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Journal of Organometallic Chemistry 564 (1998) 143–153

Journal of Organo metallic Chemistry

Synthesis, structure and reactivity of novel W–Ge chlorocarbonyl compounds. X-ray crystal structure of [WCl($GeCl_3$)$(CO)_3$$(NCEt)_2$]

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Received 23 February 1998

Abstract

The reaction of $GeCl_4$ with tungsten(0) compounds yielded heterobimetallic W–Ge complexes. The novel dinuclear complex [$(CO)_4$W(μ-Cl)$_3$W($GeCl_3$)$(CO)_3$] **1** was obtained together with [W$(CO)_5$($GeCl_2$)] **2** in a photochemical reaction of W$(CO)_6$ with $GeCl_4$. The mononuclear seven-coordinate complex [WCl($GeCl_3$)$(CO)_3$$(NCMe)_2$] **3** was formed in a reaction of complex **1** with acetonitrile or in a reaction of [W$(CO)_4$$(NCMe)_2$] with $GeCl_4$ in dichloromethane. A single-crystal X-ray diffraction study of the complex [WCl($GeCl_3$)$(CO)_3$$(NCEt)_2$] **4** showed that the environment of the tungsten atom is a distorted capped octahedron with the $GeCl_3$ anionic ligand occupying the unique capping position above an octahedral face defined by the three carbonyl groups. The position of the $GeCl_3$ ligand is approximately *trans* to the W–Cl bond. The dinuclear complex **1** and the mononuclear complex **3** show similar behavior in reaction with alkynes. Complexes were isolated in which CO or/and acetonitrile ligands were replaced by alkyne ligands. The alkyne tungsten(II) complexes **7–13** formed were structurally characterized by IR and NMR spectroscopy. However, the reaction of **1** and **3** with phenylacetylene (PA) leads to polymerization and formation of a high molecular weight polyphenylacetylene (PPA). The structures and mechanisms of the formation of various new types of complexes and their role in the catalytic process are discussed. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Tungsten(II); German; Crystal structure; Alkyne complexes; Polymerization

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1. Introduction

In 1995 we reported [1] that a photochemical reaction of W$(CO)_6$ with $SnCl_4$ led to the formation of an orange crystalline air-sensitive complex. This was structurally identified by single-crystal X-ray crystallography as the first example of a dinuclear halogenocarbonyl complex of tungsten(II) with a W–Sn bond.

The triply chloride-bridged dimer [$(CO)_4$W(μ-Cl)$_3$W($SnCl_3$)$(CO)_3$] reacts with a wide range of two-electron donor ligands L, that cleave the chloride bridges to give mononuclear disubstituted products of the type [$WCl_2$$(CO)_3$$L_2$] and [WCl($SnCl_3$)$(CO)_3$$L_2$] [2]. Further studies [3,4] with this complex showed that chlorine bridge-breaking and substitution of a CO group by alkene or alkyne occur very easily and mononuclear six- or seven-coordinate complexes are formed.

In this paper, we report a photochemical reaction of W$(CO)_6$ with $GeCl_4$ that yields a unique dinuclear compound [$(CO)_4$W(μ-Cl)$_3$W($GeCl_3$)$(CO)_3$] **1**. The dinuclear complex **1** has been found to be an active catalyst for the polymerization of PA. The mononuclear complex [WCl($GeCl_3$)$(CO)_3$$(NCMe)_2$] **3** shows similar behavior, leading to the postulate that the active species in all cases is mononuclear.

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PII S0022-328X(98)00584-1

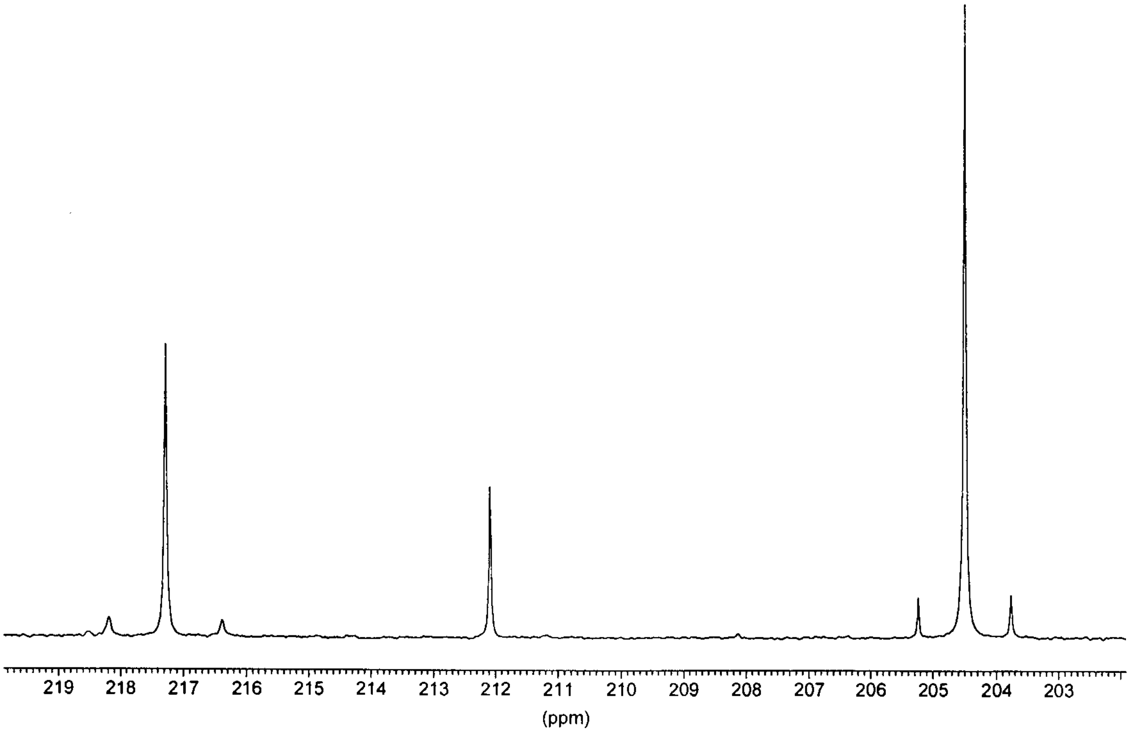

Fig. 1. Carbonyl region of $^{13}C\{^1H\}$-NMR spectrum of $[(CO)_4W(\mu\text{-}Cl)_3W(GeCl_3)(CO)_3]$ **1** in toluene-d_8.

2. Results and discussion

2.1. Tungsten(II)–germanium(II) chlorocarbonyl complexes

Following our report [1] of the synthesis, molecular structure and reactivity of the unusual dimeric, bimetallic tungsten–tin compound $[(CO)_4W(\mu\text{-}Cl)_3W(SnCl_3)(CO)_3]$, it has recently been found that the photochemical reaction of $W(CO)_6$ with $GeCl_4$ leads to an analogous W–Ge complex in moderate yields. Photolysis of a cyclohexane solution containing tungsten hexacarbonyl and germanium tetrachloride gives an orange solution, and then a yellow precipitate of $[(CO)_4W(\mu\text{-}Cl)_3W(GeCl_3)(CO)_3]$ **1** in a ca. 60% yield. This extremely air-sensitive compound **1** was further purified via crystallization from toluene/heptane under nitrogen and then characterized by IR and ^{13}C-NMR spectroscopy. The IR spectrum of **1** in KBr showed four bands in the terminal carbonyl region with the shape, frequency and intensity almost identical to the spectrum of $[(CO)_4W(\mu\text{-}Cl)_3W(SnCl_3)(CO)_3]$ [1]. The $^{13}C\{^1H\}$-NMR spectrum of compound **1** in toluene-d_8 at 293 K consists of three sharp resonances at 217.3, 212.1 and 204.5 ppm in the approximate intensity ratio 2:1:4, respectively (Fig. 1). Very similar resonances were observed for the carbonyl group of $[(CO)_4W(\mu\text{-}Cl)_3W(SnCl_3)(CO)_3]$ [1]. The spectroscopic properties of complex **1** are very similar to those of the analogue $[(CO)_4W(\mu\text{-}Cl)_3W(SnCl_3)(CO)_3]$, hence it probably has an analogous structure with a 4:3 arrangement of either $(OC)_4WCl_3$ or $(OC)_3(GeCl_3)WCl_3$ around each tungsten center. An attempt to prepare a single crystal of **1** was unsuccessful, perhaps due to the instability of **1**. Besides **1**, a side product is formed in the photochemical reaction of $W(CO)_6$ and $GeCl_4$ that was identified by IR [ν(CO) 2071 (w), 1937 (vs)] and by $^{13}C\{^1H\}$-NMR (δ 202.8 ppm, J(WC) 158 Hz, 1 CO; 198.1 ppm, J(WC) 125 Hz, 4 CO) as $[W(CO)_5GeCl_2]$ **2**. Similar compounds $[W(CO)_5(GeCl_2)(THF)]$ and $[W(CO)_5(GeClCp)]$ had been observed earlier by Jutzi et al. [5]. Compound **2** is extremely air-sensitive and readily soluble even in cyclohexane and other hydrocarbons. The appearance of compound **2** as the side product suggest that the $GeCl_3^-$ ligand very easily undergoes hydrolysis to give $GeCl_2$ and Cl^-.

The mechanism for the formation of **1** is not known but the reaction can be summarized as follows (Eq. (1)):

$$3W(CO)_6 + 2GeCl_4 \xrightarrow{h\nu} [(CO)_4W(\mu\text{-}Cl)_3W(GeCl_3)(CO)_3] + [W(CO)_5(GeCl_2)] + 6CO \qquad (1)$$

2.2. Reactivity of $[(CO)_4W(\mu\text{-}Cl)_3W(GeCl_3)(CO)_3]$ 1

The triply chloride-bridged dimer $[(CO)_4W(\mu\text{-}Cl)_3W(GeCl_3)(CO)_3]$ **1** reacts with two-electron donor ligands (L = PPh_3, acetonitrile) that cleave the chloride bridges to give mononuclear disubstituted products of the type $[WCl_2(CO)_3L_2]$ and $[WCl(GeCl_3)(CO)_3L_2]$ (Eq. (2)):

$$[(CO)_4W(\mu\text{-}Cl)_3W(GeCl_3)(CO)_3] + 4L$$
$$\rightarrow [WCl(GeCl_3)(CO)_3L_2] + [WCl_2(CO)_3L_2] + CO \qquad (2)$$

When compound **1** is dissolved in toluene and acetonitrile is added, an equimolecular mixture of $[WCl(GeCl_3)(CO)_3(NCMe)_2]$ **3** and $[WCl_2(CO)_3(NCMe)_2]$ is immediately formed. Recrystallization of the mixture from CH_2Cl_2/toluene/heptane produces quite stable yellow crystals of **3** while the considerably less stable $[WCl_2(CO)_3(NCMe)_2]$ decomposes with a loss of CO and the formation of a deep blue most probably chloride-bridged dimer insoluble in methylene chloride.

Compound **3** is very quickly hydrolyzed on exposure to air, and special precautions are necessary to exclude air from the solvents to prepare crystals.

In the reaction of **1** with PPh_3, the mixture of two compounds ($[WCl_2(CO)_3(PPh_3)_2]$ and $[WCl(GeCl_3)(CO)_3(PPh_3)_2]$) can probably be formed, but after repeated crystallization and washing with acetonitrile, the mixture gives pure $[WCl_2(CO)_3(PPh_3)_2]$ with the IR spectrum [ν(CO): 2015 (s), 1935 (vs), 1890 (s) cm^{-1}] and other data agreeing with those discussed elsewhere [2]. Compound **1** in interaction with PPh_3 undergoes a possible loss of $GeCl_2$, which is washed out together with an excess of PPh_3.

Compound **1** dissolves in acetone, initially giving a dark brown solution; however, after a few minutes, the solution becomes deep blue. The blue solid which is formed after evaporation of acetone in vacuo is characterized by the absence of ν(CO) bands and the presence of a strong ν(W=O) band at 970 cm^{-1} in the IR spectrum. This result suggests that after the coordination of acetone to tungsten, similar as with other nucleophiles, the carbon–oxygen multiple bond is cleaved to form an oxo complex. Such a process was previously observed by Bryan and Mayer in reactions of $[WCl_2(PMePh_2)_4]$ with a variety of ketones and aldehydes [6].

Surprisingly, the chemistry of heterobimetallic tungsten(II)–germanium(II) complexes has been developed very weakly. The first complex of this type to be reported and crystallographically-characterized was $[WBr(GeBr_3)(CO)_3(bipy)]$ [7]. Recently, Baker and Kendrick briefly mentioned the formation of **3** by reaction of $[W(CO)_3(NCMe)_3]$ with $GeCl_4$ in acetonitrile, but without synthetic and spectroscopic details [8]. As noted by Baker and Kendrick, their tungsten–germanium complex could not be isolated in a pure state. However, we found that compound **3** is more conveniently obtained in high yields by using CH_2Cl_2 instead of acetonitrile as the solvent for the reaction of $[W(CO)_4(NCMe)_2]$ with $GeCl_4$.

Compound **3** is readily soluble in NCMe, acetone, and chlorinated solvents (CH_2Cl_2, $CHCl_3$), but less soluble in hydrocarbon solvents. It is air-sensitive in solution but in the solid state can be stored under nitrogen for a month without decomposition. The most prominent feature of complex **3** is the facility with which acetonitrile ligands can be replaced by other ligands. Compounds **4–6**, containing nitriles with a longer carbon chain, were prepared in the reaction of **3** with an appropriate nitrile at room temperature (r.t.).

The carbonyl region of the IR spectra of compounds **3–6** in KBr is almost identical showing three carbonyl bands (see Section 3) and is similar to that for the analogous molybdenum–germanium complex first obtained by Baker and Kendrick, [ν(CO): 2040 (s), 1953 (s), 1877 (m) cm^{-1}] [8] and the tungsten–tin compound obtained by us [ν(CO): 2030 (vs), 1935 (s), 1903 (vs) cm^{-1})] [9]. However, IR spectra of **3** in a dichloromethane solution shows more than three bands in the carbonyl stretching region: 2040 (s), 2020 (s), 1970 (m), 1930 (vs) cm^{-1}. The spectral differences correspond to different coordination geometries, and, in a dichloromethane solution, distinct isomers of **3** may co-exist, as was proposed previously by Kummer and Graham [10]. In the ν(C≡N) region of the IR spectra for **3** two bands are observed. One is the ν(C≡N) band and the other a combination band resulting from the symmetrical CH_3 deformation and the C–C stretch which borrows its intensity from the ν(C≡N) [11]. For compound **3**, the bands are at 2320 and 2292 cm^{-1}, i.e. at higher frequencies than the ν(C≡N) band in the free acetonitrile observed at 2268 cm^{-1} [11]. The intensity ratio of the ν(C≡N) band to that of the combination band was found to be a major difference for *cis* and *trans* isomers [11]. Two sharp bands of comparable intensities in the ν(C≡N) region of **3** are consistent with *cis* acetonitrile ligands [11]. The ν(C≡N) frequency of coordinated propionitrile and butyronitrile in **4** and **5** was observed as a single band at 2292 cm^{-1}. The bands at about 585 and 565 cm^{-1} are attributed to the deformation vibrations of the W–CO groups. The lower frequency region of the IR spectrum is dominated by a principal absorption at 379 cm^{-1}, which can be regarded as a ν(Ge–Cl) vibration.

The ^{1}H- and ^{13}C-NMR spectra of the nitrile compounds **3–6** are very similar and are consistent with the solid-state structure of **4** (Fig. 2). The spectrum shows one carbonyl resonance of three equivalent CO groups and a single signal of the carbons of two nitriles (see Section 3).

According to the observation of Colton and Kevekordes, it is possible to distinguish between a carbonyl group in the capping and octahedral positions in the capped octahedral environment by ^{13}C-NMR spectroscopy [12]. The resonance due to the capping carbonyl appears at a high frequency, some 30 ppm above that for the carbonyls occupying the octahedral positions [12]. The ^{13}C-NMR spectrum of **3–6** does not show low-field resonance characteristic of the carbonyl

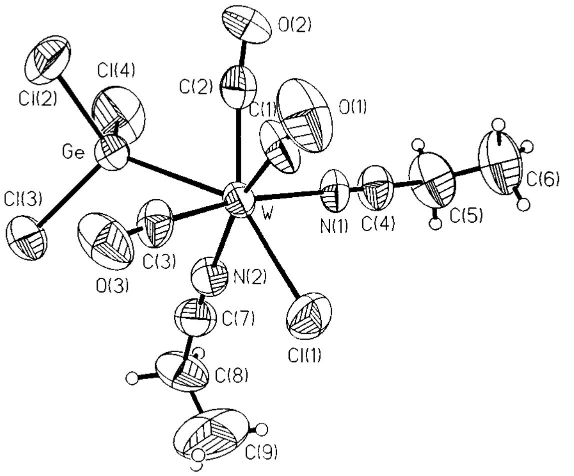

Fig. 2. Molecular structure of [WCl(GeCl$_3$)(CO)$_3$(NCEt)$_2$] **4**.

ligand in the unique capping position. Our results excluded the formation of such an isomer with carbonyl occupying the capping position as was proposed by Baker et al. for [MoCl(SnCl$_3$)(CO)$_3$(NCMe)$_2$] [13] and [MoCl(GeCl$_3$)(CO)$_3$(NCMe)$_2$] [8].

The electronic spectrum of **4** shows one strong band at 238 nm and two lower intensity bands at 322 and 386 nm. The first band, because of its high intensity and its position, is attributed to the CT transition $\pi^*(CO) \leftarrow d\pi(W)$. Two lower-energy bands, because of their relatively low intensity, can be assigned to a ligand–field transition.

Table 1
Selected bond lengths (Å) and bond angles (°) for [WCl(GeCl$_3$)(CO)$_3$(NCEt)$_2$] **4**

Bond length (Å)			
W–C(1)	1.977(9)	W–Cl(1)	2.423(3)
W–C(3)	1.979(9)	W–Ge	2.567(1)
W–C(2)	2.008(11)	Ge–Cl(2)	2.139(3)
W–N(2)	2.174(6)	Ge–Cl(3)	2.156(2)
W–N(1)	2.212(6)	Ge–Cl(4)	2.159(4)
Bond angle (°)			
C(1)–W–C(3)	75.6(3)	C(2)–W–Cl(1)	149.2(3)
C(1)–W–C(2)	74.8(4)	N(2)–W–Cl(1)	80.2(2)
C(3)–W–C(2)	109.4(4)	N(1)–W–Cl(1)	82.1(2)
C(1)–W–N(2)	165.5(4)	C(1)–W–Ge	116.9(3)
C(3)–W–N(2)	101.6(3)	C(3)–W–Ge	72.5(3)
C(2)–W–N(2)	119.0(4)	C(2)–W–Ge	67.0(3)
C(1)–W–N(1)	102.0(3)	N(2)–W–Ge	74.8(2)
C(3)–W–N(1)	169.8(3)	N(1)–W–Ge	116.9(2)
C(2)–W–N(1)	79.1(3)	Cl(1)–W–Ge	143.81(7)
N(2)–W–N(1)	78.1(2)	Cl(2)–Ge–Cl(3)	100.98(12)
C(1)–W–Cl(1)	85.5(3)	Cl(2)–Ge–Cl(4)	101.9(2)
C(3)–W–Cl(1)	87.8(3)	Cl(3)–Ge–Cl(4)	101.59(14)

2.3. Structural results

The ORTEP diagram of complex **4** is shown in Fig. 2. Selected bond lengths and angles are given in Table 1.

The environment of the tungsten atom is a distorted capped octahedron with the germanium atom occupying the unique capping position above an octahedral face defined by the three carbonyl groups. The angles subtended at the tungsten atom by the three atoms determining the capped face are 75.6(3), 74.8(4) and 109.4(4)°, compared with the opposite face, determined by Cl(1), N(1) and N(2), where the angles are 78.1(2), 80.2(2) and 82.1(2)°, respectively. In compound **4**, two acetonitrile ligands are effectively *cis* with an N(1)–W–N(1) angle of 78.1(2)° and *trans* to CO groups with N–W–C angles of 165.5(4) and 169.8(3)°. The W–N distances are not identical: 2.174(6) and 2.212(6) Å. The W–N–C angles are 175.3(7) and 174.8(8)°, which is evidence that the nitrile ligand is coordinated in a linear manner. The carbonyl groups, being strong π acceptors, prefer a mutually *cis* position, thus avoiding competition for the metal dπ electrons [14].

The tungsten–germanium bond is short, at 2.567(1) Å, compared to the sum of the relevant covalent radii of 2.80 Å [15,16]. The W–Ge distances of 2.608(6) [7], 2.573(2) [17], 2,580(1) [17], 2.632(4) [18], 2.583(2) [19], 2.605(2) [19], 2.487(2) [19] and 2.542(1) Å [20] had been observed previously. In view of the established π-acceptor properties of the GeCl$_3$ group, it seems probable that the bond does possess some double bond character [21]. The W–Cl distance of 2.423(3) Å is very close to the W–Cl distance of 2.454(2) Å observed in a monomeric seven-coordinate W–Sn compound [4].

The germanium atom is four-coordinate with a geometry that is best described as tetrahedral with Cl–Ge–Cl angles in the range 100.98(12)–101.9(2)° and Cl–Ge–W angles in the range 114.06(9)–118.85(11)°, thus indicating that the tetrahedral geometry is distorted by the greater repulsions associated with the tungsten atom.

Of particular interest is the fact that whereas in W–Sn and Mo–Sn heterobimetallic seven-coordinate complexes metal atoms are linked by a direct M–Sn bond and also by a chlorine bridge [9,22–24], an X-ray study of complex **4** showed that the GeCl$_3$ ligand occupies a position approximately *trans* to the W–Cl bond with a Cl–W–Ge angle of 143.81(7)°. To our knowledge this is the first example of a mutually *trans* position of two anionic ligands X^- and MX_3^- (M = Sn, Ge; X = Cl, Br, I) observed for seven-coordinate compounds. The molecular structure of the first W–Ge compound [WBr(GeBr$_3$)(CO)$_3$(bpy)] was described as a capped trigonal prism with a bromine atom lying above a square face formed by the germanium atom, two nitrogen atoms and one carbonyl group; two anionic ligands are approximately *cis* with a Cl–W–Ge angle of 78.8(2)° [7].

Monocapped octahedral geometries similar to those for **4**, with two mutually *trans* anionic ligands I^-, the I–W–I angles of 160.3(9) and 158.3(1)°, and two *cis* nitrile ligands, were observed only for $[WI_2(CO)_3(NCR)_2]$ (R = Me, Et) [25]. Thus, the form of the tungsten atom coordination in **4** is indeed very similar to the monocapped octahedral geometries observed for $[WI_2(CO)_3(NCR)_2]$, (R = Me, Et) [25], with the exception that those complexes contain a carbonyl ligand in the unique capping position whereas in **4** this position is occupied by $GeCl_3$.

2.4. Reactions with alkynes

The most prominent feature of complexes **1** and **3** is the facility with which carbonyl and/or acetonitrile ligands can be replaced by other ligands. This can be the basis for synthetic procedures including the preparation of alkene and alkyne derivatives as well as a model of a catalytic center. Our earlier work [3] on heterobimetallic W–Sn complexes analogous to **1** had demonstrated that they were capable of selectively polymerizing terminal alkynes. In addition, a number of alkyne complexes had been generated during that study (Eq. (3)).

$$\begin{aligned}&[(CO)_4W(\mu\text{-Cl})_3W(GeCl_3)(CO)_3]\\&+ 4RC\equiv CR \xrightarrow{-[W(CO)_5(GeCl_2)]} 2[WCl_2(CO)_2(RC\equiv CR)_2]\\&\xrightarrow{-CO} [W(\mu\text{-Cl})Cl(CO)(RC\equiv CR)_2]_2\end{aligned} \tag{3}$$

When the reaction of **1** with four molecular equivalents of PhC≡CPh at r.t. in toluene was monitored by IR, an alkyne adduct of the CO-loss product can be observed. The ν(CO) bands for **1** decrease, while those of the alkyne complexes appear at 2093 (w) and 2030 (s) cm^{-1}. However, in this reaction we also observed the appearance and growth of ν(CO) bands at 2071 (w) and 1937 (s) cm^{-1}, characteristic of complex **2**. The ^1H-, ^{13}C-NMR and IR spectral data for the reaction product indicate that it is a mixture of two alkyne compounds. One compound, with two mutually *trans* CO ligands, two *cis* PhC≡CPh ligands and two *cis* anionic ligands (Cl^-) in the coordination sphere, can be formulated as $[WCl_2(CO)_2(PhC\equiv CPh)_2]$ **7**, which probably has a structure similar to that observed by Baker et al. for $[WI_2(CO)_2(MeC\equiv CMe)_2]$ [26]. Compound **7** dimerizes with a loss of CO to give the chloride-bridged dimer $[W(\mu\text{-Cl})Cl(CO)(PhC\equiv CPh)_2]_2$ **8** (Eq. (3)). Thus, ^{13}C-NMR spectra of the reaction products show two sets of carbon signals of coordinated PhC≡CPh, with an intensity ratio 2:1. A similar monomer–dimer equilibrium was observed by Baker et al. in their molybdenum(II) and tungsten(II) diiodide alkyne complexes [26,27]. However, the repeated crystallization of compounds **7** and **8** leads to a loss of CO ligands and, in the presence of traces of air, to the hydrolysis product, the trimeric compound $[W_2^{2+}W^{4+}Cl_2(\mu_3\text{-O})(O)(OH)_2(PhC\equiv CPh)_5]$ observed by us earlier [3].

The reaction product of **1** and 3-hexyne was detected by ^1H- and ^{13}C-NMR as a mixture of monomeric and dimeric compounds $[WCl_2(CO)_2(EtC\equiv CEt)_2]$ **9** and $[W(\mu\text{-Cl})Cl(CO)(EtC\equiv CEt)_2]_2$ **10**. NMR analysis showed hydrogen and carbon resonances for **9** and **10** with an intensity of 2:1.

In the reaction of **3** with two molecular equivalents of diphenylacetylene (DPA), a mixture of alkyne complexes is formed (Eq. (4)):

$$\begin{aligned}&[WCl(GeCl_3)(CO)_3(NCMe)_2] + 2PhC\equiv CPh\\&\rightarrow [WCl_2(CO)_2(GeCl_2)(PhC\equiv CPh)]\\&\quad + [WCl_2(NCMe)_2(PhC\equiv CPh)_2]\\&\quad + [W(\mu\text{-Cl})Cl(NCMe)(PhC\equiv CPh)_2]_2\end{aligned} \tag{4}$$

The monomeric compound $[WCl_2(CO)_2(GeCl_2)(PhC\equiv CPh)]$ **11**, with two mutually *cis* CO ligands (ν(CO) 2087 (m) and 2029 (vs) cm^{-1}), which are magnetically equivalent and give one signal in ^{13}C-NMR spectra at δ 204.3 ppm, was identified as the main product. One signal of the symmetrically coordinated alkyne ($Ph\mathit{C}\equiv\mathit{C}Ph$) was observed at 219.8 ppm and one signal of the two C_{ipso} at δ 138.3 ppm. The other alkyne complex does not contain CO but two acetonitrile in the coordination sphere and most probably can be formulated as $[WCl_2(NCMe)_2(PhC\equiv CPh)_2]$ **12**. Complex **12** is initially formed only because it dimerizes to yield chloride-bridged complexes. Repetition of the reaction of **3** with PhC≡CPh always gives compound **11** as the main product with the characteristic signal in the ^{13}C-NMR spectrum (see above), but in the region of the acetylenic carbon (180–196 ppm), characteristic for **12**, the number and position of carbon signals was changed (see Section 3). Compound **2** appeared as the side product, which suggests that the $GeCl_3^-$ ligand undergoes hydrolysis to $GeCl_2$ and Cl^- in the presence of an alkyne. The mixture of the reaction product of **3** and DPA in the presence of moist air and on standing yields a pale yellow crystalline solid of the trimeric tungsten alkyne compound observed earlier by us [3].

In the reaction of **1** and **3** with PhC≡CH (PA, phenylacetylene), catalytic polymerization was observed, so several intermediate alkyne compounds were formed which were not separated, but only observed, by ^1H-, ^{13}C-NMR and IR spectroscopy. Spectral studies revealed that the precursor complex **3** is liable to loose CO and acetonitrile when it reacts with PA, but one CO and acetonitrile ligand still remains in the coordination sphere of the tungsten. The IR spectrum of the product mixture from the reaction of PA and **3** showed only one ν(CO) band at 2089 cm^{-1}. The hydrogen resonance due to PA coordinated to tungsten was observed at δ 11.90 ppm (≡C*H*) and acetonitrile (2.55 ppm). The $^{13}C\{^1H\}$-NMR spectrum of isolated products showed δ 196.2 (CO), 183.6 (≡*C*Ph), 176.7 (≡*C*H), 137.0 (C_{ipso}-Ph) ppm. Based on the spectroscopic data, the PA complex is best described as $[WCl_2(CO)(NCMe)(PhC{\equiv}CH)_2]$ **13**. It may now be deduced that the structure of the initial alkyne complex **13** is close to the one obtained and characterized crystallographically by Baker et al. in the reaction of $[WI_2(CO)_3(NCMe)_2]$ and RC≡CR (R = Me, Ph) [26,27]. However, complex **13** is not the only reaction product because several other proton signals of coordinated PA in the region 11–14 ppm appeared in the reaction of PA with **3**. Also, several lower intensity carbon signals of coordinated PA were observed in $^{13}C\{^1H\}$-NMR spectra.

2.5. Catalytic activity of 1 and 3

The starting point of the present investigation was to examine the scope of our earlier finding [28–30] that the formation of tungsten(II) might be an important event in the creation by Lewis acids (Group 14 tetrachlorides) of the catalytic activity of tungsten(0) compounds. Because $[WCl_2(CO)_3L_2]$ (L = PPh_3, $AsPh_3$) had been shown to be efficient precatalysts in a number of important catalytic reactions [31–35], we turned our attention towards the synthesis of more soluble and reactive derivatives containing acetonitrile ligands, which are often more labile than phosphines and may result in an enhanced activity. To be precise, polymerization of PA occurs very easily at r.t. in CH_2Cl_2 containing the W–Ge compounds **1** or **3**. Treatment of the resultant deep-red solution with a large amount of methanol produced quantitatively polyphenylacetylene (PPA) as a fine dark-orange powder which has a number-average molecular weight (M_w) from 1×10^4 to 5×10^4, determined by GPC. All the polymers produced were soluble in CH_2Cl_2, $CHCl_3$ and toluene. IR and ^1H-NMR spectroscopy was used to establish the stereochemistry in PPA [36]. The IR spectrum of PPA is characterized by a low intensity band at 740 cm^{-1}. The chemical shift of the =CH groups (5.85 ppm) and its intensity showed that the polymer appeared to possess both *cis* and *trans* linkages, with no more than 30% of the *cis* form.

However, the catalytic coupling of alkynes in the presence of **1** or **3** yields at least two types of product, namely polymers with conjugated polyenic structures and cyclic oligomers, especially the aromatic cyclotrimers 1,2,4- and 1,3,5-triphenylbenzene (TPB). Minor amounts of other oligomers arise, mainly linear diphenylbutadienes (DPBD), which contain, for example, hydrogen derived from the solvent and also a dimer of PA detected by MS as 1*H*-indene-1-phenylmethylene $(PA)_2$. The relative amounts of different oligomers seemed to depend on the catalyst. The dinuclear complex **1** is more selective towards polymer formation, while the mononuclear compound **3** gives the dimers and trimers of PA in greater yields. A summary of the comparative catalytic activity of complexes **1** and **3** towards PA is given in Table 2.

Table 2
GC–MS analysis of reaction mixture containing PA and compound **1** or **3** as catalyst after 24 h reaction time at r.t.[a]

Organic products/ catalyst		**1**	**3**
PA	I	5	61
	II	66.3	77
	III	93.0	92
PPA (M_w)[b]	I	51 (2×10^4)	26 (1×10^4)
	II	32 (6×10^4)	12 (2×10^4)
	III	2.2	9.0 (1×10^4)
DPBD[c,e]	I	9.3, 12.8, 7.4	9.7, 5.5, 19.2
	II	—, 3.6, 12.2	2.4, 3.9, 18.3
	III	—	2.3, 3.6, 16.2
$(PA)_2^{d,e}$	I	5.3	15.2
	II	5.9	12.2
	III	34.5	5.0
1,2,4-TPB[e]	I	49.1	31.6
	II	51.7	46.7
	III	32.8	32.9
1,3,5-TPB[e]	I	21.4	18.8
	II	23.8	39.9
	III	32.6	41.9

[a] The reaction mixture contained 0.05 mmol of catalyst and 5 mmol (I, III) or 10 mmol (II) of PA in 5 cm^3 of toluene (I, II) or CH_2Cl_2 (III). Xylene (1 mmol) was added as internal standard in GC analysis.
[b] PPA separated with methanol and weighted. [c] Three different isomers of diphenylbutadiene. [d] Dimer of PA detected by MS as 1H-indene-1-phenylmethylene. [e] Contents (%) in the residue obtained after separation of PPA.

It is very likely that the binuclear structure of **1** might not be preserved in the active catalytic species, and that, in fact, a mononuclear species could be generated in the presence of an excess of ligands, such as the PA we wished to polymerize. Such equilibria were observed for stoichiometric reactions of **1** with alkyne ligands.

Nevertheless, a general observation can be made that there is a strong similarity between the behavior of the dimer **1** and the mononuclear complex **3**. There are subtle differences in the ratio of polymeric and cyclotrimeric products (Table 2).

2.6. Attempts to detect possible intermediates

The intermediates formed in mechanisms most frequently suggested for the catalytic polymerization and cyclotrimerization of alkynes are alkylidene complexes [37] and metallacyclic species [38]. In the reactions of **1** and **3** with alkynes that we investigated, the tungsten

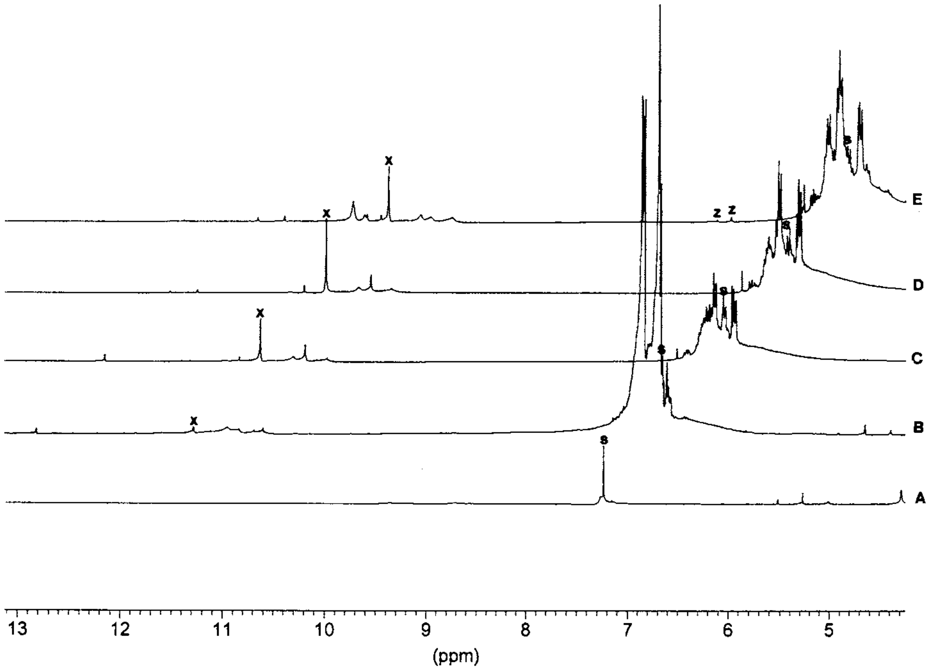

Fig. 3. Partial ^{1}H-NMR spectra of reaction mixture containing **3** and PhC≡CH in CDCl$_3$ at 293 K, demonstrating the coordination of PhC≡CH to tungsten (δ 11.90 ppm) and formation of 1,3,5-TPB and 1,2,4-TPB (δ 7–8 ppm). (A) Before addition of PhC≡CH; (B), (C), (D) and (E) after 10 min, 6 h, 24 h, and 96 h reaction, respectively. The signals are denoted as follows: (s) proton impurities in the solvent; (x) hydrogens of –CH groups in [WCl$_2$(CO)(NCMe)(PhC≡CH)$_2$] **13** (δ 11.90 ppm); (z) hydrogens in tungstenacyclopentadiene (δ 8.53, 8.67 ppm).

complexes that could be isolated usually contained a *cis* arrangement of the two alkyne ligands. Hence, if the active catalytic species is a mononuclear bis(alkyne) complex, it might be possible to detect it directly by studying the equilibria between the mononuclear complex **3** and PA. The good solubility of **3** makes it easy to follow these reactions by ^{1}H-NMR and to observe the replacement of acetonitrile by PA. Precisely speaking, when the reaction of **3** with excess PA in CDCl$_3$ was followed by ^{1}H-NMR, the disappearance of resonances due to complex **3** (δ 2.34 ppm, C*H*$_3$CN) and the free PA (δ 3.00 ppm, ≡C*H*) was accompanied by a simultaneous increase of resonances due to PA coordinated to tungsten at δ 11.90 ppm (≡C*H*) (Fig. 3). However, complex **13** is not the only reaction product because several other hydrogen signals of coordinated PA in the region 11–14 ppm appeared in the reaction of PA with **3**. The intensity ratio of those signals changed with reaction time. After 24 h, by which time all PA had been consumed and **3** decayed, there were the following hydrogen signals (intensity given in brackets): δ 13.43 (0.2), 13.17 (0.3), 12.11 (0.9), 11.90 (10), 11.58 (1.7) 11.46 (3.1) 11.25 (2.8) ppm (Fig. 3D). After a prolonged reaction time in the absence of free alkyne, PA coordinated to tungsten probably rearranges, so hydrogen signals at higher frequencies increase, but those below 12 ppm decrease: δ 13.91 (0.1), 13.17 (0.3), 12.92 (0.5), 12.44 (0.1), 12.01 (0.1), 12.00 (0.2) 11.90 (4.6), 11.58 (1.4) 11.46 (1.1) 11.25 (1.5) ppm (Fig. 3E). It is most probable that all new signals with a frequency > 11.9 ppm are due to carbene ligands which are formed after the rearrangement of alkynes coordinated to tungsten. Such a high position of carbene hydrogen was observed at δ 11.8 ppm [39] for [(W=CHPh)Cl$_2$(PhC≡CPh)(PMe$_3$)$_2$], at δ 12.33, 12.04 ppm [40] for [(W=CH$_2$)(CO)(PhC≡CMe)Tp′]PF$_6$, (Tp′ = hydridotris-3,5-dimethylpyrazolyborate) and at δ 11.45 ppm for [(WCHPh)Cl$_2$(CMe$_3$)$_2$(py)] [41]. In the region δ 7–8 ppm signals due to hydrogens of 1,3,5- and 1,2,4,-TPB appeared. Signals due to metallacyclopentadiene can also be observed at δ 8.53 ppm for the C$_\beta$*H* of the symmetric unit [W–C(Ph)=CH–CH=CPh] and at δ 8.67 ppm for the C$_\alpha$*H* of the asymmetric unit [W–C(Ph)=CH–C(Ph)=CH]. Similar hydrogen resonances had been observed earlier for analogous tantallacyclopentadienes complexes [δ 7.61 (C$_\beta$*H*), 8.67 (C$_\alpha$*H*) ppm] [42]. For asymmetric tungstenacyclopentadienone the C$_\beta$*H* resonance was observed at δ 8.33 ppm [43]. Our results provide direct information only as regards the first step and strongly suggest that the loss of a labile ligand to form a coordinatively unsaturated mononuclear center is common to all the reactions studied. The resulting unsaturated W center is conceivably capable of providing up to three sites for the coordination of alkynes or their coupled derivatives. It is clear that the lability of the acetonitrile plays a key role in the catalytic processes. We were unable to isolate any intermediates beyond the first bis(alkyne) complex. The formation of cyclotrimers and linear conjugated polyenic polymers as the major products in volves oxidative coupling and formation of a series of metalacyclic species as suggested by Vollhardt [38]. The metallacycle formed with four molecules of alkyne can then rearrange to an alkylidene ligand, as was observed by Yeh et al. [44]. The mechanism of PA polymerization induced by tungsten(II) complexes is therefore seen to involve a series of stepwise *cis* insertions of coordinated PA into a C–W bond giving a metallacycloheptatriene complex. A further PA *cis* insertion then occurs to give an alkylidene complex initiating the increase of the polymer chain.

Our results cannot rigorously exclude the possibility of other pathways involving the formation of vinylidene intermediates. However for the d^4 configuration of the catalyst the formation of vinylidene intermediates is rather disfavored [45].

2.7. Conclusion

The generation of W–Ge species was achieved in a straightforward manner utilizing two separate methods of synthesis which demonstrate that oxidative addition is a viable reaction to generate M–M bonds in organometallic compounds.

Tungsten(II)–germanium(II) complex **1** can be prepared relatively simply in good yields in the photochemical reaction of $W(CO)_6$ with $GeCl_4$. The structure of complex **1** has been proved by IR and $^{13}C\{^1H\}$-NMR spectroscopy.

Another method which proved useful in obtaining a W–Ge compound was the oxidative-addition reaction of $[W(CO)_4(NCMe_2]$ with $GeCl_4$ in dichloromethane.

It was found, that bis(alkyne) complexes can indeed be readily formed in the reaction of the dimeric complex **1** and the monomeric complex **3**. The resulting air-unstable compounds are all characterized mainly by IR, ^1H- and $^{13}C\{^1H\}$-NMR spectroscopy. The catalytic coupling of alkynes in the presence of **1** or **3** yields at least two types of product, namely polymers with conjugated polyenic structures and cyclic oligomers, especially the aromatic cyclotrimers.

3. Experimental

All operations were carried out in an inert atmosphere using standard Schlenk techniques. All solvents and liquid reagents were dried and distilled over CaH_2. Photochemical reactions were carried out in a glass reactor with a Pyrex window. An HBO 200 high-pressure mercury lamp was used as the light source. IR spectra (KBr plates) were recorded on an FT-IR Model-400 Nicolet instrument and Far-IR spectra were recorded (500–50 cm^{-1}) with a Brucker IFSv instrument in Nujol mull on a polyethylene film. NMR spectra were run using a Bruker AMX-300 spectrometer. UV–vis absorption spectra were recorded on a Hewlett-Packard 8452A spectrophotometer. The analysis of the catalytic reaction products was performed on a Hewlett-Packard GC–MS system and by ^1H-NMR spectroscopy.

3.1. Synthesis of tungsten(II) compounds

3.1.1. $[CO_4W(\mu\text{-}Cl)_3W(GeCl_3)(CO)_3]$ **1**

A sample of $W(CO)_6$ (1.0 g, 2.8 mmol) was dissolved in 100 cm^3 of cyclohexane and $GeCl_4$ (0.33 cm^3, 2.8 mmol) was added with continuous stirring under a stream of argon. The solution was irradiated for 2 h. The IR spectrum of the reaction mixture showed a decay of the absorption due to $W(CO)_6$ accompanied by the appearance of new absorptions at 2096 (w), 2072 (w), 2022 (vs), 1990 (vs) and 1940 (s, br) cm^{-1}. The amorphous brown precipitate that settled down was filtered off, washed repeatedly with cyclohexane to remove the soluble side product **2** and any unreacted $W(CO)_6$. The relatively readily soluble dark brown compound was dissolved in toluene to remove traces of a blue decarbonylation product. The solvent was evaporated in vacuo to give a yellow residue (yield = 60%) which was recrystallized from toluene–heptane. IR spectrum (KBr disc): ν(CO) 2098 w, 2021 vs, 1990 vs and 1942 s, br cm^{-1}; (Nujol) ν(GeCl) 372 cm^{-1}. $^{13}C\{^1H\}$-NMR (δ, ppm, $C_6D_5CD_3$, 293 K): 217.34 [J(WC) 135.9 Hz, 4 CO], 212.1 (1 CO), 204.5 [J(WC) 111.0 Hz, 2 CO].

3.1.2. Preparation of $[WCl(GeCl_3)(CO)_3(NCMe)_2]$ **3**

To a sample of $[W(CO)_4(NCMe)_2]$ [46] (0.5 g, 1.4 mmol) dissolved in CH_2Cl_2 (25 cm^3) with continuous stirring under a stream of nitrogen was added a stoichiometric amount of $GeCl_4$ (0.16 cm^3, 1.4 mmol) by means of a syringe. The mixture was stirred for 6 h, during which time the yellow solution gradually changed to a golden–brown color, while the ν(CO) frequency of $[W(CO)_4(NCMe)_2]$ disappeared. After the completion of the reaction, the solution was separated from some insoluble blue powder by filtration and evaporated to dryness. The crude product was contaminated with **2** but the crystallization from CH_2Cl_2/heptane produced the analytically pure golden–yellow crystalline complex **3**.

IR (ν, cm^{-1}): (KBr) ν(CO) 2033 (s), 1968 (m), 1914 (vs); ν(CN) 2320 (w), 2292 (w); ν(WCO) 584 (w), 565 (w); (Nujol) ν(GeCl) 379 (vw). ^1H-NMR (δ, ppm, $C_6D_5CD_3$, 293 K): 2.34 (s, 2 CH_3CN). $^{13}C\{^1H\}$-NMR (δ, ppm, $C_6D_5CD_3$, 293 K): 214.8 [J(WC) 120 Hz, s, 3 CO], 3.1 (s, 2 CH_3CN).

3.1.3. Preparation of $[WCl(GeCl_3)(CO)_3(NCR)_2]$ ***4*** *($R = C_2H_5$);* ***5*** *($R = C_3H_7$);* ***6*** *($R = C_6H_5$)*

Complex **3** was dissolved in an appropriate nitrile and the solution was stirred for 60 min. Filtration, followed by removal of the solvent in vacuo, gave a residue colored from golden–yellow (**4**) to red (**6**), which was recrystallized from CH_2Cl_2/heptane giving a pure bis(nitrile) complex **4–6**.

3.1.4. Spectroscopic data for ***4–6***

Complex **4** IR (ν, cm^{-1}): (KBr) ν(CO) 2035 (s), 1966 (m), 1919 (vs); ν(CN) 2292 (m); ν(WCO) 585 (w), 567 (w); (Nujol) ν(GeCl) 376 (vw). ^{1}H-NMR (δ, ppm, $CDCl_3$, 293 K): [2.8 q, *J*(HH) 7.6 Hz, 2 $\mathrm{CH_3C}\mathit{H}_2\mathrm{CN}$], 1.4 [t, *J*(HH) 7.6 Hz, 2 $\mathrm{C}\mathit{H}_3\mathrm{CH_2CN}$]. $^{13}C\{^1H\}$-NMR (δ, ppm, $CDCl_3$, 293 K): 213.3 (s, 3 *C*O), 128.7 (s, 2 $\mathrm{CH_3CH_2}\mathit{C}\mathrm{N}$), 12.6 (s, 2 $\mathrm{CH_3}\mathit{C}\mathrm{H_2CN}$), 9.4 (s, 2 $\mathit{C}\mathrm{H_3CH_2CN}$). UV–vis ($\lambda_{max}$, nm, CH_2Cl_2): 238, 322, 386 (ε/dm^3 mol^{-1} cm^{-1} 32849, 1197, 517).

Complex **5** IR (ν, cm^{-1}): (KBr) ν(CO) 2034 (s), 1968 (s), 1925 (s); ν(CN) 2292 (m). ^{1}H-NMR (δ, ppm, $CDCl_3$, 293 K): 2.8 [t, *J*(HH) 7.0 Hz, 2 $\mathrm{CH_3CH_2C}\mathit{H}_2\mathrm{CN}$), 1.87 [q, *J*(HH) 7.5 Hz, 2 $\mathrm{CH_3C}\mathit{H}_2\mathrm{CH_2CN}$], 1.15 [t, *J*(HH) 7.5 Hz, 2 $\mathrm{C}\mathit{H}_3\mathrm{CH_2CH_2CN}$]. $^{13}C\{^1H\}$-NMR (δ, ppm, $CDCl_3$, 293 K): 213.6 (s, 3 *C*O), 128.9 (s, 2 $\mathrm{CH_3CH_2CH_2}\mathit{C}\mathrm{N}$), 20.4 (s, 2 $\mathrm{CH_3CH_2}\mathit{C}\mathrm{H_2CN}$), 18.6 (s, 2 $\mathrm{CH_3}\mathit{C}\mathrm{H_2CH_2CN}$), 13.4 (s, 2 $\mathit{C}\mathrm{H_3CH_2CH_2CN}$).

Complex **6** IR (ν, cm^{-1}): (KBr) ν(CO) 2036 (s), 1968 (m), 1937 (vs); ν(CN) 2257 (w), 2264(w). ^{1}H-NMR (δ, ppm, $CDCl_3$, 293 K): 7.86 (*o*-Ph), 7.78 (*p*-Ph), 7.54 (*m*-Ph). $^{13}C\{^1H\}$-NMR (δ, ppm, $CDCl_3$, 293 K): 213.1 (s, 3 *C*O), 126.9 (s, 2 Ph*C*N), 136.0 (*p*-Ph), 133.6 (*o*-Ph), 129.8 (*m*-Ph).

3.2. Reactions with alkynes

3.2.1. Reaction of ***1*** *with alkynes*

The reaction of **1** with four molecular equivalents of PhC≡CPh at r.t. in toluene yielded a mixture of compounds which were identified by IR and NMR studies as $[WCl_2(CO)_2(PhC{\equiv}CPh)_2]$ **7**, $[W(\mu\text{-}Cl)Cl(CO)(PhC{\equiv}CPh)_2]_2$ **8** and **2**. The alkyne complexes **7** and **8** are formed in the ratio 2:1, as was detected by NMR.

Complex **7** IR (ν, cm^{-1}): (KBr) ν(CO) 2093. $^{13}C\{^1H\}$-NMR (δ, ppm, $CDCl_3$, 293 K): 201.4 (*C*O), 187.9 (Ph*C*≡CPh), 171.9 (PhC≡*C*Ph), 136.1, 133.7 (C_{ipso}-Ph).

8 IR (ν, cm^{-1}): (KBr) ν(CO) 2030. $^{13}C\{^1H\}$-NMR (δ, ppm, $CDCl_3$, 293 K): 201.4 (*C*O), 187.0 (Ph*C*≡CPh), 170.9 (PhC≡*C*Ph), 136.2, 133.9 (C_{ipso}-Ph)

In the reaction of **1** and 3-hexyne in toluene, the mixture of monomeric $[WCl_2(CO)_2(EtC{\equiv}CEt)_2]$ **9** and dimeric $[W(\mu\text{-}Cl)Cl(CO)(EtC{\equiv}CEt)_2]_2$ **10** compounds was detected by spectroscopic methods, which showed hydrogen and carbon resonances with an intensity ratio of 2:1.

Complex **9** IR (ν, cm^{-1}): (KBr) ν(CO) 2053. ^{1}H-NMR (δ, ppm, $CDCl_3$, 293 K): four quartets in the region 3.10–3.81 ($\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 1.2 ($\mathrm{CH_2C}\mathit{H}_3$). $^{13}C\{^1H\}$-NMR (δ, ppm, $CDCl_3$, 293 K): 207.1 [*J*(WC) 120 Hz, *C*O], 183.6, 180.2, 169.2, 159.7 (Et*C*≡*C*Et), 29.6, 27.7, 27.5, 27.1 ($\mathit{C}\mathrm{H_2CH_3}$), 14.5 ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$).

Complex **10** ^{1}H-NMR (δ, ppm, $CDCl_3$, 293 K): four quartets in the region 3.10–3.81, ($\mathrm{C}\mathit{H}_2\mathrm{CH_3}$) 1.22 ($\mathrm{CH_2C}\mathit{H}_3$). $^{13}C\{^1H\}$-NMR (δ, ppm, $CDCl_3$, 293 K): 207.3 (*C*O), 183.5, 174.9, 168.5, 157.0 (Et*C*≡*C*Et), 29.7, 28.8, 27.9, 26.9 ($\mathit{C}\mathrm{H_2CH_3}$), 13.8 ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$).

3.2.2. Reaction of ***3*** *with diphenylacetylene*

To a solution of **3** (0.2 g, 0.37 mmol) in 15 cm^3 of CH_2Cl_2 was added PhC≡CPh (DPA, 0.13 g, 0.75 mmol) in CH_2Cl_2 (5 cm^3). The mixture was stirred for 2 h, after which time the full conversion of **3** was observed by IR. Evaporation of the solvent followed by washing with heptane produced mixture of compounds identified by IR and NMR studies as $[WCl_2(CO)_2(GeCl_2)(PhC{\equiv}CPh)]$ **11** and $[WCl_2(NCMe)_2(PhC{\equiv}CPh)_2]$ **12**. Crystallization of the above greenish–yellow solid from CH_2Cl_2/heptane always produced mixture of compounds **11** and **12**, but with different molar ratios. The decay of compound **12** is probably due to the dimerization process and the formation of less soluble $[W(\mu\text{-}Cl)Cl(NCMe)(PhC{\equiv}CPh)_2]_2$.

Complex **11** IR (ν, cm^{-1}): (KBr) ν(CO) 2088 (m), 2029 (vs). $^{13}C\{^1H\}$-NMR (δ, ppm, $CDCl_3$, 293 K): 204.3 [*J*(WC) 97.8 Hz, *C*O], 219.8 (Ph*C*≡*C*Ph), 138.2, (C_{ipso}-Ph).

Complex **12** IR (ν, cm^{-1}): (KBr) ν(CN) 2330, 2229. ^{1}H-NMR (δ, ppm, 293 K): 2.26, 2.23 ($\mathrm{C}\mathit{H}_3\mathrm{CN}$). $^{13}C\{^1H\}$-NMR (δ, ppm, $CDCl_3$, 293 K): 196.2 (Ph*C*≡CPh), 189.3 (PhC≡*C*Ph), 138.8, 137.8 (C_{ipso}-Ph), 127.1 ($\mathrm{CH_3}\mathit{C}\mathrm{N}$), 4.5 ($\mathit{C}\mathrm{H_3CN}$).

3.2.3. Reaction of ***3*** *with phenylacetylene (PA)*

A slight excess of PA (0.05 cm^3, 0.45 mmol) was syringed into a stirred CH_2Cl_2 solution (15 cm^3) of **3** (0.1 g, 0.18 mmol) at r.t.; immediately the solution turned dark orange. Stirring for 2 h followed by the evaporation of the solvent under low pressure gave an orange solid, which was washed with a small portion of heptane and dried in vacuo to give a brownish–yellow mixture of compounds containing mainly $[WCl_2(CO)(NCMe)(PhC{\equiv}CH)_2]$ **13**, as was shown by ^{1}H and $^{13}C\{^1H\}$-NMR spectra. The heptane extract contained organic products 1,2,4-DPB (44.6%), 1,3,5-TPB (26.3%), different isomers of DPB (30.3%), and a dimer of PA detected by MS as 1*H*-indene-1-phenylmethylene (2.8%).

Complex **13** IR (ν, cm^{-1}): (KBr) ν(CO) 2089 (m). ^{1}H-NMR (δ, ppm, $CDCl_3$, 293 K): 11.90 ($\equiv CH$), 2.55 (CH_3CN). $^{13}C\{^1H\}$-NMR (δ, ppm, $CDCl_3$, 293 K): 196.2 (*C*O), 183.6 ($\equiv C$Ph), 176.7 ($\equiv C$H) 137.0 (C_{ipso}-Ph).

3.2.4. Reaction of **3** with PA in an NMR tube

Complex **3** (0.1 g, 0.18 mmol) was dissolved in $CDCl_3$ (0.7 cm^3) and then transferred under nitrogen into a 5 mm NMR tube. The tube was closed with septum rubber and analyzed using ^{1}H-NMR spectroscopy. Next, two equivalents of PA (0.04 cm^3) were added to the tube by means of a microliter syringe and a sample was periodically analyzed by ^{1}H-NMR spectroscopy at r.t. Complete transformation of PA detected by the decay of the signal at δ 3.00 ppm due to $\equiv CH$, occurred within 24 h. The hydrogen signals of organic reaction products appeared in the region δ 5–8 ppm. Several signals appeared and increased in the region (11–14 ppm) characteristic for PA coordinated to tungsten, but the signal at δ 11.90 ppm was ten times more intense than others. The signal of coordinated NC*Me* in **3** at 2.34 ppm decayed but a new signal of coordinated NC*Me* appeared at δ 2.55 ppm.

3.2.5. Procedures for testing catalytic activity and characterization of organic products

Polymerization experiments were carried out in a reaction mixture composed of toluene, *o*-xylene (the internal chromatographic standard), PA (1 mol dm^{-3}), and a tungsten complex (PA/W 100). The reaction mixture was stirred by a magnetic stirrer at r.t. in a 50 cm^3 glass reactor provided with a septum through which liquid reactants were introduced and removed by a syringe. The conversion of PA was monitored by chromatography. The gas samples were removed with a syringe and injected into the PORA PLOT-Q 15 m column of the chromatograph fitted with a flame ionization detector. For reactions in which the product could not be resolved by GLC, the GC–MS was additionally used (HP5 25 m column). For the analysis of PA reaction products, reactions were continued for 24 h and then methanol was added. The polymer was collected, washed with methanol, dried and weighed. Yield (%) is defined by comparing the polymer weight to the weight of the PA used. The polymer was analyzed by ^{1}H-NMR and IR spectroscopy and gel-permeation chromatography. Molecular weights of the PPA were measured using $CHCl_3$ solutions, a refractive index monitor and a P1gel 10 m MIXED-B column. The values recorded are the weight of polystyrene that would exhibit the chromatograms observed.

The filtrate obtained after the precipitation of the polymers was evaporated to dryness and the CH_2Cl_2 solution of the residue was investigated by GC–MS. Analysis showed mainly diphenylbutadienes and triphenylbenzenes.

^{1}H-NMR spectra of the polymers were recorded in a $CDCl_3$ solution at 300 MHz. The microstructural details of the polymers were calculated from the ^{1}H-NMR integrals [36] at about 30% *cis–transoidal*.

3.3. Crystallography

3.3.1. Crystal data for **4**

$C_9H_{10}Cl_4GeN_2O_3W$, $M_w = 592.43$, monoclinic, space group $P2_1/n$, $a = 13.321(3)$, $b = 9.928(2)$, $c = 13.980(3)$ Å, $\beta = 92.65(3)°$, $V = 1846.9(7)$ Å^3, $Z = 4$, $D_{calc.} = 2.131$ g cm^{-3}, $F(000) = 1104$, $\mu(Mo–K_\alpha) = 84.33$ cm^{-1}.

3.3.2. X-ray structal determination

A yellow crystal ca. $0.12 \times 0.15 \times 0.15$ mm was removed from the flask, rapidly coated with a light hydrocarbon oil to protect it from the atmosphere and sealed in a capillary. Data collection was performed on a KM4 K-axis computer-controlled [47] four-circle diffractometer operating in the $\omega - 2\theta$ scan mode with graphite monochromated Mo–K_α radiation ($\lambda = 0.71069$ Å) at 293 K. The accurate cell dimensions and the crystal orientation matrix were determined by a least-squares refinement of the setting angles of 50 carefully centered reflections in the range $20 < 2\theta < 40°$. A total of 3631 unique reflections were measured, of which 2155 (183 variables) with $I \geq 2\sigma(I)$ in the range 4.0–55.5° were used to solve and refine the structure in the monoclinic space group $P2_1/n$. Absorption corrections following the DIFABS [48] were applied to the data: minimum 0.867 and maximum 1.068.

The hydrogen atoms were placed in the geometrically calculated positions with the isotropic temperature factors taken as 1.2 and 1.5 U_{eq} of the neighboring heavier atoms for CH_2 and CH_3, respectively. Several cycles of refinement of the coordinates and anisotropic thermal parameters for non-hydrogen atoms (parameters of the H atoms were fixed) reduced the R_1 to 0.0376 and wR_2 to 0.0725. The maximum and minimum residual densities in the difference map were 1.185 and -1.235 e Å^{-3}, respectively. Goodness-of-fit was 0.917. The structure was given a weighting scheme in the form $w = 1/[\sigma^2(F_o^2) + (0.0278P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$.

The structure was solved by heavy-atom methods with the SHELXS-86 program [49] and refined by a full-matrix least-squares method, using the SHELXL program [50]. Neutral atomic scattering factors were taken from the SHELXL-93 program [50].

4. Supplementary material available

Atomic coordinates, thermal parameters, and bond lengths and angles were deposited at the Cambridge Crystallographic Data Centre (CCDC) and are available on request.

Acknowledgements

Financial support from the Polish State Committee for Scientific Research (grant no. 3T09A-094-10) is gratefully acknowledged.

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