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Spectroscopic properties, structure and reactivity of $[WCl(SnCl_3)(CO)_3(NCMe)_2]$

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Abstract—A series of seven-coordinate tungsten(II) nitrile complexes of the type $[WCl(SnCl_3)(CO)_3(NCR)_2]$(**1**–**4**), R=Me, Et, *n*-Bu, Ph, has been synthesized. These new complexes have been characterized by IR, NMR and UV-vis spectroscopy. In addition single-crystal X-ray diffraction was used to structurally characterize $[WCl(SnCl_3)(CO)_3(NCMe)_2]$(**1**). The most prominent feature of complex **1** is the facility by which acetonitrile and carbonyl ligands can be replaced by other ligands. Complexes were isolated in which CO and acetonitrile ligands were substituted by alkyne ligands. The alkyne tungsten(II) complexes **5**–**8** formed were structurally characterized by IR and NMR spectroscopy. The complex **1** has been found to be an active catalyst for the polymerization of phenylacetylene. 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 Ltd. All rights reserved

Keywords: tungsten; tin; crystal structure; nitrile complexes; alkyne complexes; polymerization of phenylacetylene.

A number of seven-coordinated compounds with a tungsten-tin or a molybdenum-tin bond have been prepared by reaction of tungsten- and molybdenum-substituted carbonyls, $[M(CO)_4L_2]$ (2L = 2,2′-bipyridyl, 2,5-dithiahexane, 1,2-bis(diphenylphosphino)ethane, RN=CHCH=NR, R = *i*-Pr, *n*-Bu or Cy, two molecules of acetonitrile) and tin tetrahalides or organometallic halides, R_nSnCl_{4-n}, R=Me, Bu, Ph [1–10]. Among them acetonitrile compounds are especially interesting as useful starting materials in which the labile acetonitrile groups can be easily replaced by other ligands [10–17]. This can be the basis for synthetic procedures, including the preparation of alkene and alkyne derivatives as well as a model of a catalytic centre. In the reaction of $[WCl(SnCl_3)(CO)_3(NCMe)_2]$(**1**) with norbornadiene two acetonitrile ligands are replaced by one molecule of norbornadiene and $[WCl(SnCl_3)(CO)_3(\eta^4\text{-NBD})]$ is formed [17]. In this paper we present results concerning the reactivity of complex **1** towards alkynes. Complexes were isolated in which CO and acetonitrile ligands were replaced by alkyne ligands. The complex **1** has been found to be an active catalyst for the polymerization of phenylacetylene.

The unknown coordination geometry of acetonitrile compound **1** together with the fact that compounds of this class have been used for synthetic purpose on several occasions [10–17], make it an interesting problem for X-ray structure analysis.

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. IR spectra (KBr pellets) were recorded on an FT-IR Model-400 Nicolet instrument and Far-IR spectra (500–50 cm^{-1}) were recorded with a Brücker IFSv instrument in Nujol mull on a polyethylene film. ^1H and $^{13}C\{^1H\}$ NMR spectra were run using a Bruker AMX-300 spectrometer. UV-visible 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.

Synthesis of $[WCl(SnCl_3)(CO)_3(NCMe)_2]$(**1**)

To $[W(CO)_4(NCMe)_2]$ [18] (1.8 g, 4.7 mmol) dissolved in CH_2Cl_2 (50 cm^3) with continuous stirring

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under a stream of nitrogen, was added a stoichiometric amount of $SnCl_4$ (0.56 cm^3, 4.7 mmol) by means of a syringe. The mixture was stirred for 6 hours, during which time the yellow solution gradually changed to an orange colour, 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 crystallization from CH_2Cl_2/heptane produced the analytically pure dark orange crystalline complex **1** (Table 1).

Preparation of $[WCl(SnCl_3)(CO)_3(NCR)_2]$, **2** ($R{=}C_2H_5$); **3** ($R{=}C_3H_7$); **4** ($R{=}C_6H_5$).

1 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 coloured from orange **2** to red **4**, which was recrystallized from CH_2Cl_2-heptane giving a pure crystalline bis(nitrile) complex **2-4** (Table 1).

Reaction of **1** *with* $PhC{\equiv}CPh$

To a solution of **1** (0.2 g, 0.33 mmol) in 15 cm^3 of CH_2Cl_2 was added $PhC{\equiv}CPh$ (0.12 g, 0.66 mmol) in 5 cm^3 of CH_2Cl_2. The mixture was stirred for two hours, after which time the full conversion of **1** was observed by IR. Evaporation of the solvent followed by washing with heptane produced a mixture of compounds identified by IR and NMR studies as $[WCl_2(CO)(NCMe)(PhC{\equiv}CPh)_2]$ **5**, and $[WCl_2(NCMe)_2(PhC{\equiv}CPh)_2]$ **6** (Table 2). Crystallization of the above greenish-yellow solid from CH_2Cl_2/heptane always produced mixture of the compounds **5** and **6**, but with different molar ratios depending on reaction time. Beside **5** and **6**, a side products were formed. One was identified by IR: ν(CO) 2069 (vw), 1939 (vs) and ^{13}C NMR: δ 202.47 (1 CO), 196.54 (4 CO) ppm as $[W(CO)_5SnCl_2]$ and other was separated by filtration as white, insoluble in CH_2Cl_2 solid of $SnCl_2$.

Reaction of **1** *with phenylacetylene* (*PA*)

A slight excess of PA (0.125 cm^3, 1.18 mmol) was syringed into a stirred CH_2Cl_2 solution (15 cm^3) of **1** (0.2 g, 0.33 mmol) at room temperature. Immediately the solution became dark orange. Stirring for 2 hours followed by the evaporation of the solvent under low pressure gave an orange solid, which was washed out with a small portion of heptane and dried *in vacuo* to give a greenish yellow mixture of compounds containing mainly $[WCl_2(CO)(NCMe)(PhC{\equiv}CH)_2]$ **7** and $[WCl_2(NCMe)_2(PhC{\equiv}CH)_2]$ **8** as was shown by ^{1}H and $^{13}C\{^1H\}$ NMR spectra (Table 2). The heptane extract contained organic products: 1,2,4-triphenylbenzene (41%), 1,3,5-triphenylbenzene (39%), different isomers of diphenylbutadienes (19%), and a dimer of PA detected by MS as 1*H*-indene-1-(phenylmethylene) (1%).

Procedures for testing catalytic activity and characterization of organic products

Polymerization experiments were carried out in a reaction mixture composed of toluene or CH_2Cl_2 as solvent, *ortho*-xylene (the internal chromatographic standard), phenylacetylene (PA)(1 mol dm^{-3}), and complex **1**(PA/W 100). The reaction mixture was stirred by a magnetic stirrer at room temperature in a 50 cm^3 glass reactor provided with a septum through which liquid reactants were introduced and removed by a syringe. 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. The conversion of PA, monitored by chromatography, was not higher than 10% after 24 h reaction. For the analysis of PA reaction products, reactions were continued for 24 h and then methanol was added. The polymer (PPA) was collected, washed with methanol, dried and weighed. The polymerization yield (%) is defined by comparing the polymer weight to the weight of the PA used and 24 h reaction catalyzed by **1** was about 7%. The polymer was analysed by ^{1}H NMR, IR spectroscopy and gel-permeation chromatography. Molecular weights of the PPA were measured using $CHCl_3$ solutions, a refractive index monitor and a Plgel 10 m MIXED-B column. The value recorded ($M_w = 5\times10^3$) is the weight of polystyrene that would exhibit the chromatogram 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 (HP5 25 m column). Analysis showed 1,2,4-triphenylbenzene (45%), 1,3,5-triphenylbenzene (34%), different isomers of diphenylbutadienes (16%), and a dimer of PA detected by MS as 1*H*-indene-1-(phenylmethylene) (5%).

^{1}H NMR spectra of the polymers were recorded in a $CDCl_3$ solution at 300 MHz. The microstructural details of the polymers were deduced from the ^{1}H NMR integrals [19] as mainly *trans*.

Crystallography

Crystal data for **1**. $C_7H_6Cl_4N_2O_3SnW$, $M = 610.48$, monoclinic, space group $P2_1/m$, $a = 6.803(1)$, $b = 13.669(3)$, $c = 8.640(2)$ Å, $\beta = 102.68(3)°$, $U = 783.9(3)$ Å^3, $Z = 2$, $D_c = 2.586$ g cm^{-3}, $F(000) = 556$, μ(Mo-Kα) $= 96.04$ cm^{-1}. The dark orange crystals of **1** were grown from a CH_2Cl_2/toluene/heptane solution. The crystals were stable enough when handled in an inert atmosphere or coated with a light hydrocarbon oil to protect them from the atmosphere. Crystallographic data were

Table 1. Spectroscopic data for the seven-coordinate nitrile complexes $[\mathrm{WCl(SnCl_3)(CO)_3(NCR)_2}]$ **1**–**4**; R=$\mathrm{CH_3}$ (**1**), $\mathrm{C_2H_5}$ (**2**), $\mathrm{C_3H_7}$ (**3**), $\mathrm{C_6H_5}$ (**4**)

Complex	IR(ν, $\mathrm{cm^{-1}}$)			^{1}H NMR	^{13}C{^{1}H} NMR	UV-vis, λ, nm
	ν(CO)[a]	ν(CN)[a]	ν(SnCl)[b]	(δ, ppm; J, Hz)	(δ, ppm; J, Hz)	(ϵ, $\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$
1	2030 (vs) 1935 (s,sh) 1903 (vs)	2327 (w) 2299 (w)	344 (w) 325 (w)	2.53 (s, 2 $\mathrm{C}H_3\mathrm{CN}$)[c]	211.93 (s, 3 CO), 126.80 (s, 2 $\mathrm{CH_3}C\mathrm{N}$), 4.54 (s, 2 $\mathrm{C}H_3\mathrm{CN}$)[c]	250 (9386), 290 (4225), 398 (464)[d]
2	2022 (vs) 1936 (s,sh) 1907 (vs)	2293 (m)		2.82 (q, $J_{\mathrm{HH}}=7.5$, 2 $\mathrm{CH_3C}H_2\mathrm{CN}$) 1.46 (t, $J_{\mathrm{HH}}=7.5$, 2 $\mathrm{C}H_3\mathrm{CH_2CN}$)[e]	211.01 (s, 3 CO), 129.47 (s, 2 $\mathrm{CH_3CH_2}C\mathrm{N}$), 12.75 (s, 2 $\mathrm{CH_3}C\mathrm{H_2CN}$), 9.45 (s, 2 $C\mathrm{H_3CH_2CN}$)[e]	
3	2021 (s) 1940 (s,sh) 1915 (vs)	2292 (m)		2.80 (t, $J_{\mathrm{HH}}=7.0$, 2 $\mathrm{CH_3CH_2C}H_2\mathrm{CN}$) 1.89 (q, $J_{\mathrm{HH}}=7.5$, 2 $\mathrm{CH_3C}H_2\mathrm{CH_2CN}$) 1.14 (t, $J_{\mathrm{HH}}=7.5$, 2 $\mathrm{C}H_3\mathrm{CH_2CH_2CN}$)[e]	211.27 (s, 3 CO, $J_{\mathrm{WC}}=125$, $^2J_{\mathrm{117Sn–13C}}=261$, $^2J_{\mathrm{119Sn–13C}}=277$) 128.94 (s, 2 $\mathrm{CH_3CH_2CH_2}C\mathrm{N}$), 20.49 (s, 2 $\mathrm{CH_3CH_2C}H_2\mathrm{CN}$), 18.60 (s, 2 $\mathrm{CH_3C}H_2\mathrm{CH_2CN}$), 13.48 (s, 2 $\mathrm{C}H_3\mathrm{CH_2CH_2CN}$)[e]	
4	2026 (s) 1945 (s) 1912 (s)	2263 (m)		7.86 (d, o-Ph, $J=7.3$) 7.78 (t, p-Ph, $J=7.7$) 7.59 (t, m-Ph, $J=7.8$)[e]	211.09 (s, 3 CO, $^1J_{\mathrm{WC}}=127$, $^2J_{\mathrm{117Sn–13C}}=267$, $^2J_{\mathrm{119Sn–13C}}=280$) 135.98 (s, C_p–-Ph) 133.61 (s, C_o–-Ph) 129.84 (s, C_m–-Ph) 129.05 (s, C_i–-Ph) 126.93 (s, 2 $\mathrm{Ph}C\mathrm{N}$),[e]	

[a] Spectra recorded in KBr plates. [b] Spectra recorded in Nujol mull on a polyethylene film. [c] Spectra recorded in $\mathrm{CD_2Cl_2}$ at 293 K. [d] Spectra recorded in $\mathrm{CH_2Cl_2}$. [e] Spectra recorded w $\mathrm{CDCl_3}$ at 293 K.

Table 2. Selected IR and NMR data for tungsten (II) alkyne complexes **5**–**8**

Complex	IR(ν, $\mathrm{cm^{-1}}$)[a]		^{1}H NMR[b]	^{13}C{^{1}H} NMR[b]
	ν(CO)	ν(CN)	(δ, ppm; J, Hz)	(δ, ppm; J, Hz)
$[\mathrm{WCl_2(CO)(NCMe)(PhC{\equiv}CPh)_2}]$ (**5**)	2088 (s)	2329 (w) 2298 (vw)	2.42 (s, $\mathrm{C}H_3\mathrm{CN}$)	200.73 (s, 1 CO), 176.18 (s, 2 $\mathrm{Ph}C{\equiv}\mathrm{CPh}$), 167.22 (s, 2 $\mathrm{PhC}{\equiv}C\mathrm{Ph}$), 140.44 (s, 2 C_i–Ph), 139.48 (s, 2 C_i–Ph), 126.96 (s, 1 $\mathrm{CH_3}C\mathrm{N}$), 5.17 (s, 1 $C\mathrm{H_3CN}$)
$[\mathrm{WCl_2(NCMe)_2(PhC{\equiv}CPh)_2}]$ (**6**)	—	2327 (w) 2299 (vw)	2.39 (s, 2 $\mathrm{C}H_3\mathrm{CN}$)	195.96 (s, 2 $\mathrm{Ph}C{\equiv}\mathrm{CPh}$), 189.26 (s, 2 $\mathrm{PhC}{\equiv}C\mathrm{Ph}$), 138.63 (s, 2 C_i–Ph), 137.85, (s, 2 C_i–Ph), 127.63 (s, 2 $\mathrm{CH_3}C\mathrm{N}$), 5.56 (s, 2 $C\mathrm{H_3CN}$)
$[\mathrm{WCl_2(CO)(NCMe)(PhC{\equiv}CH)_2}]$ (**7**)	2089 (s)	2329 (w) 2292 (vw)	2.55 (s, 1 $\mathrm{C}H_3\mathrm{CN}$) 11.90, (s, 2 $\mathrm{PhC{\equiv}C}H$)	196.24 (s, 1 CO), 183.63 (s, 2 $\mathrm{PhC}{\equiv}C\mathrm{H}$), 176.73 (s, 2 $\mathrm{Ph}C{\equiv}\mathrm{CH}$), 137.04 (s, 2 C_i–Ph), 4.82 (s, 1 $C\mathrm{H_3CN}$)
$[\mathrm{WCl_2(NCMe)_2(PhC{\equiv}CH)_2}]$ (**8**)	—	2326 (w) 2300 (vw)	2.42 (s, 2 $\mathrm{C}H_3\mathrm{CN}$) 11.61,11.55 (s, 2 $\mathrm{PhC{\equiv}C}H$)	196.64 (s, 2 $\mathrm{PhC}{\equiv}C\mathrm{H}$), 188.50 (s, 2 $\mathrm{Ph}C{\equiv}\mathrm{CH}$), 136.44 (s, 2 C_i–Ph), 5.22 (s, 2 $C\mathrm{H_3CN}$)

[a] Spectra recorded in KBr disc. [b] Spectra recorded w $\mathrm{CDCl_3}$ at 293 K.

obtained for a crystal approximately $0.10 \times 0.10 \times 0.15$ mm using a KM4 κ-axis computer-controlled [20] four-circle diffractometer operating in the ω-2θ scan mode. All measurements were made using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) at 293 (3) K. The accurate cell dimensions and the crystal orientation matrix were determined by a least-squares refinement of the setting angles of 30 carefully centred reflections in the range $20.6° < 2\theta < 37.3°$. A total of 2114 unique reflections were measured, of which 1995 (137 variables) with $I \geq 4\sigma\,(I)$ in the range 5 to 70° were used to solve and refine the structure in the monoclinic space group $P2_1/m$. A surprisingly high R value ($R_1 = 0.0791$, $wR_2 = 0.1981$) was obtained after first refinement. A difference synthesis at this stage revealed two regions of significant electron density (11.2, 8.0, e/Å^3) located at approximately 0.5 Å from both sides of W(1), Sn(1) and Cl(1) atoms. During refinement the molecule was found to be disordered between three adjacent positions with occupancy factor 0.76, 0.12 and 0.12 for W(1), Sn(1), Cl(1). Further refinement of this three site model gave a final R_1 value of 0.0560 ($wR_2 = 0.1546$). The largest peak in the final difference map was 2.86 e/Å^3. Goodness-of-fit was 1.130. The structure was given a weighting scheme in the form $w = 1/[\sigma^2(F_0^2) + (0.0278P)^2 + 0.0000P]$, where $P = (F_0^2 + 2F_c^2)/3$.

The structure was solved by the heavy-atom method with the SHELXS-86 program [21] and refined by a full-matrix least-squares method, using the SHELXL-93 program [22]. Neutral atomic scattering factors were taken from the SHELXL-93 program [22]. The positions of C-bonded H atoms were calculated assuming typical stereochemistry and three atoms were refined with fixed positions at 0.96 Å from the C atoms to which they were bonded.

The remaining dimensions, positional parameters and equivalent isotropic thermal parameters and anisotropic thermal parameters are deposited in supplementary material.

RESULTS AND DISCUSSION

In 1995 we reported [23] 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. When this product is dissolved in toluene and acetonitrile added, an equimolecular mixture of $[WCl(SnCl_3)(CO)_3(NCMe)_2]$(**1**) and $[WCl_2(CO)_3(NCMe)_2]$ is formed immediately [24]. Recrystallization of the mixture from CH_2Cl_2/toluene/heptane produces quite stable orange crystals of **1** while considerable less stable $[WCl_2(CO)_3(NCMe)_2]$ decomposes with loss of carbon monoxide and formation of deep blue, insoluble solid in methylene chloride, most probably the chloro-bridged dimer.

Another method which proved useful in obtaining the compound **1** was the oxidative-addition reaction of $[W(CO)_4(NCMe_2]$ with $SnCl_4$ in dichloromethane. Baker and Bury briefly mentioned the formation of mixture of compounds containing **1** by reaction of $[W(CO)_3(NCMe)_3]$ with $SnCl_4$ in acetonitrile, but without synthetic and spectroscopic details for **1** [10].

The compounds **2**–**4** containing nitriles with a longer carbon chain, were prepared in the reaction of **1** with an appropriate nitrile at room temperature. The compounds **1**–**4** are very soluble in nitriles and in acetone, less soluble in chlorinated solvents (CH_2Cl_2, $CHCl_3$) but insoluble in hydrocarbon solvents. They are air-sensitive in solution but in the solid state it can be stored under nitrogen for a month without decomposition.

Structure of **1**

The molecule $[WCl(SnCl_3)(CO)_3(NCMe)_2]$(**1**), is shown in Fig. 1 together with the atomic numering scheme Selected interatomic bond distances and angles are presented in Table 3.

The environment of the tungsten atom is an almost ideal capped octahedron with the tin atom occupying the unique capping position above an octahedral face defined by the bridging chlorine and two crystallographically equivalent carbonyl groups. The octahedral face that is capped by the $SnCl_3$ group is distorted to allow a close approach of the tin atom. The angles subtended at the tungsten atom by the three atoms determining the capped face are in the range 107.7(8)–108.2(4)°; compared with the opposite face, determined by C(2), N(1) and N(1)^i, where the angles are in the range 80.0(7)–93.3(5)°. Thus, there is a distortion of octahedral symmetry in order to accommodate the tin atom.

In addition one may notice that the molecule of **1** is remarkable in its symmetry. The crystallographic plane of symmetry extends through W, Sn, Cl(1) and

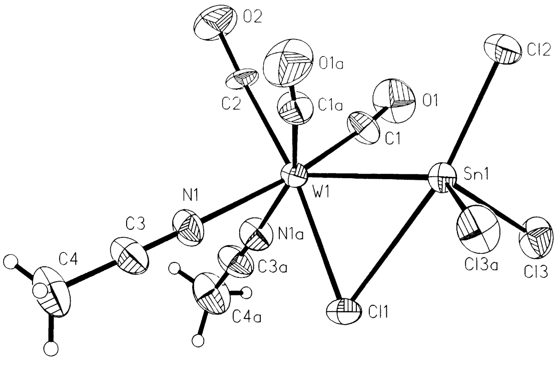

Fig. 1. Molecular geometry of $[WCl(SnCl_3)(CO)_3(NCMe)_2]$(**1**).

Table 3. Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for **1**

W(1)–Sn(1)	2.710(1)	W(1)–C(1)	1.997(13)
W(1)–Cl(1)	2.511(5)	Sn(1)–Cl(1)	2.840(5)
W(1)–N(1)	2.18(1)	Sn(1)–Cl(2)	2.333(4)
W(1)–C(2)	2.00(2)	Sn(1)–Cl(3)	2.344(5)
C(1)–W(1)–C(2)	76.6(6)	Sn(1)–W(1)–C(2)	123.1(6)
C(2)–W(1)–N(1)	93.3(5)	Sn(1)–W(1)–C(1)	70.8(4)
C(2)–W(1)–Cl(1)	171.1(6)	Cl(3)–Sn(1)–Cl(3)^{i}	101.3(3)
C(1)–W(1)–C(1)^{i}	107.7(8)	Cl(3)–Sn(1)–Cl(2)	97.9(1)
Cl(1)–W(1)–C(1)	108.2(4)	Cl(1)–Sn(1)–Cl(3)	89.5(1)
Cl(1)–W(1)–N(1)	80.0(3)	Cl(1)–Sn(1)–Cl(2)	168.4(2)
N(1)–W(1)–N(1)^{i}	80.0(7)	Cl(1)–Sn(1)–W(1)	53.7(1)
N(1)–W(1)–C(1)	161.2(5)	W(1)–Sn(1)–Cl(2)	114.6(2)
N(1)i–W(1)–C(1)	84.8(5)	W(1)–Sn(1)–Cl(3)	120.4(1)
Sn(1)–W(1)–Cl(1)	65.8(1)	W(1)–Cl(1)–Sn(1)	60.5(1)
Sn(1)–W(1)–N(1)	127.5(3)		

Symmetry elements represented by i: *x*, 0.5-*y*, *z*.

Cl(2). In such an arrangement two acetonitrile ligands are crystallographically equivalent and effectively *cis* with N(1)–W–N(1)^{i} angle 80.0(7)° and the W–N distances identical (2.18(1) Å). Two CO groups in the capped face are mutually *cis* with C(1)–W–C(1)^{i} angle 107.7(8)° and the same W–C distance 2.00(1) Å. The angles between carbonyl groups in the capped and uncapped face are smaller with 76.6(6)° for C(2)–W–C(1) angle.

The W–N–C angle is 178(1)° to evidence that the nitrile ligand is coordinated in an almost linear manner. The C–N lengths of 1.13(2) Å are not significant but are shorter than C–N distance of 1.155 Å observed in free CH$_3$CN [25]. Comparison of bond length for **1** and tungsten(0) complex, reveals that the W–N distance is shorter in **1**, being 2.18(1) Å *vs.* 2.21 Å(av) in [W(CO)$_3$(NCMe)$_3$] [26], while the tungsten-carbonyls distances in **1** are about 0.07 Å longer, being 2.00 Å (av) *vs.* 1.93 Å (av) in tungsten(0) complex. This correlates qualitatively with the expected lower electron density and π-donor ability of the tungsten in the higher oxidation state.

The tungsten atom is seven-coordinate and tin atom is five-coordinate, with one chlorine atom occupying a bridging position between the two metal atoms. The tungsten-tin bond is short at 2.710(1) Å compared to the sum of the relevant covalent radii of 2.97 Å [27, 28]. The W–Sn distances of 2.759(3) [4], 2.731(1) [18], 2.711(1) [29] and 2.737(1) [29] Å have been observed previously. In view of the established π-acceptor properties of the [SnCl$_3$]$^-$ group it seems probable that the bond does possess some double-bond character [30]. The tin to bridging chlorine distance is 2.840(5) Å, being considerably longer than the other tin-chlorine distances, which are average 2.34 Å, indicates that this bond is much weaker than a tin-chlorine single bond. The tungsten to bridging chlorine distance is 2.511(5) Å and indicates that the bridging chlorine forms a stronger bond with the tungsten while the Sn–Cl bond is weakened. The angle of 60.5(1)° subtended at the chlorine by the tungsten-tin bond agrees with the value 59.9(2)° for bridging chlorine in [WCl(MeSnCl$_2$)(CO)$_3$(C$_4$H$_{10}$S$_2$)] [4], 60.5(1)° in [MoCl(SnCl$_3$)(CO)$_3$(C$_4$H$_{10}$S$_2$)](CH$_2$Cl$_2$) [6] and 61.6(1)° in [MoCl(MeSnCl$_2$)(CO)$_3$(C$_{10}$H$_8$N$_2$)] [3]. The form of the tungsten atom coordination in **1** is indeed very similar to the monocapped octahedral geometries observed earlier in W–Sn or Mo–Sn compounds [3, 4, 6]. A common feature of those structures is the presence of a tin atom in the unique capping position and a chlorine atom bridging the W–Sn or Mo–Sn bond.

The tin atom in **1** is five-coordinate with a geometry that is best described as trigonal bipyramidal with the two chlorine atoms occupying the axial sites. The WSnCl$_2$ unit is nearly planar with the tin atom only 0.605(3) Å out of the W–Cl(1)–Cl(2) plane. The Cl(1)–Sn–Cl(3) and Cl(1)–Sn–Cl(3)^{i} angles are identical (89.5(1)°) as are the W–Sn–Cl(3) and W–Sn–Cl(3)^{i} angles (120.4(1)°). However, the Cl(1)–Sn–Cl(2) angle is 168.4(2)°, and the Cl(1)–Sn–W angle is much smaller than 90°, at 53.7(1)°; so the trigonal bipyramid is significantly distorted.

Similar capped octahedral geometry with two crystallographically equivalent nitrile and carbonyl groups seen in **1** has been detected for [WI$_2$(CO)$_3$(NCR)$_2$], R=Me, Et [31]. However, those complexes contain a carbonyl ligand in the unique capping position and two mutually *trans* iodine ligands.

The molecular structure of the recently investigated [WCl(SnCl$_3$)(CO)$_3$(η^4-NBD)] [17] is best described as a capped trigonal prism with the tin atom lying above a square face formed by the chlorine atom and three carbonyl groups. Unlike the situation in other W–Sn compounds in [WCl(SnCl$_3$)(CO)$_3$(η^4-NBD)] the chlorine attached to the tungsten does not bridge the W–

Sn bond. The W–Cl bond length is much shorter at 2.454(2) Å and W–Sn distance longer at 2.764(1) Å than in other W–Sn or Mo–Sn compounds [3, 4, 6].

Spectroscopic studies of nitrile compounds **1**–**4**

The carbonyl region of the infrared spectra of the compounds **1**–**4** in KBr are almost identical in showing three carbonyl bands (Table 1). The infrared spectrum of compound **1** shows three carbonyl bands at ν(CO) 2030vs, 1935s(sh) and 1903vs cm^{-1} and is similar to that for the analogous molybdenum-tin complex obtained first time by Baker and Bury, (ν(CO) 2026s, 1939s and 1912vs cm^{-1} [10]) but qualitatively different from that reported by Baker and Bury for the tungsten compound (ν(CO) 2017, 1978 and 1934 cm^{-1} [10]). As noted by Baker and Bury their tungsten complex was extremely unstable to exposure to air and could not be isolated in a pure state. This is marked contrast to the quite good stability of the complex obtained by us. However, IR spectra of **1** in a dichloromethane solution shows more than three bands in the carbonyl stretching region: 2040 (s), 2020 (s), 1970 (m) and 1930 (vs) cm^{-1}. The spectral differences correspond to different coordination geometries, and in a dichloromethane solution distinct isomers of **1** may co-exist, as was proposed previously by Kummer and Graham [1]. In the ν(C$\equiv$N) region of the IR spectra for **1** two bands are observed. One is the ν(C$\equiv$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$\equiv$N) [25]. For the compound **1** those bands are at 2320 and 2292 cm^{-1}, these are at higher frequencies than the ν(C$\equiv$N) band in the free acetonitrile observed at 2268 cm^{-1} [25]. The intensity ratio of the ν(C$\equiv$N) band to that of the combination band was found to differ greatly between *cis* and *trans* isomers [25]. Two sharp bands of comparable intensities in the ν(C$\equiv$N) region of **1** are consistent with *cis* acetonitrile ligands [25]. The ν(C$\equiv$N) frequencies of coordinated propionitrile and butyronitrile in **2** and **3** were observed as one band at 2292 cm^{-1}. The lower frequency region of the infrared spectrum is dominated by the principal absorptions at 344, 325 cm^{-1}, which can be regarded as ν_s and ν_{as} (Sn–Cl) vibration. This is in good agreement with increased frequencies of these bands upon coordination to metal or other ligand. Tin-halide frequencies of $[SnCl_3]^-$ ion were observed in, for example, $^1Et_4N[SnCl_3]$ at 295 (A_1) and 253 cm^{-1} (E) [32].

The similarity of the IR spectra in a solid state of the series of nitrile compounds obtained by us, shows that the most probable solid state structure for those compounds is the same as that of **1** (Fig. 1).

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

The electronic spectrum of **1** is quite similar to those of the starting tungsten (II) compound [23] and shows one strong band at 250 nm with a shoulder at 290 nm which, because of its high intensity and its position is assigned to CT transition $\pi^*(CO) \leftarrow d\pi(W)$. There is also another band at 398 nm. Because of its relatively low intensity it is assigned to a ligand-field transition.

Reaction of **1** *with alkynes*

When the reaction of **1** with two molecular equivalents of PhC$\equiv$CPh at room temperature in CH_2Cl_2 was monitored by IR, the substitution of the CO ligands by an alkyne can be observed. The ν(CO) bands for **1** decrease, while this of the alkyne complex at 2101 (s) appears. The ^{1}H, ^{13}C NMR and IR spectral data for the reaction product indicate that it is a mixture of two alkyne compounds (Table 2). One compound, with acetonitrile *trans* to CO ligand, two *cis* PhC$\equiv$CPh ligands and two *cis* anionic ligands (Cl$^-$) in the coordination sphere, can be formulated as $[WCl_2(CO)(NCMe)(PhC{\equiv}CPh)_2]$ **5**, which probably has a structure similar to that observed by Baker *et al.* for $[WI_2(CO)(MeCN)(MeC{\equiv}CMe)_2]$ [33]. The other alkyne compound does not contain CO in coordination sphere and can be formulated as $[WCl_2(NCMe)_2(PhC{\equiv}CPh)_2]$ **6**. Both compounds dimerize in solution, first with a loss of carbon monoxide and second with a loss of acetonitrile molecule to give probably the chloride-bridged dimer $[W(\mu\text{-}Cl)Cl(NCMe)(PhC{\equiv}CPh)_2]_2$. The dimeric compound is less soluble than monomeric and could not be characterized by ^{13}C NMR spectroscopy in solution. A similar dimerization process was observed by Baker *et al.* in their molybdenum(II) and tungsten(II) diiodide alkyne complexes [33, 34]. In ^{13}C NMR spectra of the reaction products two sets of carbon signals of coordinated PhC$\equiv$CPh for **5** and **6** are observed. However, after prolonged reaction time (24 h) ν(CO) band characteristic of alkyne complex **5** disappears and in the residue obtained after evaporation of solvent only compound **6** was identified by NMR. ^{13}C NMR spectra of **5** and **6** revealed acetylenic carbon resonances in the range from 196–167 ppm, as is typical for three-electron-donor alkynes. The white precipitate which appeared as the side product during the reaction of **1** with alkynes was identified as $SnCl_2$, what suggests that the $SnCl_3^-$ ligand undergoes hydrolysis to $SnCl_2$ and Cl$^-$ in the presence of an alkyne.

In the reaction of **1** with two molecular equivalents of phenylacetylene, a mixture of alkyne complexes is formed. The monomeric compound $[WCl_2(CO)(MeCN)(PhC{\equiv}CH)_2]$ **7**, with a solitary CO ligand was identified as the main product by IR and NMR spectroscopy. The other alkyne complex does not contain CO and most probably can be formulated as

$[WCl_2(NCMe)_2(PhC{\equiv}CH)_2]$ **8** (Table 2). However, complexes **7** and **8** are not the only reaction products because several other proton signals of coordinated PA in the region 11–14 ppm appeared in the reaction of PA with **1**. Also several lower intensity carbon signals of coordinated PA were observed in ^{13}C NMR spectra.

Catalytic activity of **1**. The starting point of the present investigation was to examine the scope of our earlier finding [35, 36, 37] 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. To be precise, polymerization of PA occurs at room temperature in CH_2Cl_2 containing tungsten(II) compound **1**. Treatment of the resultant deep-red solution with a large amount of methanol produced, quantitatively, poly-(phenylacetylene) (PPA) as a fine dark-orange powder with a number-average molecular weight (M_w) of 5×10^3, determined by GPC. 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 as mainly *trans* [19].

However, the catalytic coupling of alkynes in the presence of **1** 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. Minor amounts of other oligomers arise, mainly linear diphenylbutadienes, which contain, for example, hydrogen derived from the solvent and also a dimer of PA detected by MS as 1*H*-indene-1-(phenylmethylene).

The intermediates formed in mechanisms most frequently suggested for the catalytic polymerization and cyclotrimerization of alkynes are alkylidene complexes [38] and metallacyclic species [39]. The catalytically active species are, as yet, rather poorly characterized. Our results provide direct information only as regards to the first step and strongly suggest that the loss of three labile two-electron-donor ligands (CO or CH_3CN), and coordination of two alkyne molecules as three-electron-donor ligands, is common to all the reactions studied. In the reactions of **1** with alkynes that we investigated, the tungsten complexes that could be isolated contained a *cis* arrangement of the two alkyne ligands. We were unable to isolate any intermediates beyond the first bis(alkyne) complexes and their decomposition product: 1*H*-indene-1-(phenylmethylene). The formation of dimers, cyclotrimers and linear conjugated polyenic polymers involves oxidative coupling and formation of a series of metalacyclic species [39]. The metallacycle formed with four molecules of alkyne can then rearrange to an alkylidene ligand, as was observed by Yeh *et al.*[40]. The mechanism of PA polymerization induced by tungsten(II) complex 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.

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