An anionic binuclear complex of tungsten(II), $[(\mu\text{-Cl})_3\{W(SnCl_3)(CO)_3\}_2]^-$, and its reactivity towards norbornene

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Abstract

An anionic binuclear complex of tungsten(II), $[(\mu\text{-Cl})_3\{W(SnCl_3)(CO)_3\}_2]^-$ (**1⁻**), containing the protonated piperidine molecule $[Hpip]^+$ as the counter ion, has been obtained during crystallization of the product from reaction between $[W(CO)_4(pip)_2]$ and $SnCl_4$ in dichloromethane solution, and its molecular structure has been elucidated by single-crystal X-ray diffraction studies. The chemical properties of complex **1** were investigated by IR and NMR spectroscopy in solution and its catalytic activity was checked in reaction with norbornene (NBE). In the presence of complex **1**, NBE transformed to a new olefin, 2,2′-binorbornylidene with ca. 50% yield in dichloromethane solution. The spectroscopic characteristics of complex **1⁻** were compared with those of the reinvestigated analogue compound $[(\mu\text{-Cl})_3W_2(SnCl_3)(CO)_7]$ (**2**). The ^{119}Sn and ^{13}C NMR data indicated that in dichloromethane solution complex **2** transformed to the ionic complex **1⁻**.
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Keywords: Tungsten(II); Stannyl ligand; Heterobimetallic complex; X-ray crystal structure; Catalytic activity; Olefin dimerization; Carbene formation
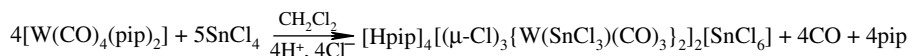
1. Introduction

Oxidative decarbonylation of low-oxidation-state tungsten and molybdenum carbonyl complexes such as $[M(CO)_4L_2]$ (L = nitrogen or phosphorous donor ligands) with halogens and tetrahalides of group 14 elements has previously been shown to be a valuable route to M(II) derivatives [1–3]. For example, using this method, we have prepared the W(II) and Mo(II) bis(nitrile) complexes $[MCl(M'Cl_3)(CO)_3(NCMe)_2]$ (M′ = Sn, Ge) and demonstrated that these compounds are useful starting materials for the synthesis of various complexes obtained by substitution of nitrile with olefin, alkyne, and phosphine [3]. Other highly versatile starting materials include heterobimetallic complexes of the type $[(\mu\text{-Cl})_3M_2(M'Cl_3)(CO)_7]$ (M = W, Mo; M′ = Sn, Ge), prepared in photochemical oxidative addition reaction of $[M(CO)_6]$ (M = W, Mo)

and tin or germanium tetrachloride [3]. The former compounds 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 [3]. A very intriguing catalytic reaction initiated by binuclear compounds is dimerization of norbornene leading to the formation of 2,2′-binorbornylidene (bi-NBE) [3–5]. The formation of bi-NBE from NBE indicates that the binuclear tungsten(II) complex can transform an olefin to a carbene ligand and this process may be applied in the synthesis of a new olefin, as a result of carbene–carbene coupling.

In this study, using the well-known piperidine (pip) complex $[W(CO)_4(pip)_2]$ [6–8] as a precursor, we introduce a binuclear anion complex of tungsten(II), $[(\mu\text{-Cl})_3\{W(SnCl_3)(CO)_3\}_2]^-$ (**1⁻**), and describe its crystal structure, molecular structure, and reactivity towards norbornene. The properties of the new compound **1** are compared with those of the binuclear complex $[(\mu\text{-Cl})_3W_2(SnCl_3)(CO)_7]$ (**2**), studied in our laboratory

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$$4[W(CO)_4(pip)_2] + 5SnCl_4 \xrightarrow[4H^+, 4Cl^-]{CH_2Cl_2} [Hpip]_4[(\mu\text{-}Cl)_3\{W(SnCl_3)(CO)_3\}_2]_2[SnCl_6] + 4CO + 4pip$$

Scheme 1.

previously, whose photochemical synthesis and ^{13}C and ^{119}Sn NMR studies have been reinvestigated.

2. Results and discussion

2.1. Synthesis and spectroscopic identification of the tungsten compound 1 in reaction of [W(CO)₄(pip)₂] with SnCl₄

Synthesis of the compound **1** was achieved via addition of SnCl₄ to [W(CO)₄(pip)₂] [6–8] in dichloromethane solution. An immediate color change from yellow to orange indicated a rapid reaction, and an insoluble colorless microcrystalline solid was deposited as the solution was stirred under ambient conditions. The solid was then determined by elemental analysis to be [Hpip][SnCl₃(OH)₂]. As was observed using IR spectroscopy, the reaction of the tungsten(0) compound with SnCl₄ leads to the formation of a new carbonyl compound of tungsten in higher than zero oxidation state. The IR spectrum of the reaction mixture exhibited $v(C\equiv O)$ stretching modes at ca. 2100 (w), 2030 (vs), and 1940 (vs) cm^{-1}, shifted to higher wave numbers relative to those of the parent compound ($v(C\equiv O)$: 2006 (w), 1925 (vs), 1868 (m, br), and 1824 (w) cm^{-1}). The IR spectrum of the new compound **1** is more similar to those of dimeric halocarbonyls of group 6 metals containing mutually *cis* carbonyl groups [3,5,9,10] than to the spectra of mononuclear seven-coordinate compounds of the type [MCl(M′Cl₃)(CO)₃L₂] (M = W, Mo; M′ = Sn, Ge, L = nitrogen donor ligand) [3]. Three $v(C\equiv O)$ bands in the IR spectrum of **1** suggests the C_{3v} local symmetry of the W(CO)₃ carbonyl moiety. In the ^{13}C NMR spectrum of the product isolated from the reaction mixture and dissolved in CD₂Cl₂, the carbonyl ligands give two resonances in the intensity ratio 2:1, at $\delta = 215.5$ and 208.6 ppm, respectively. The latter resonances differ very greatly in their tin–carbon coupling constants: $^2J_{Sn-C} = 341$ Hz for 2CO and $^2J_{Sn-C} = 88$ Hz for 1CO, while the tungsten–carbon coupling constants are only slightly different: $^1J_{W-C} = 130$ Hz and $^1J_{W-C} = 123$ Hz, respectively. This indicates a different position of the carbonyl ligands compared with the trichlorostannyl ligand in the coordination sphere of tungsten. The value of the ^{119}Sn–^{13}C coupling constant indicates a weaker interaction between one of the three carbonyl ligands and the tin atom. The ^{119}Sn chemical shift for the trichlorostannyl SnCl₃⁻ ligand in **1** was observed at $\delta = -138$ ($^1J_{W-Sn} = 614$ Hz) in CDCl₃, compared with $\delta = -146$ ($^1J_{W-Sn} = 609$ Hz) in CD₂Cl₂ solution.

Attempts to grow crystals of the compound **1** gave extremely insoluble orange crystals, which prevented their recrystallization. Their formulation was determined by means of single-crystal X-ray diffraction and elemental analysis to contain two ionic compounds, [Hpip][(μ-Cl)₃{W(SnCl₃)(CO)₃}₂] and [Hpip]₂[[SnCl₆], in the molar ratio 2:1 (Scheme 1).

The precise mechanism for the formation of compound **1** remains unclear, although the most likely scenario is the generation of HCl in reaction conditions. The similar protonation of nucleophilic species such as PPh₃ and the formation of the ionic compound [HPPh₃]₂[[SnCl₆] has previously been observed in oxidative addition reactions of a tungsten(0) phosphine compound with SnCl₄ carried out in CH₂Cl₂ solution [11,12].

2.2. X-ray crystal structure of compound 1

The unit cell of complex **1** is built up from dimeric tungsten anions [(μ-Cl)₃{W(SnCl₃)(CO)₃}₂]⁻ (**1**⁻), piperidinium cations [Hpip]⁺, and the dianion [SnCl₆]²⁻. Crystal data and structure refinement parameters for this mixture of compounds are given in Table 1. The piperidinium cations form canals along the [100] axis. In these canals the hexachlorostannate dianions are arranged as columns parallel

Table 1
Crystal data and structure refinement parameters for the 2:1 mixture of compounds [C₅H₁₀NH₂][(μ-Cl)₃{W(SnCl₃)(CO)₃}₂] and [C₅H₁₀NH₂][SnCl₆]

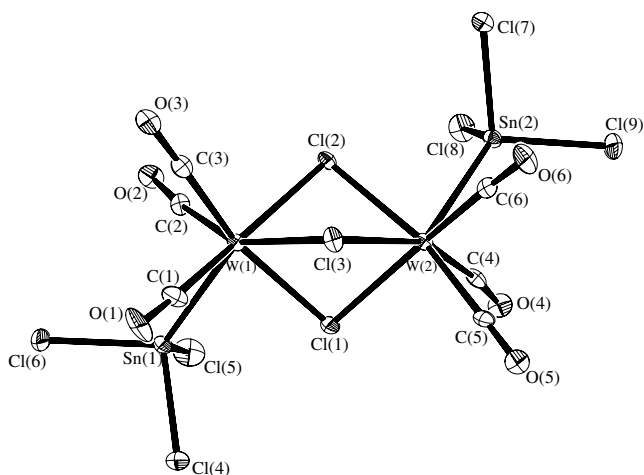| Empirical formula	C₃₂H₄₈Cl₂₄N₄O₁₂Sn₅W₄
Formula weight	2860.45
Crystal size (mm)	0.12 × 0.08 × 0.08
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
Unit cell dimensions	
a (Å)	6.813(5)
b (Å)	23.480(5)
c (Å)	23.831(5)
α (°)	92.50(3)
β (°)	95.76(3)
γ (°)	97.67(3)
V (Å³)	3753(3)
Z	2
D_{calc} (g/cm³)	2.531
Diffractometer	Kuma KM4CCD
Radiation	Mo Kα ($\lambda = 0.71073$ Å)
Temperature (K)	100(2)
μ (mm^{-1})	8.638
$F(000)$	2636
Number of data/parameters	17468/730
Index ranges	$-8 \leqslant h \leqslant 9$; $-30 \leqslant k \leqslant 31$; $-31 \leqslant l \leqslant 28$
Number of reflections collected	43692
Data collected, θ minimum/maximum (°)	2.8/28.6
R_{int}	0.060
S	1.25
Final residuals: R_1, wR_2 ($I > 2\sigma(I)$)	0.0640/0.1215
T_{min}, T_{max}	0.345, 0.789
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	2.26/−1.74

Fig. 1. ORTEP diagram, including the crystallographic labeling scheme, for one of the two very similar molecules of the binuclear anion 1^-.

Table 2
Selected bond lengths (Å) and angles (°) for $[(\mu\text{-Cl})_3\{W(SnCl_3)(CO)_3\}_2]^-$ (1^-)

Atoms	Distance	Atoms	Angle
W(1)–C(1)	2.00(1)	C(2)–W(1)–C(1)	75.7(5)
W(1)–C(2)	1.99(1)	C(3)–W(1)–C(2)	78.6(5)
W(1)–C(3)	2.02(1)	C(1)–W(1)–C(3)	114.4(5)
W(1)–Cl(2)	2.503(3)	C(2)–W(1)–Cl(2)	93.1(3)
W(1)–Cl(3)	2.526(3)	C(1)–W(1)–Cl(2)	82.1(4)
W(1)–Cl(1)	2.571(3)	C(3)–W(1)–Cl(2)	158.3(3)
W(1)–Sn(1)	2.725(1)	C(1)–W(1)–Cl(3)	157.9(4)
W(2)–C(5)	1.98(1)	C(2)–W(1)–Cl(1)	168.0(3)
W(2)–C(4)	1.99(1)	Cl(2)–W(1)–Cl(3)	77.9(1)
W(2)–C(6)	1.99(1)	Cl(2)–W(1)–Cl(1)	76.8(1)
W(2)–Cl(1)	2.522(3)	C(1)–W(1)–Cl(3)	75.8(1)
W(2)–Cl(3)	2.565(3)	C(1)–W(1)–Sn(1)	68.8(4)
W(2)–Cl(2)	2.488(3)	C(3)–W(1)–Sn(1)	70.1(3)
W(2)–Sn(2)	2.709(1)	Cl(1)–W(1)–Sn(1)	76.6(1)
Sn(1)–Cl(4)	2.340(3)	C(2)–W(1)–Sn(1)	115.3(3)
Sn(1)–Cl(5)	2.355(3)	Cl(2)–W(1)–Sn(1)	131.1(1)
Sn(1)–Cl(6)	2.337(3)	Cl(3)–W(1)–Sn(1)	132.4(1)
Sn(2)–Cl(7)	2.343(3)	W(1)–Cl(1)–W(2)	87.3(1)
Sn(2)–Cl(8)	2.337(3)	W(1)–Cl(2)–W(2)	89.6(1)
Sn(2)–Cl(9)	2.356(3)	W(1)–Cl(3)–W(2)	87.4(1)
C(1)–O(1)	1.14(1)	Cl(3)–W(2)–Cl(1)	76.0(1)
C(2)–O(2)	1.13(1)	Cl(2)–W(2)–Cl(3)	77.4(1)
C(3)–O(3)	1.14(1)	Cl(2)–W(2)–Cl(1)	77.9(1)
C(4)–O(4)	1.16(1)	Cl(3)–W(2)–C(6)	166.9(4)
C(5)–O(5)	1.15(1)	Cl(1)–W(2)–C(5)	157.9(4)
C(6)–O(6)	1.14(2)	Cl(2)–W(2)–C(4)	158.4(4)

to the c-axis. Between the structural units formed in this way, the columns of the anions $[(\mu\text{-Cl})_3\{W(SnCl_3)(CO)_3\}_2]^-$ are situated. The crystal structure is stabilized by hydrogen bonds of the type N–H···Cl, C–H···Cl, and C–H···O (see supplementary information).

An ORTEP diagram, including the crystallographic labeling scheme, for one of the two very similar molecules of the binuclear anion 1^- is shown in Fig. 1. The selected bond distances and the important bond angles are given in Table 2.

The basic structural units of an anion 1^- are two seven-coordinate tungsten atoms linked by three chlorine atoms occupying a bridging position between the two tungsten atoms. The resultant geometry at each tungsten atom is approximately a capped octahedron with the tin atom occupying the unique capping position above the centre of the trigonal face defined by the chlorine atom and two carbonyl ligands with the Cl(1)–W(1)–Sn(1) angle of 76.63(7)° and the C–W(1)–Sn(1) angles of 68.8(4)° and 70.1(3)°. The average angle between the three atoms occupying the capped face is 110.6°, while that between three carbonyl carbons occupying the uncapped face is much smaller (89.6°). The angles between the carbonyl and the chloride ligands (C–W(1)–Cl) of 168.0(3)°, 158.3(3)°, and 157.9(4)° (161.4° av.), indicate approximately *trans* positions of these ligands. The two independent W(SnCl₃)(CO)₃ moieties are bridged by three chlorine atoms which are present in a face-shared bioctahedron arrangement with an average bridging Cl–W distance of 2.53 Å and an average Cl–W–Cl angle of 76.9°. The lengths of the W–Sn bonds for two independent molecules are almost identical: W(1)–Sn(1) = 2.725(1) Å, W(2)–Sn(2) = 2.709(1) Å, W(3)–Sn(4) = 2.711(1) Å, W(4)–Sn(3) = 2.728(1) Å (2.718 Å av.), but are slightly shorter than the W–Sn bond distance of 2.731(1) Å found in the previously reported neutral compound $[(\mu\text{-Cl})_3W_2\text{-}(SnCl_3)(CO)_7]$ (2) [10], which contains a W(SnCl₃)(CO)₃ unit like 1. Although distances between the tungsten atom and relevant ligands

in compounds 1^- and 2 are only slightly different, the bond angles are somewhat different. In the neutral compound 2, the average C–W–Sn angle of 87.3° is ca. 3.4° greater than in 1^-, while the average C–W–C angle of 86.5° is ca. 3.1° smaller than in 1^-. This comparison is in agreement with different geometries observed for sometimes very similar seven-coordinate compounds [13–15]. The 4:3 piano stool geometry was suggested for compound 2 [10], while the capped octahedron for 1^-.

The tin atom in the $SnCl_3^-$ anion is nearly tetrahedral with an average bond angle of 108.95°, varying in the range 98.64(12)–118.82(9)°. However, the W(1)–Sn(1)–Cl bond angles (117.1 av.) are much larger than the Cl–Sn(1)–Cl angles (100.8° av.). The average Sn(1)–Cl bond distance of 2.34 Å in the anion $SnCl_3^-$ is distinctly shorter than the Sn(5)–Cl distances (2.43 Å av.) detected here for the dianion $[SnCl_6]^{2-}$. The geometry of $[SnCl_6]^{2-}$ is nearly octahedral with the Cl–Sn–Cl angles in the range 88.17(11)–92.55(12)° (89.7° av.). A similar geometry of the anion $[SnCl_6]^{2-}$ has been found by others [16]. In the crystal unit, a dianion $[SnCl_6]^{2-}$ is surrounded by hydrogen-bonded piperidinium cations Hpip⁺. The N···Cl distances were found to be in the range 3.28(1)–3.51(1) Å. The piperidinium cation is also involved in a hydrogen bond to the chlorine atom of the $SnCl_3^-$ anion with the N···Cl distance of 3.32(1) Å (see supplementary information). The hydrogen bond interactions in the crystal unit of 1 explain very well its low solubility in non-polar solvents.

2.3. The ^{119}Sn NMR data of compounds 1 and 2

The ^{119}Sn chemical shift for the trichlorostannyl $SnCl_3^-$ ligand in the ^{119}Sn NMR spectrum of **1** was observed at $\delta = -138$ ($^1J_{W–Sn} = 614$ Hz) in $CDCl_3$, while for compound **2** it was observed at $\delta = -115$ ($^1J_{W–Sn} = 574$ Hz). The greater value of tungsten–tin coupling observed for **1$^-$** suggests stronger interaction of the $SnCl_3^-$ ligand with the tungsten atom in **1$^-$** than in compound **2** and may result in a shorter W–Sn bond. A correlation between the W–Sn bond distance in the solid state and the value of $^1J_{W–Sn}$ observed in NMR spectra in solution has recently been noticed for a series of tungstenocene stannyl complexes [17]. The W–Sn bond distance of 2.731(1) Å was found in previously reported neutral compound **2** [10], whereas a slightly shorter (2.718 Å av.) W–Sn bond distance was detected for in **1$^-$**. However, during investigation of ^{119}Sn NMR spectra of compound **2** in $CDCl_3$ or CD_2Cl_2 solution, the signal characteristic for compound **2** disappears over time, whereas a signal very similar to that for the anionic compound **1$^-$** appears and increases in intensity. Based on the results of ^{119}Sn NMR spectroscopy investigations, the transformation of the neutral compound **2** to an ionic compound containing anion **1$^-$** may be postulated. The rearrangement of **2** to **1$^-$** was also suggested by the ^{13}C NMR spectra, in which two pairs of carbonyl carbon signals in an intensity ratio of ca. 2:1, characteristic for the $W(SnCl_3)(CO)_3$ unit, were observed in the spectrum of **2** in CD_2Cl_2 solution (see supplementary information).

2.4. Reactivity of compound 1 towards norbornene

In our previous investigations, we have shown that compound **2** reacts readily with NBE in dichloromethane solution at room temperature to give in a high yield of 2,2'-binorbornylidene (bi-NBE) [3,4]; therefore, it is interesting to compare the reactivity of **1** and **2** towards NBE.

In reaction of NBE initiated by in situ generated **1**, the formation of bi-NBE was observed with a similarly yield (ca. 50% by GC–MS) as in the presence of **2**. However, in contrast to catalysis by **2**, in the presence of **1**, the initiation of the ROMP reaction and the formation of a ROMP polymer (poly-1,3-cyclopentylenevinylene, poly-NBE) was not detected. The dimerization of NBE accompanied the formation of norbornene adducts with HCl ($M_r = 130.61$, 27%) and H_2O ($M_r = 112.17$, 2%), cyclobinorbornane ($M_r = 188.31$, 1%), binorbornene adducts with HCl ($M_r = 224.77$, 1%) and H_2O ($M_r = 206.32$, 0.5%), and norbornene trimers ($M_r = 282.46$, 14.5%). Although the reactions were performed under anhydrous conditions, we could not rule out the presence of traces of water leading to the formation of 2-hydroxylnorbornane and 3-hydroxyl-2,2'-binorbornyl during the isolation process of organic products.

The mechanism for the formation of bi-NBE may involve the coordination of NBE to the tungsten atom and its transformation to a tungstanorbornylidene species as a result of 1,2-hydride shift. A similar η^2-olefin-to-alky-lidene rearrangement has been proposed by others for catalytic systems where an olefin ligand is the only source of an alkylidene species [18]. The first direct evidence for an alkene-to-alkylidene rearrangement was obtained by Wolczanski et al. [19]. A bimolecular coupling of two carbene ligands and the formation of new olefin has been observed during mild thermolysis of chromium(0) and tungsten(0) pentacarbonylcarbene complexes [20–22] and detected by Schrock et al. in reaction of alkylidene complexes of tantalum, molybdenum and tungsten [23–25]. For the first time the carbene–carbene coupling reaction was applied in synthesis of bi-NBE from NBE in reaction catalyzed by the binuclear compound **2** [4]. Previously, the McMurry and Fleming procedure for reductive dimerization of ketones had been applied for the synthesis of compounds of that type [26,27]. 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 identified by NMR spectroscopy [4,27]. 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 disproportionate giving a new olefin as the carbene–carbene coupling product. In the presence of HCl or H_2O, the tungstanorbornylidene species decomposes to give 2-chloronorbornane or 2-hydroxylnorbornane, respectively (see supplementary information).

Although the formation of bi-NBE is a major process initiated by halocarbonyls of tungsten(II), the detection of other products such as cyclobinorbornane, 3-hydroxyl-2,2'-binorbornyl, or 3-chloro-2,2'-binorbornyl suggests the presence of one more intermediate species in addition to tungstanorbornylidene, e.g. tungstacyclopentane. The formation of the latter species may result from the splitting of chloride bridges by olefin and the coordination of two η^2-NBE ligands to a mononuclear coordinatively unsaturated tungsten species (see supplementary information). The formation of the metallacyclopentane species and its transformation to metallacarbene had previously been postulated in the ROMP of NBE catalyzed by transition metal halides such as WCl_6, $MoCl_5$, $ReCl_5$, and $RuCl_3$ [28–31]. However, in contrast to the previously investigated transition metal halides, complex **1** does not initiate the ROMP reaction. That may be the effect of its great stability in the binuclear form, which appears after bimolecular coupling of two carbene ligands.

3. Conclusions

Reaction of the light yellow tungsten(0) complex [$W(CO)_4(pip)_2$] with $SnCl_4$ in dichloromethane solution produces a deep orange solution from which orange crystals are precipitated. Unequivocal proof of the constitution and structure of the crystals comes from X-ray and elemental analyses, which showed the presence two ionic compounds: [Hpip][(μ-Cl)$_3${$W(SnCl_3)(CO)_3$}$_2$] and [Hpip]$_2$[$SnCl_6$], in the molar ratio 2:1.

The molecular structure of the new binuclear anionic complex $[(\mu\text{-Cl})_3\{W(SnCl_3)(CO)_3\}_2]^-$ ($\mathbf{1}^-$) of tungsten(II) in solution was confirmed by spectroscopic methods: IR, ^{119}Sn, ^{13}C and ^{1}H NMR, and is in good agreement with the crystal structure.

The study of the reactivity of complex **1** towards norbornene showed its catalytic activity in transformation of norbornene to a new olefin, 2,2′-binorbornylidene, similarly as the previously investigated binuclear compound **2**. The most likely route to the formation of bi-NBE is the bimolecular coupling of two norbornylidene ligands formed from η^2-NBE ligands. However, the reaction is accompanied by the formation of chloronorbornane, norbornene trimers, and binorbornene adducts with water and HCl.

Reinvestigation of the spectroscopic properties (^{119}Sn and ^{13}C NMR) of the previously studied complex $[(\mu\text{-Cl})_3\text{-}W_2(SnCl_3)(CO)_7]$ (**2**) revealed its rearrangement in dichloromethane solution to the ionic species $\mathbf{1}^-$.

Similar catalytic activity of the binuclear compounds **1** and **2** results from the similar mechanism of interaction of both compounds with olefin, i.e. the splitting of chloride bridges by olefin and the formation of a mononuclear coordinatively unsaturated tungsten species, which is able to activate an olefin molecule.

4. Experimental

4.1. General data

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 500 MHz instrument. All chemical shifts are referenced to residual solvent protons for ^{1}H NMR ($\delta 7.24$ CDCl$_3$; 5.32 CD$_2$Cl$_2$) and to the chemical shift of the solvent for ^{13}C NMR (77.0 CDCl$_3$; 54.0 CD$_2$Cl$_2$). The ^{119}Sn chemical shifts are referenced to external standard Ph$_3$SnCl ($\delta = -44.7$ ppm [32]). Analyses of the catalytic reaction products were performed on a Hewlett-Packard GC–MS system. [W(CO)$_4$(pip)$_2$] was synthesized according to a previously published procedure [6–8].

4.2. Reaction of [W(CO)$_4$(pip)$_2$] with SnCl$_4$ in dichloromethane solution and the formation of compound 1

A sample of SnCl$_4$ (0.4 g, 0.2 cm^3, 1.7 mmol) was added by means of a syringe to a stirred suspension of [W(CO)$_4$(pip)$_2$] (0.52 g, 1.1 mmol) in dichloromethane (30 cm^3). An immediate color change from light yellow to deep orange, complete dissolution of the piperidine compound, gas evolution, and precipitation of a colorless microcrystalline solid were observed when the solution

was stirred under ambient conditions. Monitoring by IR spectroscopy revealed the disappearance of the v (CO) bands of the starting material (v(C$\equiv$O): 2006 (w), 1925 (vs), 1968 (m, br), and 1824 (w) cm^{-1}) and the appearance of v (CO) bands at ca. 2100 (w), 2030 (vs), and 1940 (vs) cm^{-1}. The solution was stirred for ca. 2 h and then separated from an insoluble colorless byproduct (Anal. Calc. for C$_5$H$_{14}$Cl$_4$NO$_2$Sn: C, 17.39; H, 4.09; N, 4.06. Found: C, 17.39; H, 3.79; N, 3.51%). The solvent was evaporated in vacuo to give an orange residue, which was washed several times with n-heptane and dried under vacuum (yield = 0.8 g). The sample, relatively readily soluble in halogenated hydrocarbons, was investigated by NMR and IR spectroscopy. However, during the NMR measurements, the composition of the sample changed and precipitation of a colorless solid was observed.

Single crystals of the orange compound were obtained from the dichloromethane solution by keeping the solution of the crude reaction mixture at 273 K. X-ray and elemental analyses confirmed that they contain two ionic compounds: [Hpip][$(\mu\text{-Cl})_3\{W(SnCl_3)(CO)_3\}_2$] (**1**) and [Hpip]$_2$[SnCl$_6$] in the molar ratio 2:1 (see below).

Anal. Calc. for C$_{32}$H$_{48}$Cl$_{24}$N$_4$O$_{12}$Sn$_5$W$_4$: C, 13.44; H, 1.69; N, 1.96. Found: C, 13.33; H, 1.37; N, 1.62%. IR (KBr disc): v (CO) = 2100 (w), 2017 (vs), 1910 (vs) cm^{-1}; (CH$_2$Cl$_2$): v (CO) = 2104 (w), 2030 (s), 1940 (vs) cm^{-1}. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, 243 K): $\delta = 6.35$ (s, 2H, NH$_2$), 3.41 (s, 4H, CH$_2$), 1.90 (s, 4H, CH$_2$), 1.73 (s, 2H, CH$_2$). ^{13}C{^{1}H} NMR (125.7 MHz, CD$_2$Cl$_2$, 243 K): $\delta = 215.5$ ($^1J_{W-C} = 130$ Hz, $^2J_{Sn-C} = 341$ Hz, 2CO), 208.6 ($^1J_{W-C} = 123$ Hz, $^2J_{Sn-C} = 88$ Hz, 1CO), 47.1 (2C, CH$_2$), 23.0 (2C, CH$_2$), 21.7 (1C, CH$_2$). ^{119}Sn{^{1}H} NMR (186.5 MHz, CDCl$_3$, 253 K): $\delta = -138$ ($^1J_{W-Sn} = 614$ Hz); (186.5 MHz, CD$_2$Cl$_2$, 253 K): $\delta = -146$ ($^1J_{W-Sn} = 609$ Hz).

4.3. Photochemical reaction of W(CO)$_6$ with SnCl$_4$ in n-heptane solution – synthesis of [(μ-Cl)$_3$W$_2$(SnCl$_3$)(CO)$_7$] (2) revisited

A solution of W(CO)$_6$ (0.35 g, 1.0 mmol) and SnCl$_4$ (0.4 g, 0.2 cm^3, 1.7 mmol) in n-heptane (80 cm^3) was irradiated through quartz at room temperature for ca. 3.5 h. During photolysis, an amorphous brownish-yellow precipitate was formed. It was filtered off, washed with n-heptane, and extracted with CH$_2$Cl$_2$. After evaporation of the solvent, an orange residue was obtained. IR (KBr disc): v (CO) = 2102 (m), 2018 (vs), 1935 (s, br) cm^{-1}; (CH$_2$Cl$_2$): v (CO) = 2111 (m), 2076 (w), 2029 (sh, vs), 2018 (vs), 1976 (s), 1945 (vs) cm^{-1}. ^{13}C{^{1}H} NMR (125.7 MHz, CD$_2$Cl$_2$, 243 K): $\delta = 217.6$ ($^1J_{W-C} = 130$ Hz), 215.7 ($^1J_{W-C} = 131$ Hz, $^2J_{Sn-C} = 347$ Hz), 214.3 ($^1J_{W-C} = 134$ Hz, $^2J_{Sn-C} = 326$ and 338 Hz), 210.5, 208.9 ($^1J_{W-C} = 124$ Hz, $^2J_{Sn-C} = 91$ Hz), 207.9 ($^2J_{Sn-C} = 88$ Hz), 207.5 ($^1J_{W-C} = 111$ Hz), 206.1 ($^1J_{W-C} = 110$ Hz), 204.1 ($^1J_{W-C} = 111$ Hz). ^{119}Sn{^{1}H} NMR (186.5 MHz, CDCl$_3$, 253 K): $\delta = -94$ ($^1J_{W-Sn} = 581$ Hz), -115 ($^1J_{W-Sn} = 574$ Hz), -140 ($^1J_{W-Sn} = 613$ Hz); (186.5 MHz,

CD_2Cl_2, 253 K): $\delta = -98$ ($^1J_{W-Sn} = 523$ Hz), -119 ($^1J_{W-Sn} = 587$ Hz), -137 ($^1J_{W-Sn} = 606$ Hz); (186.5 MHz, $C_6D_5CD_3$, 253 K): $\delta = -106$ ($^1J_{W-Sn} = 551$ Hz), -131. The intensity ratio of ^{13}C and ^{119}Sn signals changed over time.

4.4. Crystallography

Crystals with approximate dimensions of $0.12 \times 0.08 \times 0.08$ mm were used for data collection. The data were collected at 100 K using a KM4-CCD chip 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 [33]. The experimental details together with crystal data are given in Table 1. The structure was solved by the heavy atom method using SHELXS 97 [34] and refined by the full-matrix least-squares method on all F^2 data [35]. Non-H atoms were included in the refinement, with anisotropic displacement parameters, and H atoms were included from the geometry of the molecules and were not refined. The data were corrected for absorption [33], min/max absorption coefficients 0.345 and 0.789.

4.5. Transformation of norbornene in CH_2Cl_2 solution in the presence of in situ generated compound 1

A catalyst solution was prepared by mixing $[W(CO)_4(pip)_2]$ (0.1 g, 0.21 mmol) and $SnCl_4$ (0.05 g, 0.02 cm^3, 0.21 mmol) with 10 cm^3 of dichloromethane. An orange solution was separated from a colorless solid and added to the solution of NBE (0.25 g, 2.7 mmol) and *n*-heptane (0.4 cm^3 as the internal chromatographic standard) in dichloromethane (9.6 cm^3). The reaction mixture was stirred at 293 K until completion (ca. 24 h). The GC–MS analysis of the residue obtained after evaporation of the solvent revealed the formation of 2,2′-binorbornylidene ($M_r = 188.32$) with 54% yield.

Acknowledgements

Appendix A. Supplementary material

CCDC 635816 contains the supplementary crystallographic data for 1. These data can be obtained free of charge via http://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.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.06.013.

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