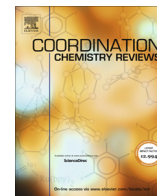




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Review

Recent advances in the chemistry of transition metal–silicon/germanium triple-bonded complexes

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This review is dedicated to Prof. Pierre Braunstein to celebrate his 70th birthday.

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ABSTRACT

The chemistry of complexes bearing triple bonds between transition metals and silicon or germanium has made considerable progress in the last two decades. For base-free complexes of this type, neutral and cationic complexes of Groups 5, 6, 7, 8, and 10 transition metals are known so far. The synthetic routes for these complexes can be categorized into two patterns: (1) reactions starting from stable divalent Group 14 element species (Category I), and (2) reactions starting from tetravalent Group 14 element species (Category II). These synthetic reactions are described first, and then characteristic structures and spectroscopic properties are discussed. Finally, several unique reactions originating from the peculiar reactivity of the metal–silicon/germanium triple bonds of silylyne and germylyne complexes are presented.

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Abbreviations: Cp, η^5 -cyclopentadienyl; Cp⁺, η^5 -pentamethylcyclopentadienyl; Cy, cyclohexyl; DFT, density functional theory; DMAP, 4-(dimethylamino)pyridine; DME, 1,2-dimethoxyethane; dmpe, 1,2-bis(dimethylphosphino)ethane; dppe, 1,2-bis(diphenylphosphino)ethane; Eind, 1,1,3,3,5,5,7,7-octaethyl-s-hydrindacen-4-yl; Idipp, 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene; IR, infrared; ⁱPr, isopropyl; Me, methyl; Mes, mesityl; ^{Me}IME, 1,3,4,5-tetramethyl-1,3-dihydro-2H-imidazol-2-ylidene; ^{Me}IPr, 1,3-diisopropyl-4,5-dimethyl-1,3-dihydro-2H-imidazol-2-ylidene; NHC, N-heterocyclic carbene; NMR, nuclear magnetic resonance; Ph, phenyl; Sldipp, 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene; ^tBu, *tert*-butyl; Tbb, C₆H₂-2,6-[CH(SiMe₃)₂]₂-4-^tBu; THF, tetrahydrofuran; Trip, 2,4,6-triisopropylphenyl; VE, valence electron; WBI, Wiberg bond indices; Xyl, 2,6-dimethylphenyl.

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1. Introduction

Multiple bonds between transition metals and main-group elements hold a prominent position in coordination chemistry and organometallic chemistry, because of the uniqueness of their bonding modes and fascinating reactions that can only be achieved by these bonds. Needless to say, the most important examples of compounds having these multiple bonds are carbene and carbyne complexes, and a number of excellent books and review articles have been published on their chemistry [1–8].

On the other hand, complexes having multiple bonds between transition metals and heavier Group 14 elements such as silicon and germanium have been much less extensively studied, mainly because the chemical properties of the compounds of silicon and germanium are greatly different from those of carbon. For instance, the double- and triple-bonded species of silicon and germanium are stable only when they have bulky groups on silicon and germanium, and this makes the research on the reactions of M=E and M≡E complexes (M = transition metal, E = Si, Ge) corresponding to alkene and alkyne metathesis reactions difficult. Nevertheless, a significant number of silylene complexes (M=Si) and germylene complexes (M=Ge) have been synthesized in these three decades, and based on the synthetic effort for these complexes, the chemistry of transition metal–silicon/germanium double bonded complexes has made steady progress. You can find several review articles on the synthesis, structures, and properties of silylene and germylene complexes [9–19].

As for the transition metal–silicon/germanium triple-bonded complexes, the first example, a germylyne complex (M≡Ge), was reported by Simons and Power in 1996, which was prepared by the reaction of chlorogermylene and an anionic molybdenum complex [20]. They used a stable divalent germanium species bearing a halogen substituent and a very bulky group as a precursor. With respect to the silicon analogue, a neutral, genuine silylyne complex (M≡Si) was first reported by Filippou et al. in 2010. They developed a new chlorosilylene having a very bulky group and stabilized by an NHC (N-heterocyclic carbene) as a precursor, and they achieved the synthesis by the reaction of this species with an anionic molybdenum complex [21]. In both cases, divalent Group 14 element species are used as key precursors.

Importantly, these synthetic routes starting from divalent Group 14 element species are different from those of carbyne complexes from the viewpoint of the reaction mode, because many carbyne complexes are derived from the corresponding carbene complexes, i.e., prepared via conversion of M=C double bonds to M≡C triple bonds. Therefore, if we can convert M=Si or M=Ge double bonds into M≡Si or M≡Ge triple bonds, the diversity of substituents and ligands in accessible silylyne and germylyne complexes will become much wider. Indeed, the authors have discovered by accident a new reaction that converts a germylene complex to a germylyne complex quantitatively, which was reported in 2012 [22]. We also subsequently reported a different type of reaction that converts a silylene complex to silylyne complex in 2016 [23,24]. During the last few years, although the number of examples is still small, the chemistry of transition

metal–silicon/germanium triple-bonded complexes is becoming increasingly clear. In this article, we will review the synthesis, structures, properties, and reactions of all reported, isolable silylyne and germylyne complexes.

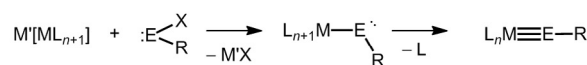
2. Synthesis of germylyne and silylyne complexes

2.1. Synthetic methods

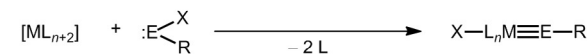
Synthetic methods for preparing M≡E triple bonded complexes (M = transition metal, E = Si, Ge) are summarized in Scheme 1. These methods are classified into two categories (I and II) depending on the starting Group 14 element species. Methods A–C in

I. Methods using Group 14 element(II) halides

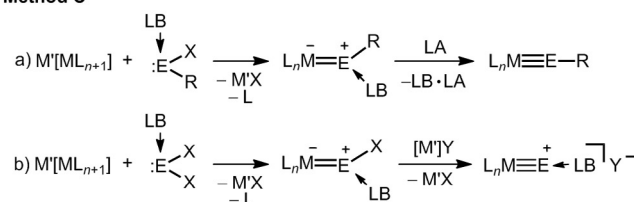
Method A



Method B

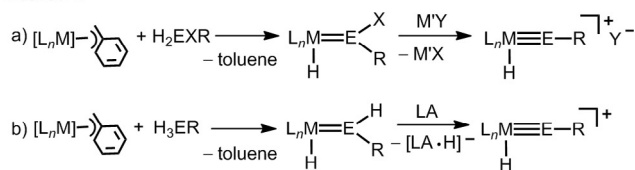


Method C

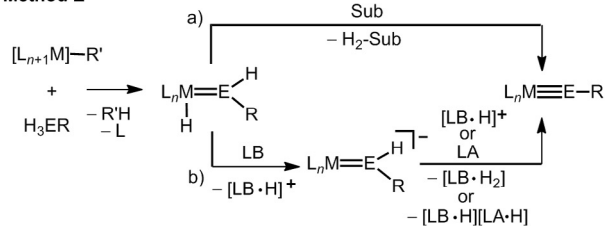


II. Methods using Group 14 element(IV) species

Method D



Method E



Scheme 1. Synthetic methods for M≡E triple bonded complexes (M = transition metal, M' = alkali metal, X = halide, Y = counter anion, L = ligand, LA = Lewis acid, LB = Lewis base, R = substituent, R' = alkyl, Sub = substrate).

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