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Germylone-Bridged Bimetallic Ir and Rh Complexes

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The reactions of germylone **1** with one equivalent of $[M(COD)Cl]_2$ ($M = Ir, Rh$) afforded the germylone-bridged bimetallic complexes **2** and **3**, that have been spectroscopically and structurally characterized. Density functional theory (DFT) studies reveal the relatively strong interactions between the Ge atom and those metals. By the reaction of $[Rh(COD)Cl]_2$ with CO followed by addition of **1**, a complex **4** involving a Rh-Ge-Rh-Ge-Rh chain was also synthesized.

Since the first isolation in the 1970s,¹ germynes bearing the Ge atoms in +II oxidation state,² the heavier analogue of singlet carbenes,³ have been extensively studied because of its diverse reactivity ranging from activation of bonds in the inorganic and organic compounds^{4,5} to coordination to various metals.⁶ Recently a new class of low-valent germanium compounds, namely germynes **A** containing the Ge atoms in zero oxidation state, has emerged (Figure 1).^{7,8} The pioneering experimental works by the several groups involving Kira,⁹ Driess,¹⁰ Roesky,¹¹ Nikonov,¹² and their co-workers, have significantly contributed to the initial advance of the germynone chemistry. Although various types of isolable germynes have been reported to date, the studies on their coordination chemistry on transition metals are still limited (Figure 1). In 2016, Driess et al. reported the formation of the mono-coordinate germynone-iron complex **B** by reaction of bis(silylene)pyridine-supported chlorogermylumidene with $K_2Fe(CO)_4$.¹³ Recently, the group of Jana and Rzepa prepared the first dicoordinate germynone-iron complex **C** by the transformation of the NHC-digermanium(0)-iron complex.¹⁴ Note that both synthetic routes to the germynone-iron complexes **B** and **C** are not straightforward from the isolable

germylones. In contrast, Driess and co-workers reported the direct complexation between an isolable germynone and excess $AlBr_3$ affording bis($AlBr_3$)-germylone adduct **D**.¹⁵

Figure 1. Germynes stabilized by donor ligands (**A**) and the reported germynone-metal complexes (**B–E**).

Recently, we have reported the isolation of germynone **1** stabilized by a bidentate imino-N-heterocyclic carbene, which can readily react with $M(CO)_5(thf)$ ($M = Cr, Mo, W$) to generate the corresponding mono-coordinate germynone-metal complexes $[1 \cdot M(CO)_5]$ (**E**).¹⁶ Our preliminary study showed

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†Electronic Supplementary Information (ESI) available: Complete experimental data, and crystallographic data (CIF) of **2–4** (CCDC: 1889621–1889623) and computational details including Cartesian coordinates for stationary points. See DOI: 10.1039/x0xx00000x

that **1** can serve as a donor of two lone pairs, as confirmed by the reaction with two equivalents of methyl trifluoromethanesulfonate (MeOTf) affording a dicationic species $[1 \cdot \text{Me}_2]^{2+} \cdot 2\text{OTf}^-$.^{16a} However, its coordination ability to two metals is hitherto unknown, which prompted us to investigate the reactions of **1** with two equivalents of transition metals. Herein, we report the synthesis, single-crystal X-ray diffraction analysis, and computational studies of germylone-supported bimetallic Ir and Rh complexes. We also show that using **1** as the synthetic precursor, a complex involving a unique Rh-Ge-Rh-Ge-Rh chain can be synthesized.

Treatment of **1** with a stoichiometric amount of $[\text{M}(\text{COD})\text{Cl}]_2$ ($\text{M} = \text{Ir}, \text{Rh}$) in benzene at room temperature immediately furnished the deep red solution. After work-up, complexes **2** ($\text{M} = \text{Ir}$) and **3** ($\text{M} = \text{Rh}$) were obtained as red crystalline solids in high yield (**2**: 86%, **3**: 77%) (Scheme 1).

Scheme 1. Synthesis of bimetallic complexes **2**, **3**.

Complexes **2** and **3** have been fully characterized by the standard spectroscopic methods and the crystallographic study. In the ^{13}C NMR spectra, the single peaks corresponding to the carbene carbon (NCN) were observed of 215.3 ppm for **2** and 215.8 ppm for **3**, which are shifted downfield compared with that (194.3 ppm) of **1**. Single crystals of **2** and **3** suitable for X-ray diffraction analysis were obtained at room temperature by slow evaporation of a saturated THF and toluene solution, respectively. In the solid-state structures of **2** and **3** (Figure 2), the $\text{C}_2\text{N}_2\text{Ge}$ five-membered ring persists the coplanar geometry (the sum of internal angles = 539.9° (**2**), 539.8° (**3**)). Both complexes involve the tetracoordinate Ge atom coordinating to two $[\text{M}(\text{COD})\text{Cl}]$ ($\text{M} = \text{Ir}, \text{Rh}$) units, that are located at the opposite sides with respect to the $\text{C}_2\text{N}_2\text{Ge}$ ring with the large bond angles of $144.04(2)^\circ$ for Ir1-Ge1-Ir2 in **2** and $142.383(13)^\circ$ for Rh1-Ge1-Rh2 in **3**, respectively. The C-Ge-N bond angles of $79.52(18)^\circ$ for **2** and $78.91(10)^\circ$ for **3** are slightly smaller than that ($80.59(6)^\circ$) of **1**. The Ge-M bond lengths (Ge1-Ir1 : 2.4954(6) Å, Ge1-Ir2 : 2.4942(6) Å in **2**; Ge1-Rh1 : 2.4912(3) Å, Ge1-Rh2 : 2.5029(3) Å in **3**) are comparable or slightly longer than those reported for germylene iridium (2.4019(13)–2.5598(11) Å)¹⁷ and rhodium complexes (2.3366(9)–2.4499(8) Å).¹⁸ The distances between two metal centres are 4.746 Å (**2**) and 4.727 Å (**3**), which are significantly longer than the sum of their van der Waals radii (4.0 Å),¹⁹ indicating no interaction between them. The Ge-C and Ge-N bond distances in **2** (1.985(5) Å, 2.044(4) Å) and **3** (1.984(3) Å, 2.044(2) Å) are longer than those (1.8870(15) Å, 1.9680(13) Å) of **1**, but comparable with those of $[1\text{-Cl}]^+[\text{GeCl}_3]^-$.^{16a} The formation of **2** and **3** demonstrates the nucleophilic nature of **1** as a two lone-pair donor. Note that **2** and **3** represent the first example of the bimetallic germylone complex with group 9 metals.

Figure 2. Solid-state structures of **2** (top) and **3** (bottom) (hydrogen atoms and solvent molecules are omitted for clarity). Thermal ellipsoids are set at the 50% probability.

Figure 3. Plots of the HOMO (top) and LUMO (bottom) of **2** calculated at the B3LYP/6-311G(d,p) level of theory, with the LANL2TZ(f) pseudo-potential applied for the Ir atoms.

DFT calculations were carried out to interrogate the origins of the structure of complexes **2** and **3**. The crystal structures of both complexes were well replicated by the complete optimized structures. The frontier orbitals of **2** are depicted in Figure 3. The similar MOs of **3** were confirmed (see the supporting information). The HOMO mainly corresponds to the interaction between the lone pair orbitals on the Ge atom and the d orbitals on the Ir atoms whereas the LUMO is mainly dominated by a π -type orbital over the C_2N_2Ge five-membered ring with some contribution from the N lone pair as well as the d-orbitals of Ir atoms. Wiberg Bond Index (WBI) values for the Ge1–Ir1 and Ge1–Ir2 bonds are 0.74 and 0.71, respectively, thus indicating a pronounced interaction between the gerymlone ligand **1** and the $[IrCl(COD)]$ units in **2**. WBI values of 0.54 for the Ge1–C1 bond and 0.29 for the Ge1–N3 bond are significantly smaller than those (1.21, 0.56) of **1** but comparable with those (0.61, 0.39) of $[1-Cl]^+[GeCl_3]^-$,^{16a} which is probably due to the loss of the aromatic property of the C_2N_2Ge ring in **2**. Natural Population Analysis (NPA) revealed an overall charge transfer of 0.80 e and 0.79 e from the ligand **1** to $[Ir1Cl(COD)]$ and $[Ir2Cl(COD)]$ fragments in **2**, respectively.

Complexes **2** and **3** are stable both in the solid-state and in solution under an inert atmosphere, but they rapidly decompose to a complex mixture upon exposure to air. We attempted to replace the COD substituents on the metal centre with CO by directly bubbling CO into the toluene solutions of **2** and **3**, which unfortunately led to a complex mixture instead of the expected products $1 \cdot [M(CO)_2Cl]_2$. Accordingly, next, we carried out the reaction of $[Rh(COD)Cl]_2$ with CO in CH_3CN first followed by addition of the benzene solution of **1** after removal of CH_3CN . While the reaction mixture was kept at room temperature overnight, a deep red crystalline appeared. After work-up, **4** was obtained in 45% yield (Scheme 2). Compound **4** does not dissolve in most of the common organic solvents such as benzene, toluene, THF and CH_3CN but slightly dissolves in DCM. However, **4** in DCM gradually decomposes at room temperature over 2 hrs. In the solid-state, compound **4** can be stored for several months without any significant decomposition at room temperature under inert atmosphere. An X-ray diffraction study (Figure 4) reveals that complex **4** involves two gerymlone units and three Rh metals featuring a Rh–Ge–Rh–Ge–Rh chain. The central Rh2 atom exhibits planar geometry with the sum of the bond angles of 360° . The Ge1 and Ge2 atoms adopt the tetrahedral geometry that coordinate to Rh2 atom in a *trans* position with the Ge1–Rh2–Ge2 bond angle of $172.380(15)^\circ$. Two terminal Rh1 and Rh3 atoms are coordinated by COD units, while the central Rh2 atom is coordinated by the CO. The bond lengths for Ge1–Rh1, Ge1–Rh2, Ge2–Rh2, Ge2–Rh3 are 2.4760(4) Å, 2.4509(4) Å, 2.4611(4) Å, 2.4963(4) Å, respectively, which are comparable to those of **3**. Compared with **3**, slightly smaller bond angles of $137.002(17)^\circ$ for Rh2–Ge1–Rh1 and $136.459(16)^\circ$ for Rh2–Ge2–Rh3 are observed, possibly due to the mitigated steric congestions of the substitutes around the Rh2 centre.

Scheme 2. Synthesis of **4**.

Figure 4. Solid-state structure of **4** (hydrogen atoms, adamantyl (Ad) and mesityl (Mes) groups and solvent molecules are omitted for clarity). Thermal ellipsoids are set at the 50% probability.

The IR spectrum of **4** shows a characteristic CO frequency (ν_{CO}) at 1921 cm^{-1} , which is significantly lower than those (1951 cm^{-1} – 1993 cm^{-1}) of *trans*- $[RhCl(CO)(PR_3)_2]$ complexes supported by common phosphine ligands,²⁰ indicating the relatively strong donor ability of the gerymlone ligand. While the detailed mechanism for the formation of **4** is still unclear, the result represents the first gerymlone-bimetallic complex involving two different metal fragments, indicating the potential coordination ability of gerymlone.

Conclusions

In summary, we have demonstrated that gerymlone **1** is able to react with two group IX metals, delivering the gerymlone bridged bimetallic complexes **2** and **3**, which represents the first examples of the direct dimetallation of gerymlone with transition metals. Thanks to the ability of **1** as a four-electron donor, the formation of complex **4** involving a Rh–Ge–Rh–Ge–Rh chain has also been achieved. Using gerymlones as the synthetic building block, the formation of complexes featuring a longer metal–Ge chain is currently under investigation.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- (a) D. H. Harris and M. F. Lappert, *J. Chem. Soc., Chem. Comm.*, 1974, 895; (b) P. J. Davidson, D. H. Harris and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1976, 2268; (c) M. J. S. Gynane, D. H. Harris, M. F. Lappert, P. P. Power, P. Rivière and M. Rivière-Baudet, *J. Chem. Soc., Dalton Trans.*, 1977, 2004.
- (a) E. Rivard, *Chem. Soc. Rev.*, 2016, **45**, 989; (b) M. Asay, C. Jones and M. Driess, *Chem. Rev.*, 2011, **111**, 354; (c) S. K. Mandal and H. W. Roesky, *Chem. Commun.*, 2010, **46**, 6016; (d) Y. Mizuhata, T. Sasamori and N. Tokitoh, *Chem. Rev.*, 2009, **109**, 3479; (e) A. V. Zabula and F. E. Hahn, *Eur. J. Inorg. Chem.*, 2008, 5165; (f) S. Nagendran and H. W. Roesky, *Organometallics*, 2008, **27**, 457; (g) O. Kühn, *Coord. Chem. Rev.*, 2004, **248**, 411; (h) J. Barrau and G. Rima, *Coord. Chem. Rev.*, 1998, **178-180**, 593; (i) C. Boehme and G. Frenking, *J. Am. Chem. Soc.*, 1996, **118**, 2039.
- (a) V. Nesterov, D. Reiter, P. Bag, P. Frisch, R. Holzner, A. Porzelt and S. Inoue, *Chem. Rev.*, 2018, **118**, 9678; (b) E. Peris, *Chem. Rev.*, 2018, **118**, 9988; (c) M. N. Hopkinson, C. Richter, M. Schedler and F. Glorius, *Nature*, 2014, **510**, 485; (d) D. J. Nelson and S. P. Nolan, *Chem. Soc. Rev.*, 2013, **42**, 6723; (e) T. Dröge and F. Glorius, *Angew. Chem. Int. Ed.*, 2010, **49**, 6940; (f) A. J. Arduengo and G. Bertrand, *Chem. Rev.*, 2009, **109**, 3209.
- (a) J. Böserle, R. Jambor, A. Růžička and L. Dostál, *J. Organomet. Chem.*, 2018, **855**, 44; (b) T. Chu and G. I. Nikonov, *Chem. Rev.*, 2018, **118**, 3608; (c) M. Usher, A. V. Protchenko, A. Rit, J. Campos, E. L. Kolychev, R. Tirfoin and S. Aldridge, *Chem. Eur. J.*, 2016, **22**, 11685; (d) Y. Wu, L. Liu, J. Su, K. Yan, T. Wang, J. Zhu, X. Gao, Y. Gao and Y. Zhao, *Inorg. Chem.*, 2015, **54**, 4423; (e) J. W. Dube, Z. D. Brown, C. A. Caputo, P. P. Power and P. J. Ragogna, *Chem. Commun.*, 2014, **50**, 1944; (f) Z. D. Brown and P. P. Power, *Inorg. Chem.*, 2013, **52**, 6248; (g) P. P. Power, *Nature*, 2010, **463**, 171; (h) Y. Peng, J.-D. Guo, B. D. Ellis, Z. Zhu, J. C. Fettingner, S. Nagase and P. P. Power, *J. Am. Chem. Soc.*, 2009, **131**, 16272.
- (a) J. Böserle, G. Zhigulin, P. Štěpnička, F. Horký, M. Erben, R. Jambor, A. Růžička, S. Ketkov and L. Dostál, *Dalton Trans.*, 2017, **46**, 12339; (b) J. Böserle, M. Alonso, R. Jambor, A. Růžička and L. Dostál, *RSC Adv.*, 2016, **6**, 19377; (c) M. Walewska, J. Hlina, J. Baumgartner, T. Müller and C. Marschner, *Organometallics*, 2016, **35**, 2728; (d) H. Arij, T. Amari, J. Kobayashi, K. Mochida and T. Kawashima, *Angew. Chem. Int. Ed.*, 2012, **51**, 6738; (e) A. Sekiguchi, R. Izumi, S. Ihara, M. Ichinohe and V. Y. Lee, *Angew. Chem. Int. Ed.*, 2002, **41**, 1598; (f) W. Ando, H. Ohgaki and Y. Kabe, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 659.
- (a) M. K. Sharma, S. Sinhababu, D. Yadav, G. Mukherjee, G. Rajaraman and S. Nagendran, *Chem. – Asian J.*, 2018, **13**, 1357; (b) N. Deak, P. M. Petrar, S. Mallet-Ladeira, L. Silaghi-Dumitrescu, G. Nemeş and D. Madec, *Chem. Eur. J.*, 2016, **22**, 1349; (c) L. Álvarez-Rodríguez, J. A. Cabeza, P. García-Álvarez and D. Polo, *Coord. Chem. Rev.*, 2015, **300**, 1; (d) J. Hlina, H. Arp, M. Walewska, U. Flörke, K. Zangger, C. Marschner and J. Baumgartner, *Organometallics*, 2014, **33**, 7069; (e) J. Hlina, J. Baumgartner, C. Marschner, P. Zark and T. Müller, *Organometallics*, 2013, **32**, 3300; (f) S. M. I. Al-Rafia, M. R. Momeni, M. J. Ferguson, R. McDonald, A. Brown and E. Rivard, *Organometallics*, 2013, **32**, 6658; (g) D. Matioszek, N. Katir, N. Saffon and A. Castel, *Organometallics*, 2010, **29**, 3039; (h) O. Kühn, P. Lönnecke and J. Heinicke, *Inorg. Chem.*, 2003, **42**, 2836; (i) Z. T. Cygan, Bender, K. E. Litz, J. W. Kampf and M. M. Banaszak Holl, *Organometallics*, 2002, **21**, 5373; (j) P. Bazinet, G. P. A. Yap and D. S. Richeson, *J. Am. Chem. Soc.*, 2001, **123**, 11162.
- N. Takagi, T. Shimizu and G. Frenking, *Chem. Eur. J.*, 2009, **15**, 8593.
- (a) P. K. Majhi and T. Sasamori, *Chem. Eur. J.*, 2018, **24**, 9441; (b) S. Yao, Y. Xiong and M. Driess, *Acc. Chem. Res.*, 2017, **50**, 2026.
- T. Iwamoto, H. Masuda, C. Kabuto and M. Kira, *Organometallics*, 2005, **24**, 197.
- Y. Xiong, S. Yao, G. Tan, S. Inoue and M. Driess, *J. Am. Chem. Soc.*, 2013, **135**, 5004.
- Y. Li, K. C. Mondal, H. W. Roesky, H. Zhu, P. Stollberg, R. Herbst-Irmer, D. Stalke and D. M. Andrada, *J. Am. Chem. Soc.*, 2013, **135**, 12422.
- T. Chu, L. Belding, A. van der Est, T. Dudding, I. Korobkov and G. I. Nikonov, *Angew. Chem. Int. Ed.*, 2014, **53**, 2711.
- Y.-P. Zhou, M. Karni, S. Yao, Y. Apeloig and M. Driess, *Angew. Chem. Int. Ed.*, 2016, **55**, 15096.
- D. Mandal, D. Dhara, A. Maiti, L. Klemmer, V. Huch, M. Zimmer, H. S. Rzepa, D. Scheschkewitz and A. Jana, *Chem. Eur. J.*, 2018, **24**, 2873.
- Y. Wang, M. Karni, S. Yao, Y. Apeloig and M. Driess, *J. Am. Chem. Soc.*, 2019, DOI: 10.1021/jacs.8b11605.
- (a) B. Su, R. Ganguly, Y. Li and R. Kinjo, *Angew. Chem. Int. Ed.*, 2014, **53**, 13106; (b) B. Su, R. Ganguly, Y. Li and R. Kinjo, *Chem. Commun.*, 2016, **52**, 613.
- (a) J. Brugos, J. A. Cabeza, P. García-Álvarez and E. Pérez-Carreño, *Organometallics*, 2018, **37**, 1507; (b) M. L. B. Ismail, F.-Q. Liu, W.-L. Yim, R. Ganguly, Y. Li and C.-W. So, *Inorg. Chem.*, 2017, **56**, 5402; (c) M. H. Mobarok, R. McDonald, M. J. Ferguson and M. Cowie, *Inorg. Chem.*, 2012, **51**, 4020; (d) M. H. Mobarok, R. McDonald, M. J. Ferguson and M. Cowie, *Inorg. Chem.*, 2012, **51**, 9249; (e) R. D. Adams, F. Fang, Q. Zhang, M. B. Hall and E. Trufan, *Organometallics*, 2012, **31**, 2621; (f) R. D. Adams, B. Captain and J. L. Smith, *Inorg. Chem.*, 2005, **44**, 1413.
- (a) L. Álvarez-Rodríguez, J. A. Cabeza, J. M. Fernández-Colinas, P. García-Álvarez and D. Polo, *Organometallics*, 2016, **35**, 2516; (b) D. Matioszek, N. Saffon, J.-M. Sotiropoulos, K. Miqueu, A. Castel and J. Escudié, *Inorg. Chem.*, 2012, **51**, 11716; (c) J. M. García, E. Ocampo-Mavárez, T. Kato, D. S. Coll, A. Briceño, N. Saffon-Merceron and A. Baceiredo, *Inorg. Chem.*, 2012, **51**, 8187; (d) M. Veith, A. Müller, L. Stahl, M. Nötzel, M. Jarczyk and V. Huch, *Inorg. Chem.*, 1996, **35**, 3848.
- (a) S. S. Batsanov, *Inorg. Mater.*, 2001, **37**, 871; (b) S.S. Batsanov, *Neorg. Mater.*, 2001, **37**, 1031.
- D. Gudmunson, E. G. Hope, D. R. Paige and A. M. Stuart, *J. Fluorine Chem.*, 2009, **130**, 942.