Photochemical reaction of W(CO)$_6$ with GeCl$_4$ as a source of germyl and germylene compounds acting as initiators for ring-opening metathesis polymerization of norbornene

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Abstract

Photolysis of W(CO)$_6$ in a solution of *n*-heptane containing GeCl$_4$ leads to the formation of two seven-coordinate compounds with direct W—Ge bonds: [(CO)$_4$W(μ-Cl)$_3$W(GeCl$_3$)(CO)$_3$] (**1**) and [(μ-GeCl$_2$){W(CO)$_5$}$_2$] (**2**). The molecular structures of these two tungsten–germanium compounds have been established by single-crystal X-ray diffraction studies. The germyl compound **1** is a previously synthesized binuclear complex of tungsten(II) with a d^4 electronic configuration, while in the new germylene compound **2** the tungsten atom is formally in the zero oxidation state with a d^6 electronic configuration and a direct W—W bond. In an attempt to establish whether compounds **1** and **2** could be used as precatalysts for the ring-opening metathesis polymerization (ROMP) of cyclic olefins, their reactivity towards norbornene has been studied. In chloroform-d_1 solution the ROMP reaction is accompanied by the formation of a new olefin, 2,2′-binorbornylidene (bi-(NBE)), as a result of carbene–carbene coupling. In reaction of norbornene carried out in benzene solution the ROMP reaction is accompanied by the formation of 2-phenylnorbornane (hydroarylation product) and small amounts of bi-(NBE). In general, in the presence of olefin, compound **2** undergoes rearrangement to give an olefin compound of the type [(WCO)$_5$(η^2-olefin)].
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Keywords: Tungsten; Germanium; Photochemistry; X-ray structure; Metathesis polymerization; Hydroarylation; Germyl; Germylene complex

1. Introduction

Heterobimetallic complexes with a direct metal—metal bond have attracted particular interest owing to their strikingly different activity relative to the separate metal complex, possible as a result of the cooperative effects of two metals. Thus, a great number of group 6 metal complexes containing germyl [1–14] or germylene ligands [15–24] have been synthesized and characterized, and some of them have proved to be very active and selective initiators for many catalytic and stoichiometric processes [25]. Heterobimetallic complexes of the type [(CO)$_4$M(μ-Cl)$_3$M(M′Cl$_3$)(CO)$_3$] M = W, Mo; M′ = Sn, Ge, prepared in photochemical oxi-

dative addition reaction of M(CO)$_6$ M = W, Mo, and tin or germanium tetrachloride [25], have emerged as versatile initiators for synthetically important transformations such as metathesis polymerization of alkynes, ring-opening metathesis polymerization (ROMP), dimerization, and hydroarylation of cyclic olefin [7,25].

The earlier-reported photochemical reaction of W(CO)$_6$ with GeCl$_4$ has been reinvestigated and found to give the previously synthesized trichloro-bridged dinuclear tungsten(II) compound [(CO)$_4$W(μ-Cl)$_3$W(GeCl$_3$)(CO)$_3$] (**1**) and a previously unknown germylene-bridged tungsten(0) dimer [(μ-GeCl$_2$){W(CO)$_5$}$_2$] (**2**) (Scheme 1). We have isolated a ditungsten complex bridged by a germanium center substituted with two chlorides. Here, we report the results of our studies on the crystal structure of both compounds, **1** and **2**, and on their reactivity towards olefin.

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$$4W(CO)_6 + 2GeCl_4 \xrightarrow[n\text{-heptane}]{h\nu} [(CO)_4W(\mu\text{-Cl})_3W(GeCl_3)(CO)_3] \text{ (1)} + [(\mu\text{-GeCl}_2)\{W(CO)_5\}_2] \text{ (2)} + 7CO$$

Scheme 1. Photochemical synthesis of W–Ge compounds **1** and **2**.

2. Results and discussion

2.1. Synthesis and spectroscopic characteristic

As was observed using IR and NMR spectroscopy several years ago, the photochemical reaction of tungsten hexacarbonyl with GeCl$_4$ in cyclohexane solution leads to the formation of two compounds, the dimeric tungsten(II) compound (**1**), an analogue of [(CO)$_4$W(μ-Cl)$_3$W-(SnCl$_3$)(CO)$_3$], and a not-fully characterized pentacarbonyltungsten–dichlorogermylene adduct [7]. Reinvestigation of this reaction and change of the reaction solvent from cyclohexane to *n*-heptane, in which all compounds are more soluble, allowed us to isolate two compounds, the germyl **1** and the germylene compound **2** in pure crystalline form and characterize both by spectroscopic methods in solution and by X-ray diffraction studies in the solid state. The IR spectrum of compound **1** is typical for dimeric halocarbonyls of group 6 metals containing mutually *cis* four and three carbonyl groups (Fig. 1A) [25]. The pentacarbonyl moiety of compound **2**, instead of the typical three-band pattern commonly observed in the IR spectra of complexes of the type [M(CO)$_5$L] with a local C_{4v} symmetry, gives at least five v(C≡O) bands in the IR spectrum (Fig. 1B), indicating a substantial lowering of the local C_{4v} symmetry arising from the presence of seven atoms around the central tungsten atom. In the ^{13}C NMR spectrum of compound **2** the carbonyl ligands give two resonances in the intensity ratio 1:4 at $\delta = 194.5$ and 192.9, respectively, differing very greatly in the tungsten–carbon coupling constant: $^1J_{W–C} = 147$ Hz, (1CO), $^1J_{W–C} = 120$ Hz (4CO). This indicates a stronger interaction of one of the five carbonyl groups with the tungsten atom than the other four carbonyl groups and suggests this unique CO group is *trans* to the germylene ligand, which is a poorer π-acceptor than the CO ligand. In the ^{13}C NMR spectrum of the tungsten(II) compound **1**, three resonances in the intensity ratio 2:1:4 at $\delta = 217.3$, 212.1 and 204.5, respectively, were observed [7], i.e. at lower field than for the tungsten(0) compound **2**. The lowest-field resonance of CO ligands at $\delta = 217.3$ differs from the highest-field resonance at $\delta = 204.5$ in the tungsten–carbon coupling constant ($^1J_{W–C} = 136$ Hz, (2CO), $^1J_{W–C} = 111$ Hz (4CO)), indicating a stronger interaction of two of the seven CO ligands with the tungsten atoms.

2.2. X-ray crystal structure

Although the structure of compound **1** has been proposed earlier based on the results of IR and NMR spectroscopic investigations, here we report the single crystal structure of **1** determined by X-ray diffraction studies
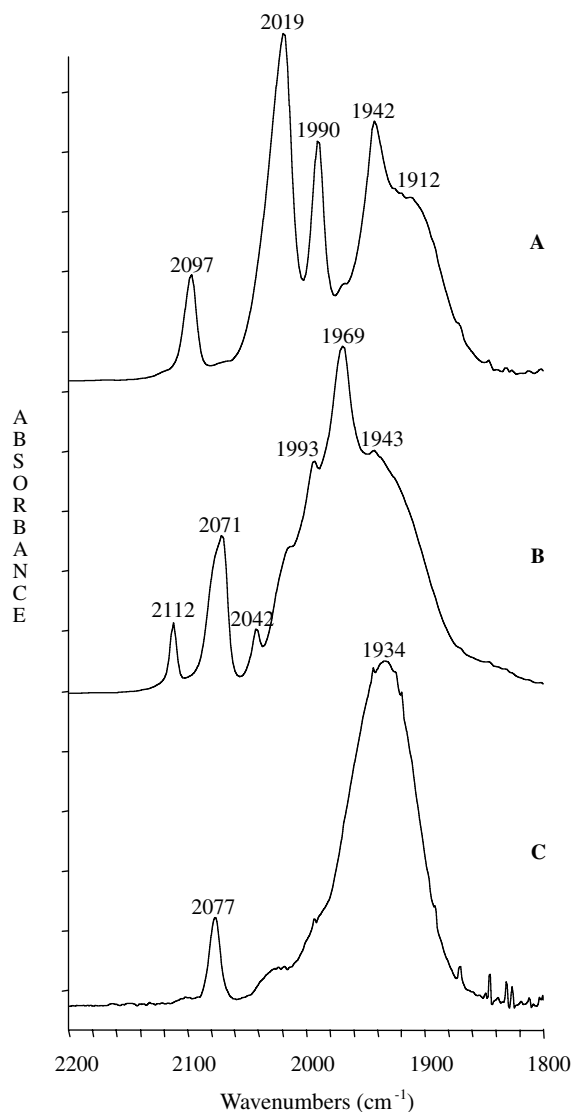

Fig. 1. Comparison of the v(C≡O) region of IR spectra in KBr pellets of compounds **1** (A) and **2** (B), and an insoluble product formed in reaction of **2** with olefin (C).

(Fig. 2, Table 1). Selected bond lengths and angles are listed in Table 2. The geometry of the coordination sphere of the tungsten atom in **1** approximates that of the 4:3 piano stool structure identified in analogous W–Sn and Mo–Sn complexes [25]. The angles between the plane defined by three chlorine atoms and the tetragonal base defined by four carbon atoms and the other plane defined by the germanium atom and three carbon atoms are 3.6(1)° and 3.7(8)°, respectively. Four carbonyl carbon atoms are at a slightly longer distance from the tungsten atom W(1) (W(1)–CO = 2.03 Å av.) than three carbonyl carbon atoms from the tungsten atom W(2) (W(2)–CO = 1.99 Å av.). In contrast to carbonyl groups,
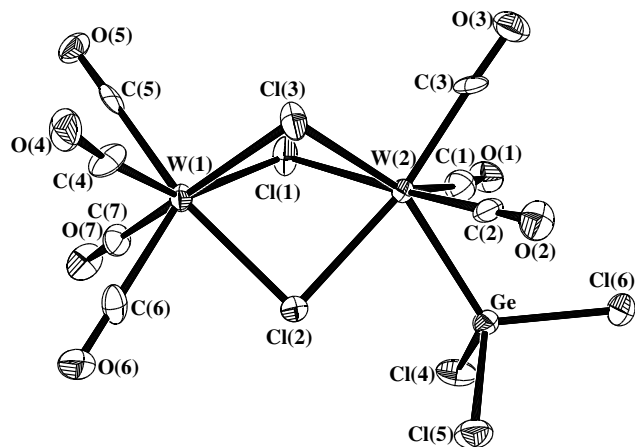
Fig. 2. Crystal structure of **1**.

Table 1
Crystal data and structure refinement parameters for $[(CO)_4W(\mu\text{-}Cl)_3W(GeCl_3)(CO)_3]$ (**1**) and $[(\mu\text{-}GeCl_2)\{W(CO)_5\}_2]$ (**2**)

	1	**2**
Empirical formula	$C_7Cl_6GeO_7W_2$	$C_{10}Cl_2GeO_{10}W_2$
Formula weight	849.06	791.29
Crystal size (mm)	$0.07 \times 0.05 \times 0.03$	$0.12 \times 0.10 \times 0.08$
Crystal system	Orthorombic	Monoclinic
Space group	*Pbca* (No. 61)	$P2_1/c$ (No. 14)
Unit cell dimensions		
a (Å)	15.578(3)	9.236(2)
b (Å)	13.646(3)	12.762(3)
c (Å)	17.258(3)	16.833(2)
β (°)	90.0	119.16(2)
V (Å^3)	3668.7(12)	1732.6(8)
Z	8	4
D_{calc} (g/cm^3)	3.074	3.033
Diffractometer	Kuma KM4CCD	Kuma KM4CCD
Radiation	Mo Kα ($\lambda = 0.71073$ Å)	Mo Kα ($\lambda = 0.71073$ Å)
Temperature (K)	100(2)	100(2)
μ (mm^{-1})	15.037	15.324
$F(000)$	3040	1416
No. of data/ restraints/ parameters	4479/0/209	4157/0/226
Index ranges	$-20 \leqslant h \leqslant 20$; $-17 \leqslant k \leqslant 17$; $-22 \leqslant l \leqslant 22$	$-12 \leqslant h \leqslant 12$; $-13 \leqslant k \leqslant 17$; $-21 \leqslant l \leqslant 21$
No. of reflections collected	40,214	22,756
Data collected, θ minimum/ maximum (°)	3.01/28.58	3.13/28.54
R_{int}	0.1412	0.0729
S	1.577	1.239
Final residuals: R_1, wR_2 ($I > 2\sigma(I)$)	0.1024, 0.1634	0.0343, 0.0598
T_{min}, T_{max}	0.137, 0.608	0.260, 0.373
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	1.970/−2.028	0.961/−1.802

Table 2
Selected bond lengths (Å) and angles (°) for **1**

Atoms	Distance	Atoms	Angle
W(1)—C(4)	2.01(2)	C(4)—W(1)—C(6)	114.8(9)
W(1)—C(6)	2.02(2)	C(4)—W(1)—C(5)	73.9(8)
W(1)—C(5)	2.04(2)	C(6)—W(1)—C(5)	75.5(8)
W(1)—C(7)	2.04(2)	C(4)—W(1)—C(7)	72.2(9)
W(1)—Cl(1)	2.475(5)	C(6)—W(1)—C(7)	72.7(8)
W(1)—Cl(2)	2.506(5)	C(5)—W(1)—C(7)	116.6(8)
W(1)—Cl(3)	2.515(5)	C(4)—W(1)—Cl(1)	145.2(6)
W(2)—C(1)	1.95(2)	C(5)—W(1)—Cl(2)	165.6(6)
W(2)—C(3)	1.99(2)	C(6)—W(1)—Cl(3)	164.9(6)
W(2)—C(2)	2.03(2)	Cl(1)—W(1)—Cl(2)	77.1(2)
W(2)—Cl(3)	2.487(5)	C(1)—W(2)—C(3)	73.4(7)
W(2)—Cl(2)	2.553(5)	C(1)—W(2)—C(2)	111.2(8)
W(2)—Cl(1)	2.553(5)	C(1)—W(2)—Cl(3)	148.0(5)
W(2)—Ge	2.551(2)	C(1)—W(2)—Ge	67.8(5)
Ge—Cl(4)	2.162(5)	C(3)—W(2)—Ge	114.9(6)
Ge—Cl(6)	2.167(6)	C(2)—W(2)—Ge	71.7(5)
Ge—Cl(5)	2.178(5)	Cl(3)—W(2)—Ge	143.8(1)
C(1)—O(1)	1.17(2)	C(3)—W(2)—Cl(2)	165.8(6)
C(2)—O(2)	1.10(2)	C(2)—W(2)—Cl(1)	166.2(6)
C(3)—O(3)	1.11(2)	Cl(3)—W(2)—Cl(2)	76.6(2)
C(4)—O(4)	1.13(3)	Cl(3)—W(2)—Cl(1)	76.2(2)
C(5)—O(5)	1.11(2)	Cl(2)—W(2)—Cl(1)	75.2(2)
C(6)—O(6)	1.15(2)	W(2)—Cl(3)—W(1)	89.3(1)
C(7)—O(7)	1.10(3)	W(2)—Cl(2)—W(1)	88.0(2)
		W(2)—Cl(1)—W(1)	89.3(1)

the W···W contact distance of 3.514(1) Å was found. The W—Ge distance of 2.551(2) Å in **1** is comparable with those reported for other germyl compounds of tungsten [1–14], and is very close to that found in the germylene compound **2** (2.561(1) and 2.569(1) Å) (Fig. 3, Table 3). The structure of compound **2** is very similar to that found for μ-(dibromogermylene)-bis(pentacarbonyltungsten) [3], and to other structurally characterized binuclear carbonyl complexes of tungsten containing bridging silylene or carbene ligands [26,27]. However, as can be expected, the W—W bond length of 3.360(1) Å in **2** is longer than in analogous silylene (3.265(2) Å in $[(\mu\text{-}SiPh_2)\{W(CO)_5\}_2]$ [26]) and carbene (3.118(1) Å in $[(\mu\text{-}CHPh)\{W(CO)_5\}_2]$ [27]) compounds.

Fig. 3. Crystal structure of **2**.
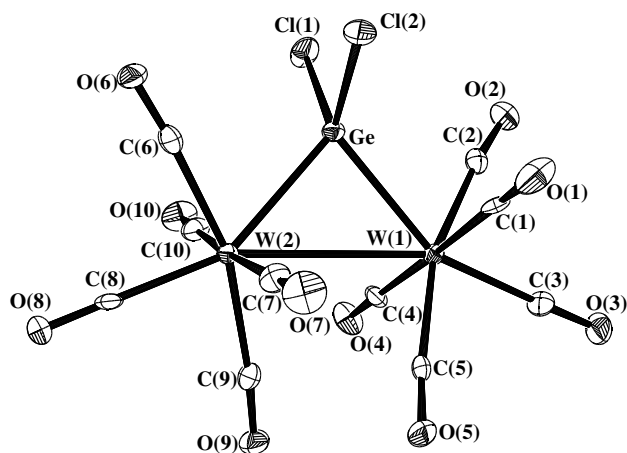
the bridging Cl atoms are slightly closer to W(1) than to W(2) (average W(1)—Cl = 2.499 Å and W(2)—Cl = 2.531 Å). The average angles, Cl—W(1)—Cl = 77.1°, Cl—W(2)—Cl = 76.0°, and W(1)—Cl—W(2) = 88.6°, ensure that there is no metal—metal bonding in **1**, in which

Table 3
Selected bond lengths (Å) and angles (°) for **2**

| Atoms	Distance	Atoms	Angle
W(1)—C(3)	2.022(6)	C(3)—W(1)—C(2)	80.4(3)
W(1)—C(2)	2.037(7)	C(3)—W(1)—C(1)	90.1(2)
W(1)—C(1)	2.046(6)	C(2)—W(1)—C(1)	90.4(2)
W(1)—C(4)	2.060(6)	C(3)—W(1)—C(4)	91.2(2)
W(1)—C(5)	2.070(6)	C(2)—W(1)—C(4)	89.5(2)
W(1)—Ge(1)	2.561(1)	C(1)—W(1)—C(4)	178.6(2)
W(1)—W(2)	3.360(1)	C(3)—W(1)—C(5)	84.3(3)
W(2)—C(8)	2.006(7)	C(2)—W(1)—C(5)	164.3(2)
W(2)—C(6)	2.031(7)	C(3)—W(1)—Ge(1)	154.1(2)
W(2)—C(7)	2.050(6)	C(6)—W(2)—C(8)	81.9(2)
W(2)—C(10)	2.058(6)	C(8)—W(2)—C(7)	91.7(3)
W(2)—C(9)	2.076(6)	C(6)—W(2)—C(7)	91.5(3)
W(2)—Ge(1)	2.569(1)	C(7)—W(2)—C(10)	175.6(3)
Ge(1)—Cl(1)	2.155(2)	C(6)—W(2)—C(9)	163.9(2)
Ge(1)—Cl(2)	2.170(2)	C(8)—W(2)—C(9)	82.5(2)
C(1)—O(1)	1.133(7)	C(7)—W(2)—Ge(1)	91.4(2)
C(2)—O(2)	1.136(8)	C(6)—W(2)—Ge(1)	70.7(2)
C(3)—O(3)	1.128(8)	C(8)—W(2)—Ge(1)	152.5(2)
C(4)—O(4)	1.124(7)	C(9)—W(2)—Ge(1)	124.6(2)
C(5)—O(5)	1.132(8)	C(10)—W(2)—Ge(1)	84.8(2)
C(6)—O(6)	1.140(8)	Cl(1)—Ge(1)—Cl(2)	99.64(8)
C(7)—O(7)	1.131(8)	Cl(1)—Ge(1)—W(1)	121.44(6)
C(8)—O(8)	1.142(8)	Cl(2)—Ge(1)—W(1)	119.31(5)
C(9)—O(9)	1.137(8)	Cl(1)—Ge(1)—W(2)	117.83(6)
C(10)—O(10)	1.126(8)	Cl(2)—Ge(1)—W(2)	118.04(6)
		W(1)—Ge(1)—W(2)	81.82(3)

The W—CO bond length in **2** falls in the range 2.006(7)–2.070(6) Å. The shortest W—CO bond distance is observed for CO in the *cis* position to the remaining four carbonyl ligands, which are at an average distance of 2.053 Å from the tungsten atom.

In **1** and **2**, the germanium atom is four-coordinate with a geometry that is best described as distorted tetrahedral. The average bond angle at the germanium atom is 109° in **1** and 109.5° in **2**. However, in **1** the W—Ge—Cl average angle (115.9°) is larger than the Cl—Ge—Cl average angle (102.1°), whereas in **2** the W—Ge—W angle (81.82(3)°) is noticeably smaller than other tetrahedral angles (Cl—Ge—Cl = 99.64(8)° and W—Ge—Cl = 119.1° av.).

2.3. Reactivity of compound 1 towards norbornene

In our previous investigations, we have shown that compound **1** reacts rapidly at room temperature with phenylacetylene to give red poly(phenylacetylene) in high yield [7,25]. Here we tested the reactivity of **1** and **2** towards bicyclic olefins – norbornene (NBE).

In reaction of NBE carried out in C_6H_6 solution at 70 °C in the presence of **1**, the yield of ROMP polymer (poly-1,3-cyclopentylenevinylene, poly-NBE) reached *ca.* 50% (by mass), but the rest of NBE transforms to 2,2′-binorbornylidene (bi-(NBE)), and to the hydroarylation product (2-phenylnorbornane) in a 1:6 molar ratio, respectively (Scheme 2). An identical distribution of products was detected during the reaction carried out in C_6D_6 solution,
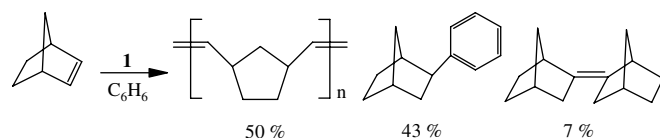
Scheme 2. Transformation of NBE in reaction carried out in benzene solution in the presence of **1**.

monitored by ^{1}H NMR spectroscopy (Fig. 4). It should be noted that poly-(NBE) is poorly soluble in benzene and for that reason its characteristic olefinic proton signals at $\delta = 5.53$ for *trans* and $\delta = 5.39$ for *cis* (—CH=CH—) units are of low intensity [28]. The most intense signals in the spectrum are due to protons of *exo*-2-phenyl-d_5-3-d_1-norbornane δ: 2.64 (t, $J_{HH} = 7.2$ Hz, 1H, C^2H), 2.31 (s, 1H, C^1H), 2.23 (s, 1H, C^4H), 1.64 (d, $J_{HH} = 7.2$, 1H; C^3HD), 1.49 (m, 3H; $C^{6,5,7}H_2$), 1.23 (m, 1H; C^6H_2), 1.18 (m, 1H; C^5H_2), 1.08 (d, $J_{HH} = 9.6$, 1H; C^7H_2) [29]. The simultaneous formation of four stereoisomers (*anti–cis*, *syn–cis*, *anti–trans*, and *syn–trans*) of bi-(NBE) is indicated by signals characteristic for their methine protons (HC^1) at $\delta = 2.93$, 2.88, 2.78, and 2.75 [30,31]. During the conversion of NBE in the presence of **1** monitored by ^{1}H NMR spectroscopy in chloroform-d_1 solution, the decay of NBE and the appearance of poly-(NBE) as well as bi-(NBE) are nicely detected (Fig. 5). The formation of small amounts of *exo* and *endo*-2-chloronorbornane in this solvent is indicated by signals characteristic for the methine proton (HC^2) at δ 3.8 and 4.2, respectively [29]. Although the reaction was performed under anhydrous conditions, we could not exclude the presence of traces of water leading
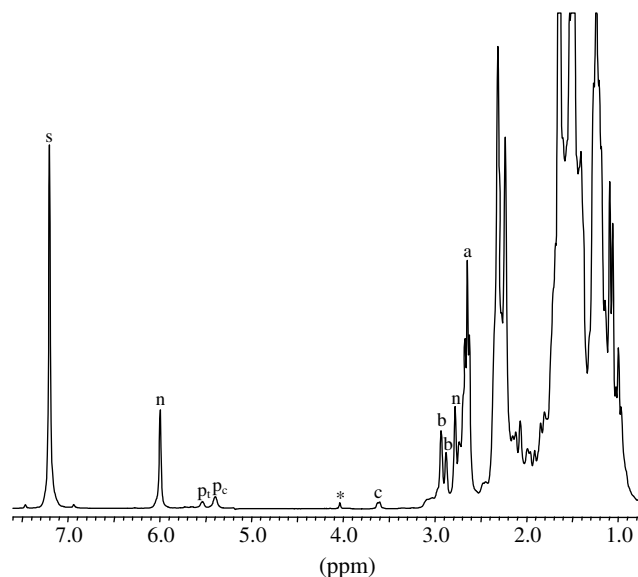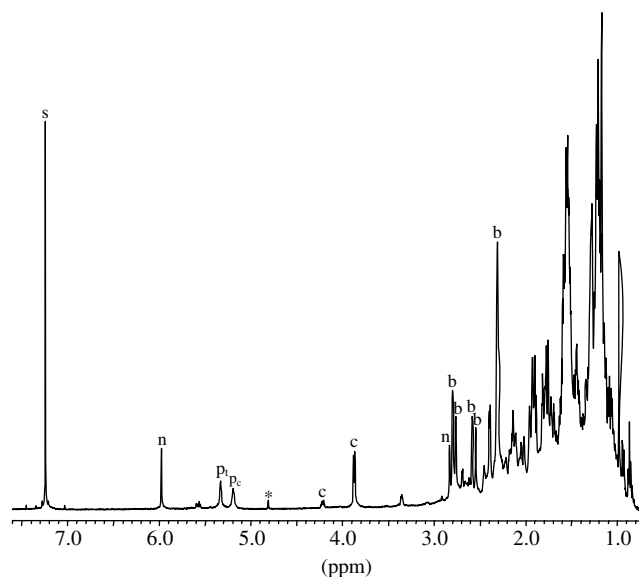

Fig. 4. The ^{1}H NMR spectrum (500 MHz, C_6D_6 (s)) obtained during reaction of **1** with NBE (n) showing the formation of poly-(NBE) (p) and bi-(NBE) (b). Signals characteristic for *exo*-2-phenyl-d_5-3-d_1-norbornane are denoted by (a), those characteristic for chloronorbornane by (c), and signals of $[W(CO)_5(\eta^2\text{-}C_7H_{10})]$ are labeled by an asterisk (*).

Fig. 5. The ^{1}H NMR spectrum (500 MHz, CDCl$_3$) obtained during reaction of **1** with NBE showing the formation of poly-(NBE) (p) and bi-(NBE) (b). Signals characteristic for chloronorbornane are denoted by (c) and those characteristic for [W(CO)$_5$(η^2-C$_7$H$_{10}$)] labeled by an asterisk (∗).

to the formation of 3-hydroxyl-2,2′-binorbornyl, observed in the latter spectrum due to a characteristic signal at $\delta = 3.35$ and subsequently identified by GC–MS analysis ($M_r = 206.32$). The η^2-coordination of NBE to the tungsten atom is indicated by a proton signal at $\delta = 4.8$ [29]. The NMR experiment provides very important information about the initiation of ROMP reaction by **1**. The mechanism for the formation of poly-(NBE) as well as bi-(NBE) involves the coordination of NBE to the tungsten atom and its transformation to a tungstanorbornylidene species as a result of 1,2-hydride shift (Scheme 3). A similar η^2-olefin-to-alkylidene rearrangement has been proposed by others for catalytic systems where an olefin ligand is the only source of an alkylidene species [28]. The first direct evidence for an alkene-to-alkylidene rearrangement was obtained by Wolczanski et al. [32]. In our study it was observed that a bimolecular coupling of the tungstanor-bornylidene intermediate species led to the formation of bi-(NBE) and regenerated the binuclear compound **1**. A similar bimolecular coupling of two carbene ligands has been observed during mild thermolysis of chromium(0)
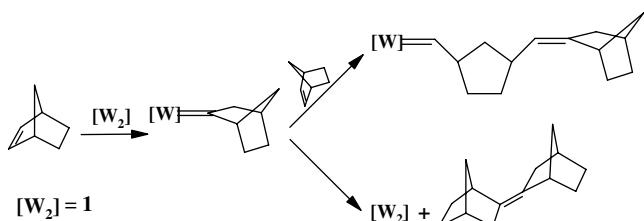
and tungsten(0) pentacarbonylcarbene complexes [33–35] and detected by Schrock et al. in reaction of alkylidene complexes of tantalum, molybdenum, and tungsten [36–38]. For the first time the carbene–carbene coupling reaction was applied in synthesis of bi-(NBE) from NBE in reaction catalyzed by a W—Sn compound [30]. Previously, the McMurry and Fleming procedure for reductive dimerization of ketones had been applied for the synthesis of compounds of that type [31,39]. As shown here, compound **1** can also be used as a catalyst in synthesis of bi-(NBE), which is formed as a mixture of four stereoisomers. It is worth pointing out that the detection of bi-(NBE) provides direct evidence for tungsten(II)-promoted transformation of olefin to metallacarbene, which is able to initiate the ROMP of NBE or to disproportionate giving a new olefin as the carbene–carbene coupling product.

2.4. Reactivity of compound 2

To investigate the reactivity of a new analogue of the bridging carbene compound **2**, its reactions with various olefins were examined. Thus, reaction of **2** in *n*-heptane solution with ethene at room temperature cleanly yields two tungsten carbonyl compounds: an η^2-ethene complex soluble in *n*-heptane, [W(CO)$_5$(η^2-C$_2$H$_4$)], [40,41] and a compound insoluble in *n*-heptane, with an IR spectrum characteristic for a pentacarbonyl moiety with a local C_{4v} symmetry, containing one weak and one strong band at 2077 and 1934 cm^{-1}, respectively (Fig. 1C). The very poorly soluble solid studied by ^{13}C NMR spectroscopy in CDCl$_3$ solution has shown only a low-intensity broad signal at $\delta = 194.99$. In a similar reaction of **2** with NBE the formation of [W(CO)$_5$(η^2-C$_7$H$_{10}$)] [29] and the initiation of ROMP reaction were observed by ^{1}H NMR spectroscopy in benzene-d_6 and chloroform-d_1 solutions. Similarly as for compound **1**, ROMP reaction initiated by **2** in benzene solution was accompanied by the formation of bi-(NBE) and 2-phenylnorbornane.

2.5. Conclusions

In photochemical reaction of W(CO)$_6$ and GeCl$_4$, tri-chlorogermyl and dichlorogermylene species are formed which bind to the tungsten atom to give compounds **1** and **2**, respectively. Compound **1** is a binuclear complex of tungsten(II) with a d^4 electronic configuration, while in compound **2**, which has a direct W—W bond, the tungsten atom is formally in the zero oxidation state with a d^6 electronic configuration.

Investigation of the reactivity of compounds **1** and **2** revealed that both compounds can be used as precatalysts for the ROMP of NBE. In reaction of complexes **1** and **2** with NBE the initiation of ROMP reaction as well as the formation of bi-(NBE) were observed. This experiment provided direct evidence that the mechanism for the formation of poly-(NBE) as well as bi-(NBE) must involve the

Scheme 3. Initiation of ROMP of NBE and formation of 2,2′-binor-bornylidene in reaction carried out in CDCl$_3$ solution in the presence of **1**.

coordination of NBE to the tungsten atom and its transformation to a tungstanorbornylidene species as a result of 1,2-hydride shift (the activation of the olefin C—H bond by the tungsten atom). Tungstanorbornylidene species are able to initiate the ROMP of NBE or, in carbene–carbene coupling reaction, give a new olefin bi-(NBE). In that way direct evidence was obtained for the transformation of a cyclic olefin ligand to a carbene species as a result of the activation of the olefin C—H bond by the tungsten atom in a low oxidation state.

In benzene solution the ROMP reaction is accompanied by the hydroarylation reaction of NBE, which indicates that compounds **1** and **2** are also able to activate the C–H bond of arene.

The very reactive germylene compound **2**, in reaction with olefin undergoes rearrangement to give an olefin and bis(germylene) compounds. The pentacarbonylnorbornene complex of tungsten(0) very easily transforms to a carbene species initiating the ROMP reaction.

Further efforts to explore these germyl and germylene complexes of tungsten in ROMP reaction of different derivatives of norbornene are in progress [43].

3. Experimental

3.1. General information

The synthesis and manipulation of all chemicals were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Solvents and liquid reagents were pre-dried with CaH_2 and vacuum transferred into small storage flasks prior to use. IR spectra were measured with a Nicolet-400 FT-IR instrument. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AMX 300 or 500 MHz instrument. All chemical shifts are referenced to residual solvent protons for ^{1}H NMR (δ 7.24 CDCl$_3$; 7.20 benzene-d_6; 4.65 D$_2$O) and to the chemical shift of the solvent for ^{13}C NMR (77.00 CDCl$_3$; 128.00 benzene-d_6). The photolysis source was an HBO 200 W high-pressure Hg lamp. Analyses of the catalytic reaction products were performed on a Hewlett–Packard GC–MS system. The average molecular weights (M_n) of the polymers were determined by gel permeation chromatography (GPC) of the solution in CHCl$_3$ on a Hewlett–Packard 1090II instrument equipped with a refractive index detector HP 1047A and Plgel 10 μ MIXED-B or Plgel 5 μ MIXED-C columns previously calibrated using commercially available polystyrene standards in the molecular mass range 11.6×10^3 to 2.9×10^6.

3.2. Synthesis of W—Ge complexes 1 and 2

A solution of W(CO)$_6$ (100 mg, 0.28 mmol) and GeCl$_4$ (0.3 cm^3, 1.1 mmol) in *n*-heptane (30 cm^3) was irradiated through quartz at room temperature by *ca.* 1.5 h. The volatile materials were then stripped off the reaction mixture under reduced pressure at room temperature and the unreacted W(CO)$_6$ sublimated off at *ca.* 320 K. The residue was

extracted with a few portions (5 cm^3) of *n*-heptane to give, after evaporation of the solvent, compound **2** (32 mg, 29% yield). IR (KBr disc): $\nu = 2112$ (w), 2071 (s), 2042 (w), 1993 (s,sh), 1969 (vs), 1943 (s,sh), 577 (w), 557 (w) cm^{-1}. ^{13}C NMR (125 MHz, CDCl$_3$): $\delta = 194.5$ ($^1J_{W-C} = 147$ Hz, 1CO), 192.9 ($^1J_{W-C} = 120$ Hz, 4CO). Anal. Calc. for C$_{10}$Cl$_2$GeO$_{10}$W$_2$: C, 15.18; Cl, 8.96. Found: C, 15.35; Cl, 9.09%. Compound **1**, insoluble in *n*-heptane, was recovered (40 mg, 33% yield) [7].

3.3. X-ray diffraction studies

Crystal data for a yellow plate of **1** with approximate dimensions of $0.07 \times 0.05 \times 0.03$ mm and a for red block of **2** with approximate dimensions of $0.12 \times 0.10 \times 0.08$ mm were collected at 100 K, using a KM4-CCD diffractometer and graphite-monochromated Mo Kα radiation, generated from a diffraction X-ray tube operated at 50 kV and 35 mA. The images were indexed, integrated, and scaled using the KUMA data reduction package CrysAlis RED (Oxford Diffraction Poland Sp., CCD data collection and reduction GUI, Version 1.173.13 beta, release 14.11.2003, Copyright 1995–2003). The structure was solved by the heavy atom method using SHELXS97 (Program for the Solution of Crystal Structure, University of Göettingen, Göettingen, Germany, 1997), and refined by the full-matrix least-squares method on all F^2 data (Program for the Refinement of Crystal Structure, University of Göettingen, Göettingen, Germany, 1997). All atoms were included in the refinement, with anisotropic displacement parameters. The data were corrected for absorption, min/max absorption coefficients 0.137/0.608 for **1** and 0.260/0.373 for **2**.

3.4. Reaction of compound 2 with ethene

The ethene was bubbled into a freshly prepared solution of **2** in *n*-heptane at room temperature. The decay of **2** was complete after 60 min (IR spectroscopy). The clear, yellow solution was then decanted and separated from an yellow precipitate to give clean [W(CO)$_5$(η^2-C$_2$H$_4$)] [40,41]. The compound, insoluble in *n*-heptane, was not fully identified. (Anal. Found C, 13.55). IR (KBr disc): $\nu = 2077$ (w), 1934 (vs), 595 (w), 571 (w) cm^{-1}. ^{13}C NMR (125 MHz, CDCl$_3$): $\delta = 194.99$ (broad).

3.5. Reaction of compound 2 with NBE in n-heptane

During the reaction of **2** with NBE in *n*-heptane at room temperature the decay of ν(C≡O) bands of germylene compound of tungsten, and simultaneous appearance of ν(C≡O) bands at 2078 (w) and 1951 (vs) cm^{-1}, characteristic for a norbornene complex [W(CO)$_5$(η^2-C$_7$H$_{10}$)] [29], were observed by IR spectroscopy. The reaction solution changed from orange to yellow, and the light yellow precipitate was settled out, leaving the η^2-norbornene complex in the *n*-heptane solution.

3.6. Reaction of compound 1 and 2 with NBE in benzene solution

NBE (*ca.* 0.3 g, 3.5 mmol) in solution of C_6H_6 (5 cm^3) was added to *ca.* 0.03 g (0.035 mmol) of compound **1** or **2** and stirred at 343 K until completion (*ca.* 6 h). The conversion was determined by ^{1}H NMR spectroscopy, with D_2O as the external standard. The polymer was then precipitated in methanol, isolated, and dried under vacuum (*ca.* 0.15 g, 50%). The GC–MS analysis of the residue obtained after separation of polymer revealed the formation of 2-phenylnorbornane ($M_r = 172.27$) [42] and 2,2′-binorbornylidene ($M_r = 188.32$) [30,31] in a molar ratio of *ca.* 6:1. The average molecular weights M_n of poly-(NBE) obtained in reaction initiated by **1** and **2** were 58,490 and 25,090, respectively.

3.7. General procedure for reaction of NBE in the NMR tube

Under a nitrogen atmosphere, complex **1** or **2** (*ca.* 0.03 g, 0.035 mmol) was weighed into an NMR tube. The tube was then capped with a septum. A portion of NBE (*ca.* 0.03 g, 0.32 mmol) in (0.7 cm^3) appropriate solution (CDCl$_3$, C$_6$D$_6$) was then added to the NMR tube via a syringe. The tube was shaken very briefly and transferred to the NMR probe. The conversion of NBE was observed by ^{1}H NMR spectroscopy at room temperature and the desired time.

4. Supplementary material

The X-ray crystallographic data for compounds **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre with deposition Nos. CCDC 250426 (**1**) and 250427 (**2**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk).

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