  (35.8 mg, 0.07 mmol) were dissolved into benzene (1 mL). The resulting orange solution was stirred for 4 h at room temperature. All volatiles were removed under reduced pressure to give

germylene-rhodium(I) complex **2** (57.8 mg, 66%) as orange crystals. Mp. 165–167 °C (decomp.).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 500 MHz):  $\delta$  = 1.34 (s, 18H,  $\text{CH}_3$ ), 1.71–1.78 (m, 4H,  $\text{CH}_2$ ), 2.12 (br s, 2H,  $\text{CH}_2$ ), 2.25 (br s, 2H,  $\text{CH}_2$ ), 4.43 (br s, 2H, CH), 5.62 (br s, 2H, CH), 6.93–6.95 (m, 3H, Ph), 8.03–8.05 (m, 2H, Ph).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 101 MHz):  $\delta$  29.3 ( $\text{CH}_2$ ), 31.0 ( $\text{CH}_3$ ), 33.5 ( $\text{CH}_2$ ), 56.1 (C), 70.2 (CH,  $J_{\text{Rh-C}}$  = 14 Hz, cod), 101.0 (CH, cod), 128.6 (CH, Ph), 129.9 (CH, Ph), 133.8 (CH, Ph), 147.3 (C, Ph). Anal. Calcd. for  $\text{C}_{22}\text{H}_{35}\text{Cl}_2\text{GeN}_2\text{RhS}$ : C, 43.60; H, 5.82; N, 4.62. Found: C, 43.98; H, 5.71; N, 4.46. See Supplementary Materials.

### 3.3. Reaction of **2** with CO

A pressure-tight NMR tube containing a solution of **2** in  $\text{C}_6\text{D}_6$  (0.5 mL) under a CO pressure (ca. 3 atm) was kept for 1 h at room temperature. The color of the solution changed immediately from orange to yellow. The reaction was completed within 1 h.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 500 MHz):  $\delta$  1.28 (s, 9H,  $\text{CH}_3$ ), 1.58 (s, 9H,  $\text{CH}_3$ ), 6.95 (t, 1H,  $^3J$  = 7 Hz, *p*-Ph), 7.06 (t, 2H,  $^3J$  = 8 Hz, *m*-Ph), 7.51 (d, 2H,  $^3J$  = 8 Hz, *o*-Ph).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 101 MHz):  $\delta$  33.0 ( $\text{CH}_3$ ), 33.6 ( $\text{CH}_3$ ), 60.0 (C), 62.4 (C), 128.6 (CH, Ph), 129.2 (CH, Ph), 131.2 (CH, Ph), 145.6 (C, Ph), 185.8 (C, CO). IR ( $\text{C}_6\text{D}_6$ ): 2005, 2069  $\text{cm}^{-1}$  [ $\nu(\text{CO})$ ]. See Supplementary Materials. Concentration of the reaction mixture resulted in the decomposition of the expected product **3**.

### 3.4. SCXRD Analysis of **2**

An orange single crystal of **2** was grown from a saturated benzene solution at 25 °C. The intensity data were collected at 100 K on a Bruker SMART APEX II diffractometer employing graphite-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda$  = 0.71073 Å). The structure was solved by direct methods (SHELXT) [42] and refined by full-matrix least-squares procedures on  $F^2$  for all reflections (SHELXL) [43]. Hydrogen atoms were located by assuming ideal geometry and were included in the structure calculations without further refinement of the parameters.

Crystal data for  $\text{C}_{28}\text{H}_{41}\text{Cl}_2\text{GeN}_2\text{RhS}$  (**2**):  $M$  = 684.09  $\text{g mol}^{-1}$ , triclinic,  $P-1$ ,  $a$  = 8.3881(7),  $b$  = 12.5836(11),  $c$  = 14.1437(12) Å,  $\alpha$  = 88.7760(10),  $\beta$  = 88.8650(10),  $\gamma$  = 89.9720(10)°,  $V$  = 1492.3(2) Å<sup>3</sup>,  $Z$  = 2,  $D_x$  = 1.522  $\text{g cm}^{-3}$ ,  $F(000)$  = 700, and  $\mu$  = 1.829  $\text{mm}^{-1}$ . CCDC deposition number: 2324776.

## 4. Conclusions

A novel germylene-rhodium(I) complex **2** was synthesized and structurally characterized by spectroscopic data and SCXRD. To estimate the electron-donating ability of diimidosulfinato germylene ligand **1**, the corresponding *cis*-dicarbonyl Rh(I) complex **3** was prepared through the reaction of **2** with carbon monoxide. The donor property of **1** was determined from the Tolman electronic parameter of **3** and revealed to be intermediate between NHCs and cAACs.

**Supplementary Materials:** The following are available online: all spectroscopic data for **2** and **3** and crystallographic data for **2** in Crystallographic Information File (CIF) format. CCDC 2324776 also contains the supplementary crystallographic data for this paper.

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**Data Availability Statement:** CCDC 2324776 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) (accessed on 11 January 2024), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

**Conflicts of Interest:** The authors declare no conflicts of interest.

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