Journal of Organometallic Chemistry 575 (1999) 98–107

Synthesis and reactivity of Mo–Sn compounds: X-ray crystal structure of a novel $[Mo(SnCl_3)_2(CO)_2(NCEt)_3]$

Teresa Szymańska-Buzar *, Tadeusz Głowiak

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

Received 7 August 1998

Abstract

$[Mo(CO)_4(NCMe)_2]$ reacts with $SnCl_4$ in CH_2Cl_2 to produce a mixture of compounds which can be regarded as the results of oxidative addition with the elimination of CO and the formation of a Mo–Sn bond. The compound $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ **1** is the main product but others containing Mo–Sn bond compounds can be formed also in variable amounts, as was shown by IR and NMR investigation of the reaction mixture. The structure of a novel $[Mo(SnCl_3)_2(CO)_2(NCEt)_3]$ **4** was established by X-ray crystallography. This is the first structurally characterized molybdenum(II) carbonyl complex containing two anionic $SnCl_3$ ligands and the very rare example of the 4:3 piano stool seven-coordinate geometry. In the reaction of **1** with alkynes, complexes were isolated in which CO and/or acetonitrile ligands were replaced by alkyne ligands. The alkyne molybdenum(II) complexes formed were characterized structurally by IR and NMR spectroscopy. However, the reaction of **1** with phenylacetylene leads to the catalytic coupling of alkyne molecules and the formation of cycloligomers and polymers. The possible mechanisms for the formation of molybdenum(II) complexes and their role in the catalytic process are discussed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Molybdenum(II); Tin; Crystal structure; Seven-coordinate; Heterobimetallic complexes; Nitrile complexes; Alkyne complexes; Cyclooligomerization of alkynes

1. Introduction

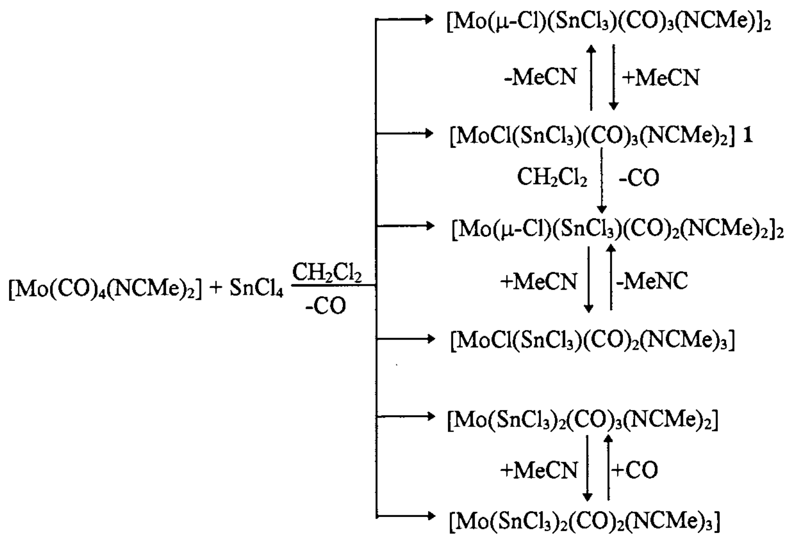
In recent years work in this laboratory involving Group 6 metal carbonyls has largely focused on the catalytic activity of compounds with d^4 electronic configuration in reaction of alkenes and alkynes [1–3]. Such compounds can be formed easily in oxidative-addition reactions of d^6 Group 6 metal complexes and Group 14 metal halides. Particularly heterobimetallic complexes with Mo–Sn or W–Sn bonds are intriguing because of the possibility that on reaction with alkene or alkyne the unsaturated carbon–carbon bond may be activated.

It has been long known that compounds $[Mo(CO)_4L_2]$, L = N-, P-donor ligands, react with R_nSnCl_{4-n} to form the seven-coordinate compounds with Mo–Sn bond [4–9]. Among them bis(nitrile) compounds are especially interesting as useful starting materials in which the labile nitrile groups can be easily replaced by other ligands [9–17]

In 1989 Baker and Bury reported the synthesis of $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ **1** in the reaction of $[Mo(CO)_3(NCMe)_3]$ and $SnCl_4$ in acetonitrile [9]. The complex **1** was characterized by elemental analysis, IR and NMR spectroscopy and showed three carbonyl bands at $\nu(CO)$ 2026 (s), 1939 (s), 1912 (s) cm^{-1} but 12 resonances in the carbonyl region δ 227.84–201.97 ppm of ^{13}C-NMR spectrum [9]. This is in contrast to the results for $[WCl(SnCl_3)(CO)_3(NCMe)_2]$ [18] and $[WCl(GeCl_3)(CO)_3(NCMe)_2]$ [19] which showed similar IR spectrum containing three carbonyl bands, but only

* Corresponding author. Fax: + 48-71-222348; e-mail: tsz@chem.uni.wroc.pl.

PII: S0022-328X(98)00982-6



Scheme 1.

one carbonyl resonance of three equivalent CO groups; at δ 211.9 ppm [18] for W–Sn and at δ 214.8 ppm [19] for the W–Ge compound. The possibility of forming several different isomers of **1** was particularly intriguing to us, so we decided to repeat the synthesis of **1** and to verify the nature of the Mo–Sn compounds formed in the oxidative-addition reaction of molybenum(0) and tin tetrahalide. An X-ray diffraction study of one of these products was desirable to confirm the existence of different seven-coordinate molybdenum compounds containing the Mo–Sn bond.

It was also interesting to compare structural, spectroscopic and catalytic properties investigated by us earlier [WCl($SnCl_3$)$(CO)_3$$(NCMe)_2$] with a similar compound of molybdenum.

2. Experimental

2.1. General data

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. Solution IR spectra were obtained using KBr or NaCl plates while solid samples were recorded using KBr pellets on an FT-IR Model-400 Nicolet instrument. Far-IR spectra were recorded (500–50 cm^{-1}) with a Brücker IFSv instrument in nujol mull on a polyethylene film. NMR spectra were run using a Bruker AMX-300 spectrometer. The analysis of the catalytic reaction products was performed on a Hewlett-Packard GC-MS system and by ^{1}H-NMR and IR spectroscopy.

2.2. Synthesis

2.2.1. [MoCl($SnCl_3$)$(CO)_3$$(NCMe)_2$] 1

To [Mo$(CO)_4$$(NCMe)_2$] [20] (2.0 g, 6.9 mmol) dissolved in CH_2Cl_2 (50 cm^3) with continuous stirring under a stream of nitrogen, a stoichiometric amount of $SnCl_4$ (0.8 cm^3, 6.9 mmol) was added by means of a syringe. The mixture was stirred for 1 h, during which time the yellow solution gradually changed to a redish–orange colour, while the ν(CO) frequency of [Mo$(CO)_4$$(NCMe)_2$] disappeared. After this reaction time IR spectroscopy confirmed the reaction to be complete. Volatiles were removed in vacuo to yield an orange solid. The crude product was washed with heptane (3 × 10 cm^3) to remove $Mo(CO)_6$ and a compound with characteristic for [$Mo(CO)_5$] unit ν(CO) bands at 2072 vw and 1949 vs cm^{-1}. The residue was treated with CH_2Cl_2 (50 cm^3). The solution was separated from less soluble orange powder by filtration and heptane was added (10 cm^3). Overnight cooling in a refrigerator afforded orange crystals. They were washed with heptane and dried under vacuum. By analysis and by their IR and NMR spectra were identified as pure **1** (2.88 g, 80%). Less soluble in CH_2Cl_2 residue was identified as a mixture of mononuclear and dinuclear compounds of the type: [MoCl($SnCl_3$)$(CO)_2$$(NCMe)_3$], [Mo(μ-Cl)($SnCl_3$)$(CO)_3$-(NCMe)]$_2$, [Mo(μ-Cl)($SnCl_3$)$(CO)_2$$(NCMe)_2$]$_2$ [Mo($SnCl_3$)$_2$$(CO)_3$$(NCMe)_2$], and [Mo($SnCl_3$)$_2$$(CO)_2$$(NCMe)_3$]. The dimers react with acetonitrile to give the bridge cleaved mononuclear compounds (Scheme 1).

Satisfactory analysis has been obtained only for compound **1**. Anal. found: C, 16.04; H, 1.26; N, 5.20. $C_7H_6Cl_4MoN_2O_3Sn$ calc.: C, 16.09; H, 1.16; N, 5.36. Remaining compounds were not separated and detected only by IR and NMR spectroscopy in the reaction mixture (Table 1).

*2.2.2. [MoCl(SnCl$_3$)(CO)$_3$(NCR)$_2$], **2** (R = C_2H_5); **3** (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 which was recrystallized from CH_2Cl_2–heptane giving a pure bis(nitrile) complex **2** and **3**. For **2** anal. found: C, 19.65; H, 1.89; N, 4.50. $C_9H_{10}Cl_4MoN_2O_3Sn$ calc.: C, 19.63; H, 1.83; N, 5.09. For **3** anal. found: C, 30.09; H, 1.99; N, 4.34. $C_{17}H_{10}Cl_4MoN_2O_3Sn$ calc.: C, 31.57; H, 1.56; N, 4.33.

*2.2.3. [Mo(SnCl$_3$)$_2$(CO)$_2$(NCEt)$_3$] **4***

The insoluble in the CH_2Cl_2 mixture of Mo–Sn compounds separated from **1** (Section 2.2.1) was dissolved in propionitrile. The removal of the solvent in vacuo, gave a residue which was recrystallized from CH_2Cl_2–heptane giving the large redish–orange crystals, which could be separated easily by hand as **4**. Anal. found: C, 17.58; H, 2.18; N, 5.09. $C_{11}H_{15}Cl_6MoN_3O_2Sn_2$ calc.: C, 17.22; H, 1.97; N, 5.48. The residue contained several other propinitrile compounds (see Table 1) and presumably molybdenum chlorides, which could not be separated.

2.3. Reactions with alkynes

*2.3.1. Reaction of **1** with diphenylacetylene (DPA)*

To a solution of **1** (0.6 g, 1.1 mmol) in 15 cm^3 of CH_2Cl_2 was added PhC≡CPh (0.41 g, 2.2 mmol) in CH_2Cl_2 (5 cm^3). The mixture was stirred and the progress of the reaction was monitored by the disappearance of ν(CO) bands due to **1**. At the begining of the reaction (2–4 h), one new ν(CO) band appears and increases at about 2100 cm^{-1} which next decays after prolonged reaction time. The solution was filtered to remove an insoluble white solid containing $SnCl_2$. Evaporation of the solvent followed by washing with heptane produced a compounds identified by IR and NMR studies (Table 2) as [MoCl$_2$(NCMe)$_2$(PhC≡CPh)$_2$]. In dichloromethane this compound very easily releases acetonitrile and dimerizes to give an insoluble in CH_2Cl_2 and $CHCl_3$ most probably [Mo(μ-Cl)Cl(NCMe)(PhC ≡ CPh)$_2$]$_2$. Crystallization of the above greenish–yellow solid from acetonitrile restores the mononuclear bis(acetonitrile) compound.

*2.3.2. Reaction of **2** with DPA*

The alkyne (0.16 g, 0.9 mmol) was added to a solution of complex **2** (0.25 g, 0.45 mmol) in CH_2Cl_2 (15 cm^3) at room temperature. The procedure was the same as in Section 2.3.1. The resulting compound was characterized by IR and NMR spectroscopy (see Table 2).

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

The addition of four equivalents of PA (0.16 cm^3, 1.52 mmol) to a stirred CH_2Cl_2 solution (15 cm^3) of **1** (0.2 g, 0.38 mmol) at room temperature resulted in a color change from light orange to dark orange. The progress of the reaction was monitored by disappearance of ν(CO) bands of **1**. Stirring for 2 h followed by the filtration and 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 brownish–yellow mixture of compounds containing mainly [MoCl$_2$-(NCMe)$_2$(PhC≡CH)$_2$], as was shown by ^{1}H- and ^{13}C-NMR spectra. (Table 2). In CH_2Cl_2 solution this compound dimerizes but crystallization of the mixture from MeCN restores a better soluble in the CH_2Cl_2 mononuclear compound. The heptane extract contained organic products: 1,2,4-triphenylbenzene (66.2%), 1,3,5-triphenylbenzene (31.1%), diphenylbutadiene (0.9%) and 1*H*-indene-1-(phenylmethylene) (1.8%).

*2.3.4. Reaction of **1** with PA in an NMR tube*

To the NMR tube containing the solution of **1** (0.05 g, 0.09 mmol) in CD_2Cl_2 (0.7 cm^3) two equivalents of PA (0.02 cm^3, 0.19 mmol) were added by means of a microlitre syringe and a sample was periodically analyzed by ^{1}H-NMR spectroscopy at room temperature. Complete transformation of **1** detected by the decay of the signal at δ 2.46 due to protons of coordinated C*H*$_3$CN, occurred within 24 h. At the same time new signals of free and coordinated NC*Me* appeared at δ 1.97 and 2.20 ppm, respectively. The signal of free PA, (≡C*H*) at δ 3.13 ppm had decayed but three signals appeared and increased in the region characteristic for PA coordinated to molybdenum at δ 11.15, 10.97 and 10.88 ppm. After a prolonged reaction time, the intensity of the latter three signals decreased but several new signals appeared in the region δ 11.3–10.8 ppm The hydrogen signals of organic reaction products were observed in the region δ 5–8 ppm. The organic products based on GC-MS characterization were 1,2,4-triphenylbenzene (64.9%), 1,3,5-triphenylbenzene (32.4%), diphenylbutadiene (2.3%) and 1*H*-indene-1-(phenylmethylene) (0.4%).

*2.3.5. Reaction of **3** with PA*

The PA (0.11 cm^3, 1 mmol) was added to a solution of **3** (0.16 g, 0.25 mmol) in CH_2Cl_2 (15 cm^3). The progress of the reaction was monitored by the disappearance of ν(CO) bands of **1**. Stirring for 2 h 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 brownish–yellow mixture of compounds with signals in ^{1}H-NMR spectrum characteristic for PA coordinated to tungsten probably in the mixture of compounds such as [MoCl$_2$(NCPh)$_2$(PhC≡CH)$_2$] (δ 10.86 ppm) and [MoCl(μ-Cl)(NCPh)(PhC≡CH)$_2$]$_2$ (δ 11.23 and 11.06

Table 1
IR and NMR spectral data for the seven-coordinate nitrile complexes with Mo–Sn bonds

Complex	IR(ν, cm^{-1})		^{1}H-NMR (δ, ppm)[b]	^{13}C-NMR (δ, ppm)[b]
	ν(CO)[a]	ν(CN)[a]		
$[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ **1**	2033 s, 1959 s, 1917 vs	2317 w, 2290 w	2.46 (s, 2 CH_3CN)	219.39 (s, 3 CO), 128.24 (s, 2 CH_3CN), 5.40 (s, 2 CH_3CN)
$[MoCl(SnCl_3)(CO)_2(NCMe)_3]$	1949 vs, 1890 s	2320 m, 2290 w	2.41 (s, 3 CH_3CN)	218.98 (s, 2 CO), 128.41 (s, 3 CH_3CN), 3.65 (s, 3 CH_3CN)
$[Mo(SnCl_3)_2(CO)_3(NCMe)_2]$	2037 s, 1950 s, 1915 vs	1960 vs, 1893 s	2.63 (s, 2 CH_3CN)	230.54 (s, 3 CO), 132.32, (s, 2 CH_3CN), 5.71 (s, 2 CH_3CN)
$[Mo(SnCl_3)_2(CO)_2(NCMe)_3]$	2326 w, 2298 w	2326 m, 2298 w	2.76 (s, 3 CH_3CN)	230.39 (s, 2 CO), 132.32, (s, 3CH_3CN), 6.90 (s, 3 CH_3CN)
$[MoCl(SnCl_3)(CO)_3(NCEt)_2]$ **2**	2029 vs, 1960 s, 1925 vs	2291 m	2.75 (q, 2 CH_3CH_2CN), 1.41 (t, 2 CH_3CH_2CN)	219.55 (s, 3 CO), 131.80 (s, 2 CH_3CH_2CN), 13.90 (s, 2 CH_3CH_2CN), 10.81 (s, 2 CH_3CH_2CN)
$[MoCl(SnCl_3)(CO)_2(NCEt)_3]$	1950 s, 1893	2290 m	2.85 (q, 3 CH_3CH_2CN), 1.45 (t, 3 CH_3CH_2CN)	218.79 (s, 2 CO), 131.27 (s, 3 CH_3CH_2CN), 13.82 (s, 3 CH_3CH_2CN), 10.45 (s, 3 CH_3CH_2CN)
$[Mo(SnCl_3)_2(CO)_3(NCEt)_2]$	2029 sv, 1960 s, 1936 vs	2287 m	2.94 (q, 2 CH_3CH_2CN), 1.48 (t, 2 CH_3CH_2CN)	229.62, (s, 3 CO), 134.83 (s, 2 CH_3CH_2CN), 14.56 (s, 2 CH_3CH_2CN), 10.81 (s, 2 CH_3CH_2CN)
$[Mo(SnCl_3)_2(CO)_2(NCEt)_3]$ **4**	1960 s, 1893 vs	2287 m	2.81 (q, 3 CH_3CH_2CN), 1.45 (t, 3 CH_3CH_2CN)	230.63, (s, 2 CO), 136.91 (s, 3 CH_3CH_2CN), 14.72 (s, 3 CH_3CH_2CN), 10.69 (s, 3 CH_3CH_2CN)
$[MoCl(SnCl_3)(CO)_3(NCPh)_2]$ **3**	2026 s, 1958 s, 1936 vs	2263 m	7.96 (d, *o*-Ph), 7.83 (t, *p*-Ph), 7.50 (t, *m*-Ph)[c]	217.5 (s, 3 CO, 135.94 (s, C_p-Ph), 133.68 (s, C_o-Ph), 130.02 (s, C_m-Ph) 129.26 (s, C_i-Ph), 127.0 (s, 2 PhCN)[c]

[a] Spectra recorded in KBr pellets.
[b] Spectra recorded in CD_2Cl_2 at 293 K.
[c] Spectra recorded w $CDCl_3$ at 293 K.

Table 2
Selected IR and NMR data for molybdenum(II) alkyne complexes

Complex	IR(ν, cm^{-1})		^{1}H-NMR (δ, ppm)	^{13}C-NMR (δ, ppm)
	ν(CO)	ν(CN)		
$[MoCl_2(CO)(NCMe)(PhC{\equiv}CPh)_2]$	2100[a]	–[b]	–[b]	–[b]
$[MoCl_2(NCMe)_2(PhC{\equiv}CPh)_2]$		2319 w, 2289 vw[c]	2.30 (s, 2 CaH_3CN)[a]	191.23 (s, 2 Ph$C{\equiv}$CPh), 186.65 (s, 2 PhC$\equiv$$C$Ph), 136.22 (s, 2 C_i-Ph), 135.06, (s, 2 C_i-Ph), 126.60 (s, 2 $CH_3$$C$N), 4.75 (s, 2 CH_3CN)[d]
$[MoCl_2(NCEt)_2(PhC{\equiv}CPh)_2]$		2291	2.47 (q, 2 CH_3CH_2CN), 1.26 (t, 2 CH_3CH_2CN)[e]	193.26 (s, 2 Ph$C{\equiv}$CPh), 188.49 (s, 2 PhC$\equiv$$C$Ph), 138.13 (s, 2 C_i-Ph), 136.72, (s, 2 C_i-Ph), 132.86 (s, 2 CH_3CH_2CN), 15.21(s, 2 CH_3CH_2CN), 10.14 (s, 2 CH_3CH_2CN)[e]
$[MoCl_2(CO)(NCMe)(PhC{\equiv}CMe)_2]$	2087[a]	–[b]	–[b]	
$[MoCl_2(NCMe)_2(PhC{\equiv}CMe)_2]$		2325 w, 2397 vw[c]	3.25 (s, 2 PhC$\equiv$CMe), 2.16 (s, CH_3CN)[d]	194.99 (s, 2 Ph$C{\equiv}$CMe), 178.71 (s, 2 PhC$\equiv$$C$Me), 135.99 (s, 2 C_i-Ph), 126.60 (s, 2 $CH_3$$C$N), 18.89 (s, 2 PhC$\equiv$C$Me$), 3.99 (s, 2 CH_3CN)[e]
$[MoCl_2(CO)(NCMe)(PhC{\equiv}CH)_2]$	2095[a]	–[b]	–[b]	–[b]
$[MoCl_2(NCMe)_2(PhC{\equiv}CH)_2]$		2325 w, 2397 vw[c]	2.20 (s, 2 CH_3CN), 10.88 (s, 2 PhC$\equiv$CH)[d]	182.88. (s, 2 Ph$C{\equiv}$CH), 169.58 (s, 2 PhC$\equiv$$C$H, $^{1}J_{CH} = 224$ Hz), 134.50 (s, 4 C_i-Ph), 4.24 (s, 2 CH_3CN)[d]
$[MoCl_2(NCPh)_2(PhC{\equiv}CH)_2]$		2269 w[c]	10.86 (s, 2 PhC$\equiv$CH)[d]	–[b]

[a] Spectra recorded w CH_2Cl_2.
[b] Not observable.
[c] Spectra recorded in KBr disc.
[d] Spectra recorded w $CDCl_3$.
[e] Spectra recorded in CD_2Cl_2 at 293 K.

ppm). The heptane extract contained organic products: 1,2,4-triphenylbenzene (81.2%), 1,3,5-triphenylbenzene (18.3%), diphenylbutadiene (0.5%).

2.3.6. Reaction of **1** with 1-phenylprop-1-yne (PhC≡CMe)

The alkyne (0.3 cm^3, 2.4 mmol) was added to a solution of complex **1** (0.27 g, 0.5 mmol) in CH_2Cl_2 (15 cm^3) at room temperature. The procedure was the same as for the PA reaction. The spectral data for alkyne compound are shown in Table 2. The organic products based on GC-MS characterization were mainly cyclotrimers 1,2,4-trimethyltriphenylbenzene and 1,3,5-trimethyltriphenylbenzene in the ratio 8/1.

2.4. Procedures for testing catalytic activity

Catalytic reactions of alkynes were carried out in a reaction mixture composed of CH_2Cl_2, *ortho*-xylene (the internal chromatographic standard), phenylacetylene (PA) (1 M), and a molybdenum complex (PA/Mo 100 or PA/Mo 50). The conversion of PA monitored by chromatography after 24 h reached the higher value 46%. Small amounts of the acetonitrile added to the reaction mixture protect the catalyst against deactivation. For the analysis of PA reaction products, reactions were continued for 24 h and then methanol was added. The polymer was collected, washed with methanol, dried and weighed. The polymerization yield (%) defined by comparing the polymer weight to the weight of the PA used was no greater than 22%. The polymer was analyzed 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 values recorded are the weight of polystyrene that would exhibit the chromatograms observed. Molecular weights of the PPA achieved the value from 5000 to 6000. ^{1}H-NMR spectra of the polymers were recorded in a $CDCl_3$ solution at 300 MHz. The microstructural details of the polymers were calculated from the ^{1}H-NMR integrals ($\%cis = A_{5.85} \times 10^4/A_t \times 16.66$, where $A_{5.85}$ is the area of the signal at $\delta = 5.85$ ppm and A_t is the total integral of the NMR spectrum [21]). The chemical shift of the =CH groups (5.85 ppm) and its intensity showed that the polymer appeared to possess both *cis* and *trans* linkages, with about 75% *cis* form.

The filtrate obtained after the precipitation of the polymers was evaporated to dryness and the CH_2Cl_2 solution of the residue was investigated by GC-MS. Analysis showed mainly 1,2,4-triphenylbenzene and 1,3,5-triphenylbenzene in an average ratio 3/1.The PA dimers, 1*H*-indene-1-(phenylmethylene) and diphenylbutadiene were formed in low yield, below 2%. Yield of oligomerization calculated as the difference between the conversion (%) and yield of polymerization reaction was about 24% after 24 h reaction time.

2.5. Crystal and refinement data for compound **4**

Crystal data and relevant refinement details are collected in Table 3. A redish–orange crystal ca. $0.12 \times 0.12 \times 0.15$ mm was removed from the flask and rapidly coated with a light hydrocarbon oil to protect it from the atmosphere. Data collection was performed on a KM4 κ-axis computer-controlled [22] four-circle diffractometer operating in the $\omega - 2\theta$ scan mode with graphite-monochromated Mo–K_α radiation ($\lambda = 0.71069$ Å) at 293 K. The accurate cell dimensions and the crystal orientation matrix were determined by a least-squares refinement of the setting angles of 50 carefully centred reflections in the range $20 < 2\theta < 40°$. A total of 4199 unique reflections were measured, of which 2484 (229 variables) with $I \geq 2\sigma(I)$ in the range 5–50° were used to solve and refine the structure in the monoclinic space group $P2_1/n$. Absorption corrections following the DIFABS [23] were applied to the data: minimum 0.7968 and maximum 1.094.

The hydrogen atoms were placed in the geometrically calculated positions with the isotropic temperature factors taken as 1.2 and 1.5 U_{eq} of the neighbouring

Table 3
Crystal data and details of refinement for $[Mo(SnCl_3)_2(CO)_2(NCEt)_3]$ **4**

Chemical formula	$C_{11}H_{15}Cl_6MoN3O_2Sn_2$
Molecular weight	767.28
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	8.791(2)
b (Å)	25.682(5)
c (Å)	11.622(2)
β (°)	103.32(3)
V (Å^3)	2553.3(9)
Z	4
Reflections determining lattice	50
T (K)	293(2)
Crystal size (mm)	$0.12 \times 0.12 \times 0.15$
$D_{calc.}$ (g cm^{-3})	1.996
λ(Mo–K_α) (Å)	0.71069
μ(Mo–K_α) (cm^{-1})	30.62
F(000)	1448
Method of collection	$\omega/2\theta$ scan
2θ Range (°)	$5 < 2\theta < 50$
Index ranges	$-10 \leq h \leq 10$, $0 \leq k \leq 30$, $0 \leq l \leq 13$
No. of unique data	4199
No. of data with $I \leq 2\sigma(I)$	2484
Correction factors (min, max)	0.7968, 1.0940
Residuals R_1, wR_2	0.0362, 0.0778
Goodness-of-fit	0.923
Final ($\Delta\rho$) (e Å^3)	0.525/−0.625

heavier atoms for CH_2 and CH_3, respectively. Several cycles of refinement of the coordinates and anisotropic thermal parameters for non-hydrogen atoms (parameters of the H atoms were fixed) reduced the R_1 to 0.0362 and wR_2 to 0.0778. The maximum and minimum residual densities in the difference map were 0.525 and -0.625 e Å^{-3}, respectively. Goodness-of-fit was 0.923. The structure was given a weighting scheme in the form $w = 1/[\sigma^2(F_o^2) + (0.0380P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$.

The structure was solved by heavy-atom methods with the SHELXS-86 program [24] and refined by a full-matrix least-squares method, using the SHELXL program [25]. Neutral atomic scattering factors were taken from the SHELXL-93 program [25].

2.6. Supplementary material available

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

3. Results and discussion

3.1. Synthesis of Mo–Sn compounds

A number of seven-coordinated compounds containing molybdenum–tin bonds have been prepared by reaction of molybdenum(0)-substituted carbonyls and tin tetrahalides or organometallic halides, R_nSnCl_{4-n}, R = Me, Bu, Ph [4–9,26]. The first time bis(nitrile) compound **1** was obtained in the reaction of $[Mo(CO)_3(NCMe)_3]$ and $SnCl_4$ in acetonitrile [9]. However, we found that compound **1** is more conveniently obtained in high yields by using CH_2Cl_2 instead of acetonitrile as solvent for the reaction of $[Mo(CO)_4(NCMe)_2]$ with $SnCl_4$.

Treatment of a slurry of $[Mo(CO)_4(NCMe)_2]$ in CH_2Cl_2 with an equimolar amount of $SnCl_4$ gives the oxidative-addition product compound **1** in good yield (80%). Besides **1**, others containing Mo–Sn bond compounds are formed (Scheme 1). They include seven-coordinated monomeric and dimeric compounds with a varying number (from 3 to 2) of CO and nitrile ligands. We found, that the equilibrium between mononuclear and dinuclear species was dependent upon the molar ratio of Mo and Sn compounds used in the oxidative-addition reaction (Scheme 1). The higher Sn/Mo molar ratio favour the formation of dinuclear compounds is probably due to removing the nitrile ligands from the coordination sphere of Mo by the stronger Lewis acid, $SnCl_4$. In this interaction the very well known complex $[SnCl_4(NCMe)_2]$ [27] can be formed. We observed the decrease of the intensity of ν(CN) bands (2290 and 2320 cm^{-1}) in comparison to ν(CO) bands in IR spectrum of the reaction product mixture with the increase of Sn/Mo molar ratio. Simultaneously, the intensity of weak ν(CO) band at about 2100 cm^{-1} characteristic for metal (II) halocarbonyl dimers formed in oxidation of Group 6 metal carbonyls, $M(CO)_6$, M = W, Mo, with such oxidants as Cl_2, Br_2 [28–30], CCl_4 [3], $SnCl_4$ [31] and $GeCl_4$ [19], increases. The yield of dimer formed as the result of CO loss (Scheme 1) depends mainly on solvent. The dichloromethane as solvent favours especially the CO loss. The insoluble in CH_2Cl_2 or $CHCl_3$ dimers can be restore to soluble monomers by recrystallization from nitrile (Scheme 1). The formation of compounds with two $SnCl_3$ groups coordinated to molybdenum centre was observed also (Scheme 1). These compounds can be formed in disproportionation reaction giving $[MoCl_2(CO)_{5-n}L_n]$ and next $MoCl_2$ solvated by nitrile. Such a course of the reaction may well be a consequence of lower thermal stability of $[MoCl_2(CO)_{5-n}L_n]$ by-product in comparison to $[Mo(SnCl_3)_2(CO)_{5-n}L_n]$ as a result of the π-acceptor character of the $SnCl_3$ ligand [32] in relation to the π-donor character of the chloride ligand.

3.2. Spectroscopic studies of Mo–Sn compounds

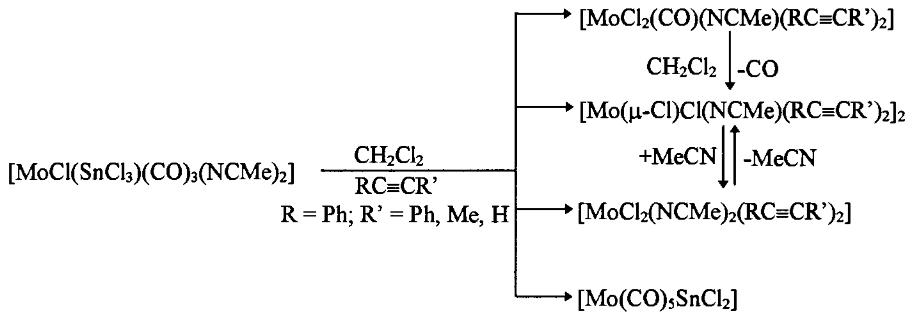
The IR spectra of $[MoCl(SnCl_3)(CO)_3(NCR)_2]$ compounds (R = Me, Et and Ph) in KBr show a common profile which includes three bands in the CO region (Table 1) and are similar to that for the analogous molybdenum–tin complex obtained first time by Baker and Bury, (ν(CO) 2026s, 1939s and 1912vs cm^{-1}[9]) and are in excellent agreement with the data reported for comparable compounds of the type $[WCl(MCl_3)(CO)_3(NCMe)_2]$, M = Sn [18], Ge [19].

The ^{1}H-NMR spectrum of bis(nitrile) compounds show single resonance consistent with two identical nitrile groups. The room-temperature ^{13}C-NMR spectra show one carbonyl resonance of the three equivalent CO group at δ ~220 ppm in keeping with the symmetry of these compounds in the solid state analogous to tungsten compounds [18].

However, compounds containing two $SnCl_3$ groups coordinated to molybdenum have different spectral data (Table 1). First of all there are down-field shifts of carbon resonance of two equivalents of the CO group to ~230 ppm in the ^{13}C-NMR spectra.

3.3. Reactions of molybdenum(II) compounds with alkynes

The complexes obtained in reaction of **1** and alkynes (Scheme 2) are listed in Table 2 along with certain of their IR and NMR spectral properties. As was mentioned in Section 2.3 we were unable to prepare the alkyne complexes containing Mo–Sn bonds, because



Scheme 2.

the hydrolysis of $SnCl_3$ occurred and a white precipitate of $SnCl_2$ together with [$Mo(CO)_5SnCl_2$] resulted. The latter, good solubility compound was identified due to the characteristics for pentacarbonyl unit ν(CO) bands at 2072 w and 1949 vs cm^{-1} in IR spectrum and two carbon resonances at δ 211.60 (1CO) and δ 205.12 (4CO) in intensity ratio 1/4, in ^{13}C-NMR spectrum. These data are in a good agreement with the spectral data for compounds of that type [$Mo(CO)_5(SnX_2)$] [32].

When the reaction of **1** with two molecular equivalents of diphenylacetylene at room temperature in CH_2Cl_2 was monitored by IR, at the beginning, decay of ν(CO) bands due to **1** was accompanied by appearance of one ν(CO) band at 2100 cm^{-1}. But after prolonged reaction time (24 h), new ν(CO) band of alkyne complex decays. Based on the IR data the initial complex can be described as [$MoCl_2$(CO)(NCMe)(PhC≡CPh)$_2$] with the structure close to the one obtained and characterized crystallographically by Baker et al. in the reaction of [$WI_2(CO)_3(NCMe)_2$] and RC≡CR (R = Me, Ph) [33,34]. The loss of the CO group leads to formation of chloride-bridged dimer [W(μ-Cl)Cl(NCMe)(PhC≡CPh)$_2$]$_2$ (Scheme 2). The IR and NMR spectral data for the reaction product indicate that it is a mixture of compounds but without CO in coordination sphere of the molybdenum. The mononuclear compound [$MoCl_2(NCMe)_2$(PhC≡CPh)$_2$], with two mutually *cis* alkyne ligands, which are magnetically equivalent and give two signals of acetylenic carbons in ^{13}C-NMR spectra at δ 191.23 and 186.65 ppm, was identified as the main product. In CH_2Cl_2 solution this compound dimerizes with a loss of acetonitrile molecule to yield less soluble chloride-bridged complexes. This process is reversible in the presence of an excess of acetonitrile (Scheme 2). Thus, nitrile effects the nucleophilic cleavage of an Mo(μ-Cl)$_2$Mo bridge.

Spectral studies revealed that in the reaction of **1** with PhC≡CH (PA) the precursor complex **1** is liable to loose CO and acetonitrile, but at the beginning one CO and acetonitrile ligand still remains in the coordination sphere of the molybdenum. The IR spectrum of this product showed one ν(CO) band at 2095 cm^{-1}. However, the isolated product does not contain carbonyl ligand and after recrystallization from acetonitrile was identified as [$MoCl_2(NCMe)_2$(PhC≡CH)$_2$]. The ^{13}C-NMR spectrum of this compound showed acetylenic carbon signals at δ 182.19 (≡*C*Ph) and 169.58 (≡*C*H). The hydrogen resonance due to phenylacetylene coordinated to molybdenum was observed at δ 10.88 ppm (≡C*H*) and acetonitrile at δ 2.20 ppm.

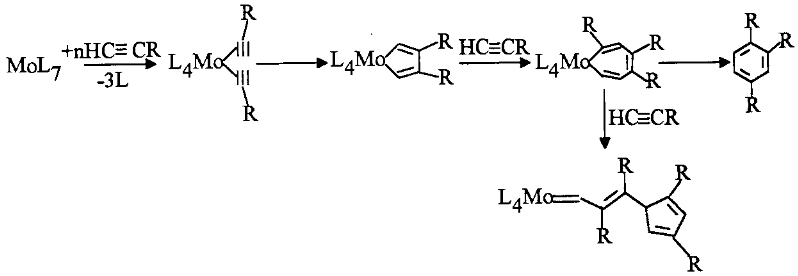
The acetylenic ^{1}H- and ^{13}C-NMR chemical shift values observed here (Table 2) are comparable to literature values for other three-electron-donor alkyne ligands [33–35].

3.4. Catalytic activity of 1

Polymerization of PA occurs very smoothly at room temperature in CH_2Cl_2 containing the compound **1**. Treatment of the reaction mixture with a large amount of methanol produced quantitatively poly(phenylacetylene) (PPA) as a fine dark-orange powder which has a number-average molecular weight (M_w) from 5 to 6×10^3, determined by GPC. All the polymers produced were soluble in CH_2Cl_2, $CHCl_3$ and toluene. IR and ^{1}H-NMR spectroscopy was used to establish the stereochemistry in PPA [21]. The IR spectrum of PPA is characterized by a low intensity band at 740 cm^{-1}. The ^{1}H-NMR spectra of PPA in $CDCl_3$ displayed a sharp singlet due to the vinylic protons at δ 5.85 ppm in addition to a set of multiplets at δ 6.60–7.00 ppm which has been correlated to the *cis*-transoidal (75%) structure of PPA [21].

However, the catalytic coupling of alkynes in the presence of **1** yields at least two types of products in the approximately ratio 1/1, namely polymers with conjugated polyenic structures and cyclic oligomers, especially the aromatic cyclotrimers 1,2,4- and 1,3,5-triphenylbenzene (TPB). Minor amounts of other oligomers arise, mainly linear diphenylbutadienes (DPBD), which contain, for example, hydrogen derived from the solvent and also a dimer of PA detected by MS as 1*H*-indene-1-(phenylmethylene).

A reasonable mechanism for the formation of cyclotrimers from PA involves the initial coordination of



Scheme 3.

two alkynes to the metal, rearrangement to a metallacyclopentadiene, insertion of third alkyne into the Mo–C bond and reductive cyclization to the cyclotrimers (Scheme 3). The formation of linear conjugated polyenic polymers involves oxidative coupling and formation of a series of metallacyclic species. The metallacycle formed with four molecules of alkyne can then rearrange to an alkylidene ligand initiating the increase of the polymer chain, as was observed by Yeh et al. [36] (Scheme 3).

Our results provide direct information only as regards the first step. In the reactions of **1** with alkynes that we investigated, the molybdenum complexes that could be isolated usually contained a *cis* arrangement of the two alkyne ligands.

The compound **1** has shown similar catalytic activity to that investigated by us earlier in the W–Sn compound [18]. However, yield of oligomerization products in case of molybdenum catalyst is much greater.

3.5. Structure of $[Mo(SnCl_3)_2(CO)_2(NCEt)_3]$ 4

Although the structures of numerous seven-coordinate complexes containing molybdenum–tin bonds have been determined crystallographically [12–14,26,37,38], no bis(trichlorotin) complexes have thus far been studied.

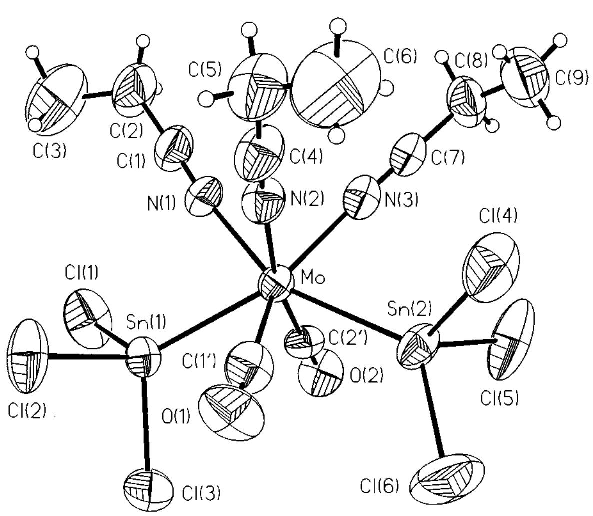


Fig. 1. Molecular structure of $[Mo(SnCl_3)_2(CO)_2(NCEt)_3]$ **4**.

The structure of compound **4**, is shown in Fig. 1 with the atom-numbering scheme. Table 3 gives a summary of the crystal data and refinement obtained for **4**. The principal interatomic bond distances and angles are presented in Table 4.

The geometry of the coordination sphere of molybdenum atom in **4** approximates that of the 4:3 piano stool structure identified in several molybdenum(II) complexes ($[Mo(CNPh)_7]^{2+}$ [39], $[Mo_2Cl_3(CO)_4\{P(OMe)_3\text{-}\}_4]^+$ [40] and $[MoBr(CO)_3$(1,4,7-triazacyclononane)$]^+$ [41]. In this description the tetragonal base is defined by two carbon atoms, Mo–C = 1.981 Å (average) and two tin atoms, Mo–Sn = 2.693 Å (average). In

Table 4
Bond lengths (Å) and bond angles (°) for $[Mo(SnCl_3)_2(CO)_2(NCEt)_3]$ **4**

Bond lengths (Å)			
Mo–C(1′)	1.984(9)	Sn(1)–Cl(2)	2.334(2)
Mo–C(2′)	1.978(8)	Sn(1)–Cl(3)	2.339(2)
Mo–N(1)	2.179(6)	Sn(2)–Cl(4)	2.342(3)
Mo–N(2)	2.201(6)	Sn(2)–Cl(5)	2.342(3)
Mo–N(3)	2.158(7)	Sn(2)–Cl(6)	2.313(3)
Mo–Sn(1)	2.6864(9)	N(1)–C(1)	1.135(8)
Mo–Sn(2)	2.6989(9)	N(2)–C(4)	1.106(9)
Sn(1)–Cl(1)	2.334(2)	N(3)–C(7)	1.150(9)
Bond angles (°)			
C(1′)–Mo–C(2′)	105.0(3)	N(2)–Mo–Sn(2)	94.3(2)
C(1′)–Mo–N(1)	130.1(3)	Sn(1)–Mo–Sn(2)	129.10(3)
C(1′)–Mo–N(2)	81.3(3)	Cl(1)–Sn(1)–Cl(3)	98.95(11)
C(1′)–Mo–N(3)	142.4(3)	Cl(1)–Sn(1)–Cl(2)	98.37(9)
C(2′)–Mo–N(1)	99.5(2)	Cl(2)–Sn(1)–Cl(3)	98.61(11)
C(2′)–Mo–N(2)	169.7(3)	Cl(2)–Sn(1)–Mo	119.85(7)
C(2′)–Mo–N(3)	89.3(3)	Cl(1)–Sn(1)–Mo	118.65(7)
N(1)–Mo–N(2)	81.9(2)	Cl(3)–Sn(1)–Mo	118.11(7)
N(1)–Mo–N(3)	79.3(2)	Cl(4)–Sn(2)–Cl(5)	98.26(13)
N(2)–Mo–N(3)	80.9(2)	Cl(4)–Sn(2)–Cl(6)	98.61(12)
C(1′)–Mo–Sn(1)	69.3(2)	Cl(5)–Sn(2)–Cl(6)	99.0(2)
C(2′)–Mo–Sn(1)	77.5(2)	Cl(4)–Sn(2)–Mo	112.74(7)
N(1)–Mo–Sn(1)	74.8(2)	Cl(5)–Sn(2)–Mo	115.20(6)
N(1)–Mo–Sn(2)	154.4(2)	Cl(6)–Sn(2)–Mo	128.06(11)
N(2)–Mo–Sn(1)	112.6(2)	C(1)–N(1)–Mo	173.4(6)
N(3)–Mo–Sn(1)	148.3(2)	C(4)–N(2)–Mo	177.0(7)
N(3)–Mo–Sn(2)	75.1(2)	C(7)–N(3)–Mo	177.7(5)
C(1′)–Mo–Sn(2)	73.6(2)	O(1)–C(1′)–Mo	172.9(8)
C(2′)–Mo–Sn(2)	80.0(2)	O(2)–C(2′)–Mo	178.4(6)

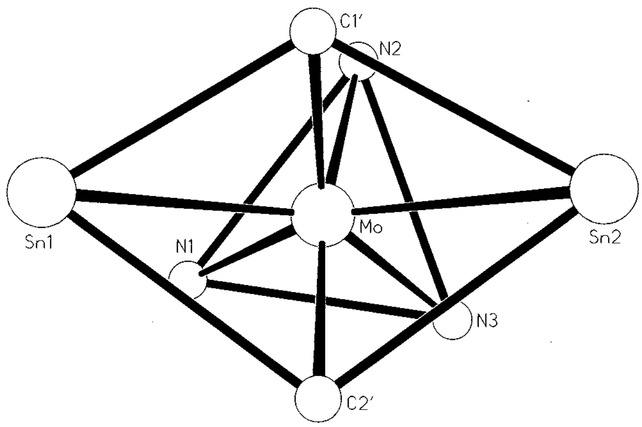


Fig. 2. Projection of the coordination sphere of Mo on the trigonal base illustrating the 4:3 geometry of **4**. Lines joining the atoms are drawn to define the planes. The angle between tetragonal and trigonal base is 4.6(2)°.

the trigonal base are three nitrogen atoms with a mean Mo–N bond length of 2.179(6), 2.201(6) and 2.158(7) Å and *cis* N–Mo–N bond angles 81.9(2), 80.9(2) and 79.3(2)°. The angle between tetragonal and trigonal base is 4.6(2)° confirming the 4:3 geometry [42]. One atom (N(2)) of the trigonal base and one atom (C(1′)) of the tetragonal base almost overlap (Fig. 2).

The Mo–Sn distance of 2.699(1) and 2.686(1) Å is comparable with those noted for other Mo–Sn compounds, e.g. for $[MoCl(SnCl_3)(CO)_3(C_4H_{10}S_2)](CH_2Cl_2)$ 2.688(2) Å [26], $[MoCl(MeSnCl_2)(CO)_3(C_{10}H_8N_2)]$ 2.753(3) Å [37], $[Mo(SnCl_3)(CO)_4(dppe)]^+$ 2.729(4) Å [38], $[MoCl(SnBuCl_2)(CO)_2\{P(OMe)_3\}_3]$ 2.774(1) Å [12,13] and $[Mo(SnBuCl_2)\{S_2P(OEt)_2\}(CO)_2\{P(OMe)_3\}_2]$ 2.709(7) Å [14]. The Mo–Sn bond is short compared to the sum of the relevant covalent radii of 3.00 Å [43,44]. 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 [32,45].

Acknowledgements

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

References

[1] T. Szymańska-Buzar, J. Mol. Catal. 68 (1991) 177.
[2] T. Szymańska-Buzar, J. Mol. Catal. 93 (1994) 137.
[3] T. Szymańska-Buzar, J. Mol. Catal. A: Chem. 123 (1997) 113.
[4] R. Kummer, W.A.G. Graham, Inorg.Chem. 7 (1968) 310.
[5] K. Edgar, B.F.G. Jonson, J. Lewis, S.B. Wild, J. Chem. Soc. A (1968) 2851.
[6] M. Iglesias, A. Lorente, C. Del Pino, A. Santos, J. Organomet. Chem. 256 (1983) 73.
[7] A. Bell, R.A. Walton, J. Organomet.Chem. 290 (1985) 341.
[8] M. Panizo, M. Cano, J. Organomet. Chem. 287 (1985) 221.
[9] P.K. Baker, A. Bury, J. Organomet. Chem. 359 (1989) 189.
[10] P.K. Baker, A. Bury, Polyhedron 8 (1989) 917.
[11] P.K. Baker, A.J. Quinlan, Inorg. Chim. Acta 162 (1989) 179.
[12] D. Miguel, J.A. Pérez-Martinez, V. Riera, S. Garcia-Granda, Polyhedron 10 (1991) 1717.
[13] D. Miguel, J.A. Pérez-Martinez, V. Riera, S. Garcia-Granda, J. Organomet. Chem. 455 (1993) 121.
[14] G. Barrado, D. Miguel, J.A. Pérez-Martinez, V. Riera, S. Garcia-Granda, J. Organomet. Chem. 463 (1993) 127.
[15] M. Cano, M. Panizo, J.A. Campo, J. Tornero, N. Menéndez, J. Organomet. Chem. 463 (1993) 121.
[16] M. Cano, J.A. Campo, M. Panizo, Polyhedron 16 (1997) 1095.
[17] D. Miguel, J.A. Pérez-Martinez, V. Riera, S. Garcia-Granda, Angew. Chem. Int. Ed. Engl. 31 (1992) 76.
[18] T. Szymańska-Buzar, T. Głowiak, Polyhedron (in press).
[19] T. Szymańska-Buzar, T. Głowiak, J. Organomet. Chem. 564 (1998) 143.
[20] G.R. Dobson, M.F. Amr El Sayed, I.W. Stolz, R.K. Sheline, Inorg. Chem. 1 (1961) 526.
[21] C.J. Simionescu, V. Percec, S. Dumitrescu, J. Polym. Sci. Polym. Chem. 15 (1977) 2497.
[22] KUMA KM4 Software, User's Guide, Version 3.1, KUMA Diffraction, Wrocław, Poland, 1989.
[23] N. Walker, D. Stuart, Acta Crystallogr. Sect. A 39 (1983) 158.
[24] G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467.
[25] G.M. Sheldrick, SHELXL-93. Program for the refinement of crystal structure. University of Göttingen, Germany, 1993.
[26] R.A. Anderson, F.W.B. Einstein, Acta Crystallogr. Sect. B 32 (1976) 966.
[27] N. Ohkaku, K. Nakamoto, Inorg. Chem. 12 (1973) 2440.
[28] R. Colton, I.B. Tomkins, Aust. J. Chem. 19 (1966) 1143.
[29] J.A. Bowden, R. Colton, Aust. J. Chem. 21 (1968) 2657.
[30] F.A. Cotton, L.R. Falvello, J.H. Meadows, Inorg. Chem. 24 (1985) 514.
[31] T. Szymańska-Buzar, T. Głowiak, J. Organomet. Chem. 489 (1995) 207.
[32] W. Petz, Chem. Rev. 86 (1986) 1019 and references therein.
[33] E.M. Amstrong, P.K. Baker, M.G.B. Drew, J. Organomet. Chem. 336 (1987) 377.
[34] E.M. Amstrong, P.K. Baker, M.G.B. Drew, Organometallics 7 (1988) 313.
[35] J.L. Templeton, B.C. Ward, J. Am. Chem. Soc. 102 (1980) 3288.
[36] W.-Y. Yeh, S.-M. Pengband, G.-H. Lee, J. Chem. Soc. Chem. Commun. (1993) 1056.
[37] M. Elder, D. Hall, Inorg. Chem. 8 (1969) 1268.
[38] F.W.B. Einstein, J.S. Field, J. Chem. Soc. Dalton Trans. (1975) 1628.
[39] J.C. Dewan, S.J. Lippard, Inorg. Chem. 21 (1982) 1682.
[40] M.G.B. Drew, J.D. Wilkins, J. Chem. Soc. Dalton Trans. (1975) 1984.
[41] P. Chaudhuri, K. Wieghardt, Y.-H. Tsai, C. Krüger, Inorg. Chem. 23 (1984) 427.
[42] M. Melnik, P. Sharrock, Coord. Chem. Rev. 65 (1985) 49.
[43] F.C. Wilson, D.P. Shoemaker, J. Chem. Phys. 27 (1957) 809.
[44] D.H. Olson, R.E. Rundle, Inorg. Chem. 2 (1963) 1310.
[45] E. O'Connor, E.R. Corey, J. Am. Chem. Soc. 89 (1967) 3930.