



Carbonyl complexes of transition metals with stabilized germylenes

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ABSTRACT

Germylenes based on substituted diethylenetriamine (**1**), diethanolamines (**2, 3**) and pyridine-containing dialcohols (**4, 5**) were used as ligands in molybdenum and tungsten carbonyl complexes. Synthesis of new mono- and disubstituted (*cis*- or *trans*-) germanium(II) containing molybdenum (**8, 9, 14, 15, 17**) and tungsten (**6, 7, 10–13, 16**) carbonyl complexes were described. Composition of the complexes obtained was established by elemental analysis data and their structures were investigated by multinuclear NMR spectroscopy, IR and X-ray diffraction analysis (**7, 13** and **17**). The germylenes based on dialkanolamines and pyridine-containing dialcohols (O-ligands) give *cis*-digermanium complexes in contrast to the germylenes based on diethylenetriamines (N-ligands) which form *trans*-digermanium complexes.

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1. Introduction

Complexes of germylenes with metal carbonyls (Ru [1], VI Group metals (Cr, Mo, W) [2], Co [3], Rh [4], Fe [5], Mn [6] and others [7]) are intensively investigated due to academic interest in coordination chemistry of these compounds. Especial interest has been paid to the complexes of N-heterocyclic germylenes (NHGe's) [8]. We have an on-going interest in chemistry of heavy carbene analogs stabilized by transannular interaction – germylenes and stannylenes based on functionalized ligands. Chemistry and coordination properties of tricoordinated germanium(II) compounds have been reviewed recently [9]. We have reported the most appropriate method for synthesis of the germylenes/stannylenes stabilized by substituted alkanolamine [10], the related pyridine-containing ligands [11] or similar diethylenetriamine ligands [12] and presented their properties in [1 + 4]-cycloaddition, insertion and oxidation reactions. In this work, we describe the investigation of the interaction of the germylenes based on diethylenetriamines, dialkanolamines and the related ligands (pyridine-containing dialcohols) with molybdenum and tungsten carbonyl complexes.

2. Results and discussion

2.1. Synthesis

Molybdenum and tungsten hexacarbonyl complexes do not react with heavy carbene analogs under ambient conditions [13]. The use of more reactive $M(\text{CO})_5 \cdot \text{THF}$ ($M = \text{Mo}, \text{W}$) complexes instead of $M(\text{CO})_6$ ($M = \text{Mo}, \text{W}$) allows to carry out the reaction without irradiation, and the desired products are formed in higher yields [14]. For this reason, $M(\text{CO})_5 \cdot \text{THF}$ ($M = \text{Mo}, \text{W}$) were preferred as starting materials containing transition metal. These reactive complexes were prepared in THF solution before each experiment and used immediately.

In this work three types of germylenes were used as ligands for transition metal complexes (Chart 1): 1) the germylene **1** based on NNN-ligands (substituted diethylenetriamine); 2) the germylenes **2, 3** based on ONO-ligands (substituted dialkanolamines); 3) the germylenes **4, 5** based on ONO-ligands (substituted pyridine-containing dialcohols). It is noteworthy, that the germylenes **1, 3–5** are monomeric and the germylene **2** is dimeric in solid state [10].

In our hands, the treatment of THF solutions of $M(\text{CO})_6$ ($M = \text{Mo}, \text{W}$), which have been irradiated for 5 h, with the germylenes **1, 2, 4** resulted in two kinds of products in each case. The former – the major product – is the expected monosubstituted germylene-containing carbonyl complex, the latter is another carbonyl

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complex (the minor product), which was found to be carbonyl complexes containing two germylene species as ligands. Both of the products (mono- (**6**, **8**, **10**, **14**) and digermylene (**7**, **9**, **11**, **15**) complexes) were isolated from the crude reaction mixture on the basis of their different solubility (Scheme 1, Chart 2). Complexes **8** and **10** are proposed to have a dinuclear structure bridged by a dimeric germylene based on theoretical consideration (*vide infra*).

Forming the mixture of the two products in these reactions can be explained by the generation of unstable $M(CO)_4 \cdot 2THF$ species from initially formed $M(CO)_5 \cdot THF$ under prolonged irradiation. Such cases are very rare [15].

To obtain only monogermylene complexes we supposed to diminish the time of irradiating THF solutions of $M(CO)_6$. In fact, the irradiation of THF solutions of $M(CO)_6$ for 3 h, with subsequent treatment with germylene, resulted in the synthesis of only one product in each case (Scheme 2).

Composition of the complexes **6**, **8**, **10**, **12**, **14**, **16**, **18**, **20** was established on the basis of elemental analysis data and the structures were characterized by multinuclear NMR and IR spectroscopy. The compounds were obtained as white solids which were soluble in ether or toluene.

In these cases ^{13}C NMR spectroscopy data confirmed the structures of complexes with two types of nonequivalent CO groups (*cis*-/*trans*- = 4:1). This fact indicates the almost idealized octahedral geometry at W, Mo atoms. In comparison with $Mo(CO)_6$ (201.0 ppm) [16] and $W(CO)_6$ (191.1 ppm [17], $^1J_{W-C} = 191$ Hz) the downfield shift of the resonance signals of carbonyl groups in germylene-containing carbonyl complexes appears to be due to the increasing π -backbonding of CO [18] (for *trans*-CO group for W: 198.3–200.0 ppm; for *trans*-CO group for Mo: 209.9–211.1 ppm). It is noteworthy, that the type of the germylene used has only small effect on π -backbonding of *trans*-CO group in tungsten carbonyl complexes (for comparison: 198.3 ppm in complex **6** with diethylenetriamine based germylene; 199.2–199.6 ppm for the complexes **10**, **12** with the germylenes based on diethanolamines; 199.3–200.0 ppm for the complexes **14**, **18** with the germylenes based on pyridine-containing dialcohol) or molybdenum complexes (211.0 ppm for complex **8** with the germylene based on diethanolamine; 209.9–211.1 ppm for the complexes **16**, **20** with the germylenes based on pyridine-containing dialcohol). In the ^{13}C NMR spectra of tungsten carbonyl complexes (**6**, **10**, **12**, **14**, **18**), the values of $^1J_{W-C}$ (122–125 Hz for *cis*-CO; 145–152 Hz for *trans*-CO) indicate the stronger π -acceptor ability of CO ligand than that of germylene one [19].

The treatment of a monogermylene carbonyl complex with the corresponding free germylene in THF under UV irradiation is a preparative method for the synthesis of carbonyl complexes containing two germylene molecules as ligands (Scheme 3). It should be pointed out that the digermylene carbonyl complexes **7**, **9**, **15** were not formed under the same conditions without UV irradiation.

The 1H and ^{13}C NMR spectra of digermylene carbonyl compounds contain only one set of signals for ligand framework. In ^{13}C NMR spectrum of compound **7** there is only one signal for CO group (*trans*-isomer, C_s -symmetry), the rest digermylene complexes are characterized by two signals for CO groups (1:1, *cis*-isomer, C_2 -symmetry). In the majority of the cases, the signals of CO groups in digermylene

complexes are deshielded in comparison with the corresponding monogermylene ones (see Experiment). This fact can be explained by increasing π -backdonation of CO when the additional strong σ -donor germylene ligand is introduced to W or Mo.

Thus all digermylene-containing complexes except **7** were obtained as *cis*-isomers. The compounds were isolated as yellowish powders which were poorly soluble in ether or toluene. Composition of the complexes **7**, **9**, **11**, **13**, **15**, **17**, **19**, **21** was established on the basis of elemental analysis and structure was characterized by multinuclear NMR and IR spectroscopy. In solid state the crystal structures of one *trans*- (**7**) and two *cis*-isomers (**13**, **17**) were investigated by single crystal X-ray diffraction analysis.

The geometric isomers (corresponding *cis*- for **7**, *trans*- for **9**, **11**, **13**, **15**, **17**, **19** and **21**) are not formed. This is the case of the previously described systems. The germylenes formed by amides ($[R_2N]_2Ge$) give digermylene carbonyl complexes with *trans*-geometry [20,21]. The exceptions are the digermanium systems, in which two Ge subligands are covalently fixed in such a way, that it is impossible to form *trans* complexes. On contrary, alcoholate groups at Ge $[(RO)_2Ge]$ lead to *cis*-complexes. Apparently, this difference can be explained by steric factors.

2.2. IR spectroscopy

According to IR spectroscopy data the monogermylene complexes obtained in the course of the work have almost ideal octahedral coordination of M (C_{4v} symmetry, 3 bands in IR spectrum ($2A_1 + E$)).

σ -Donor ability of ligands in carbonyl complexes reflects in position of $A_1^{(1)}$ and the stronger donors result in decreasing frequency. Reducing the difference between the $A_1^{(2)}$ and E bands reflects the decreasing of π -acceptor ability of germylene [22]. For the monogermylene complexes obtained in this work, the positions of IR bands ($A_1^{(1)}$: 2067–2071 (Mo, W); $A_1^{(2)}$: 1942–1956 (Mo), 1928 (W); E: 1902–1918 cm^{-1} (Mo, W)) indicate the similarity to the germylene analogs studied previously (based on the related N- or O-ligands) or phosphines (strong σ -donor and weak π -acceptor ability) [2a, 2g].

IR spectrum of digermylene **7** showed only one band. It is characteristic for *trans*-isomer (D_{4h} symmetry). The rest digermylene complexes had 4 bands in IR (C_{2v} symmetry, $2A_1 + B_1 + B_2$ bands). This is the case for *cis*-geometry. Band shifts toward the lower frequencies (including in comparison with monogermylene complexes) indicated a strong σ -donation/weak π -acceptance of two germylene ligands at one metal atom.

The poor π -acceptor properties of all complexes investigated can be explained by the additional intramolecular N \rightarrow Ge coordination. Thus, such type germylenes would be perspective ligands in late transition metal (Pd, Pt) complexes.

2.3. X-ray crystallographic study

Attempts to isolate the crystals of digermanium complexes suitable for X-ray analysis failed. The crystal structures of digermanium substituted complexes: one molybdenum (**17**) and two tungsten (**7**, **13**) derivatives were investigated by single crystal X-ray analysis. Molecular structures and selected geometric parameters of these compounds are presented in Figs. 1–3.

According to X-ray analysis, the germylenes **1** [12], **4** [11] and **3** [10] which are used for synthesis of corresponding Mo, W digermylene complexes, are monomeric in solid state. The corresponding complexes **7**, **13**, **17** are also monomeric in solid state. It is known that the related tin compounds $[RN(CH_2CR'_2O)_2Sn]_2$ (R = Me, *t*-Bu, R' = H [23]; R = $Me_2NCH_2CH_2$, $MeOCH_2CH_2$, R' = Me

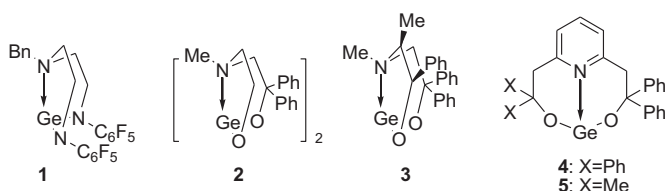


Chart 1. The germylenes investigated in this work.

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