Available online at www.sciencedirect.com

ScienceDirect

Journal of Organometallic Chemistry 692 (2007) 4067–4072

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Germylene complexes of tungsten pentacarbonyls $W(CO)_5{=}GeCl_2$ and $W(CO)_5{=}Ge{=}W(CO)_5$: Electrochemical synthesis and quantum-chemical computations

Yulia G. Budnikova [a], Tatyana V. Gryaznova [a,*], Oleg G. Sinyashin [a], Sergey A. Katsyuba [a], Tatyana P. Gryaznova [a,c], Mikhail P. Egorov [b,1]

[a] A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, 420088 Kazan, Russian Federation
[b] N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 117913 Moscow, Russian Federation
[c] Kazan State University, Russian Federation

Received 28 September 2006; received in revised form 26 May 2007; accepted 4 June 2007

Abstract

Convenient synthetic route to prepare the germylene complexes of tungsten pentacarbonyls, $W(CO)_5{=}GeCl_2$ and $W(CO)_5{=}Ge{=}W(CO)_5$, electrochemically is developed. Combined quantum-chemical/IR spectroscopic approach is used for identification of the synthesized compounds. Good agreement between theoretical and experimental spectra can be regarded as one of the proofs of their supposed structures.

Keywords: Dichlorogermylene complex of tungsten pentacarbonyls; Germylenebis(tungsten pentacarbonyl) complex; Electrolysis; Cyclic voltammetry; Combined quantum-chemical/IR spectroscopic approach; Vibrational frequencies

1. Introduction

The chemistry of transition metals complexes has been studied extensively in last decade. In particular, the stabilization of short-lived intermediates of organic reactions by means of their coordination with transition metals is one of the focuses of modern synthetic chemistry. The studies of organometallic carbene analogues such as germylene, phosphinidene and silylene complexes are of special interest. The known procedure to obtain dichlorogermylene complexes of metal carbonyls includes the reaction of $GeCl_2 \cdot$ dioxane with photochemically generated species $(CO)_5M \cdot THF$ [1]. Germylene particles are generated by thermal or photochemical decomposition of suitable precursors [2], mainly by the thermal decomposition of 7-germanorbornadienes. Methods to obtain dichlorogermylene complexes of metal carbonyls on photochemical reaction of tungsten hexacarbonyl and $CsGeCl_3$ [3], and from $W_2(CO)_{10}$ and germanium tetrachloride [4] was reported also. The possibilities of the synthesis of germylene complexes using the electrochemical methods have not yet been explored.

An electrolysis and a cyclic voltammetry were used for germylene complexes of tungsten pentacarbonyl synthesis.

Previously it has been shown that an electrolysis of solution of tungsten hexacarbonyl **1** in acetonitrile (10^{-3} mol) in presence of Et_4NBF_4 as a supporting electrolyte after passing 2F per initial metal carbonyl yielded to highly nucleophilic anion of tungsten pentacarbonyl $[W(CO)_5]^{2-}$ **2** [5]:

$$\underset{\mathbf{1}}{W(CO)_6} \xrightarrow[-CO]{e} [W(CO)_5] \xrightarrow{e} \underset{\mathbf{2}}{[W(CO)_5]^{2-}} \quad (1)$$

---

[*] Corresponding author. Tel.: +7 843 2734893; fax: +7 843 2732253.
E-mail addresses: yulia@iopc.kcn.ru (Y.G. Budnikova), tatyanag@iopc.knc.ru (T.V. Gryaznova), katsyuba@iopc.knc.ru, skatsyuba@yahoo.com (S.A. Katsyuba).

[1] Fax: +7 095 1355328.

0022-328X/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2007.06.010

We have assumed, that the interaction of such electrochemically generated in situ anion **2** with dihalogen germanium derivatives will, probably, result in the formation of various germanium complexes of tungsten pentacarbonyls. With this purpose in view germanium tetrachloride was used as the second reagent.

Anion **2** was treated with an equimolar amount of germanium tetrachloride, $GeCl_4$, at ambient temperature in acetonitrile. The yellow precipitate was obtained. The analysis of physico-chemical and spectroscopic data of the obtained compound allows to attribute to it the structure of complex **3**:

$$[W(CO)_5]^{2-} + GeCl_4 \rightarrow \underset{\mathbf{3}}{(CO)_5W{=}GeCl_2} + 2Cl^- \qquad (2)$$

The electrolysis of $W(CO)_6$ and $GeCl_2 \cdot$ dioxane complex (1:1) resulted in the same product **3**. Comparative cyclic voltammetry studies of the obtained compound and dichlorogermylene complex of tungsten pentacarbonyl **3**, obtained in traditional chemical way [6], also confirms the supposed structure (Table 1).

Thus, the results of spectroscopy, elemental analysis and voltammetry studies have shown the identity of **3**, prepared electrochemically, with reference compound [6].

Over all electrochemical reduction of $W(CO)_6$ and $GeCl_4$ in acetonitrile does not yield germylene complexes. Probably, dichlorogermylene particles $GeCl_2$ are generated in this case, instead of expected anions of tungsten pentacarbonyl. Being extremely reactive, dichlorogermylene particles, apparently, cause process of polymerization.

We have also attempted to prepare a bridging complex with two W=Ge bonds, $(CO)_5W{=}Ge{=}W(CO)_5$ (**4**). Reaction of electrochemically generated anion **2** with germanium tetrachloride in situ at a ratio 2:1 resulted in hydrolytically unstable crystal product of pistachio color.

$$2[W(CO)_5]^{2-} + GeCl_4 \rightarrow \underset{\mathbf{4}}{(CO)_5W{=}Ge{=}W(CO)_5} + 4Cl^- \qquad (3)$$

There are no absorption bands of Ge–Cl bond in the IR spectrum of the obtained compound. Vibrations of carbonyl groups are displayed as absorption bands with frequencies 1819, 1900, and 1934 s m^{-1}. These data allow to assume that the bridging germylene complex **4** is obtained. This complex has not been described earlier. Only a bridging germylene complex of manganese $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2]_2Ge$ is known, its X-ray analysis [7] being described.

Table 1
Electrochemical properties of $(CO)_5W{=}GeCl_2$ and $(CO)_5W{=}Ge{=}W(CO)_5$ in CH_3CN, 0.1 M Et_4NBF_4, glass-carbon electrode

Compound, $C = 5 \times 10^{-3}$ M (Method)	$-E_p$, V ref. Ag/$AgNO_3$, 10^{-2} M	I_p, μA	n_e^b
$W(CO)_5 \cdot GeCl_2$ (electrochem.)	1.15	28	1.6
$W(CO)_5 \cdot GeCl_2 \cdot$ THF (chem., reference)	1.19 [4][a]	28	1.6
$(CO)_5W{=}Ge{=}W(CO)_5$ (electrochem.)	1.88	18	1.0
$W(CO)_6$	2.35	36	2.0
$GeCl_4$	1.80	47	2.5

[a] CH_3CN, Bu_4NPF_6, Ag/AgCl/KCl (saturated).

[b] Ref. ferrocene.

The same complex **4** is formed as a result of joint $W(CO)_6$ and $W(CO)_5 \cdot GeCl_2$ (1:1) electrolysis:

$$[W(CO)_5]^{-2} + \underset{\mathbf{3}}{(CO)_5W{=}GeCl_2} \rightarrow \underset{\mathbf{4}}{(CO)_5W{=}Ge{=}W(CO)_5} + 2Cl^- \qquad (4)$$

The mass spectrum of **4** is not accessible owing to non-volatility of this product.

To confirm the supposed structure of the title compound **4** we have used quantum-chemical computations. In the last years, *ab initio* MO theory has become an important tool for structural studies. Reliable prediction of vibrational frequencies and other spectroscopic characteristics of various molecules is used to aid their experimental identification. Recent evidence [8] shows that density functional theory (DFT) [9] produces accurate molecular force fields and vibrational frequencies. In particular, it is possible to use the DFT vibrational spectra simulation practically as an analytical tool for studies of organoelement compounds [10]. Nevertheless this technique has not yet been applied to studies of tungsten germylenes. So, to validate the method we, first of all, have calculated vibrational and structural characteristics of related molecules $W(CO)_6$ **1**, $GeCl_4$ (**5**) and $W(CO)_5GeCl_2$ **3**, which were thoroughly studied, both theoretically [11] and experimentally [6,12–15].

The most exhaustive data on the structure [11–13] and spectra [11,14,15] are available for the molecules **1** and **5** which were used in this work as benchmark systems. The optimized bond lengths $l_{calc}(WC) = 2.070$ Å and $l_{calc}(CO) = 1.151$ Å of the molecule **1** and $l_{calc}(GeCl) = 2.142$ Å of the molecule **5** were in reasonable agreement with the corresponding experimental values $l_{expt}(WC) = 2.058$ Å [12], $l_{expt}(CO) = 1.141$ Å [12] and $l_{expt}(GeCl) = 2.113$ Å [13]. Deviations of the calculated vibrational frequencies from the experimental frequencies of the fundamentals did not exceed 4% for the molecule **1** (Table 2). The quality of the computational predictions for the molecule **5** (Table 3) was a little lower. Nevertheless even the maximal difference 31 cm^{-1} between the calculated and the experimental frequencies would not hamper spectral identification of the molecule on the basis of the comparison of the calculated frequencies with the experimentally registered spectrum.

The similar quality of computations was observed in case of molecule **3** (Table 4). At least part of the deviation between the computed and the experimental frequencies was caused by intermolecular interactions in the solid compound **3**. E.g., experimental frequencies of CO stretching vibrations of solid sample **3** were ca. 200 cm^{-1} lower than corresponding frequencies of gaseous compound **1**. This lowering was the main reason of more pronounced deviations of the frequencies calculated for the isolated molecule

Table 2
Infrared spectra of $W(CO)_6$

IR, gas[a] ν/cm^{-1}, I[b]	Computations ν/cm^{-1} (I/km × mol^{-1})	Assignment[c]
2126.2[d,e]	2193.8 (0)	νCO (A_{1g})
2021.1[d,e]	2099.6 (0)	νCO (E_g)
1997.6 vvs[e]	2075.5 (1948)	νCO (T_{1u})
586.6 vs[f]	608.9 (92)	δCO (T_{1u})
521.3[d]	539.8 (0)	δCO (T_{2u})
482.0[d]	489.4 (0)	δCO (T_{2g})
426.0[d]	436.3 (0)	νCW (A_{1g})
410.0[d]	416.2 (0)	νCW (E_g)
374.4 s	383.2 (51)	νCW (T_{1u})
361.6[d]	362.3 (0)	δCWC (T_{1g})
82.0[d]	89.4 (0)	δCWC (T_{2g})
81.4[d]	89.2 (0)	δCWC (T_{1u})
61.4[d]	65.3 (1)	δCWC (T_{2u})

[a] Ref. [9].

[b] s, strong; v, very.

[c] ν, stretch; δ, bend. In parenthesis – symmetry type of the vibrations.

[d] These frequencies were not observed in the gas phase. They were estimated from observed combination bands [9].

[e] Stretching vibrations of the carbonyls are strongly dependent on the phase state. The νCO frequencies in solid state (in nujol, this work) are 1997, 1966 and ca. 1930 cm^{-1}.

[f] in nujol (this work) 580 cm^{-1}.

Table 3
Infrared spectra of $GeCl_4$

IR, gas[a] ν/cm^{-1}	Computations ν/cm^{-1} (I/km mol^{-1})	Assignment[b]
459.1	428.0 (264)	νGeCl (T_2)
396.9	365.1 (0)	νGeCl (A_1)
171.0	164.6 (27)	δClGeCl (T_2)
125.0	122.5 (0)	δClGeCl (E)

[a] Ref. [10].

[b] ν, stretch; δ, bend. In parenthesis – symmetry type of the vibrations.

Table 4
Infrared spectra of $[W(CO)_5]GeCl_2$

IR, solid[a] ν/cm^{-1}, I[b]	Computations ν/cm^{-1} (I/km mol^{-1})	Assignment[c]
1913 vs	2168 (383)	νCO
	2100 (0)	νCO
	2082 (789)	νCO
1873 s	2078 (1795)	νCO
	2073 (1720)	νCO
	608 (94)	δOCW
593 s	585 (66)	δOCW
	584 (73)	δOCW
	536 (2)	δOCW
	518 (0)	δOCW
	513 (5)	δOCW
	493 (0)	δOCW
	437 (0)	νCW
	419 (6)	νCW
	417 (2)	νCW
	413 (21)	δOCW, νCW
	411 (40)	δOCW
384 s	405 (185)	νWGe, ν_sClGeCl
356 mw	392 (84)	νCW, νGeCl, δOCW
	386 (1)	νCW, νGeCl
	381 (28)	νCW, δOCW
	364 (0)	δOCW
	206 (13)	νWGe, δClGeCl
	149 (2)	δOCW, δCWGe, torsion
	138 (1)	δWGeCl, νWGe
	114 (1)	δWGeCl, νWGe, νCW
	91 (0)	δOCW, δCWC
	90 (0)	δOCW, δCWC
	89 (0)	δOCW, δCWC
	86 (0)	δOCW, δCWC, νWGe
	76 (1)	δOCW, δCWC
	68 (0)	δOCW, δCWC, δWGeCl
	66 (0)	δCWC, δOCW, δCWGe
	43 (0)	δWGeCl, δCWGe
	37 (1)	δCWGe
	11 (0)	Torsion

[a] This work. Mixture of **3** with buffer salt Et_4NBF_4.

[b] w, weak; m, medium; s, strong; v, very.

[c] ν, stretch; δ, bend.

3 from the solid-state experiment (Table 4) as compared to the case of molecule **1** (see footnote e of Table 2). According to the computations most of the IR bands of **3** were of very low intensity, and the registered spectrum, indeed, contained only five more or less strong bands (Table 4).

The simplicity of the IR spectra of the molecules **1**, **3** and **5** is their general feature alleviating comparison of the calculated frequencies with their experimental counterparts, despite the fact that the deviations amount to ca. 10%. As a result, a reliable spectral identification of the molecules is possible on the basis of a simple comparison of the computational predictions with the registered spectrograms. The results of such comparison for the title compound **4** are presented in Table 5. The deviations of the computed IR spectra of both possible conformers of **4** from the experiment lie in the same range as the deviations, discussed above for the test set of molecules **1**, **3** and **5**. According to our computations vibrational frequencies of the more energetically stable staggered conformer (Fig. 1, **4b**) practically coincide with the frequencies of the eclipsed conformer (Fig. 1, **4a**). So, on the basis of present results it is impossible to decide which of the abovementioned conformations (or both of them) is adopted by the molecule **4**. The most outstanding distinction of both calculated and registered spectra of **4** from the spectra of the compounds **1**, **3** and **5** is a presence of strong band of antisymmetric stretching vibration ν_{as}GeWGe at ca. 290 cm^{-1}. Another IR active bands in this region are observed about 60 cm^{-1} higher. So, the misassignment is practically impossible and the good agreement between theoretical and experimental spectra can be regarded as a proof of the supposed structure of compound **4**.

It should be mentioned though that there remain two unassigned bands of medium intensity (234 and 159 cm^{-1}) and the weak doublet band (ca. 260 cm^{-1}) in far IR region of the experimental spectrum of **4**. They can be attributed to neither the presence of the buffer salt Et_4NBF_4 nor compounds **1**, **3** or **5**. Probably the bands

Table 5
Infrared spectra of $[W(CO)_5]_2Ge$

IR, solid[a]	Computations			
ν/cm^{-1}, I[c]	Eclipsed conformation (**4a**)[b]		Staggered conformation (**4b**)[b]	
	ν/cm^{-1} (I/km mol^{-1})	Assignment[d]	ν/cm^{-1} (I/km mol^{-1})	Assignment[d]
	2172 (0)	νCO (A_{1g})	2171 (0)	νCO (E_2)
1934 sh	2138 (1942)	νCO (A_{1u})	2138 (1948)	νCO (E_2)
	2092 (0)	νCO (B_{1g})	2089 (0)	νCO (E_2)
	2089 (0)	νCO (A_{1g})	2089 (0)	νCO (E_2)
	2085 (0)	νCO (B_{2u})	2087 (0)	νCO (E_2)
1919 sh	2085 (1754)	νCO (A_{2u})	2085 (1745)	νCO (E_2)
1900 vs	2074 (3261)	νCO (E_u)	2073 (3281)	νCO (E_2)
1819 s	2058 (0)	νCO (E_g)	2059 (2)	νCO (E_2)
	606 (0)	δOCW (A_{1g})	606 (0)	δOCW (E_2)
595 m	601 (296)	δOCW (A_{2u})	601 (296)	δOCW (E_2)
554 w	584 (128)	δOCW (E_u)	584 (127)	δOCW (E_1)
	578 (0)	δOCW (E_g)	578 (0)	δOCW (E_1)
	534 (0)	δOCW (B_{1g})	533 (0)	δOCW (E_2)
	531 (0)	δOCW (B_{2u})	532 (0)	δOCW (E_2)
	495 (0)	δOCW (B_{2g})	494 (0)	δOCW (E_1)
	494 (12)	δOCW (E_u)	493 (0)	δOCW (E_1)
	493 (0)	δOCW (B_{1u})	493 (12)	δOCW (E_1)
	488 (0)	δOCW (E_g)	488 (0)	δOCW (E_2)
	435 (0)	νCW (A_{1g})	435 (0)	νCW (E_2)
415 vw	434 (11)	νCW (A_{2u})	434 (12)	νCW (E_2)
410 vw	423 (32)	δOCW, νCW (E_u)	422 (32)	δOCW, νCW (E_1)
	421 (0)	νCW (B_{1g})	420 (0)	νCW (E_1)
	419 (0)	νCW (B_{2u})	419 (0)	νCW (E_1)
	405 (0)	δOCW, νCW (E_g)	405 (0)	δOCW, νCW (E_1)
	395 (0)	νCW (A_{1g})	395 (0)	νCW (E_2)
358 s	391 (49)	νCW (A_{2u})	391 (49)	νCW (E_2)
352 sh	389 (51)	νCW (E_u)	389 (52)	νCW (E_1)
	383 (0)	δOCW, νCW (E_g)	383 (0)	δOCW, νCW (E_1)
	366 (0)	δOCW (A_{2g})	365 (0)	δOCW (B_1)
	365 (0)	δOCW (A_{1u})	364 (0)	δOCW (B_1)
293 s	297 (226)	ν_{as}GeWGe (A_{2u})	298 (226)	ν_{as}GeWGe (E_2)
	145 (0)	δWGeW, δOCW (E_u)	145 (0)	δWGeW, δOCW (E_1)
	136 (0)	ν_sGeWGe (A_{1g})	137 (0)	ν_sGeWGe (E_2)
	89 (0)	δOCW, δCWC (B_{2g})	89 (0)	δOCW, δCWC (E_1)
	88 (0)	δOCW (A_{2u})	89 (0)	δOCW (E_1)
	88 (0)	δOCW, δCWC (B_{1u})	88 (0)	δOCW, δCWC (E_2)
	88 (0)	δOCW (E_u)	87 (0)	δOCW (E_1)
	87 (0)	δOCW (E_g)	87 (0)	δOCW (E_1)
	78 (0)	δOCW (E_g)	77 (0)	δOCW (E_2)
	69 (0)	δCWC, δOCW (E_u)	68 (0)	δCWC, δOCW (E_2)
	68 (0)	δCWC, δOCW (A_{1g})	68 (0)	δCWC, δOCW (E_1)
	63 (0)	δCWC, δCWGe (B_{1g})	63 (0)	δCWC, δCWGe (E_2)
	61 (0)	δCWC, δCWGe (B_{2u})	61 (0)	δCWC, δCWGe (E_2)
	44 (0)	δCWGe (E_g)	42 (0)	δCWC (E_1)
	20 (0)	δWGeW (E_u)	18 (0)	δWGeW (E_2)
	14 (0)	torsion (A_{1u})	5 (0)	torsion (B_1)

[a] This work. Mixture of **4** with buffer salt Et_4NBF_4.

[b] See Fig. 1.

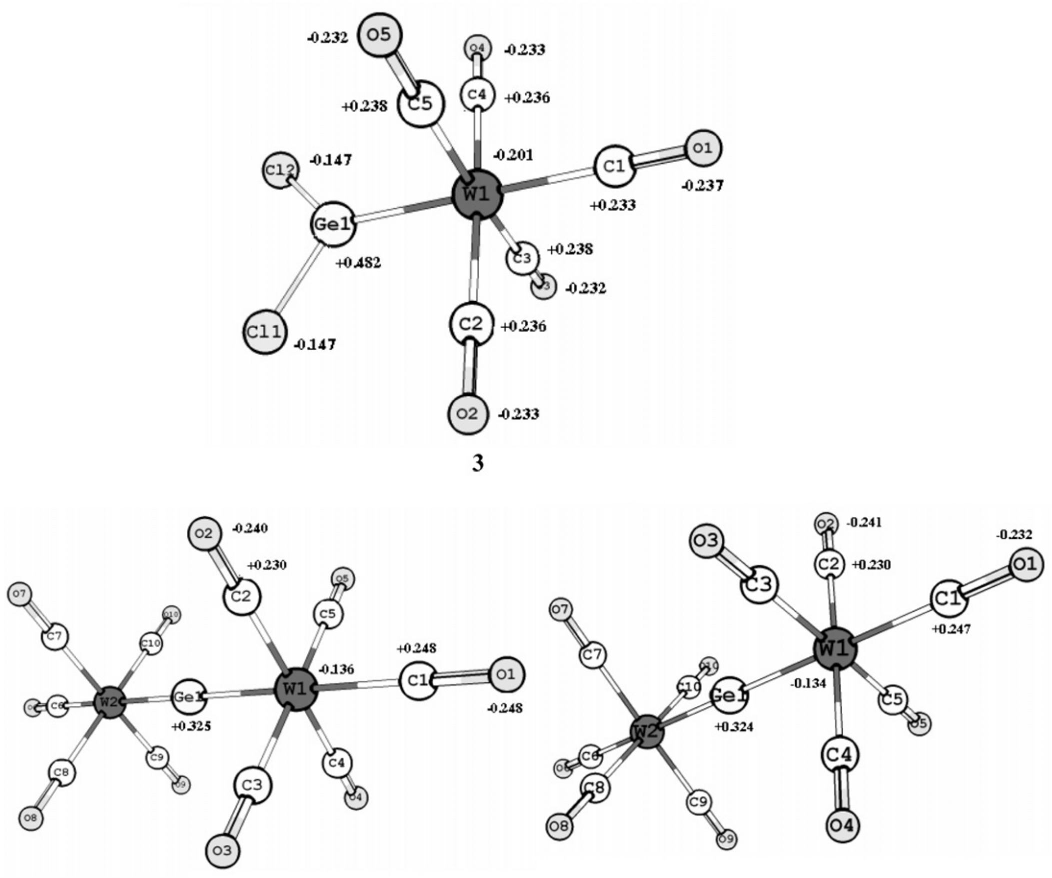
[c] w, weak; m, medium; s, strong; v, very, sh, shoulder.

[d] ν, stretch; δ, bend. In parenthesis – symmetry type of the vibrations.

belong to certain by-product(s) which cannot be identified on the basis of present spectroscopic data.

The structural parameters of the title compounds have never been determined experimentally. So, our computational data represent their first evaluation. The optimized bond length $l_{calc}(WGe) = 2.513$ Å for the molecule **3** and $l_{calc}(WGe) = 2.473$ Å for the molecule **4**. The shortening of the WGe bond in complex **4** comparative to the molecule **3** is accompanied with the lowering of polarisation of the WGe bond in **4** (Fig. 1) and the corresponding growth of the force constant f(WGe) from 1.498 mdin Å^{-1} in **3** to 1.82 mdin Å^{-1} in **4**.

Thus, electrosynthesis allows to carry out the preparation of the germylene complexes of tungsten pentacarbonyl. The



3

4a

4b

Fig. 1. Quantum-chemically optimised structures and atomic Mulliken charges of the complexes **3** (top) and **4** (bottom). **4a** – eclipsed conformation ($E = -3343.856328$H); **4b** – staggered conformation ($E = -3343.856481$H).

good agreement between the quantum-chemically computed and registered IR spectra of the complexes confirms their supposed structure. According to computational estimates, the WGe bond of complex **4** is more strong and less polar than in complex **3**.

1.1. Computations

All quantum chemical calculations were carried out by using the GAUSSIAN-98 suite of programs [16]. We used Becke‘s three-parameter exchange functional [17] in combination with the Lee–Yang–Parr correlation functional [18] (B3LYP) and standard 6–31G* basis set [19] for C, O, Cl and Ge atoms and LanL2DZ [20] for W atoms. Starting geometries of the molecules under study either were taken from electron diffraction data [11–13] or were constructed from the fragments of the related molecules. Both eclipsed and staggered conformations were calculated. For this purpose the starting geometries were fully optimised and characterised as minima or saddle points by analysis of the Hessian matrices. Both the eclipsed and the staggered conformations of the molecule **4** corresponded to minima, but only the eclipsed conformation of **3** turned out to be stable.

2. Experimental

Stationary disk glassy-carbon electrode with the efficient surface area of 3.14 mm^2 was used as the working electrode in electrochemical studies. Cyclic voltammograms were detected using a PI-50-1 potentiostat with a PR-49 programmer and an electrochemical cell switched-on *via* a three-electrode scheme. Curves were recorded at a linear potential sweep of 50 mV s^{-1} on a two-coordinate recorder. An Ag/0.01 M $AgNO_3$ system in MeCN served as the reference electrode. A platinum wire 1 mm in diameter was used as the auxiliary electrode. Measurements were carried out in a cell at the temperature kept constant at 25 °C under argon in acetonitrile at presence Et_4NBF_4 as the supporting electrolyte ($C = 5 \times 10^{-3}$ M). The complex $Ni(bpy)_3(BF_4)_2$ was used as the standard to determine the number of electrons involved in the electrochemical reaction ($I_p = 36$ μA at $C = 1 \times 10^{-2}$ mol L^{-1}). The preparative electrolysis was carried out using a B5-49 DC source in a 40 mL three-electrode cell. The working electrode potential was determined using a Shch 50-1 DC voltmeter *vs.* the reference electrode, Ag/0.01 M $AgNO_3$ in MeCN. The working surface of the cylindrical platinum cathode used as the working electrode was 20.0 cm^2. The diaphragm was made of paper; a glass carbon plate with a working area of 4 cm^2 was used as the anode, and a saturated solution of Et_4NBF_4 in MeCN was the anolyte.

IR spectra of the compounds were recorded on a FTIR spectrometer "Vector 22" (Bruker) in the 400–4000 cm^{-1} range and on a FTIR spectrometer IFS 113v (Bruker) in the 100–600 cm^{-1} range at a resolution of 1 cm^{-1}. Solid samples were prepared as KBr or polyethylene pellets, respectively.

The element analysis of metals was determined on laser-ionization mass-spectrometer EMAL2.

Acetonitrile was purified by fractional distillation over phosphorus pentoxide and potassium permanganate; Et_4NBF_4 was recrystallized from ethanol. Commercial $W(CO)_6$ (DalKhim, Nizhny Novgorod) was used.

All reactions were carried out under argon.

2.1. *Electrochemical generation of anion of tungsten hexacarbonyl* **2**

Tungsten hexacarbonyl 0.3519 g (10^{-3} mol) and 0.0325 g Et_4NBF_4 in MeCN (30 mL) were placed in an electrochemical cell and electricity (2 F per mol of $W(CO)_6$, $I = 53.8$ mA) was passed, while the solution was stirred on a magnetic stirrer under a constant flow of argon.

2.2. *Dichlorogermylene of tungsten pentacarbonyl complex* **3**

Germanium tetrachloride 0.214 g (10^{-3} mol) or $GeCl_2 \cdot$ dioxane 0.231 g (10^{-3} mol) in MeCN was added dropwise at ambient temperature to a freshly prepared solution of the tungsten pentacarbonyl anion **2**. Next day the precipitate was filtered, the resulting extract was concentrated to remove acetonitryl and the crystalline residue was washed with diethyl ether to give compound **3** yield 0.32 g (68.5%), m.p. 128–129 °C. It is found: C, 12.97; Cl, 15.20; Ge, 15.12; W, 38.92%. $C_5O_5WGeCl_2$. It is counted: C, 12.84; Cl, 15.17; Ge, 15.53; W, 39.34.

2.3. *Germylenebis(tungsten pentacarbonyl) complex* **4**

Germanium tetrachloride 0.108 g (5×10^{-4} mol) in MeCN was added dropwise at ambient temperature to a freshly prepared solution of the tungsten pentacarbonyl anion **2**. Next day the precipitate was filtered, the resulting extract was concentrated to remove acetonitryl and the crystalline residue was washed with diethyl ether to give compound **4** yield 0.3215 (44.6%), m.p. 80 °C (with decomposition). It is found: C, 16.99; Ge, 9.62; W, 51.47%. $C_{10}O_{10}W_2Ge$. It is counted: C, 16.66; Ge, 10.08; W, 51.05.

Acknowledgements

This work was financially supported by the Russian Foundation for Basic Research (Project No. 07-03-0013), the Program for Support of the Leading Scientific Schools (Grant N.Sh 5148.2006.3), the Ministry of Industry and Science (Federal Target Scientific Technical Program "Investigation and Developments on Priority Directions of Science and Technology," theme "Highly Reactive Intermediates in Chemical Reactions"), and the Russian Academy of Sciences (Complex Programs of the Division of Chemistry and Materials Sciences of the Russian Academy of Sciences Nos. 1 and 8).

References

[1] P. Jutzi, W. Steiner, Chem. Ber. B. 109 (1976) 3473.
[2] W.P. Neumann, Chem. Rev. 91 (1991) 311.
[3] Von D. Uhling, H. Behrens, E. Linder, Z. Anorg. Allg. Chem. 401 (1973) 233.
[4] H. Behrens, M. Moll, E. Sixtus, Z. Naturforsch. B Anorg. Chem. 32B (1977) 1105.
[5] Yu.G. Budnikova, O.E. Petrukhina, Z.S. Titova, Yu.M. Kargin, Zhurn. Obshch. Khim. 66 (1996) 1239, Russ. J. Gen. Chem. 66 (1996) (Engl. Transl.).
[6] M.P. Egorov, A.A. Basova, A.M. Gal'minas, O.M. Nefedov, A.A. Moiseeva, R.D. Rakhimov, K.P. Butin, J. Organomet. Chem. 574 (1999) 279.
[7] W. Gade, E. Weiss, J. Organomet. Chem. 213 (1981) 451.
[8] J. Baker, A. Jarzecki, P. Pulay, J. Phys. Chem. A. 102 (1998) 1412.
[9] R.G. Parr, W. Yang, Density Functional Methods of Atoms and Molecules, Oxford University Press, New York, 1989.
[10] S.A. Katsyuba, E.E. Vandyukova, Chem. Phys. Lett. 377 (2003) 658.
[11] A.W. Ehlers, Y. Ruiz-Morales, E.J. Baerends, T. Ziegler, Inorg. Chem. 36 (1997) 5031.
[12] S.P. Amesen, H.M. Seip, Acta Chem. Scand. 20 (1966) 271.
[13] Y. Morino, Y. Nacamura, T. Iijima, J. Chem. Phys. 32 (1960) 643.
[14] L.H. Jones, R.S. McDowell, M. Goldblatt, Inorg. Chem. 8 (1969) 2349.
[15] H. Fujii, M. Kimura, Bull. Chem. Soc. Jpn. 43 (1970) 1933.
[16] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. H ead-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN 98 (Revision A.2), Gaussian, Inc., Pittsburgh (PA) USA, 1998.
[17] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[18] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B37 (1988) 785.
[19] P.C. Hariharan, J.A. Pople, Theor. Chim. Acta 28 (1973) 213.
[20] P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 270;
W.R. Wadt, P.J. Hay, J. Chem. Phys. 82 (1985) 284;
P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 299.