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Cumulative 2c–2e *vs.* 3c–2e π-back donations: conformation preferences in germylene gold(I) complexes†

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The first homoleptic and heteroleptic cationic germylene-gold(I) complexes **3**, **4**, and **7** have been synthesized and structurally characterized, accompanied by the discovery of novel types of π-back donations. These complexes exhibit distinct conformation preferences (vertical *vs.* quasi-planar) modulated by the π-acceptor capacity of germylene and NHC ligands. Our bonding analyses further indicated that the homoleptic complex **3** exhibits marvellous cumulative two-center–two-electron (2c–2e) π-back donations, whereas the heteroleptic complexes **4** and **7** demonstrate extraordinary three-center–two-electron (3c–2e) π-back donations. These findings offer a comprehensive explanation for the atypical disruption of extensive π-systems, along with the transition from quasi-planar to vertical conformations.

Introduction

Molecular structures are fundamentally governed by the nature of chemical bonds between atoms and the electronic distribution within the molecule. A comprehensive understanding of molecular reactivity and catalytic activity necessitates a thorough elucidation of its structural properties, which can be comprehensively characterized through both experimental and theoretical investigations.[1,2] As an illustrative example, *N*-heterocyclic carbenes (NHCs) have become prevalent neutral ligands in coordination chemistry over recent decades.[3–8] Since Arduengo's pioneering work on the first isolation of NHC in 1991,[9] numerous homoleptic NHC metal complexes have been synthesized and characterized,[10–15] primarily motivated by their applications in various transformations,[16–19] providing access to crucial building blocks for organic synthesis and catalysis,[20,21] as well as antitumor and antimicrobial agents.[22–24]

Regarding the conformations of these complexes, the majority (Fig. 1a, **I**) display a quasi-planar arrangement of carbene ligands within their crystal structures,[25–30] whereas a minority adopt a vertical configuration, driven by the necessity of minimizing steric repulsion between the coordinated ligands.[31–36] The leaning for taking quasi-planar geometries is

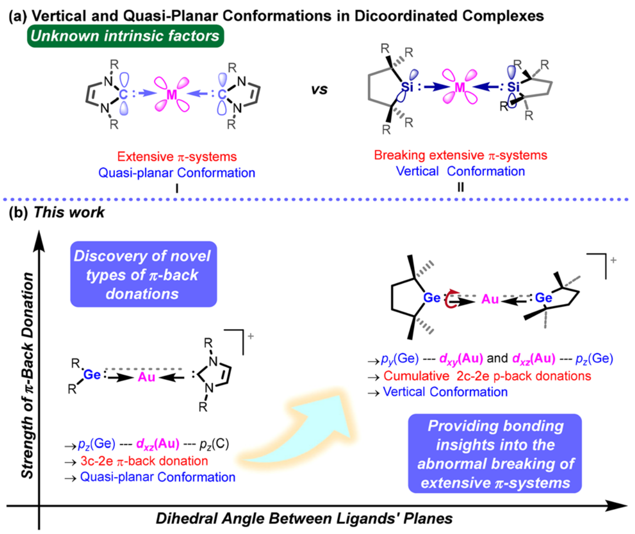

Fig. 1 Representative examples of structurally characterized dicoordinated metal complexes exhibiting vertical and quasi-planar geometries include: (a) dicoordinated NHC and dialkylsilylene metal complexes; and (b) this work: the homoleptic and heteroleptic dicoordinated germylene gold(I) complexes, where these conformation preferences are tuned by ligand's π-acceptor capacity and types of π-back donations.

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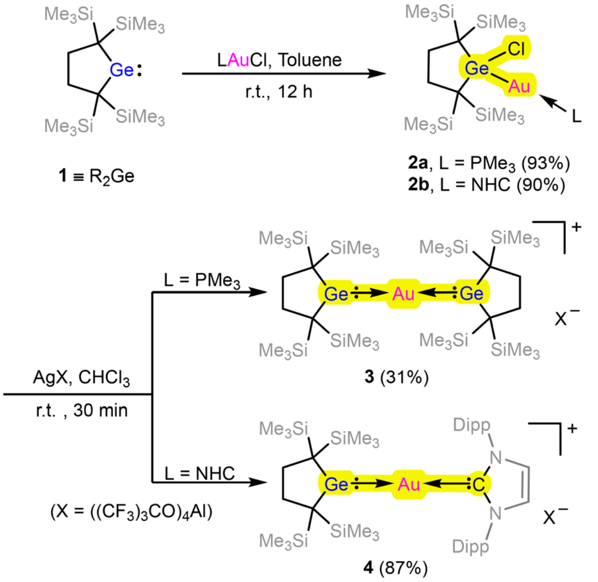
again pronounced in cyclic(alkyl)(amino)carbene (CAAC) metal complexes,[37–46] and cyclic (alkyl)(amino)germylene (CAAGe) metal complexes.[47] The tendency to adopt a quasi-planar geometry in these complexes should arise from the enhanced stability provided by the extensive π-systems formed in such conformation.

While this inclination is generally considered reasonable, dialkylsilylene, one of the strongest π-acceptor silylene ligands,[48] constitutes an exception. Three dicoordinated metal complexes (Fig. 1a, **II**) of dialkylsilylene have been isolated and characterized by Iwamoto and coworkers,[49–51] all exhibiting vertical geometry. These complexes engender a different conformation preference from the aforementioned NHC examples. The atypical breaking of extensive π-systems evokes our interests. To date, the essential determinants of such phenomena remain elusive. Furthermore, despite the burgeoning interest in gold(I)-main group chemistry,[52–55] the conformational preferences are underexplored.

Herein, we report the synthesis and structural characterization of both homoleptic and heteroleptic cationic germylene gold(I) complexes derived from dialkyl- and acyclic diaminogermylene (Fig. 1b), which exhibit vertical and quasi-planar geometry respectively. The selection of ligands is driven by the versatile bonding capacity of germylenes in the formation of transition metal complexes.[56–65] Additionally, the choice of gold(I) metal centers leverages the advantage of d^{10} shell, facilitating the construction of stable dicoordinated metal complexes, whether in a vertical or quasi-planar arrangement. Investigation of these homoleptic and heteroleptic complexes with varying conformations helps to uncover the intrinsic factors that determine conformation preferences (vertical *vs.* quasi-planar). Our bonding analyses further discovered two novel types of π-back donations, the unique cumulative two-center–two-electron (2c–2e) π-back donations among homoleptic complexes as well as the unprecedented three-center–two-electron (3c–2e) π-back donation among heteroleptic complexes. These findings afford a profound bonding insight into the impressive phenomenon of conformation preference, providing explanations for the unusual disruption of vast π-systems.

Results and discussion

As reported previously,[64,65] dialkylgermylene[66] (R_2Ge:) **1** is smoothly inserted into the Au–Cl bond of chlorotrimethylphosphinegold(I) (Me_3PAuCl) and chloro[1,3-bis(2,6-diisopropylphenyl)imidazoline-2-ylidene] gold(I) (NHCAuCl), respectively, in toluene at ambient temperature, yielding germylgolds **2a** (L = PMe_3) and **2b** (L = NHC) as off-white powders in high yields (Scheme 1). Germylgold **2a** subsequently reacts with $Ag[Al(OC(CF_3)_3)_4]$ at room temperature for 30 minutes, resulting in the formation of the first homoleptic cationic digermylene gold(I) complex **3** in 31% isolated yield as a white solid (Scheme 1). We propose that the formation of **3** involves the generation of a transient heteroleptic cationic gold(I) complex coordinated by both R_2Ge **1** and PMe_3, which subsequently decomposes to generate the more stable homoleptic cationic gold(I) complex **3**. The heteroleptic cationic germylene gold(I) complex **4** is obtained in 87% yield from germylgold **2b** *via* a similar process (Scheme 1).



Scheme 1 Synthesis of homoleptic and heteroleptic cationic germylene gold(I) complexes **3** and **4**.

Alternative chloride abstraction reagents, including AgOTf, $AgBF_4$, and $AgPF_6$, were explored under identical conditions; however, these attempts proved unsuccessful in isolating homoleptic or heteroleptic cationic germylene gold(I) complexes. The difference in reactivity between **2a** and **2b** can be attributed to the stronger σ-donating character of NHCs compared to even electron-rich phosphines such as tBu_3P.[67] This enhanced carbene-gold interaction, further strengthened by the involvement of the empty p-orbital of NHC in bonding within heteroleptic gold(I) complexes **4**, contributes to their increased resistance to dissociation. Experimental details are provided in the ESI.†

Both **2b**, **3** and **4** are isolated as pure materials and characterized by multinuclear NMR spectroscopy and single-crystal X-ray diffraction analysis (Fig. 2 and S1†).[68] The Ge1–Au1 bond

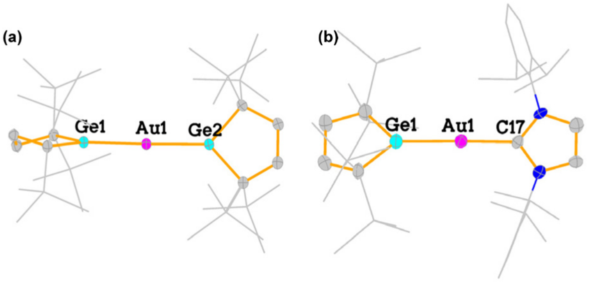


Fig. 2 Solid structures of **3** (a) and **4** (b). Thermal ellipsoids are shown at 30% probability level. Hydrogen atoms and $Al(OC(CF_3)_3)_4$ anion are omitted in **3** and **4** for clarity.

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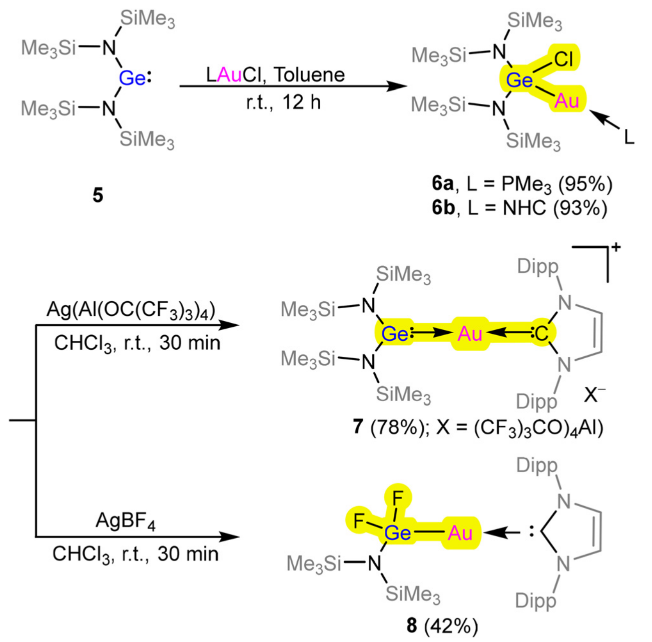
lengths of **3** (2.3798(4) Å) are remarkably shorter than those of **2a** (2.4159(5) Å), **2b** (2.4055(8) Å) and **4** (2.3848(11) Å), which suggests that **3** exhibits a stronger π-back donation compared to **4**. The observed Ge1–Au1–Ge2 angles of 178.169(16)° in **3** indicate a linear coordination geometry, consistent with the expected structure for two-coordinate gold(I) species. The Ge1–Au1–C17 angles of 177.4(2)° in **4** suggest a linear coordination geometry, consistent with that of **II** (176.62(15)°).[47] The dihedral angle of **3** between the C–Ge–C plane of dialkylgermylene moieties is 83.643°, indicating that these two planes are almost perpendicular to each other. Moreover, this dihedral angle of **4** (39.766°) is comparable to that of **II** (31.335°),[47] suggesting quasi-planar geometries.

The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of **3** and **4**, acquired at ambient temperature, align with the structural assignments of X-ray crystallography. In ^{1}H NMR spectrum of **3**, the trimethylsilyl protons exhibit a singlet resonance at 0.31 ppm (Fig. S11†). In contrast, these protons are observed as two singlets at 0.51 ppm and 0.60 ppm for **2a**.[64] The CH_2 protons of the five-membered ring are observed at 2.55 ppm in **3** and at 2.20 ppm in **4** (Fig. S15†). The ^{1}H NMR spectrum of **4** exhibits a multiplet at 2.61–2.54 ppm, assignable to the CH protons of the isopropyl groups in the NHC ligand. This signal is shifted downfield relative to the corresponding signal in **II**, which appears at 2.45–2.28 ppm.[47]

To further investigate the effects of different germylene ligands on the structural properties of heteroleptic cationic germylene gold(I) complexes, acyclic diaminogermylene **5** was employed to synthesize the germylgold complexes **6a** and **6b** through a comparable process (Scheme 2).[69] Upon treatment of germylgold **6a** with Ag[Al(OC(CF_3)$_3$)$_4$] at room temperature, decomposition was observed. We propose a mechanism involving the initial formation of a transient heteroleptic gold(I) complex coordinated by both germylene **5** and PMe_3. However, this intermediate species is not stable enough, preventing its isolation. The heteroleptic cationic germylene gold(I) complex **7** is obtained in 78% yield from germylgold **6b** *via* a similar process. Under identical conditions, the reaction of **6b** with $AgBF_4$ unexpectedly yielded germylgold **8** *via* B–F bond activation, rather than the expected analogue of **7** (Scheme 2). This result suggests that the heteroleptic cationic germylene gold(I) complex acts as a Lewis acid, facilitating B–F bond activation.



Scheme 2 Synthesis and reactivity studies of germylgolds **6** toward different silver salts.

6a, **6b**, **7**, and **8** were also isolated and fully characterized by multinuclear NMR spectroscopy and single-crystal X-ray diffraction (Fig. 3, S2 and S3†).[64] The Ge1–Au1 bond lengths of **7** (2.3780(8) Å) are remarkably shorter than those of **6a** (2.4127(3) Å) and **6b** (2.4064(4) Å), but comparable to are comparable to those in **4** (2.3848(11) Å) and **8** (2.3668(27) Å). The nearly linear coordination geometry of **7** and **8**, with angles of Ge1–Au1–C2 angle of 177.7° and 168.0° respectively, is comparable to that of **4** (177.4°). The germylene and NHC moieties of **7** exhibit quasi-planar geometries, with a dihedral angle of 14.608°.

Bonding analysis

To elucidate the nature of π-back donation in complexes **3**, **4**, and **7**, comprehensive bonding analyses were performed. The gold centers in these complexes can be formally assigned an oxidation state of +1, resulting in a $5d^{10}$ electron configuration. Consequently, the sp^2 lone pairs of the carbene and germylene ligands are expected to donate into the sp orbitals of the gold centers, forming cumulative σ-bonds (Fig. 4a–c). However, the nature of the π-back donation differs significantly among these complexes, concomitant with conformational variations. In complex **3**, a pair of cumulative two-center–two-electron (2c–2e) π-back donation interactions are proposed. This involves donation from the d_{xz} (Au) lone pair into the p_z (Ge) orbital of one germylene ligand, and concurrently, donation from the d_{xy} (Au) lone pair into the p_y (Ge) orbital of the opposing germy-

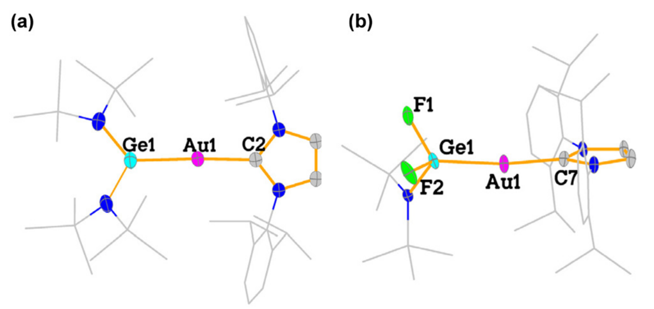


Fig. 3 Solid structures of **7** (a) and **8** (b). Thermal ellipsoids are shown at 30% probability level. Hydrogen atoms are omitted in **7** and **8**; while the Al(OC(CF_3)$_3$)$_4$ anion is omitted in **7** for clarity.

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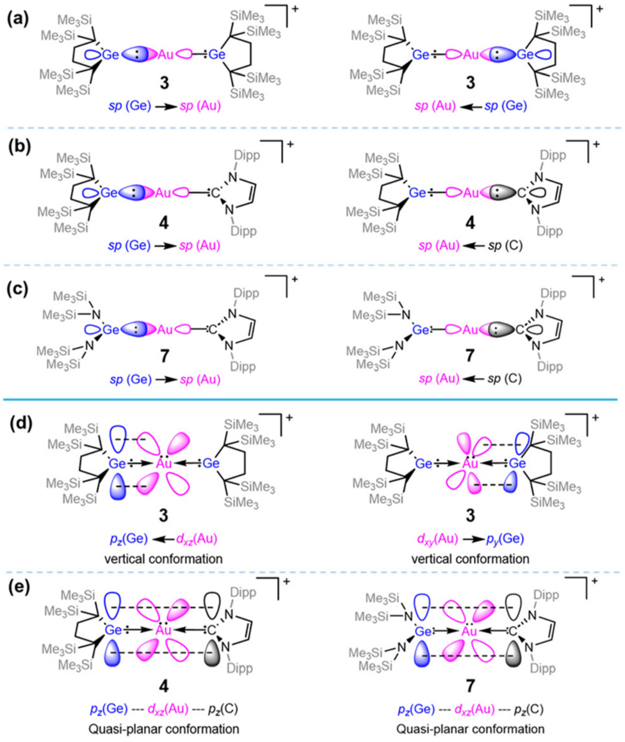

Fig. 4 Orbital interactions between Au centers and coordinating atoms. σ dative bonds in complexes **3** (a), **4** (b), and **7** (c), along with their contributing orbitals. Cumulative 2c–2e π-back donations in complex **3** (d) and 3c–2e π-back donations in complexes **4** and **7** (e), along with their contributing orbitals.

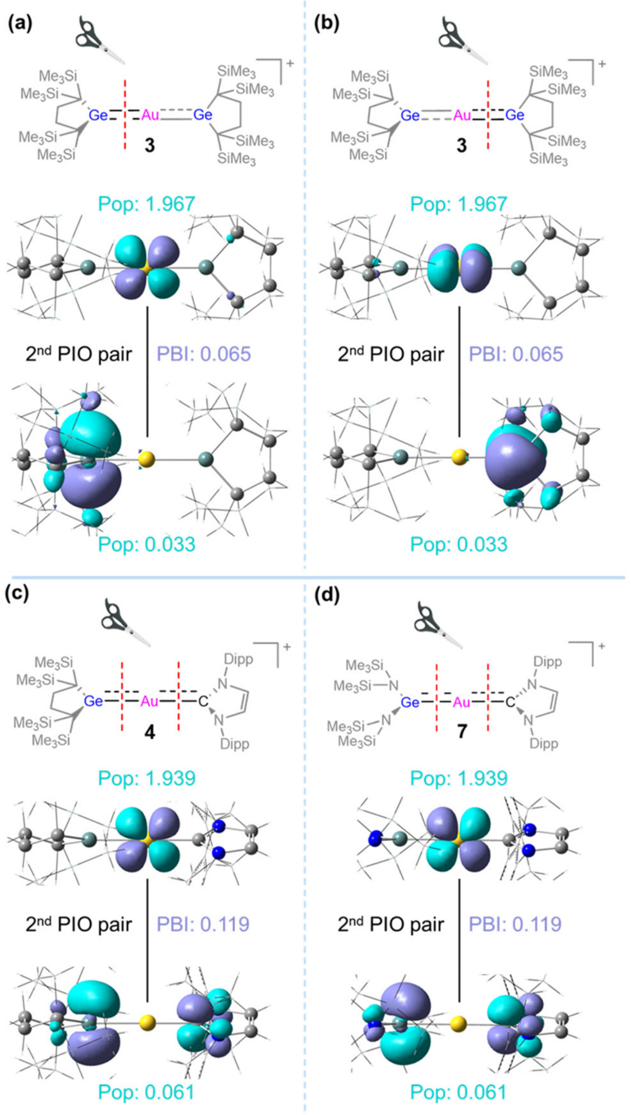

Fig. 5 Selected principal interacting with orbital (PIO) plots (isovalue = 0.05). PIO pairs representing cumulative 2c–2e π-back donations in complex **3** (a and b), with corresponding populations (Pop) and PIO-based bond indices (PBI). PIO pairs representing 3c–2e π-back donations in complexes **4** (c) and **7** (d), with corresponding populations (Pop) and PIO-based bond indices (PBI).

lene ligand (Fig. 4d). In contrast, complexes **4** and **7** exhibit a three-center–two-electron (3c–2e) π-back donation. Specifically, the d_{xz} (Au) lone pair is delocalized over the p_z (Ge) orbitals of both germylene ligands (Fig. 4e). These observed differences in π-back donation could be attributed to the varying π-acceptor capabilities of the carbene and germylene ligands. Dialkylgermylene ligand, owing to greater electronegativity, generally exhibits stronger π-acceptor properties compared to NHC ligands. As the π-electron acceptor capacity of ligand increases, the stabilization afforded by cumulative 2c–2e π-back donation is enhanced, thereby promoting a deviation from quasi-planar geometry in two-coordinate gold(I) complexes and disrupting extended π-conjugation.

We further conducted the principal interacting orbital (PIO) analysis to generate chemically interpretable orbital plots and to assess bonding strength using PIO-based bond indices (PBI).[70,71] As illustrated in Fig. 5a and b, the two PIO pairs represent the cumulative 2c–2e π-back donations among complex **3**, aligning with the preceding bonding analyses. Additionally, Fig. 5c and d displays the π interactions between Au centers and coordinating ligands within complexes **4** (Fig. 5c) and **7** (Fig. 5d), further certifying the presence of 3c–2e π-back donations. The PBI for each PIO pair corresponding to 2c–2e π-back donation in complex **3** is 0.065 (cumulative PBI = 0.130), while in complexes **4** and **7**, the PBI for each PIO pair pertaining to 3c–2e π-back donation is 0.119. This analysis suggests that complex **3** would exhibit enhanced stability derived from π-back donation interactions compared to complexes **4** and **7**. Additionally, to investigate whether the chloroform solvent would influence the strength of π-back donations, we further performed the PIO analysis in the presence of SMD solvation model (Fig. S10†).[72] Remarkably, the PBI for each PIO pair associated with 2c–2e π-back donation in complex **3** is 0.067 (cumulative PBI = 0.134), whereas the PBI for each PIO pair related to 3c–2e π-back donation is 0.123. The relatively larger PBI confirms that the presence of polar solvent would facilitate the π-back donations.

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Conclusions

In summary, we report the synthesis and characterization of the first homoleptic and heteroleptic cationic germylene-gold(I) complexes (**3**, **4**, and **7**), characterized by distinct conformation conformations (vertical *vs.* quasi-planar). By investigating these complexes, we have revealed that the conformation preferences in such dicoordinated metal complexes are tuned by the π-acceptor capabilities of enveloping ligands. Our bonding analyses have further revealed two extraordinary types of π-back donations, cumulative 2c–2e π-back donations in homoleptic complexes, as well as 3c–2e π-back donations in heteroleptic complexes. These findings offer intrinsic bonding insights into why the established trend of forming extensive π-systems through quasi-planar geometry can be broken to afford a vertical conformation. Moreover, the germylene-gold(I) complexes demonstrated the B–F bond activation, highlighting their potential in the field of catalysis and coordination chemistry.

Author contributions

L. W. directed the research. L. W. and L. K. conceived and designed the experiments. J. L. conducted and analyzed the X-ray diffraction data. J. C. and L. W. performed and analyzed the DFT calculations. L. W., R. Z., X. W., W. Z., L. Z., and Y. G. performed the synthetic experiments. L. W. contributed to the writing of the manuscript. J. C. and L. W. revised the manuscript. All authors discussed the results and contributed to the preparation of the final manuscript.

Data availability

All experimental procedures, computational sections, and associated data are included in the article and ESI.†

The data supporting this article have been included as part of the ESI.†

Crystallographic data for [**2b**, **3**, **4**, **6a**, **6b**, **7**, and **8**] has been deposited at the CCDC under [accession number: 2401588, 2401589, 2401590, 2401591, 2401592, 2401593 and 2401594] contains the supplementary crystallographic data for this paper.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References

1 A. J. Pounds, Valency and Bonding: A Natural Bond Orbital Donor–Acceptor Perspective (Frank Weinhold and Clark Landis), *J. Chem. Educ.*, 2007, **84**, 43.
2 F. Weinhold and C. R. Landis, *Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective*, Cambridge University Press, Cambridge, 2005.
3 J. Vignolle, X. Cattoën and D. Bourissou, Stable Noncyclic Singlet Carbenes, *Chem. Rev.*, 2009, **109**, 3333–3384.
4 C. D. Martin, M. Soleilhavoup and G. Bertrand, Carbene-stabilized main group radicals and radical ions, *Chem. Sci.*, 2013, **4**, 3020–3030.
5 A. J. Arduengo and G. Bertrand, Carbenes Introduction, *Chem. Rev.*, 2009, **109**, 3209–3210.
6 D. Bourissou, O. Guerret, F. P. Gabbaï and G. Bertrand, Stable Carbenes, *Chem. Rev.*, 2000, **100**, 39–92.
7 D. Martin, M. Soleilhavoup and G. Bertrand, Stable singlet carbenes as mimics for transition metal centers, *Chem. Sci.*, 2011, **2**, 389–399.
8 C. S. J. Cazin, *N-Heterocyclic Carbenes in Transition Metal Catalysis and Organocatalysis*, Springer Science+Business Media B.V., Dordrecht, 2011.
9 A. J. Arduengo III, R. L. Harlow and M. Kline, A stable crystalline carbene, *J. Am. Chem. Soc.*, 1991, **113**, 361–363.
10 J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang and I. J. B. Lin, Coinage Metal−N-Heterocyclic Carbene Complexes, *Chem. Rev.*, 2009, **109**, 3561–3598.
11 S. Guo, H. Sivaram, D. Yuan and H. V. Huynh, Gold and Palladium Hetero-Bis-NHC Complexes: Characterizations, Correlations, and Ligand Redistributions, *Organometallics*, 2013, **32**, 3685–3696.
12 P. C. Kunz, C. Wetzel, S. Kögel, M. U. Kassack and B. Spingler, $[(C_3H_4N_2)_2Au]Cl$—a bis protic gold(I)-NHC, *Dalton Trans.*, 2011, **40**, 35–37.
13 A. Priante-Flores, V. Salazar-Pereda, A. L. Rheingold and D. Mendoza-Espinosa, Synthesis and characterization of a gold(I) bis(triazolylidene) complex featuring a large $[(TpMe_2)_2K]$ anion, *New J. Chem.*, 2018, **42**, 15533–15537.
14 W. Liu, K. Bensdorf, M. Proetto, A. Hagenbach, U. Abram and R. Gust, Synthesis, Characterization, and in Vitro Studies of Bis[1,3-diethyl-4,5-diarylimidazol-2-ylidene]gold (I/III) Complexes, *J. Med. Chem.*, 2012, **55**, 3713–3724.
15 J. Ruiz, L. García, D. Sol and M. Vivanco, Template Synthesis, Metalation, and Self-Assembly of Protic Gold(I)/$(NHC)_2$ Tectons Driven by Metallophilic Interactions, *Angew. Chem., Int. Ed.*, 2016, **55**, 8386–8390.
16 H. Jacobsen, A. Correa, A. Poater, C. Costabile and L. Cavallo, Understanding the M(NHC) (NHC=N-heterocyclic carbene) bond, *Coord. Chem. Rev.*, 2009, **253**, 687–703.
17 S. Díez-González and S. P. Nolan, Copper, Silver, and Gold Complexes in Hydrosilylation Reactions, *Acc. Chem. Res.*, 2008, **41**, 349–358.
18 M. Rudolph and A. S. K. Hashmi, Gold catalysis in total synthesis—an update, *Chem. Soc. Rev.*, 2012, **41**, 2448–2462.

Published on 24 April 2025. Downloaded by Yunnan University on 8/2/2025 2:53:59 PM.

19 S. Gaillard, C. S. J. Cazin and S. P. Nolan, N-Heterocyclic Carbene Gold(I) and Copper(I) Complexes in C–H Bond Activation, *Acc. Chem. Res.*, 2012, **45**, 778–787.

20 D. J. Nelson and S. P. Nolan, Quantifying and understanding the electronic properties of N-heterocyclic carbenes, *Chem. Soc. Rev.*, 2013, **42**, 6723–6753.

21 P. de Frémont, N. Marion and S. P. Nolan, Carbenes: Synthesis, properties, and organometallic chemistry, *Coord. Chem. Rev.*, 2009, **253**, 862–892.

22 W. Liu and R. Gust, Metal N-heterocyclic carbene complexes as potential antitumor metallodrugs, *Chem. Soc. Rev.*, 2013, **42**, 755–773.

23 D. Tapu, D. A. Dixon and C. Roe, ^{13}C NMR Spectroscopy of "Arduengo-type" Carbenes and Their Derivatives, *Chem. Rev.*, 2009, **109**, 3385–3407.

24 I. J. B. Lin and C. S. Vasam, Preparation and application of N-heterocyclic carbene complexes of Ag(I), *Coord. Chem. Rev.*, 2007, **251**, 642–670.

25 H. M. J. Wang, C. Y. L. Chen and I. J. B. Lin, Synthesis, Structure, and Spectroscopic Properties of Gold(I)−Carbene Complexes, *Organometallics*, 1999, **18**, 1216–1223.

26 K. Arentsen, S. Caddick, F. G. N. Cloke, A. P. Herring and P. B. Hitchcock, Suzuki–Miyaura cross-coupling of aryl and alkyl halides using palladium/imidazolium salt protocols, *Tetrahedron Lett.*, 2004, **45**, 3511–3515.

27 G. J. Kruger, P. J. Olivier, R. Otte and H. G. Raubenheimer, Bis[bis(4-methylthiazolin-2-ylidene)gold(I)] Tetrachlorozincate Dichloromethane, *Acta Crystallogr., Sect. C:Cryst. Struct. Commun.*, 1996, **52**, 1159–1161.

28 A. J. Arduengo III, D. Tapu and W. J. Marshall, The Generation of a Metallocene-Fused Imidazol-2-ylidene and Its Mercury Complex, *Angew. Chem., Int. Ed.*, 2005, **44**, 7240–7244.

29 K. Chen, M. M. Nenzel, T. M. Brown and V. J. Catalano, Luminescent Mechanochromism in a Gold(I)–Copper(I) N-Heterocyclic Carbene Complex, *Inorg. Chem.*, 2015, **54**, 6900–6909.

30 Q.-X. Liu, L.-N. Yin, X.-M. Wu, J.-C. Feng, J.-H. Guo and H.-B. Song, New N-heterocyclic carbene mercury(II) and silver(I) complexes, *Polyhedron*, 2008, **27**, 87–94.

31 A. J. Arduengo III, S. F. Gamper, J. C. Calabrese and F. Davidson, Low-Coordinate Carbene Complexes of Nickel (0) and Platinum(0), *J. Am. Chem. Soc.*, 1994, **116**, 4391–4394.

32 D. Marchione, L. Belpassi, G. Bistoni, A. Macchioni, F. Tarantelli and D. Zuccaccia, The Chemical Bond in Gold (I) Complexes with N-Heterocyclic Carbenes, *Organometallics*, 2014, **33**, 4200–4208.

33 C. W. K. Gstöttmayr, V. P. W. Böhm, E. Herdtweck, M. Grosche and W. A. Herrmann, A Defined N-Heterocyclic Carbene Complex for the Palladium-Catalyzed Suzuki Cross-Coupling of Aryl Chlorides at Ambient Temperatures, *Angew. Chem., Int. Ed.*, 2002, **41**, 1363–1365.

34 P. L. Arnold, F. G. N. Cloke, T. Geldbach and P. B. Hitchcock, Metal Vapor Synthesis as a Straightforward Route to Group 10 Homoleptic Carbene Complexes, *Organometallics*, 1999, **18**, 3228–3233.

35 J. Du, W. Chen, Q. Chen, X. Leng, Y.-S. Meng, S. Gao and L. Deng, Reactivity of a Two-Coordinate Cobalt(0) Cyclic (Alkyl)(amino)carbene Complex, *Organometallics*, 2020, **39**, 729–739.

36 K. C. Mondal, P. P. Samuel, Y. Li, H. W. Roesky, S. Roy, L. Ackermann, N. S. Sidhu, G. M. Sheldrick, E. Carl, S. Demeshko, S. De, P. Parameswaran, L. Ungur, L. F. Chibotaru and D. M. Andrada, A Catalyst with Two-Coordinate Nickel: Theoretical and Catalytic Studies, *Eur. J. Inorg. Chem.*, 2014, **2014**, 818–823.

37 G. D. Frey, R. D. Dewhurst, S. Kousar, B. Donnadieu and G. Bertrand, Cyclic (alkyl)(amino)carbene gold(I) complexes: A synthetic and structural investigation, *J. Organomet. Chem.*, 2008, **693**, 1674–1682.

38 P. Jerabek, H. W. Roesky, G. Bertrand and G. Frenking, Coinage Metals Binding as Main Group Elements: Structure and Bonding of the Carbene Complexes [TM(cAAC)$_2$] and [TM(cAAC)$_2$]$^+$ (TM = Cu, Ag, Au), *J. Am. Chem. Soc.*, 2014, **136**, 17123–17135.

39 D. Bawari, S. K. Thakur, K. K. Manar, B. Goswami, V. R. Sabari, A. R. Choudhury and S. Singh, Syntheses and characterization of neutral and cationic cyclic (alkyl)(amino)carbene mercury [cAAC-Hg(II)] complexes, *J. Organomet. Chem.*, 2019, **880**, 108–115.

40 A. S. Romanov and M. Bochmann, Synthesis, structures and photoluminescence properties of silver complexes of cyclic (alkyl)(amino)carbenes, *J. Organomet. Chem.*, 2017, **847**, 114–120.

41 L. Tendera, M. S. Luff, I. Krummenacher and U. Radius, Cationic Nickel d9-Metalloradicals [Ni(NHC)$_2$]$^+$, *Eur. J. Inorg. Chem.*, 2022, **2022**, e202200416.

42 A. P. Singh, P. P. Samuel, H. W. Roesky, M. C. Schwarzer, G. Frenking, N. S. Sidhu and B. Dittrich, A Singlet Biradicaloid Zinc Compound and Its Nonradical Counterpart, *J. Am. Chem. Soc.*, 2013, **135**, 7324–7329.

43 P. P. Samuel, K. C. Mondal, H. W. Roesky, M. Hermann, G. Frenking, S. Demeshko, F. Meyer, A. C. Stückl, J. H. Christian, N. S. Dalal, L. Ungur, L. F. Chibotaru, K. Pröpper, A. Meents and B. Dittrich, Synthesis and Characterization of a Two-Coordinate Manganese Complex and its Reaction with Molecular Hydrogen at Room Temperature, *Angew. Chem., Int. Ed.*, 2013, **52**, 11817–11821.

44 D. S. Weinberger, N. Amin SK, K. C. Mondal, M. Melaimi, G. Bertrand, A. C. Stückl, H. W. Roesky, B. Dittrich, S. Demeshko, B. Schwederski, W. Kaim, P. Jerabek and G. Frenking, Isolation of Neutral Mononuclear Copper Complexes Stabilized by Two Cyclic (Alkyl)(amino)carbenes, *J. Am. Chem. Soc.*, 2014, **136**, 6235–6238.

45 Z. Mo, Z. Ouyang, L. Wang, K. L. Fillman, M. L. Neidig and L. Deng, Two- and three-coordinate formal iron(I) compounds featuring monodentate aminocarbene ligands, *Org. Chem. Front.*, 2014, **1**, 1040–1044.

46 P. P. Samuel, K. C. Mondal, N. Amin SK, H. W. Roesky, E. Carl, R. Neufeld, D. Stalke, S. Demeshko, F. Meyer, L. Ungur, L. F. Chibotaru, J. Christian, V. Ramachandran,

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J. van Tol and N. S. Dalal, Electronic Structure and Slow Magnetic Relaxation of Low-Coordinate Cyclic Alkyl(amino) Carbene Stabilized Iron(I) Complexes, *J. Am. Chem. Soc.*, 2014, **136**, 11964–11971.

47 Z. Feng, L. Wang, S. N. B. S. Mohammed, B. Rao and R. Kinjo, Reactivity of Cyclic (Alkyl)(amino)germylene towards Copper(I) and Gold(I) Complexes, *Chem. – Asian J.*, 2023, **18**, e202300634.

48 L. Wang, Y. Li, Z. Li and M. Kira, Isolable silylenes and their diverse reactivity, *Coord. Chem. Rev.*, 2022, **457**, 214413.

49 S. Abe, Y. Inagawa, R. Kobayashi, S. Ishida and T. Iwamoto, Silyl(silylene) Coinage Metal Complexes Obtained from Isolable Cyclic Alkylsilylenes, *Organometallics*, 2022, **41**, 874–882.

50 Y. Inagawa, S. Ishida and T. Iwamoto, Two-coordinate Dialkylsilylene–Coinage Metal Complexes, *Chem. Lett.*, 2014, **43**, 1665–1667.

51 C. Watanabe, T. Iwamoto, C. Kabuto and M. Kira, Fourteen-Electron Bis(dialkylsilylene)palladium and Twelve-Electron Bis(dialkylsilyl)palladium Complexes, *Angew. Chem., Int. Ed.*, 2008, **47**, 5386–5389.

52 T. J. Hadlington, Heavier tetrylene- and tetrylyne-transition metal chemistry: it's no carbon copy, *Chem. Soc. Rev.*, 2024, **53**, 9738–9831.

53 C. Hu, X.-F. Wang, R. Wei, C. Hu, D. A. Ruiz, X.-Y. Chang and L. L. Liu, Crystalline monometal-substituted free carbenes, *Chem*, 2022, **8**, 2278–2289.

54 S. Jeltsch, J. Schulz, C. Schrenk and A. Schnepf, Insertion Behavior of Dialkylgermylene Ge(FluTMS)$_2$ in Different E–X σ Bonds (E = Au, Si, Ge, Sn) and Its Relevance for Germanium Cluster Formation, *Inorg. Chem.*, 2025, **64**, 785–795.

55 D. Vesseur, K. Miqueu and D. Bourissou, Combining ligand-enhanced backdonation and steric shielding to stabilize a mono-substituted Au(I) carbene, *Chem. Commun.*, 2023, **59**, 5387–5390.

56 M. He, C. Hu, R. Wei, X.-F. Wang and L. L. Liu, Recent advances in the chemistry of isolable carbene analogues with group 13–15 elements, *Chem. Soc. Rev.*, 2024, **53**, 3896–3951.

57 M. Veith and M. Grosser, Cyclische Diazastannylene, XVI [1]. Ringe und Käfige mit Ge(II), Sn(II) und Pb(II)/Cyclic Diazastannylenes, XVI [1]. Rings and Cages with Ge(II), Sn (II) and Pb(II), *Z. Naturforsch., B*, 1982, **37**, 1375–1381.

58 Y. Li, K. C. Mondal, P. Stollberg, H. Zhu, H. W. Roesky, R. Herbst-Irmer, D. Stalke and H. Fliegl, Unusual formation of a N-heterocyclic germylene via homolytic cleavage of a C–C bond, *Chem. Commun.*, 2014, **50**, 3356–3358.

59 L. Kristinsdóttir, N. L. Oldroyd, R. Grabiner, A. W. Knights, A. Heilmann, A. V. Protchenko, H. Niu, E. L. Kolychev, J. Campos, J. Hicks, K. E. Christensen and S. Aldridge, Synthetic, structural and reaction chemistry of N-heterocyclic germylene and stannylene compounds featuring N-boryl substituents, *Dalton Trans.*, 2019, **48**, 11951–11960.

60 Z. Dong, K. Bedbur, M. Schmidtmann and T. Müller, Hafnocene-based Bicyclo[2.1.1]hexene Germylenes – Formation, Reactivity, and Structural Flexibility, *J. Am. Chem. Soc.*, 2018, **140**, 3052–3060.

61 J. Brugos, J. A. Cabeza, P. García-Álvarez, E. Pérez-Carreño and D. Polo, Synthesis and some coordination chemistry of the PSnP pincer-type stannylene Sn(NCH$_2$PtBu$_2$)$_2$C$_6$H$_4$, attempts to prepare the PSiP analogue, and the effect of the E atom on the molecular structures of E(NCH$_2$PtBu$_2$)$_2$C$_6$H$_4$ (E = C, Si, Ge, Sn), *Dalton Trans.*, 2018, **47**, 4534–4544.

62 Z. Benedek and T. Szilvási, Theoretical Assessment of Low-Valent Germanium Compounds as Transition Metal Ligands: Can They Be Better than Phosphines or NHCs?, *Organometallics*, 2017, **36**, 1591–1600.

63 Z. Benedek and T. Szilvási, Can low-valent silicon compounds be better transition metal ligands than phosphines and NHCs?, *RSC Adv.*, 2015, **5**, 5077–5086.

64 L. Wang, G. Zhen, Y. Li, M. Kira, L. Yan, X.-Y. Chang, L. Huang and Z. Li, Structure and reactivity of germylene-bridged digold complexes, *Nat. Commun.*, 2022, **13**, 1785.

65 Y. Li, G. Zhen, L. Huang, R. Zhang, L. Wang, F. Qi, M. Kira and Z. Li, Trinuclear anionic gold clusters bridged by dialkylsilylene and dialkylgermylene, *Chem. Commun.*, 2022, **58**, 6705–6708.

66 M. Kira, S. Ishida, T. Iwamoto, M. Ichinohe, C. Kabuto, L. Ignatovich and H. Sakurai, Synthesis and Structure of a Stable Cyclic Dialkylgermylene, *Chem. Lett.*, 2003, **28**, 263–264.

67 A. A. Tukov, A. T. Normand and M. S. Nechaev, N-heterocyclic carbenes bearing two, one and no nitrogen atoms at the ylidene carbon: insight from theoretical calculations, *Dalton Trans.*, 2009, **35**, 7015–7028.

68 Deposition numbers 2401588 (for **6a**), 2401589 (for **4**), 2401590 (for **7**), 2401591 (for **2b**), 2401592 (for **8**), 2401593 (for **3**) and 2401594 (for **6b**) contain the supplementary crystallographic data for this paper.†

69 J. A. Cabeza, J. M. Fernández-Colinas, P. García-Álvarez and D. Polo, Diaminogermylene and Diaminostannylene Derivatives of Gold(I): Novel AuM and AuM$_2$ (M = Ge, Sn) Complexes, *Inorg. Chem.*, 2012, **51**, 3896–3903.

70 J.-X. Zhang, F. K. Sheong and Z. Lin, Unravelling Chemical Interactions with Principal Interacting Orbital Analysis, *Chem. – Eur. J.*, 2018, **24**, 9639–9650.

71 J.-X. Zhang, F. K. Sheong and Z. Lin, Principal interacting orbital: A chemically intuitive method for deciphering bonding interaction, *Wiley Interdiscip. Rev.:Comput. Mol. Sci.*, 2020, **10**, e1469.

72 A. V. Marenich, C. J. Cramer and D. G. Truhlar, Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions, *J. Phys. Chem. B*, 2009, **113**, 6378–6396.