Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Coordination Chemistry Reviews 249 (2005) 2195–2202

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Review

Structure and reactivity of tungsten(II) and molybdenum(II) compounds containing an M–M′ bond

Teresa Szymańska-Buzar*

Faculty of Chemistry, University of Wrocław, ul. F. Joliot-Curie 14, 50-383 Wrocław, Poland

Received 27 October 2004; accepted 25 February 2005

Contents

Abstract

The synthesis of heterobimetallic W–Sn, W–Ge, Mo–Sn, and Mo–Ge seven-coordinate chlorocarbonyl complexes of the type: $[(CO)_4M(\mu\text{-}Cl)_3M(M'Cl_3)(CO)_3]$, $[MCl(M'Cl_3)(CO)_3(NCR)_2]$, $[M(M'Cl_3)(CO)_3(\eta^2,\eta^2\text{-}C_7H_8)]$ (M = W, Mo; M′ = Sn, Ge) is described. The crystal structures of these compounds together with their spectroscopic characteristics in solution are discussed. The reactivity and catalytic activity of these compounds in reactions with alkenes and alkynes is also reviewed. Special attention is given to catalytic reactions that lead to the formation of new carbon–carbon bonds such as polymerization of terminal alkynes, metathesis, and ring-opening metathesis polymerization of cyclic olefins (ROMP).

Keywords: Tungsten(II); Molybdenum(II); Seven-coordinate compounds; M–M′ bond; Homogeneous catalyst; Organometallic compounds

1. Introduction

Tungsten(II) and molybdenum(II) seven-coordinate complexes have been attracting great interest for the past 50 years. During this time several good reviews concerning the synthesis, crystal structure, and reactivity of compounds of this type have been published [1–5]. However, no one has paid special attention to the unusual properties of seven-coordinate heterobimetallic compounds formed in oxidative addition reactions of halide group 14 elements and carbonyls of group 6 transition metals. One of the major factors stimulating interest in compounds of this type is their application in homogeneous catalysis, particularly of metathesis reactions [6]. The catalytic activity of heterobimetallic W–Sn, W–Ge, Mo–Sn, and Mo–Ge seven-coordinate chlorocarbonyl complexes was studied during investigations of photochemically generated catalysts for metathesis of olefins from group 6 metal carbonyls. It has long been known that photolysis of $W(CO)_6$ in tetrachlorocarbon solution creates a very active catalyst for

---

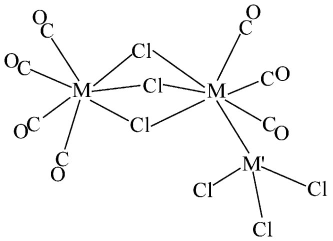
* Tel.: +48 71 375 7221; fax: +48 71 328 2348.
E-mail address: tsz@wchuwr.chem.uni.wroc.pl.

0010-8545/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2005.02.023

metathesis of olefins and polymerization of alkynes [7–10]. Later, it was observed that more active and tractable catalysts can be photogenerated in reaction of $W(CO)_6$ and halide group 4, 13, or 14 elements [6]. In the course of the search for catalytically active species formed in this photochemical reaction, seven-coordinate compounds of a new type, containing a metal–metal bond, were accidentally discovered. The first compound of that type was a binuclear compound of tungsten(II) containing a W–Sn bond [11]. Subsequently numerous heterobimetallic compounds containing W–Sn, W–Ge, Mo–Sn, and Mo–Ge bonds were synthesized [12–20]. All seven-coordinate compounds obtained in the oxidative addition reaction of group 6 metal carbonyls and halide group 14 elements initiate the metathesis of olefins, ring opening metathesis polymerization of cyclic olefins (ROMP), and polymerization of terminal alkynes [21–25]. Recently, it has been discovered that chlorocarbonyl binuclear complexes can be used as catalysts in hydroarylation reaction of acyclic and cyclic olefins [23,26]. Exploration of the rich and diverse chemistry of such compounds should be continued.

2. Binuclear complexes of the general formula $[(CO)_4M(\mu\text{-}Cl)_3M(M'Cl_3)(CO)_3]$ (M = W, Mo; M′ = Sn, Ge)

The heterobimetallic binuclear tungsten(II) seven-coordinate compound $[(CO)_4W(\mu\text{-}Cl)_3W(SnCl_3)(CO)_3]$ (**1**) was prepared in a photochemical reaction of $W(CO)_6$ and $SnCl_4$. The formation of the W–Sn bond, between one of the tungsten atom and the trichlorostannyl moiety, was proved by X-ray diffraction studies [11] (Fig. 1).



	M	M'
1	W	Sn
2	W	Ge
3	Mo	Sn

Fig. 1. Schematic view of the ligand arrangement in compounds of the type $[(CO)_4M(\mu\text{-}Cl)_3M(M'Cl_3)(CO)_3]$.

A similar photochemically induced oxidative addition reaction takes place between $W(CO)_6$ and $GeCl_4$. The structure of the binuclear compound $[(CO)_4W(\mu\text{-}Cl)_3W(GeCl_3)(CO)_3]$ (**2**) was earlier proposed based on the results of spectroscopic investigations [13], but recently has also been proved by X-ray diffraction analysis [27]. Additionally, a new and unusual tungsten–germanium compound has been separated from the reaction mixture. It contains two pentacarbonyltungsten moieties connected by a direct tungsten–tungsten bond and a dichlorogermylene bridge (Scheme 1) [27].

A crystal structure similar to that of the tungsten compounds **1** and **2** is also shown by the product formed in the photochemical reaction of $Mo(CO)_6$ and $SnCl_4$, i.e. $[(CO)_4Mo(\mu\text{-}Cl)_3Mo(SnCl_3)(CO)_3]$ (**3**) [17]. The triply chloride-bridged dimers **1**–**3** are stable and tractable enough. They are soluble even in hydrocarbon solutions and can be obtained in good yield in the solid state but are very reactive in solution. They react very easily at room temperature with phosphorus and nitrogen atom donor ligands that cleave the chloride bridges to give mononuclear seven-coordinate compounds (Scheme 2). They react similarly with alkenes and alkynes [11–19].

3. Seven-coordinate bis(nitrile) complexes of the type $[MCl(M'Cl_3)(CO)_3(NCR)_2]$ (M = W, Mo = Sn, Ge; R = Me, Et, *n*-Pr, Ph)

The main role of nitriles in coordination chemistry stems from their ability to act as labile ligands. This reactivity has been widely employed in numerous ligand exchange processes. As far as the chemistry of tungsten(II) and molybdenum(II) is concerned, the ready accessibility of the complexes $[MCl(M'Cl_3)(CO)_3(NCR)_2]$ (M = W [13,14], Mo [15–17]; R = Me, Et, *n*-Pr and Ph) has allowed them to be used as useful precursors to a wide range of derivatives, prompting the development of a chemistry of both stoichiometric and catalytic transformations.

In the oxidative addition reaction of $[W(CO)_4(NCMe)_2]$ with $SnCl_4$, $[WCl(SnCl_3)(CO)_3(NCMe)_2]$ (**4**) has been isolated and then characterized structurally (Scheme 2). Compound **4** contains two mutually *cis* nitrile ligands and a trichlorostannyl moiety coordinated to tungsten through a direct tungsten–tin bond and a chloride bridge [14] (Fig. 2). The

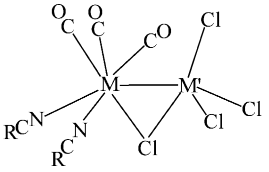
$$4W(CO)_6 + 2GeCl_4 \xrightarrow[n\text{-hexane}]{h\nu} [(CO)_4W(\mu\text{-}Cl)_3W(GeCl_3)(CO)_3]\ (\mathbf{2}) + [(\mu\text{-}GeCl_2)W_2(CO)_{10}] + 7CO$$

Scheme 1. Photochemical synthesis of W–Ge compounds.

$$[W(CO)_4(NCMe)_2] + SnCl_4 \xrightarrow{CH_2Cl_2} [WCl(SnCl_3)(CO)_3(NCMe)_2]\ (\mathbf{4}) + CO$$

$$[(CO)_4W(\mu\text{-}Cl)_3W(SnCl_3)(CO)_3]\ (\mathbf{1}) \xrightarrow{NCMe} \mathbf{4} + [WCl_2(CO)_3(NCMe)_2] + CO$$

Scheme 2. Synthetic routes to $[WCl(SnCl_3)(CO)_3(NCMe)_2]$ (**4**),



	M	M'	R
4	W	Sn	Me
6	Mo	Sn	Et

Fig. 2. The arrangement of ligands in bis(nitrile) compounds of the type [MCl(M′Cl$_3$)(CO)$_3$(NCR)$_2$].

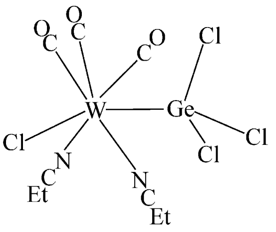


Fig. 3. The arrangement of ligands in [WCl(GeCl$_3$)(CO)$_3$(NCEt)$_2$] (**5**) proved by X-ray diffraction study [13].

same compound is formed in reaction of compound **1** with acetonitrile (Scheme 2). Re-crystallization of compound **4** from another nitrile, NCR, makes it very easy to exchange acetonitrile and obtain [WCl(SnCl$_3$)(CO)$_3$(NCR)$_2$] (R = Et, *n*-Pr, Ph).

In a reaction analogous to the one presented in Scheme 2 a heterobimetallic tungsten-germanium bis(nitrile) compound has been prepared [13]. Although crystal structure investigations revealed that the compound [WCl(GeCl$_3$)(CO)$_3$(NCEt)$_2$] (**5**) has a distorted octahedron geometry analogous to that of W–Sn bis(nitrile) compound **4**, in **5** two anionic ligands, GeCl$_3$ and Cl, are mutually *trans* (Fig. 3, Table 1). The germanium atom in **5** occupies the unique capping position above the octahedral face defined by the three carbonyl groups.

The crystal structure of [MoCl(SnCl$_3$)(CO)$_3$(NCEt)$_2$] (**6**) is similar to that observed for the analogous tungsten compound **4**, with a direct metal–metal bond and one chlorine atom occupying a bridging position between the two metal atoms [17] (Fig. 2).

The carbonyl region of the infrared spectra of bis(nitrile) compounds is almost identical, showing a common profile with three strong ν(CO) bands (Table 2), which is in excellent agreement with X-ray data indicating three mutually *cis* carbonyl ligands (Table 1). At ambient temperature (293 K) all of the complexes exhibit only one ^{13}C NMR signal at ca. 210 ppm for three carbonyl carbons and one signal at ca. 120 ppm for two nitrile carbons, indicating that the coordinated ligands are not rigidly held.

A characteristic feature of the heterobimetallic bis(nitrile) compounds is their good stability in the solid state and in hydrocarbon solution, much better than that of analogous compounds without a metal–metal bond. For example,

Table 1
Selected structural data for the seven-coordinate heterobimetallic nitrile complexes of W(II) and Mo(II)

Compound	Space group	Bond lengths (Å)				Bond angles (°)				Reference
		M–M′	M–Cl	M–CO	M–N	OC–M–CO	*trans*-OC–M–N	*trans*-OC–M–Cl	M′–M–Cl or M′–M–M′	
[WCl(SnCl$_3$)(CO)$_3$(NCMe)$_2$] (**4**)	$P2_1/m$	2.710 (1)	2.511 (5)	1.997 (13)	2.18 (1)	76.6 (6)	161.2 (5)	171.1 (6)	65.8 (1)	[14]
				2.00 (2)	2.18 (1)	76.6 (6)	161.2 (5)			
				2.00 (2)		107.7 (8)				
[WCl(GeCl$_3$)(CO)$_3$(NCEt)$_2$] (**5**)	$P2_1/n$	2.567 (1)	2.423 (3)	1.977 (9)	2.174 (6)	74.8 (4)	165.5 (4)	149.2 (7)	143.81 (7)	[13]
				1.979 (9)	2.212 (6)	75.6 (3)	169.8 (3)			
				2.008 (11)		109.4 (4)				
[MoCl(SnCl$_3$)(CO)$_3$(NCEt)$_2$] (**6**)	$P2_1/a$	2.694 (1)	2.556 (2)	1.999 (6)	2.176 (4)	76.2 (2)	159.7 (2)	172.8 (2)	56.22 (3)	[17]
				1.991 (4)	2.208 (4)	77.1 (2)	166.7 (2)			
				1.980 (5)		105.7 (2)				
[Mo(SnCl$_3$)$_2$(CO)$_2$(NCEt)$_3$] (**7**)	$P2_1/n$	2.686 (1)		1.984 (9)	2.158 (7)	105.0 (3)	142.4 (3)		129.10 (3)	[15]
		2.699 (1)		1.978 (8)	2.179 (6)		169.7 (3)			
					2.201 (6)					
[Mo(GeCl$_3$)$_2$(CO)$_2$(NCEt)$_3$] (**8**)	$P\bar{1}$	2.529 (1)		1.962 (7)	2.186 (5)	106.0 (2)	141.9 (2)		124.6 (3)	[16]
		2.539 (1)		1.974 (6)	2.193 (5)		171.3 (2)			
					2.212 (5)					

Table 2
Selected spectroscopic data for the seven-coordinate heterobimetallic bis(acetonitrile) complexes of the type $[MCl(M'Cl_3)(CO)_3(NCMe)_2]$ (M = W, Mo; M′ = Sn, Ge)

Compound	IR in KBr pellets (cm^{-1})		^{1}H and ^{13}C{^{1}H} NMR in CD_2Cl_2 at 293 K				Reference
	ν(C≡O)	ν(C≡N)	δ_H CH_3	δ_C CO	δ_C CN	δ_C CH_3	
[W—Sn] (**4**)	2030(vs), 1935(s,sh), 1903(vs)	2327(w), 2299(w)	2.53	211.93	126.80	4.54	[14]
[W—Ge]	2033(s), 1968(m), 1914(vs)	2320(w), 2292(w)	2.34	214.8		3.10	[13]
[Mo—Sn]	2033(vs), 1959(s), 1917(vs)	2317(w), 2290(w)	2.46	219.39	128.24	5.40	[15]
[Mo—Ge]	2041(vs), 1988(s), 1949(vs)	2316(w), 2289(w)	2.45	219.34	125.56	4.60	[16]

dichloro molybdenum and tungsten compounds of the type $[MCl_2(CO)_3(NCR)_2]$ (Scheme 2) are very unstable and undergo decarbonylation reaction to give non-soluble and poorly characterized mixtures of compounds. To our knowledge, to date the molecular structure of diiodide compounds of the type $[MI_2(CO)_3(NCR)_2]$, M = W [28,29], M = Mo [30], R = Me, Et, and Ph, has only been characterized crystallographically. Although diiodide compounds have a distorted capped octahedral geometry analogous to that detected for the bimetallic compounds **4–6**, the mutual positions of the seven ligands are drastically different, the two iodide ligands being mutually *trans* with the I–W–I angle of ca. 160° [28–30].

Bis(nitrile) molybdenum compounds containing a Mo—Sn or Mo—Ge bond undergo disproportionation reaction in a nitrile solution to give compounds with two Mo–M′ bonds such as $[Mo(SnCl_3)_2(CO)_2(NCEt)_3]$ (**7**) [15] or $[Mo(GeCl_3)_2(CO)_2(NCEt)_3]$ (**8**) [16] (Fig. 4).

As shown in Fig. 4, compounds **7** and **8** have structures similar to the so-called 4:3 "piano stool" arrangement of the seven ligands. In this description the tetragonal base is defined by the two carbon atoms and the two tin atoms. The trigonal base consists of the three nitrogen atoms. The angle between the tetragonal and the trigonal bases is 4.6(2)° in the bis(stannyl) compound **7** and 2.6(1)° in the bis(germyl) compound **8**.

In the reaction of bis(nitrile) compounds **4–6** with alkynes, the substitution of two carbonyl groups and one nitrile ligand by two molecules of alkyne and the formation of six-coordinate compounds has been observed [13–16]. Templeton [31] and Baker [4] showed that in compounds of this kind two alkyne ligands are mutually *cis* and together donate six electrons to the transition metal atom. The coordination of terminal alkyne to the metal atom can be very easily observed by ^{1}H NMR spectroscopy due to the low field resonance (ca. 10 ppm) of alkyne protons. However, such compounds are very unstable and undergo transformation to a species initiating the polymerization reaction of alkynes. With compounds **4–6** used as catalysts, the polymerization of phenylacetylene [13–16,23] and *tert*-butylacetylene [24] proceeds smoothly at room temperature to give high-molecular-weight soluble polymers.

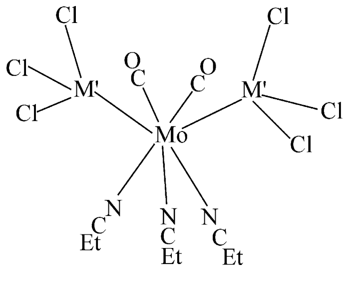
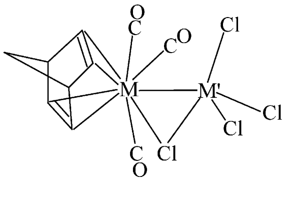


Fig. 4. Schematic view of the 4:3 "piano stool" geometry found by X-ray diffraction study for compounds of the type $[Mo(M'Cl_3)_2(CO)_2(NCEt)_3]$ (M′ = Sn, and Ge).

4. Seven-coordinate norbornadiene complexes of the general composition $[MCl(M'Cl_3)(CO)_3(\eta^2,\eta^2\text{-}C_7H_8)]$ (M = W, Mo; M′ = Sn, Ge)

As part of our current interest in the chemistry of seven-coordinate molybdenum(II) and tungsten(II) complexes of the type $[MCl(M'Cl_3)(CO)_3(NCMe)_2]$ and $[(CO)_4M(\mu\text{-}Cl)_3M(M'Cl_3)(CO)_3]$ (M = W, Mo; M′ = Sn, Ge), we have undertaken a study of their reactivity towards cyclic olefins such as bicyclo[2.2.1]hepta-2-ene (norbornene = NBE) and bicyclo[2.2.1]hepta-2,5-diene (norbornadiene = NBD) [12,17–20,25]. These heterobimetallic complexes readily react with cyclic olefins under mild conditions to give nitrile or CO substitution products, but in the presence of an excess of these organic reagents such compounds initiate the ROMP reaction. However, only in reaction with cyclic diene such as NBD has it been possible to isolate and characterize by X-ray diffraction studies the seven-coordinate complexes [12,17–20] (Fig. 5).

A bimetallic tungsten-tin compound containing the NBD ligand, $[WCl(SnCl_3)(CO)_3(\eta^2,\eta^2\text{-}C_7H_8)]$ (**9**), can be isolated in a reaction of the substitution of two nitrile ligands by a diene molecule in the bis(nitrile) compound **4** [12] or in reaction of the binuclear compound **1** with NBD.



	M	M'
10	Mo	Sn
11	W	Ge

Fig. 5. The arrangement of ligands in norbornadiene compounds of the type $[MCl(M'Cl_3)(CO)_3(\eta^2,\eta^2\text{-}C_7H_8)]$.

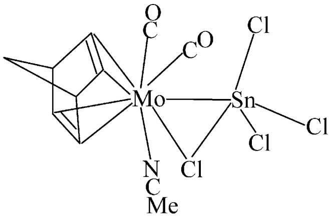


Fig. 6. The environment of the molybdenum atom in [$MoCl(SnCl_3)(CO)_2(\eta^2,\eta^2-C_7H_8)(NCMe)$] (**12**) [19].

Similar reactivity towards NBD has been observed for binuclear molybdenum compound **3** [17]. The compound [$MoCl(SnCl_3)(CO)_3(\eta^2,\eta^2-C_7H_8)$] (**10**) was separated in reaction of **3** with NBD [18]. The coordination of the NBD ligand in the molybdenum and the analogous seven-coordinate tungsten complex is arranged in two ways (Fig. 6). One of the olefinic bonds is *trans* to CO and the other *trans* to the chloride ligand, with different olefinic carbon–molybdenum atom distances: one longer by 10 pm *trans* to the CO ligand and a shorter one *trans* to the chloride ligand [12,18] (Table 3).

Similar distorted pentagonal bipyramid geometry and spectroscopic characteristics have been shown for a norbornadiene carbonyl compound of tungsten containing a W–Ge bond: [$WCl(GeCl_3)(CO)_3(\eta^2,\eta^2-C_7H_8)$] (**11**) [20] (Fig. 5).

Asymmetrical coordination of the diene ligand in seven-coordinate tungsten(II) and molybdenum(II) compounds leads to different spectroscopic characteristics and reactivities of the two olefinic bonds of the norbornadiene ligand in such compounds. One of the olefinic bonds is very loosely coordinated to the transition metal, which is reflected in a very small coordination shift of one of the olefinic proton and olefinic carbon signals (Table 4).

The development of new norbornadiene complexes **9–11** and their catalytic activity in ROMP of cyclic olefins induced us to study their chemistry more carefully. Recent results have shown that the molybdenum complex **10** appears more labile in solution than its tungsten analogue **9**. Also, the reactivity of bis(nitrile) compounds of W and Mo towards NBD is different. The reaction of [$MoCl(SnCl_3)(CO)_3(NCMe)_2$] with NBD at room temperature in dichloromethane solution gives a mixture of compounds containing the norbornadiene ligand. Compound **10** (isolated earlier in reaction of the binuclear compound **3** with NBD [18]) is one of the products but others (containing one or two carbonyl groups) are also formed in varying amounts, as shown by IR and NMR studies of the reaction mixture. From this mixture one compound was isolated in crystalline form. X-ray diffraction studies revealed that it is a novel norbornadiene complex: [$MoCl(SnCl_3)(CO)_2(\eta^2,\eta^2-C_7H_8)(NCMe)$] (**12**) [19] (Fig. 6).

The environment of the molybdenum atom in **12** can be described as a distorted pentagonal bipyramid. The two carbonyl ligands are mutually *cis* and two *ν*(CO) frequencies are observed in IR spectra of **12**, at 2012 and 1963 cm^{-1} [19].

Table 3
Selected structural data for the seven-coordinate heterobimetallic norbornadiene complexes of W(II) and Mo(II)

Compound	Space group	Bond lengths (Å)				Bond angles (°)			Reference
		M–M′	M–Cl	M–CO	M–C_{olef}	*trans*-OC–M–CO or OC–M–N	*cis*-OC–M–CO	M′–M–Cl	
[$WCl(SnCl_3)(CO)_3(\eta^2,\eta^2-C_7H_8)$] (**9**)	*P*2$_1$/*c*	2.764 (1)	2.454 (2)	2.029 (9)	2.306 (9)	166.8 (4)	92.4 (4)	69.32 (6)	[12]
				2.032 (9)	2.326 (8)		93.8 (4)		
				2.06 (1)	2.413 (8)				
					2.407 (9)				
[$WCl(GeCl_3)(CO)_3(\eta^2,\eta^2-C_7H_8)$] (**11**)	*P*2$_1$/*c*	2.636 (1)	2.443 (2)	2.056 (12)	2.325 (10)	166.4 (4)	92.3 (4)	71.87 (7)	[20]
				2.056 (10)	2.325 (10)		94.9 (4)		
				2.063 (11)	2.412 (11)				
					2.427 (10)				
[$MoCl(SnCl_3)(CO)_3(\eta^2,\eta^2-C_7H_8)$] (**10**)	*P*2$_1$/*n*	2.752 (1)	2.474 (1)	2.032 (3)	2.330 (3)	172.4 (1)	87.9 (1)	66.87 (3)	[18]
				2.064 (3)	2.335 (3)		94.8 (1)		
				2.071 (3)	2.431 (3)				
					2.423 (3)				
[$Mo(SnCl_3)_2(CO)_2(\eta^2,\eta^2-C_7H_8)(NCMe)$] (**12**)	*P*2$_1$/*c*	2.739 (1)	2.484 (2)	1.984 (9)	2.288 (7)	170.2 (2)	92.1 (2)	67.06 (4)	[19]
				1.978 (8)	2.338 (7)				
					2.403 (6)				
					2.455 (6)				

Table 4
Selected spectroscopic data for the seven-coordinate heterobimetallic norbornadiene complexes of the type $[MCl(M'Cl_3)(CO)_2L\ (\eta^2,\eta^2\text{-}C_7H_8)]$ (M = W, Mo; M′ = Sn, Ge; L = CO, NCMe)

Compound	IR in KBr pellets (cm^{-1})		^1H and $^{13}C\{^1H\}$ NMR in CD_2Cl_2 at 293 K										Reference
	$\nu(C\equiv O)$	$\nu(C\equiv N)$	δ_H: =CH	CH	CH_2	CH_3	δ_C: CO	=CH	CH_2	CH	CN	CH_3	
[W—Sn] (**9**)	2087(w)		5.04	3.97	1.50		202.28	81.81	64.00	44.24			[12]
	2040(s,sh)		3.71		1.48		193.47	43.11					
	2021(s,sh)												
	2006(vs)												
[W—Ge] (**11**)	2089(w)		5.00	3.89	1.46		203.34	81.13	64.40	44.10			[20]
	2046(m)		3.57				193.70	42.67					
	2038(m)												
	2007(vs)												
[Mo—Sn] (**10**)	2088(vw)		5.27	3.90	1.78		211.17	88.88	64.08	46.32			[18]
	2017(vs)		4.02		1.77		205.09	46.10					
[Mo—Sn] (**12**)	2012(s)	2291(w)	5.43	3.81	1.77	2.46	219.67	96.00	62.09	45.67	128.45	4.83	[19]
	1963(s)		4.84	3.76			214.17	94.07		45.42			
			4.00					53.86					
			3.91					52.31					

The ^1H NMR spectrum of **12** shows seven well-separated signals due to the protons of the norbornadiene ligand. Four peaks at $\delta_H = 5.43$, 4.84, 4.00, and 3.91, which appear as pseudo-triplets with J_{HH} = ca. 4 Hz, are due to protons attached to the olefinic carbons of double C=C bonds, while the broad peaks at $\delta_H = 3.81$ and 3.76 are due to protons attached to the bridgehead methine carbons. The signal at $\delta_H = 1.77$ appears as a pseudo-quartet, i.e. two doublets with second-order distortion, and can be assigned to two protons of the bridge methylene group. In ^1H NMR spectra of **12** four resonances of the olefinic protons are 1.22–2.74 ppm upfield compared with free NBD. Thus, the ^1H NMR data for **12** prove that the NBD ligand coordinates asymmetrically to the metal atom (Table 3).

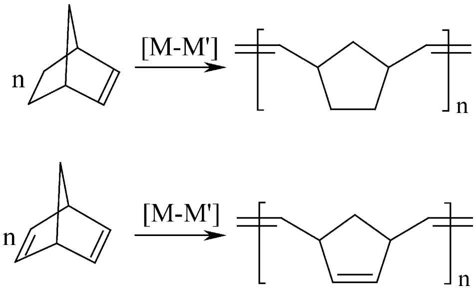
For the more symmetrically coordinated NBD ligand in the molybdenum compound **10**, only two olefinic proton signals were observed in the ^1H NMR spectrum at $\delta_H = 5.27$ and 4.02 [18]. The lower-field norbornadiene signals of **12** and **10** were assigned to the protons of the HC=CH unit trans to the CO group and the signals at a higher field to the protons of the double bond trans to the chlorine ligand. Similar conclusions can be drawn from NMR data for compounds **9** and **11** (Table 4). The NMR data for the norbornadiene complexes **9**–**12** are in very good agreement with the results of X-ray diffraction studies (Table 3).

The observed M–C bond distances are in excellent agreement with the degree of electron back-donation from the dπ-orbitals of the transition metal to the ligands whose π acidity is taken into account. As CO is a better π acid than the olefinic bond, back-donation to CO is much preferred. For C=C and its *trans* Cl ligand, the electron density due to back-donation is almost completely accepted by C=C, resulting in shortened M–C(olefin) distances. Thus the structure of compounds **9**–**12** provides a good model for comparing the effect of the relative position of olefin and CO ligands on the M–C bond distances.

5. Catalytic activity of tungsten(II) and molybdenum(II) heterobimetallic compounds

Seven-coordinate molybdenum(II) and tungsten(II) complexes provide a rich variety of reactions with unsaturated hydrocarbons and can be used as catalysts for the metathesis of acyclic olefins and ROMP of cyclic olefins [6,21–23,25,32–35]. All the seven-coordinate compounds obtained in the oxidative addition reaction of group 6 metal carbonyls and halide group 14 elements initiate the ROMP reaction of cyclic olefins as NBE and NBD [21,25] (Scheme 3).

A very important step in the initiation of ROMP by seven-coordinate complexes is the coordination of olefin to the transition-metal atom. As has been shown by NMR investigations during the catalytic reaction, the coordination of the NBD molecule to the transition metal is accompanied by the formation of a ROMP polymer. In a reaction between the previously isolated norbornadiene complex **10** and an excess of NBD monitored by ^1H NMR, the initiation of the ROMP of NBD and the formation of the ROMP polymer, with characteristic olefinic proton signals at ca. 5 ppm, starts immediately, and norbonadiene polymerizes till the end. In the analogous reaction of the tungsten norbornadiene complex **9** with norbornadiene monitored by ^1H NMR, the de-



Scheme 3. ROMP reactions catalyzed by seven-coordinate complexes containing M—M′ bonds.

cay of signals due to the norbornadiene ligand coordinated to tungsten is accompanied by an increase in signals due to polynorbornadiene.

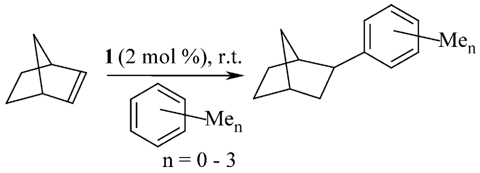
A similar picture was obtained when ROMP of NBE initiated by a chlorocarbonyl compound containing a norbornadiene ligand was followed by means of NMR. The decay of signals due to the norbornadiene ligand coordinated to tungsten is accompanied by an increase in the intensity of signals due to polynorbornene. With norbornadiene complexes used as initiators in the ROMP reaction, evidence was obtained that true catalytically active carbene species must derive from olefin ligands. The mechanism of this transformation is an intriguing problem that so far has remained unresolved.

To explain how the carbene species can be formed from the cyclic olefin ligands during the initiation of ROMP, we have recently concentrated our efforts on the study of tungsten carbonyl complexes containing norbornene ligands. Coordination of NBE to the tungsten atom can be very easily achieved by photochemical substitution of carbonyl groups by NBE in tungsten hexacarbonyl. In such a photochemical reaction very stable *trans*-$[W(CO)_4(\eta^2\text{-}C_7H_{10})_2]$ is formed. The intermediate product, $W(CO)_5(\eta^2\text{-}C_7H_{10})]$, very labile in solution, has been characterized by IR and NMR spectroscopy and by X-ray diffraction studies [26].

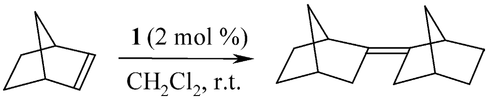
The two-electron chemical oxidation of the very stable *trans*-bis(norbornene) complex of tungsten(0) by tin tetrachloride gives a very labile norbornene complex of tungsten in the second oxidation state. Characterization of this complex has been possible only by low temperature NMR studies. This unstable norbornene compound decomposes to give chloronorbornane in chloroform solution, whereas in benzene or toluene solution the products of the hydroarylation of norbornene are formed. The simultaneous formation of the very well known binuclear compound **1** has also been observed [26].

Using compound **1** as a catalyst in solvents such as benzene, toluene, *para*-xylene, or mesitylene, norbornene can be transformed with good, over-90% yield to hydroarylation products of norbornene (Scheme 4) [36]. The reaction is accompanied by ROMP, cyclotrimerization, and dimerization processes. The last of those is the dominating reaction in solution of an arene such as chlorobenzene.

The same binuclear catalyst (**1**), but in reaction carried out in chloroform, dichloromethane, or chlorobenzene solution, leads to the formation of 2,2′-binorbornylidene (norbornene dimer containing a carbon–carbon double bond) [37] (Scheme 5).



Scheme 4. Hydroarylation of norbornene by simple arene catalyzed by complex **1** [36].



Scheme 5. Dimerization of norbornene catalyzed by complex **1** [37].

The mechanism for the formation of 2,2′-binorbornylidene involves coordination of NBE to the transition metal atom and its transformation to a carbene species as a result of 1,2-hydride shift. Bimolecular decomposition of the carbene compound leads to the formation of 2,2′-binorbornylidene and the regeneration of the binuclear compound. In that way was obtained direct evidence for the transformation of a cyclic olefin ligand to a carbene species as a result of the activation of the C–H bond by a tungsten(II) compound [37]. A similar η^2-alkene to carbene rearrangement was observed by others [38,39].

6. Formation of a W–Si bond in photochemical reaction of $W(CO)_6$ with Ph_2SiH_2

Our recent results have shown that photochemically activated $W(CO)_6$ undergoes oxidative addition reactions with hydrosilanes in which a W–Si bond is formed [40]. The photochemical reaction of $W(CO)_6$ and diphenylsilane proceeds by the activation of the silicon–hydrogen bond and the formation of an intermediate seven-coordinate hydride compound of tungsten, which decomposes to give first the silylene-bridged tungsten compound $[(\mu\text{-}SiPh_2)W_2(CO)_{10}]$ (**13**) (Fig. 7).

The oxidative addition reaction of $W(CO)_6$ and hydrosilanes is a very important step in the hydrosilylation of C=C or C=O double bonds. During the irradiation of $W(CO)_6$, diphenylsilane and acetone in alkane solution two hydrosilylation products, $Ph_2HSiOCHMe_2$ and $Ph_2Si(OCHMe_2)_2$, were detected in a 10 to 1 molar ratio.

7. Prospects and outlook

The work summarized in this review shows that the most prominent feature of seven-coordinate tungsten(II) and molybdenum(II) compounds containing W–Sn, W–Ge,

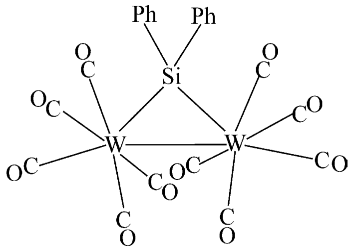


Fig. 7. Schematic view of the ligand arrangement in the silylene compound $[(\mu\text{-}SiPh_2)W_2(CO)_{10}]$ (**13**) [40].

Mo–Sn, and Mo–Ge bonds is the facility with which they react with organic compounds such as alkenes and alkynes.

This review presents several examples showing that seven-coordinate compounds of this type are very reactive and may be used as long-lived precatalytic intermediates in the transformation of alkenes and alkynes proceeding under extremely mild conditions. The products of tungsten(II) and molybdenum(II) interaction with organic substrates (unsaturated hydrocarbons) have sometimes been isolated but frequently such compounds have only been observed in situ by spectroscopic investigations during the catalytic reaction. Also, it is worth pointing out that by changing the reaction conditions it is possible to carry out the catalytic reaction selectively to one of the products of the C–C bond forming reaction: dimerization, cyclotrimerization, polymerization, or hydroarylation.

The results presented suggest that heterobimetallic seven-coordinate compounds of tungsten(II) and molybdenum(II) have considerable potential and further exploration of their unusual reactivity is required.

Acknowledgements

I would like to thank all my co-workers who have been involved in tungsten(II) and molybdenum(II) studies: Prof. Tadeusz Głowiak and Dr Andrzej Kochel – X-ray diffraction analysis; Dr Izabela Czeluśniak – the catalytic activity of tungsten and molybdenum compounds in polymerization of terminal alkynes and ROMP reaction; Marcin Górski – photochemical reactions of $W(CO)_6$ with olefins; Agnieszka Gądek – photochemical reactions of $W(CO)_6$ with hydrosilanes; and Anna Malinowska – hydroarylation reactions of norbornene. I am also grateful to Dr M. Kowalska and S. Baczyński for the measurement of NMR spectra and M. Hojniak for GC–MS analysis. Support for this work was generously provided by the Polish State Committee for Scientific Research (KBN grant No 4T09A 19125).

References

[1] R. Colton, Coord. Chem. Rev. 6 (1971) 269.
[2] M.G.B. Drew, Prog. Inorg. Chem. 23 (1977) 67.
[3] M. Melnik, P. Sharrock, Coord. Chem. Rev. 65 (1985) 49.
[4] P.K. Baker, Adv. Organomet. Chem. 40 (1996) 46.
[5] P.K. Baker, Chem. Soc. Rev. 27 (1998) 125.
[6] T. Szymańska-Buzar, J. Mol. Catal. 48 (1988) 43.
[7] P. Krausz, F. Garnier, J.E. Dubois, J. Am. Chem. Soc. 97 (1975) 437.
[8] A. Agapiou, E. McNeils, J. Organomet. Chem. 99 (1975) C47.
[9] C. Tanielan, R. Kieffer, A. Harfouch, Tetrahedron Lett. 52 (1977) 4589.
[10] T. Masuda, T. Higashimura, Adv. Polym. Sci. 81 (1986) 121.
[11] T. Szymańska-Buzar, T. Głowiak, J. Organomet. Chem. 489 (1995) 207.
[12] T. Szymańska-Buzar, T. Głowiak, Polyhedron 16 (1997) 1599.
[13] T. Szymańska-Buzar, T. Głowiak, J. Organomet. Chem. 564 (1998) 143.
[14] T. Szymańska-Buzar, T. Głowiak, Polyhedron 17 (1998) 3419.
[15] T. Szymańska-Buzar, T. Głowiak, J. Organomet. Chem. 575 (1999) 98.
[16] T. Szymańska-Buzar, T. Głowiak, I. Czeluśniak, J. Organomet. Chem. 585 (1999) 215.
[17] T. Szymańska-Buzar, T. Głowiak, I. Czeluśniak, Inorg. Chem. Commun. 3 (2000) 102.
[18] T. Szymańska-Buzar, T. Głowiak, I. Czeluśniak, J. Organomet. Chem. 640 (2001) 72.
[19] T. Szymańska-Buzar, T. Głowiak, I. Czeluśniak, Polyhedron 21 (2002) 2505.
[20] T. Szymańska-Buzar, T. Głowiak, I. Czeluśniak, M. Górski, Inorg. Chem. Commun. 5 (2002) 682.
[21] K.J. Ivin, J.C. Mol, Olefin Metathesis and Metathesis Polymerization, Academic Press, London, 1997.
[22] T. Szymańska-Buzar, J. Mol. Catal. 68 (1991) 177.
[23] T. Szymańska-Buzar, J. Mol. Catal. A: Chem. 123 (1997) 113.
[24] T. Szymańska-Buzar, I. Czeluśniak, J. Mol. Catal. A: Chem. 160 (2000) 133.
[25] I. Czeluśniak, T. Szymańska-Buzar, J. Mol. Catal. A: Chem. 190 (2002) 131.
[26] M. Górski, A. Kochel, T. Szymańska-Buzar, Organometallics 23 (2004) 3037.
[27] M. Górski, A. Kochel, T. Szymańska-Buzar, in preparation.
[28] M.G.B. Drew, P.K. Baker, E.M. Armstrong, S.G. Fraser, D.J. Muldoon, A.J. Lavery, A. Shawcross, Polyhedron 14 (1995) 617.
[29] P.K. Baker, D.J. Muldoon, M.B. Hursthouse, S.J. Coles, A.J. Lavery, A. Shawcross, Z. Naturforsch. Sect. B 51 (1996) 263.
[30] P.K. Baker, M.M. Meehan, M.G.B. Drew, Transition Met. Chem. 24 (1999) 333.
[31] J.L. Templeton, Adv. Organomet. Chem. 29 (1989) 1.
[32] M.A. Jahdali, P.K. Baker, A.J. Lavery, M.M. Meehan, D.J. Muldoon, J. Mol. Catal. A: Chem. 159 (2000) 51.
[33] L. Bencze, A. Kraut-Vass, J. Organomet. Chem. 270 (1984) 211.
[34] L. Bencze, A. Kraut-Vass, L. Prókai, J. Chem. Soc., Chem. Commun. (1985) 911.
[35] L. Bencze, G. Szalai, J.G. Hamilton, J.J. Rooney, J. Mol. Catal. A: Chem. 115 (1997) 193.
[36] A. Malinowska, I. Czeluśniak, M. Górski, T. Szymańska-Buzar, Tetrahedron Lett. 46 (2005) 1427.
[37] A. Malinowska, I. Czeluśniak, M. Górski, T. Szymańska-Buzar, J. Mol. Catal. A: Chem. 226 (2005) 259.
[38] A.S. Veige, P.T. Wolczanski, E.B. Lobkovsky, Angew. Chem. Int. Ed. 40 (2001) 3629.
[39] J.N. Coalter III, J.C. Bollinger, J.C. Huffman, U. Werner-Zwanziger, K.G. Caulton, E.R. Davidson, H. Gérard, E. Clot, O. Eisenstein, New J. Chem. 24 (2000) 9.
[40] A. Gądek, A. Kochel, T. Szymańska-Buzar, Organometallics 22 (2003) 4869.