



# Germylene and stannylene (Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>E as strong σ-donor ligands for transition metal complexes [ML(CO)<sub>n</sub>] (E = Ge, Sn; M = Cr, Mo, W, n = 4 or 5; M = Fe, n = 4). Synthesis, spectroscopic and theoretical study

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## ABSTRACT

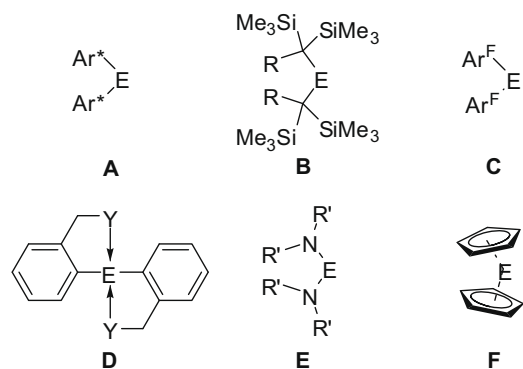
A series of germylene and stannylene (Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>E (E = Ge, **1**; E = Sn, **2**) complexes of group 6 metals and iron carbonyls L·M(CO)<sub>n</sub> (M = Cr, Mo, W, n = 5 (**3–8**), n = 4 (**9, 10**); M = Fe, n = 4 (**11, 12**)) were prepared. These complexes were characterized by <sup>1</sup>H, <sup>13</sup>C NMR, FTIR and elemental analysis. Ligand properties of **1** and **2** were compared to PPh<sub>3</sub> and dmly (N,N'-dimethylimidazolin-2-ylidene) using theoretical calculations (PBE/TZ2P) and FTIR. Ligand dissociation energies increase in the order Ph<sub>3</sub>P < **2** < **1** < dmly, while donor strength rise in the order PPh<sub>3</sub> < dmly < **2** < **1**.

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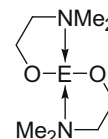
## 1. Introduction

Germynes and stannynes R<sub>2</sub>E (E = Ge, Sn) are heavy analogs of carbenes. This type of compounds bearing simple alkyl or aryl substituents are highly reactive towards both nucleophiles and electrophiles. This is due to the presence of a lone electron pair as well as a vacant p<sub>z</sub>-orbital on the central E atom. Non-stabilized germynes and stannynes undergo rapid oligomerization or insertion into C–H, C–X (X = halogen) or multiple bonds [1].

Several types of stable germynes and stannynes are known to date. Kinetic stabilization is achieved by the introduction of bulky substituents (steric stabilization, types **A** [2] and **B** [3]), while thermodynamic stabilization stems from electronic effects [4] such as: (i) introduction of acceptor substituents X on the central atom E (type **C** [5]); (ii) formation of intramolecular coordination bonds Y → E (Y – heteroatom bearing a lone electron pair, N, P, O, S; type **D** [6]); (iii) conjugation and delocalization (types **E** [7] and **F** [8]). In 2003 Zemlyansky et al. reported on the synthesis and solid state structure of germylene **1** and stannylene **2**, stabilized by a combination of factors (i) and (ii) without the introduction of sterically bulky groups [9].



E = Ge, Sn  
Ar\* - bulky aryl ligand  
Ar<sup>F</sup> = 2,4,6-trifluoromethylphenyl  
R = H, Alk; R' = Alk, Ar



E = Ge (**1**), Sn (**2**)

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Owing to the presence of a lone electron pair at E atom, germynes and stannylenes are utilized as ligands in transition metal complexes. Transitional metal complexes of unstable germynes and stannylenes bearing alkyl and aryl substituents were first synthesized in 1971 by Marks [10]. Complexes of stable derivatives of the types **A**, **B**, **D**, **E** and **F** were later reported [11].

Recently we reported on the synthesis of an iron carbonyl complex of stannylene **2** [12]. It was found that stannylene **2** is a strong  $\sigma$ -donor ligand, stronger than conventional phosphanes and N-heterocyclic carbenes. Strongly donating neutral ligands are of particular interest for transition metal catalysis since they may provide the metal center with the electron density sufficient for the activation of unreactive bonds such as H–H [13], C–H [14] and  $C_{Ar}$ –Cl [15]. In this contribution we report on the synthesis, spectroscopic and theoretical studies of germylene **1** and stannylene **2** transition metal carbonyl complexes  $[M(R_2E)(CO)_n]$  ( $E = Ge, Sn$ ;  $R = Me_2NCH_2CH_2O$ ;  $M = Cr, Mo, W, n = 4, 5$ ;  $M = Fe, n = 4$ ).

## 2. Results and discussion

### 2.1. Synthesis

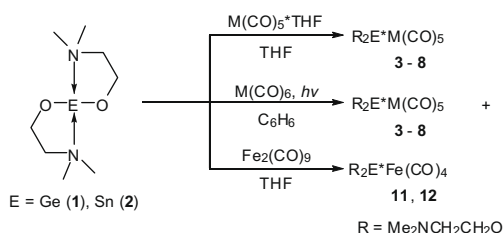
Two approaches were used for the synthesis of Cr, Mo and W carbonyl complexes **3–8** (Scheme 1): (i) interaction of germylene **1** or stannylene **2** with preformed complex  $[M(THF)(CO)_5]$  or ii) UV irradiation of the mixture of germylene **1** or stannylene **2** and metal hexacarbonyl. Irradiation of the mixtures of stannylene **2** with chromium and tungsten hexacarbonyls lead to formation of tetracarbonyls **9** and **10** in addition to pentacarbonyls **6** and **8**. Iron complexes **11** and **12** were obtained in the reactions of germylene **1** and stannylene **2** with  $Fe_2(CO)_9$ .

Complexes **3–12** are colored materials highly sensitive to traces of moisture and air. Compounds **3–8**, **11**, and **12** are very soluble in THF, diethyl ether and hot benzene, and poorly soluble in hexane. These compounds were characterized by  $^1H$ ,  $^{13}C$  NMR, FTIR and elemental analysis. Although we were previously able to obtain single crystals suitable for X-ray for **12** [12], no crystals were obtained for the new complexes reported here. Complexes **9** and **10** are virtually insoluble in organic solvents, and decompose in refluxing  $CHCl_3$  and  $CH_2Cl_2$ . These complexes were characterized by solid state  $^{13}C$  NMR, FTIR (Nujol) and elemental analysis.

### 2.2. NMR spectroscopy

Room temperature  $^1H$  NMR spectra of complexes **3–8**, **11**, **12** display two  $A_2X_2$  multiplets for the  $OCH_2CH_2N$  groups and a singlet for the  $NMe_2$ -group. All signals are broadened, indicating the fast opening–closing of the intramolecular  $N \rightarrow E$  coordination bonds. This is also observed (albeit at a faster rate) in the case of free germylene **1** and stannylene **2** [9].

In the  $^{13}C$  NMR spectra of the Group 6 metal pentacarbonyl complexes  $[ML(CO)_5]$  **3–8** two types of signals were found in the carbonyl group region, corresponding to *cis*- and *trans*-CO. Only one signal was observed in the case of iron complexes **11** and **12**.



Scheme 1.

This is due to the fast (on the NMR timescale) interconversion of two isomers in which the germylene and stannylene ligands adopt axial and equatorial positions (Scheme 2) [12]. Analogous dynamic processes were observed previously for phosphane and arsane complexes of group 8 metal carbonyls [16].

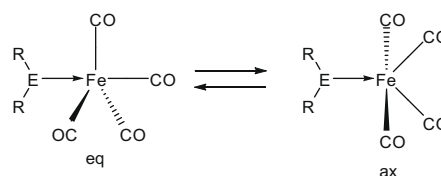
We studied the dynamics of this process at the DFT level of theory. It was found that for both **11** and **12** equatorial isomers lie lower in energy. Although axial isomers have slightly higher energies,  $\Delta E^0$  are only 1.5 and 0.1 kcal/mol, respectively for **11** and **12**. Moreover the barriers for the isomerisation are also very low;  $\Delta E^\ddagger$  are only 1.6 and 0.7 kcal/mol, respectively for **11** and **12**. Such barriers allow for the very fast interconversion of the isomers on the NMR timescale.

### 2.3. Ligand properties

The main questions under consideration in the study of ligands for transition metal complexes are (i) ligand dissociation energies, (ii) ligand donor/acceptor properties, (iii) ligand steric demand. At present the most versatile neutral donor ligands in organometallic chemistry are phosphanes and N-heterocyclic carbenes (NHCs) [17]. We performed a comparative study of germylene **1** and stannylene **2** with  $Ph_3P$  and the simple NHC – 1,3-dimethylimidazolin-2-ylidene (dmly). Free ligands as well as chromium  $[CrL(CO)_5]$  ( $L = Ph_3P$  [18], dmly [19]) and iron  $[FeL(CO)_4]$  ( $L = Ph_3P$  [20], dmly [21]) complexes were considered. The results are summarized in Table 1.

In all ligands under consideration in this work, the highest molecular orbitals (HOMO) are lone electron pairs (LEP), localized respectively on phosphorus, carbon, germanium and tin atoms [9]. The energies of HOMO increase in the order  $PPH_3 < dmly < 2 < 1$ . Thus germylene **1** is expected to be the strongest donor among the ligands studied.

Ligand dissociation energies ( $D^0$ ) were calculated as energy difference between the relaxed structures of complexes  $[CrL(CO)_5]$ ,  $[FeL(CO)_4]$  and isolated fragments L and  $[Cr(CO)_5]$  and  $[Fe(CO)_4]$ . For both chromium and iron complexes ligand dissociation energies increase in the order  $Ph_3P < 2 < 1 < dmly$ . Thus germylene **1** and stannylene **2** occupy intermediate position between aryl phosphanes and NHCs. Although the considerably higher value of  $D^0$  for dmly might be a consequence of its very low degree of steric bulk. Detailed analyses of chemical bonding in stannylene and germylene complexes have been done previously [22].



Scheme 2.

$E = Ge, M = Cr (3), Mo (4), W (5)$   
 $E = Sn, M = Cr (6), Mo (7), W (8)$

$E = Sn, M = Cr (9), W (10)$

$E = Ge (11), Sn (12)$

**Table 1**

Calculated and experimental ligand properties. (HOMO in eV;  $D^0$  ligand dissociation energies in kcal/mol;  $\nu(\text{CO}) - A_1$  stretching frequencies in  $\text{cm}^{-1}$ , experimental values in parenthesis;  $V_{\text{bur}}$  in%).

L	HOMO	L-Cr(CO) <sub>5</sub>		L-Fe(CO) <sub>4</sub>		$V_{\text{bur}}$
		$D^0$	$\nu(\text{CO})$	$D^0$	$\nu(\text{CO})$	
Ph <sub>3</sub> P	-5.28	34.1	2034(2066)	39.5	2022(2051)	22 <sup>a</sup>
dmly	-4.73	46.7	2027(2056)	53.5	2018(2043)	18 <sup>b</sup>
<b>2</b>	-4.57	38.2	2021(2049)	44.1	2009(2029)	24
<b>1</b>	-4.36	36.9	2013(2043)	45.7	2003(2026)	26

<sup>a</sup> Ref. [30].

<sup>b</sup> Ref. [31].

Direct experimental comparison of the overall electronic properties of ligands can be derived from the carbonyl stretching frequencies of their complexes with transition metals – the so-called Tolman electron parameter (TEP, or  $\nu(\text{CO})$ , in  $\text{cm}^{-1}$ ) [23,24]. Lower values of  $\nu(\text{CO})$  correspond to stronger ligand-to-metal  $\sigma$ -donation and/or lower metal-to-ligand  $\pi$ -back-donation [25]. Although TEP was initially developed as a stretching frequency in [NiL(CO)<sub>3</sub>], it was later shown that there is a linear correlation between the values obtained for different metal carbonyls and those for [NiL(CO)<sub>3</sub>] [26].

Experimental and calculated data on  $\nu(\text{CO})$  are collected in Table 1. A good linear correlation was found between experimental and calculated  $\nu(\text{CO})$  for [CrL(CO)<sub>5</sub>] ( $R^2 = 0.98$ ) and [FeL(CO)<sub>4</sub>] ( $R^2 = 0.96$ ). Both calculated and experimental values of  $\nu(\text{CO})$  simultaneously decrease in the order PPh<sub>3</sub> < dmly < **2** < **1**. Thus germylene **1** and stannylene **2** are stronger net donors than phosphanes and even imidazolium-based NHCs. It should also be stressed that there is a good linear correlation between experimental  $\nu(\text{CO})$  of chromium and iron carbonyls ( $R^2 = 0.96$ ). This further supports previous findings that the order of relative ligand donor strength is independent from the nature of the metal carbonyls [26].

The most commonly used parameter for the measurement of phosphanes steric properties is ligand cone angle  $\theta$ , proposed by Tolman [23]. Phosphanes and NHCs have different steric profiles, since the substituents on the phosphorus atom in phosphanes point away from the lone electron pair (“umbrella” shape) while those on the nitrogen atom of NHCs point towards it [27]. Therefore, Tolman’s steric parameter is inapplicable for the comparison of phosphanes and NHCs. However, Cavallo and Nolan recently developed the  $V_{\text{bur}}$  (%) parameter, the volume buried by overlap between the ligand and a sphere with a radius of 3 Å centered around the metal [28–31]. This parameter enables a reliable comparison of steric properties of virtually any type of ligands.

We performed calculations of  $V_{\text{bur}}$  for germylene **1** and stannylene **2**. It was found that dmly, bearing small methyl groups at the nitrogen atoms, is the least sterically demanding ligand ( $V_{\text{bur}} = 18\%$ ). PPh<sub>3</sub> is more bulky ( $V_{\text{bur}} = 22\%$ ), while germylene **1** and stannylene **2** exhibited the highest steric demand ( $V_{\text{bur}} = 26\%$  and  $24\%$ , respectively). Thus germylene **1** possess steric properties of the same magnitude as IMes (*N,N*-bis(2,4,6-trimethylphenyl)imidazolium-2-ylidene), however it is less bulky than P<sup>t</sup>Bu<sub>3</sub> and IPr (*N,N*-bis(2,6-diisopropylphenyl)imidazolium-2-ylidene),  $V_{\text{bur}} = 30\%$  [30].

Steric properties of germylene **1** and stannylene **2** can be easily enhanced by the insertion of more bulky groups on the nitrogen atom of the amino group or on the alkoxy group. One might also speculate that **1** and **2** are ligands with variable steric bulk. Due to the fluxional nature of the N → E coordination bonds (see above), the steric demands of **1** and **2** can be tuned using different factors. For example, increasing the temperature or addition of a Lewis acid (LA) to form a R<sub>3</sub>N → LA adduct should favor the opening of the N → E bonds, thus decreasing steric demand [32].

### 3. Conclusion

In this contribution, we report on the straightforward synthesis of a series of Cr, Mo, W and Fe carbonyl complexes of stable germylene **1** and stannylene **2**. Using experimental and theoretical techniques we have shown that these ligands: (i) exhibit relatively high binding energies to transition metals, (ii) are very strong donors, stronger than imidazolium-based NHCs, and (iii) possess tunable steric properties. Thus, utilization of germylens and stannylens as ligands opens intriguing perspectives for the stabilization of coordinatively unsaturated transition metals as well as in the activation of unreactive substrates such as H<sub>2</sub> and alkanes. Such studies are currently under way in our group.

### 4. Experimental

#### 4.1. General procedure

All manipulations were carried out under a purified argon atmosphere using standard Schlenk techniques. Commercially available solvents were purified by conventional methods and distilled immediately prior to use. Ge(OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub> (**1**) and Sn(OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub> (**2**) were synthesized as described earlier [9].

NMR spectra were recorded on an “AVANCE-400” NMR spectrometer at 400.13 MHz (<sup>1</sup>H) and 100.62 MHz (<sup>13</sup>C) in THF-*d*<sub>8</sub>. Chemical shifts are indirectly referenced to TMS via the solvent signals. The accuracy of chemical shift measurements is ±0.01 ppm (<sup>1</sup>H) and ±0.05 ppm (<sup>13</sup>C). Solid-state <sup>13</sup>C NMR investigations of powdered samples of **9** and **10** with magic angle spinning (5–6 kHz) and cross-polarization were obtained on “Bruker MSL-300” NMR spectrometers. Elemental analyses were performed on a Carlo Erba EA1108 CHNSO elemental analyzer. FTIR spectra were recorded on a Magna-750IR (Nicolet) Fourier spectrometer with a resolution of 2  $\text{cm}^{-1}$ . The samples were prepared as THF solutions and Nujol mulls under a dry argon atmosphere.

#### 4.2. General procedure for syntheses of Group 6B Metal complexes

**Method A:** A 350-mL THF solution of metal carbonyl (~10 mmol) was transferred under argon into a 500-mL quartz reaction vessel. The solution was irradiated with a low pressure lamp at room temperature for 6 h. The equimolar amount of divalent germanium (**1**) or tin (**2**) compound in 50 mL of THF was added and the mixture was stirred for 2 h. After stirring the solvent was evaporated and the residue was re-crystallized from hexane.

**Method B:** A 350-mL benzene solution of divalent germanium (**1**) or tin (**2**) compound (~10 mmol) was transferred under argon into 500-mL quartz reaction vessel containing equimolar amount of metal carbonyl. Then the solvent was evaporated and the residue was re-crystallized from hexane. In cases of complexes **9** and **10** precipitates formed under irradiation. After irradiation the precipitate was filtered and washed with THF. The pure complexes **9** and **10** were obtained. The solvent was evaporated from filtrate and the residue was re-crystallized from hexane. The pure complexes **6** and **8** were obtained.

#### 4.3. (Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>Ge-Cr(CO)<sub>5</sub> (**3**)

**Method A.** Yield: 38.5%. **Method B.** Yield: 32.4%. Green powder. Found: C, 35.20; H, 4.71; N, 6.22. Calcd for C<sub>13</sub>H<sub>20</sub>CrGeN<sub>2</sub>O<sub>7</sub>: C, 35.41; H, 4.57; N, 6.35. <sup>1</sup>H NMR (THF-*d*<sub>8</sub>):  $\delta = 2.44$  (s, 12H, NMe<sub>2</sub>), 2.62–2.69 (m, 4H, CH<sub>2</sub>N), 3.91–3.99 (m, 4H, CH<sub>2</sub>O). <sup>13</sup>C NMR (THF-*d*<sub>8</sub>):  $\delta = 45.20$  (Me<sub>2</sub>N), 61.96 (CH<sub>2</sub>N), 62.37 (CH<sub>2</sub>O), 219.98 (*cis*-CO), 224.94 (*trans*-CO). FTIR (THF,  $\text{cm}^{-1}$ ): 2043 m, 1963 w, 1922 s (CO).

4.4.  $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{O})_2\text{Ge}\cdot\text{Mo}(\text{CO})_5$  (**4**)

**Method A:** Yield: 20.1%. **Method B:** Yield: 71.8%. Yellow powder. Anal. Calc. for  $\text{C}_{13}\text{H}_{20}\text{GeMoN}_2\text{O}_7$ : C, 32.20; H, 4.16; N, 5.78. Found: C, 32.03; H, 4.21; N, 5.68%.  $^1\text{H}$  NMR (THF- $d_8$ ):  $\delta = 2.34$  (s, 12H,  $\text{NMe}_2$ ), 2.44–2.52 (m, 4H,  $\text{CH}_2\text{N}$ ), 3.86–3.95 (m, 4H,  $\text{CH}_2\text{O}$ ).  $^{13}\text{C}$  NMR (THF- $d_8$ ):  $\delta = 44.27$  ( $\text{Me}_2\text{N}$ ), 61.11 ( $\text{CH}_2\text{N}$ ), 63.63 ( $\text{CH}_2\text{O}$ ), 208.06 (*cis*-CO), 211.54 (*trans*-CO). FTIR (THF,  $\text{cm}^{-1}$ ): 2061 m, 1981 w, 1930 s (CO).

4.5.  $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{O})_2\text{Ge}\cdot\text{W}(\text{CO})_5$  (**5**)

**Method A:** Yield: 40%. Yellow powder. Anal. Calc. for  $\text{C}_{13}\text{H}_{20}\text{GeN}_2\text{O}_7\text{W}$ : C, 27.26; H, 3.52; N, 4.89. Found: C, 27.03; H, 3.70; N, 4.78%.  $^1\text{H}$  NMR (THF- $d_8$ ):  $\delta = 2.43$  (s, 12H,  $\text{NMe}_2$ ), 2.63–2.71 (m, 4H,  $\text{CH}_2\text{N}$ ), 3.95–3.98 (m, 4H,  $\text{CH}_2\text{O}$ ).  $^{13}\text{C}$  NMR (THF- $d_8$ ):  $\delta = 45.46$  ( $\text{Me}_2\text{N}$ ), 61.50 ( $\text{CH}_2\text{N}$ ), 63.62 ( $\text{CH}_2\text{O}$ ), 198.32 (*cis*-CO), 200.32 (*trans*-CO). FTIR (THF,  $\text{cm}^{-1}$ ): 2060 m, 1971 w, 1926 s (CO).

4.6.  $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{O})_2\text{Sn}\cdot\text{Cr}(\text{CO})_5$  (**6**) and  $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{O})_2\text{Sn}\cdot\text{Cr}(\text{CO})_4$  (**9**)

**Method A:** Yield of **6**: 28%. **Method B:** Yield of **6**: 31%. Yield of **9**: 48%. For **6**: green powder. Anal. Calc. for  $\text{C}_{13}\text{H}_{20}\text{CrN}_2\text{O}_7\text{Sn}$ : C, 32.06; H, 4.14; N, 5.75. Found: C, 31.76; H, 4.20; N, 5.69%.  $^1\text{H}$  NMR (THF- $d_8$ ):  $\delta = 2.28$  (s, 12H,  $\text{NMe}_2$ ), 2.38–2.54 (m, 4H,  $\text{CH}_2\text{N}$ ), 3.57–4.04 (m, 4H,  $\text{CH}_2\text{O}$ ).  $^{13}\text{C}$  NMR (THF- $d_8$ ):  $\delta = 45.86$  ( $\text{Me}_2\text{N}$ ), 62.32 ( $\text{CH}_2\text{N}$ ), 62.79 ( $\text{CH}_2\text{O}$ ), 220.91 (*cis*-CO,  $^2J(\text{Sn}-^{13}\text{C}) = 134.8$  Hz), 225.05 (*trans*-CO). FTIR (THF,  $\text{cm}^{-1}$ ): 2049 m, 1983 w, 1925 s (CO). For **9**: orange powder. Anal. Calc. for  $\text{C}_{12}\text{H}_{20}\text{CrN}_2\text{O}_6\text{Sn}$ : C, 31.40; H, 4.39; N, 6.10. Found: C, 30.81; H, 4.53; N, 6.10%.  $^{13}\text{C}$  NMR (solid):  $\delta = 44.73$  ( $\text{Me}_2\text{N}$ ), 57.34 ( $\text{CH}_2\text{N}$ ), 61.16 ( $\text{CH}_2\text{O}$ ), 213.10 (*cis*-CO), 225.71 (*trans*-CO). FTIR (Nujol,  $\text{cm}^{-1}$ ): 1995 m, 1866 s, 1849 s, 1815 s (CO).

4.7.  $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{O})_2\text{Sn}\cdot\text{Mo}(\text{CO})_5$  (**7**)

**Method A:** Yield: 20.1%. Yellow powder. Anal. Calc. for  $\text{C}_{13}\text{H}_{20}\text{MoN}_2\text{O}_7\text{Sn}$ : C, 29.41; H, 3.80; N, 5.28. Found: C, 29.27; H, 3.95; N, 5.19%.  $^1\text{H}$  NMR (THF- $d_8$ ):  $\delta = 2.26$  (s, 12H,  $\text{NMe}_2$ ), 2.35–2.47 (m, 4H,  $\text{CH}_2\text{N}$ ), 3.95–4.04 (m, 4H,  $\text{CH}_2\text{O}$ ).  $^{13}\text{C}$  NMR (THF- $d_8$ ):  $\delta = 45.20$  ( $\text{Me}_2\text{N}$ ), 62.22 ( $\text{CH}_2\text{N}$ ), 62.90 ( $\text{CH}_2\text{O}$ ), 209.41 (*cis*-CO), 211.95 (*trans*-CO). FTIR (THF,  $\text{cm}^{-1}$ ): 2062 m, 1979 w, 1936 s (CO).

4.8.  $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{O})_2\text{Sn}\cdot\text{W}(\text{CO})_5$  (**8**) and  $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{O})_2\text{Sn}\cdot\text{W}(\text{CO})_4$  (**10**)

(**A**) Yield of **8**: 30.6%. (**B**) Yield of **8**: 35.9%. Yield of **10**: 46%. For **8**: yellow powder. Anal. Calc. for  $\text{C}_{13}\text{H}_{20}\text{N}_2\text{O}_7\text{SnW}$ : C, 25.23; H, 3.26; N, 4.53. Found: C, 25.05; H, 3.39; N, 4.38%.  $^1\text{H}$  NMR (THF- $d_8$ ):  $\delta = 2.38$  (s, 12H,  $\text{NMe}_2$ ), 2.45–2.59 (m, 4H,  $\text{CH}_2\text{N}$ ), 3.84–4.14 (m, 4H,  $\text{CH}_2\text{O}$ ).  $^{13}\text{C}$  NMR (THF- $d_8$ ):  $\delta = 44.80$  ( $\text{Me}_2\text{N}$ ), 61.96 ( $\text{CH}_2\text{N}$ ), 62.83 ( $\text{CH}_2\text{O}$ ), 198.52 (*cis*-CO), 199.46 (*trans*-CO). FTIR (THF,  $\text{cm}^{-1}$ ): 2061 m, 1975 w, 1927 s (CO). For **10**: yellow powder. Anal. Calc. for  $\text{C}_{12}\text{H}_{20}\text{N}_2\text{O}_6\text{SnW}$ : C, 24.39; H, 3.41; N, 4.74. Found: C, 24.35; H, 3.41; N, 4.61%.  $^{13}\text{C}$  NMR (solid):  $\delta = 43.85$ , 45.61 ( $\text{Me}_2\text{N}$ ), 57.93, 58.52 ( $\text{CH}_2\text{N}$ ), 60.86, 66.73 ( $\text{CH}_2\text{O}$ ), 207.82 (*cis*-CO), 215.15 (*trans*-CO). FTIR (Nujol,  $\text{cm}^{-1}$ ): 1994 m, 1861 s, 1835s, 1824 s (CO).

## 4.9. General procedure for syntheses of iron complexes

A solution of divalent germanium (**1**) or tin (**2**) compound (5.00 mmol) in THF (30 mL) was added to a stirred suspension of  $\text{Fe}_2(\text{CO})_9$  (4.00 mmol) in THF (50 mL) at room temperature. After stirring for 16 h, the brown precipitate was separated by filtration

and all volatiles were removed in vacuo. The crude product was recrystallised from a 5:1 hexane–THF mixture.

4.10.  $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{O})_2\text{Ge}\cdot\text{Fe}(\text{CO})_4$  (**11**)

Yield: 61%. Yellow powder. Anal. Calc. for  $\text{C}_{12}\text{H}_{20}\text{FeGeN}_2\text{O}_6$ : C, 34.59; H, 4.84; N, 6.72. Found: C, 34.40; H, 4.95; N, 6.60%.  $^1\text{H}$  NMR (THF- $d_8$ ):  $\delta = 2.43$  (12H, s,  $\text{NMe}_2$ ), 2.69–2.81 (m, 4H,  $\text{CH}_2\text{N}$ ), 3.98–4.06 (m, 4H,  $\text{CH}_2\text{O}$ ).  $^{13}\text{C}$  NMR (THF- $d_8$ ):  $\delta = 45.19$  ( $\text{Me}_2\text{N}$ ), 61.32 ( $\text{CH}_2\text{N}$ ), 62.182 ( $\text{CH}_2\text{O}$ ), 217.16 (CO). FTIR (THF,  $\text{cm}^{-1}$ ): 2026 m, 1922 s (CO).

4.11.  $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{O})_2\text{Sn}\cdot\text{Fe}(\text{CO})_4$  (**12**)

Yield: 73%. Yellow crystals. Anal. Calc. for  $\text{C}_{12}\text{H}_{20}\text{FeN}_2\text{O}_6\text{Sn}$ : C, 31.1; H, 4.4; N, 6.05. Found: C, 31.1; H, 4.5; N, 6.0%.  $^1\text{H}$  NMR (THF- $d_8$ ):  $\delta = 2.28$  (12H, s,  $\text{NMe}_2$ ), 2.42–2.45 (m, 4H,  $\text{CH}_2\text{N}$ ), 3.86–3.88 (m, 4H,  $\text{CH}_2\text{O}$ ).  $^{13}\text{C}$  NMR (THF- $d_8$ ):  $\delta = 45.70$  ( $\text{Me}_2\text{N}$ ), 60.80 ( $\text{CH}_2\text{N}$ ), 64.22 ( $\text{CH}_2\text{O}$ ), 216.91 (CO). FTIR (THF,  $\text{cm}^{-1}$ ): 2029 m, 1928 s (CO).

## 5. Calculation procedure

All molecules were studied at the DFT level. Molecular geometries were optimized using generalized gradient-corrected functional PBE [33]. Valence electrons were treated using TZ2P basis set [34]. Innermost electrons of Cr, Fe, Ge, Sn, P, C, N, O atoms were emulated using effective core potentials ECP-SBKJC [35].  $E$ ,  $E^0$ ,  $H^0$ ,  $G^0$  were calculated for all stationary points. All calculations were made using the PRIRODA program [34,36]. This approach and program were previously used by us in studies of germynes and stannynes [12,37], ionic and covalent Ge(IV) and Sn(IV) compounds, stabilized by intramolecular coordination [38], and organometallic betaines comprising 14-group elements (Si, Ge, Sn) in the main chain [39].

$V_{\text{bur}}$  was calculated using the script provided by Luigi Cavallo [29,40].

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## Appendix A. Supplementary material

MOLEKEL 4.3 orbital plots [41],  $\nu(\text{CO})$  correlation plots, details of  $V_{\text{bur}}$  calculations.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.05.017.

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