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Organometallic derivatives of multidentate phosphines [*o*-(methylthio)phenyl]diphenylphosphine and bis(*o*-(methylthio)phenyl(phenylphosphine: preparation and characterization of group 6 metal carbonyl derivatives

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Abstract

Heterodonor phosphines [*o*-(methylthio)phenyl]diphenylphosphine and bis[*o*-(methylthio)phenyl]phenylphosphine react with group 6 metal carbonyls to form chelate complexes with bidentate bonding through P and S atoms. Only $Cr(CO)_6$ forms also monodentate derivative with [*o*-(methylthio)phenyl]diphenylphosphine. The complexes are characterized by X-ray crystallography, ^{1}H-, ^{13}C-$\{^{1}H\}$ and ^{31}P-$\{^{1}H\}$-NMR spectroscopy, IR spectroscopy, and elemental analyses. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Carbonyl; Complex; Heterodonor ligand; Phosphine; Sulfur

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1. Introduction

Heterodonor ligands form one important field in the developement of new homogeneous catalysts. For that purpose, the co-ordination chemistry of such ligands has to be studied. In this work we report the preparation and charaterization of a series of group 6 chelate complexes with thioether type phosphorus-sulfur donor ligands [*o*-(methylthio)phenyl]diphenylphosphine (PS) and bis[*o*-(methylthio)phenyl]phenylphosphine (PSS). Characterization has been performed with ^{1}H-, ^{13}C-$\{^{1}H\}$- and ^{31}P-$\{^{1}H\}$-NMR spectroscopy, IR spectroscopy, X-ray crystallography and elemental analysis.

Group 6 phosphinous pentacarbonyl complexes are widely studied [1]. Several reports have also been published concerning bidentate phosphorus–sulfur bound group 6 tetracarbonyl complexes [2–21]. Most of them contain five membered chelate ring with double bond, for example $M(CO)_4(P(Ph)_2CH_2P(Ph)_2{=}S)$ (M = Cr, Mo, W) [3]. Corresponding structures with four membered chelate rings are also known, e.g. $[M(CO)_4(P(Ph_2)C\{N(CH_3)_2\}{=}S)]$ [4]. There are only a few examples of structures containing thioether type sulfur atom in the chelate ring: $[Mo(CO)_4(P(Ph)_2CH_2CH_2SCH_3)]$, $[Mo(CO)_4(P(Ph)_2CH_2CH_2S(CH_3)_2)]$ [5,6] and $[Cr(CO)_4(P(Ph)_2C\{=P(Ph)_3\}SPh)]$ [7].

2. Experimental

All reactions were carried out with standard Schlenk tube techniques under a nitrogen atmosphere. Solvents and commercial reagents were used as received. The chromium, molybdenum and tungsten hexacarbonyl

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were obtained from Aldrich. Trimethylamine *N*-oxide dihydrate was obtained from Fluka Chemica, dichloromethane (99.8%) from FF Chemicals and hexane (95%) from Lab Scan. The ligands [*o*-(methylthio)phenyl]diphenylphosphine (PS) and bis[*o*-(methylthio)phenyl]phenylphosphine (PSS) were prepared according to literature methods [22].

2.1. NMR and IR spectra

^{1}H-NMR spectra were recorded on a Bruker AM 200 spectrometer (200.1 MHz) with chemical shifts (δ) in ppm to high frequency of $SiMe_4$. ^{13}C-{^{1}H}-, ^{31}P-{^{1}H}- and HSQC-NMR spectra were recorded at Bruker DPX 400 spectrometer. In ^{13}C-{^{1}H}-NMR spectra (100.6 MHz) $CDCl_3$ was set to 77.0 ppm, and in ^{31}P-{^{1}H}-NMR spectra (162.0 MHz) the chemical shifts were in ppm to high frequency of 85% H_3PO_4 (external standard). All spectra were recorded at room temperature. $CDCl_3$ (D 99.8, 0.03% TMS, CIL) was used as solvent. IR spectra were recorded on a Bruker IFS 66 spectrometer in dichloromethane (99.8%, 4×10^{-3} M solutions).

2.2. Elemental analyses

C, H and S analyses were performed with a Perkin–Elmer 2400 CHNS analyser.

2.3. X-ray crystallography

All data were collected at 20°C on an Enraf–Nonius KappaCCD diffractometer with a kcd (Enraf–Nonius) or Collect [23] software using ϕ- or combined ϕ–ω-scan and Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Cell refinement and data reduction were done with Denzo and Scalepack programs [24]. The structures were solved by direct methods and successive difference Fourier synthesis using the SHELXS86 or SHELXS-97 program [25,26]. The structure refinement was carried out with the SHELXL-97 program [27]. All non-hydrogen atoms were refined anisotropically. Methyl and phenyl pro-

Table 1
Crystal data and collection parameters for complexes **1**–**7**

	1	**2**	**3**	**4**	**5**	**6**	**7**
Formula	$Cr(CO)_5(PS)$	$Cr(CO)_4(PS)$	$Mo(CO)_4(PS)$	$W(CO)_4(PS)$	$Cr(CO)_4(PSS)$	$Mo(CO)_4(PSS)$	$W(CO)_4(PSS)$
Formula weight (g mol^{-1})	500.41	472.40	516.34	604.25	518.48	562.42	650.33
Colour, habit	Yellow	Yellow	Yellow	Yellow	Yellow	Yellow	Yellow
Crystal size (mm)	$0.3\times0.2\times0.1$	$0.3\times0.1\times0.1$	$0.3\times0.3\times0.2$	$0.3\times0.3\times0.2$	$0.4\times0.4\times0.2$	$0.3\times0.2\times0.2$	$0.4\times0.2\times0.2$
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Ortorhombic	Monoclinic
Space group	$P2_1/c$	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$	$P2_1/c$	$P2_12_12_1$	$P2_1/c$
a (Å)	9.729(2)	9.352(2)	9.464(2)	9.432(2)	9.777(2)	11.253(2)	9.886(2)
b (Å)	10.687(2)	10.456(2)	10.576(2)	10.497(2)	15.177(3)	13.129(3)	15.166(3)
c (Å)	23.125(3)	12.155(2)	12.296(2)	12.251(2)	16.331(3)	16.329(3)	16.477(3)
a (°)	90	110.30(3)	110.17(3)	110.18(3)	90	90	90
b (°)	99.72(3)	98.96(3)	98.12(3)	98.42(3)	98.21(3)	90	97.96(3)
g (°)	90	90.92(3)	91.46(3)	91.67(3)	90	90	90
V (Å^3)	2369.9(8)	1098.0(4)	1140.0(4)	1118.8(4)	2398.4(8)	2412.5(8)	2446.6(8)
Z	4	2	2	2	4	4	4
m (mm^{-1})	0.670	0.715	0.763	5.338	0.746	0.811	4.985
Calculated density (g cm^{-3})	1.403	1.429	1.504	1.788	1.436	1.549	1.766
Scan range θ (°)	4.16–25	2.92–25	4.12–26.29	4.15–26.38	1.84–26.00	2.94–25	2.96–24.99
h range	$-11\rightarrow0$	$-11\rightarrow0$	$0\rightarrow11$	$0\rightarrow11$	$-12\rightarrow12$	$-13\rightarrow13$	$0\rightarrow11$
k range	$0\rightarrow12$	$-12\rightarrow12$	$-12\rightarrow13$	$-13\rightarrow13$	$-18\rightarrow18$	$-15\rightarrow15$	$0\rightarrow18$
l range	$-27\rightarrow27$	$-14\rightarrow14$	$-15\rightarrow14$	$-15\rightarrow15$	$-20\rightarrow20$	$-19\rightarrow19$	$-19\rightarrow19$
Number of unique reflections	3943	3586	1841	4082	4713	4246	3923
Number of observed data ($I>2\sigma(I)$)	2538	1697	1492	3478	3723	3187	3097
Number of parameters	290	272	272	272	290	290	290
R%	9.99	8.14	3.23	4.10	3.73	3.00	7.08
wR_2%	24.25	16.62	6.72	10.00	8.60	4.64	17.47
GOOF	1.150	1.019	1.059	1.020	1.059	0.936	1.177

Table 2
Metal–carbon, metal–phosphorus, metal–sulphur and carbon–oxygen bond lengths (Å) in compounds **1**–**7**

	1	**2**	**3**	**4**	**5**	**6**	**7**
M(1)–C(1)	1.850(11)	1.846(9)	1.996(6)	1.977(8)	1.851(3)	1.963(4)	1.99(2)
M(1)–C(2)	1.895(11)	1.831(9)	1.946(6)	1.949(8)	1.843(3)	1.967(4)	1.99(2)
M(1)–C(3)	1.898(11)	1.893(9)	2.043(6)	2.026(8)	1.878(3)	2.023(4)	2.03(2)
M(1)–C(4)	1.885(11)	1.880(9)	2.037(6)	2.032(9)	1.900(3)	2.019(5)	2.01(2)
M(1)–C(5)	1.886(10)						
M(1)–P(1)	2.431(3)	2.354(2)	2.4980(14)	2.484(2)	2.3628(7)	2.5223(9)	2.482(4)
M(1)–S(1)		2.394(2)	2.5444(15)	2.527(2)	2.3995(8)	2.5370(10)	2.528(4)
C(1)–O(1)	1.153(12)	1.148(9)	1.147(7)	1.158(9)	1.151(3)	1.161(4)	1.14(2)
C(2)–O(2)	1.138(12)	1.163(8)	1.170(7)	1.155(9)	1.151(3)	1.154(4)	1.12(2)
C(3)–O(3)	1.146(12)	1.146(8)	1.142(6)	1.140(9)	1.144(3)	1.141(4)	1.16(2)
C(4)–O(4)	1.140(12)	1.146(9)	1.149(7)	1.138(10)	1.143(3)	1.154(4)	1.14(2)
C(5)–O(5)	1.145(12)						

tons were placed in idealized positions with C–H distances 0.96 and 0.93 Å and isotropic temperature factors $U(H) = 1.5 \cdot U(C)$and $U(H) = 1.2 \cdot U(C)$. Crystallographic data are summarized in Table 1 and selected bond lengths and angles in Tables 2 and 3.

2.4. Synthetic procedure

Metal carbonyl, ligand and trimethylamine *N*-oxide dihydrate (1:1:2 molar ratio in case of PS and 1:1:3 molar ratio in case of PSS ligand) were dissolved in dichloromethane and the resulting yellow solution was stirred in room temperature for 3 h. The solvent was removed in vacuo and product was purified by column chromatography using silica gel 60 as stationary phase. Height of silica was about 15 cm. A mixture of dichloromethane and hexane was used as eluent (1:1 in case of PS and 2:1 in case of PSS complexes). The first colourless fraction was unreacted metal carbonyl and the second, yellow fraction, was the complex. The fractions of the complexes **1** and **2**, which were prepared simultaneously, were difficult to isolate from each other. Complex **1**, however, was eluted slightly faster than **2**. Yellow crystals were grown from dichloromethane–hexane mixtures by slow evaporation at room temperature.

2.4.1. Preparation of [Cr(CO)$_5$(PS)] (1) and [Cr(CO)$_4$(PS)] (2)

Chromium hexacarbonyl (1.04 mmol, 228 mg), [*o*-(methylthio)phenyl]diphenylphosphine (1.04 mmol, 319 mg) and trimethylamine *N*-oxide dihydrate (2.07 mmol, 230 mg) were dissolved in 20 ml of dichloromethane. A mixture of **1** and **2** was obtained (402 mg). After separation with column chromatography complexes were isolated as yellow (**1**) and yellow–green (**2**) solids.

Almost pure **1** was gained by performing both the reaction and the separation at low temperature (ice bath) with 1 h reaction time. Unfortunately, the yield (8%) and the reproducibility of the reaction were low. Longer reaction times led to formation of the complex **2** as well. Pure **2** was gained by refluxing the reaction mixture for 3 h (yield 60%).

1: IR (CH_2Cl_2)(cm^{-1}): ν(CO) 2062(s), 1983(m), 1937 (vs). **2:** Anal. Found C, 58.85; H, 3.80; S, 7.38. $CrC_{23}H_{17}O_4PS$ Anal. Calc.: C, 58.49; H, 3.63; S, 6.79%. IR (CH_2Cl_2): ν(CO) 2015(s), 1917(sh), 1899(vs), 1869(s) cm^{-1}.

2.4.2. Preparation of [Mo(CO)$_4$PS)] (3)

Molybdenum hexacarbonyl (0.979 mmol, 259 mg), [*o*-(methylthio)phenyl]diphenylphosphine (0.979 mmol, 302 mg) and trimethylamine *N*-oxide dihydrate (1.96 mmol, 218 mg) were dissolved in 30 ml of dichloromethane. After chromatographic separation the yield was 390 mg, 77%. Anal. Found C, 53.40; H, 3.10; S,6.04. $MoC_{23}H_{17}O_4PS$ Anal. Calc.: C, 53.51; H, 3.32; S,6.21%. IR (CH_2Cl_2): ν(CO) 2024(s), 1918(sh), 1909(vs), 1877(s) cm^{-1}.

2.4.3. Preparation of [W(CO)$_4$(PS)] (4)

Tungsten hexacarbonyl (0.741 mmol, 261 mg), [*o*-(methylthio)phenyl]diphenylphosphine (0.741 mmol, 229 mg) and trimethylamine *N*-oxide dihydrate (0.741 mmol, 83 mg) were dissolved in 17 ml of dichloromethane. After chromatographic separation the yield was 239 mg, 53%. Anal. Found C, 45.79; H, 2.94; S, 5.49. $WC_{23}H_{17}O_4PS$ Anal. Calc.: C, 45.72; H, 2.84; S, 5.31%.

IR (CH_2Cl_2): ν(CO) 2020(s), 1911(sh), 1898(vs), 1872(s) cm^{-1}.

2.4.4. Preparation of [Cr(CO)$_4$(PSS)] (5)

Chromium hexacarbonyl (1.00 mmol, 221 mg), bis[*o*-(methylthio)phenyl]phenylphosphine (1.00 mmol, 355 mg) and trimethylamine *N*-oxide dihydrate (3.01 mmol, 334 mg) were dissolved in 26 ml of dichloromethane. After chromatographic separation the yield was 303 mg, 58%. Anal. Found C, 55.53; H, 3.70; S, 12.17. $CrC_{24}H_{19}O_4PS_2$ Anal. Calc.: C, 55.60; H, 3.69;

Table 3
Selected bond angles (°) for compounds **1**–**7**

	1	**2**	**3**	**4**	**5**	**6**	**7**
P(1)–M(1)–C(1)	176.3(3)	173.5(3)	170.8(2)	171.3(2)	176.42(8)	171.21(12)	174.5(5)
P(1)–M(1)–C(2)	90.8(4)	96.4(3)	98.00(2)	97.6(2)	93.77(7)	97.43(11)	94.6(5)
P(1)–M(1)–C(3)	87.7(3)	92.2(3)	92.3(2)	87.4(2)	91.16(8)	93.58(11)	91.3(6)
P(1)–M(1)–C(4)	95.2(3)	87.8(2)	87.8(2)	92.3(2)	91.32(8)	93.53(12)	90.3(5)
P(1)–M(1)–C(5)	92.7(4)						
P(1)–M(1)–S(1)		80.76(8)	77.48(5)	77.86(5)	81.35(3)	78.08(3)	78.62(13)
C(1)–M(1)–C(2)	88.5(5)	90.0(4)	91.1(2)	91.0(3)	89.79(10)	91.3(2)	90.9(6)
C(1)–M(1)–C(3)	88.8(4)	89.1(4)	89.2(3)	91.4(3)	89.06(11)	87.5(2)	88.5(7)
C(1)–M(1)–C(4)	88.2(5)	90.9(4)	90.8(2)	89.0(3)	88.21(11)	86.1(2)	89.5(7)
C(1)–M(1)–C(5)	88.5(5)						
C(2)–M(1)–C(3)	92.9(5)	89.4(4)	89.4(2)	90.1(3)	91.61(11)	88.01(13)	91.8(7)
C(2)–M(1)–C(4)	83.6(5)	90.3(4)	89.7(2)	89.4(3)	92.36(11)	86.88(15)	93.1(7)
C(2)–M(1)–C(5)	173.5(5)						
C(3)–M(1)–C(4)	175.5(4)	179.7(4)	179.1(2)	179.4(2)	175.17(10)	171.7(2)	174.7(7)
C(3)–M(1)–C(5)	92.7(5)						
C(4)–M(1)–C(5)	90.6(5)						
S(1)–M(1)–C(1)		92.9(3)	93.5(2)	93.5(2)	95.09(8)	93.20(12)	95.9(5)
S(1)–M(1)–C(2)		177.2(3)	175.3(2)	175.3(2)	174.77(8)	175.17(11)	173.1(5)
S(1)–M(1)–C(3)		90.5(2)	91.91(15)	88.6(2)	86.62(8)	90.49(11)	89.6(5)
S(1)–M(1)–C(4)		89.8(2)	89.00(2)	91.8(2)	89.66(8)	95.11(11)	85.8(5)

S, 12.37%. IR (CH_2Cl_2): ν(CO) 2013(s), 1917(sh), 1894(vs), 1870(s) cm^{-1}.

2.4.5. *Preparation of [Mo(CO)$_4$(PSS)]* **(6)**

Molybdenum hexacarbonyl (0.919 mmol, 243 mg), bis[*o*-(methylthio)phenyl]phenylphosphine (0.919 mmol, 326 mg) and trimethylamine *N*-oxide dihydrate (2.76 mmol, 307 mg) were dissolved in 30 ml of dichloromethane. After chromatographic separation the yield was 365 mg, 71%. Anal. Found C, 51.11; H, 3.23; S, 11.36. $MoC_{24}H_{19}O_4PS_2$ Anal. Calc: C, 51.25; H, 3.41; S, 11.40%. IR (CH_2Cl_2)(cm^{-1}): ν(CO) 2022(s), 1918(sh), 1904(vs), 1877(s).

2.4.6. *Preparation of [W(CO)$_4$(PSS)]* **(7)**

Tungsten hexacarbonyl (0.691 mmol, 243 mg), bis[*o*-(methylthio)phenyl]phenylphosphine (0.691mmol, 245 mg) and trimethylamine *N*-oxide dihydrate (2.072 mmol, 230 mg) were dissolved in 24 ml of dichloromethane (24 ml). After chromatographic separation the yield was 323 mg, 72%. Anal. Found C, 44.36; H, 2.98; S, 9.56. $WC_{24}H_{19}O_4PS_2$ Anal. Calc: C, 44.32; H, 2.94; S, 9.86%. IR (CH_2Cl_2): ν(CO) 2018(s), 1911(sh), 1894(vs), 1873(s) cm^{-1}.

3. Results and discussion

3.1. *Reactions*

The reaction of PS and PSS ligands with $M(CO)_6$ (M = Cr, Mo, W) in the presence of $Me_3NO{\cdot}2H_2O$ in dichloromethane at room temperature produced yellow, crystalline bidentate complex [M(CO)$_4$(ligand)]. Only the PS complex of $Cr(CO)_6$ was formed as a mixture of mono- and bidentate complexes. Synthesis was modified from a reported method [28], where $Me_3NO{\cdot}2H_2O$ was used to facilitate CO-release from metal carbonyls.

Molybdenum and tungsten carbonyls reacted more readily than chromium carbonyl. In the case of PS derivatives of $Cr(CO)_6$, some monodentate phosphorus bound complex [Cr(CO)$_5$(PS)] was formed together with bidentate one, and refluxing was needed to produce only bidentate analogue. In the case of PSS derivatives of $Cr(CO)_6$, some signs of the monodentate product was detected by the methyl signal intensities in ^{1}H-NMR, but only the bidentate complex could be isolated.

The higher tendency of Mo and W to form bidentate compounds can be explained in terms of atomic radius [1] or kinetic effects.

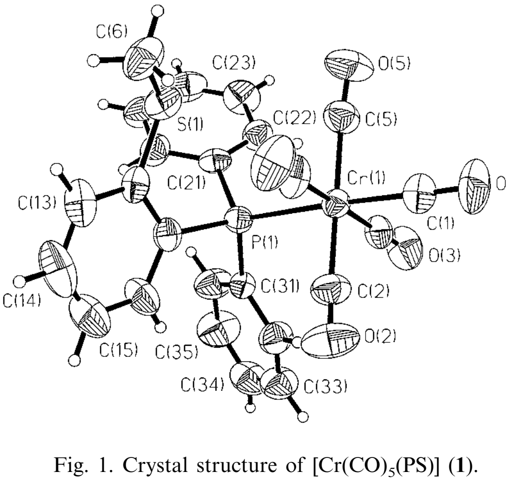

Fig. 1. Crystal structure of [Cr(CO)$_5$(PS)] (**1**).

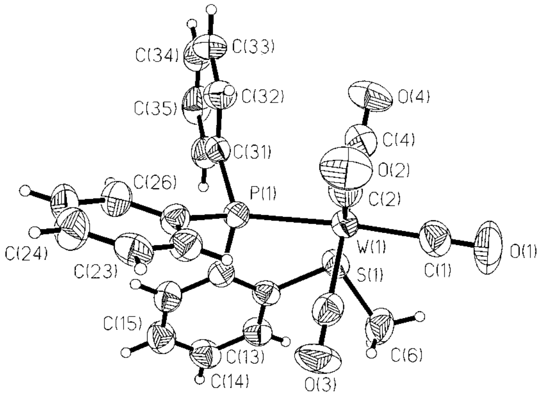

Fig. 2. Crystal structure of $[W(CO)_4(PS)]$ (**4**). The structures and numbering of $[Cr(CO)_4(PS)]$ (**2**) and $[Mo(CO)_4(PS)]$ (**3**) are similar.

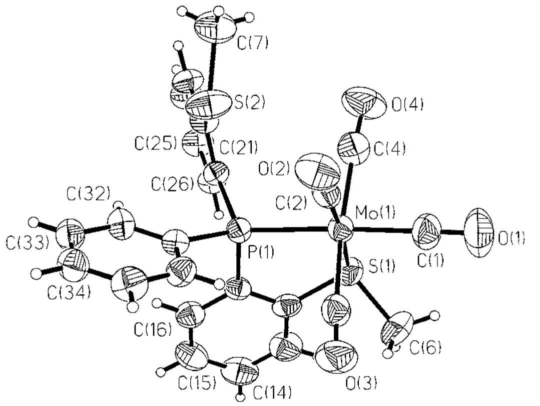

Fig. 3. Crystal structure of $[Mo(CO)_4(PSS)]$ (**6**). The structures and numbering of $[Cr(CO)_4(PSS)]$ (**5**) and $[W(CO)_4(PSS)]$ (**7**) are similar.

No tridentate products were observed for PSS ligands. For example, an unsuccessful attempt was made to prepare tridentate product from bidentate complex **7** by refluxing it in THF for 3 h. A couple of tridentate PSS-bound Mo and W derivates have been published: for Mo mononuclear tridentate complex with cyclic ligand 1-phenyl-1-phospha-4,7-dithiacyclononane [29], and for both Mo and W binuclear complexes $[\{M(CO)_3\}_2\ \{\mu\text{-}P(C_6H_4SR\text{-}2)_2\ (CH_2)_n\ P((C_6H_4SR\text{-}2)_2\}]$ ($n = 1$ and R = Me or $n = 2$ and R = Me,Pr) [30,31].

Some attempts were made to prepare also derivates with potentially tetradentate ligand tris[*o*-(methylthio)phenyl]phosphine, but no complexes could be isolated with the used method, although some reaction seemed to occur.

3.2. *Crystal structures*

The structures of complexes **1**–**7** was determined by single-crystal X-ray diffraction study. Tables 2 and 3 show selected bond distances and angles. The crystal structures are shown in Figs. 1–3. The structures show octahedral symmetry of the ligands around the metal center. The phosphine ligand has replaced one or two of the carbonyl ligands.

Comparison of bond lengths between compounds **1**–**7** show no unexpected values. M–P bond length ranged from 2.354 (**2**) to 2.522 Å (**6**), and M–S bond length ranged from 2.394 (**2**) to 2.544 Å (**3**). Mo–P bonds are slightly longer than W–P bonds, which has been observed previously for $[M(CO)_5(PPh_3)]$ complexes [32]. M–P bond length of the monodentate complex **1** is 0.08 Å longer compared to bidentate analogue **2**. The M–C bond distances are closely similar to the values of the binary carbonyl compounds (Average M–C and bond values are 1.909 [33], 2.059 [34] and 2.059 [35] for $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$, respectively). In the mono and bidentate chromium derivatives **1** and **2** the M–C bond lengths are almost identical, only M(1)–C(2) bond is 0.064 Å longer in the monodentate complex, showing that sulfur coordination causes shortening of the M–C bond *trans* to the sulfur. Complexation causes some changes in bond angles. In bidentate complexes the P(1)–M(1)–S(1) angle is less than 90° ranging from 77.48° (**3**) to 81.35(3)

Table 4
^{1}H-NMR chemical shifts (ppm) for complexes **1**–**7**[a]

	$CH_3(6)$	H(15)	H(16)	–	–	H(13,14,22–36)
PS	2.43	7.04	6.76	–	–	7.32
1	2.44	6.95–7.70[b]	6.95–7.70[b]	–	–	6.95–7.70[b]
2	2.70	7.53	7.80	–	–	7.35–7.48[b]
3	2.76	7.51	7.81	–	–	7.35–7.45[b]
4	2.95	7.51	7.83	–	–	7.32–7.45[b]
	$CH_3(6)$, $CH_3(7)$	H(15)	H(16)	H(25)	H(26)	H(13,14,23,24,32–36)
PSS	2.45	7.06	6.74	7.06	6.74	7.30
5	2.67, 2.44	7.18–7.79[b]	7.72	7.00	6.17	7.18–7.79[b]
6	2.73, 2.44	7.19–7.70[b]	7.75	7.01	6.28	7.19–7.70[b]
7	2.92, 2.45	7.28–7.78[b]	7.78	7.01	6.25	7.28–7.78[b]

[a] Protons are numbered after carbons in Figs. 1–3.

[b] Resonances could not be interpreted more precisely because of overlapping.

Table 5
^{13}C-{^{1}H}-NMR chemical shifts (ppm)^{a} and coupling constants (Hz) for complexes **1**–**4**^{b}

	CH_3(6)	C(11)	C(12)	C(13)	C(14)	C(15)	C(16)	C(21,31)^{c}	C(22,26,32,36)^{c}	C(23,25,33,35)^{c}	C(24,33)^{c}	CO(1)	CO(2)	CO(3 and 4)
PS	17.24	136.77 (9.9)^{d}	143.67 (27.5)^{e}	126.62	129.33	125.35	133.91	136.25 (9.8)	134.01 (19.9)^{e}	128.57 (6.8)^{f}	128.82			
1	18.33	132.21 (36.0)^{d}	134.70 (36.1)^{e}	128.40	130.11	125.36 (5.7)^{f}	132.14 (8.0)^{e}	134.99 (36.1)^{d}	133.44 (11.2)^{e}	128.58 (9.1)^{f}	128.62	221.7	217.0^{g} (2.5)^{e}	
2	30.55	136.62 (33.9)^{d}	146.09 (35.5)^{e}	129.89	133.70	131.01	130.50 (10.1)^{e}	135.94 (37.5)^{d}	132.06 (11.1)^{e}	128.69 (8.5)^{f}	128.72	226.9	228.1 (11.0)^{e}	218.1 (11.0)^{e}
3	32.36	136.44 (33.3)^{d}	144.73 (33.1)^{e}	129.92	134.30	131.11	131.58 (9.6)^{e}	136.51 (35.8)^{d}	132.30 (12.9)^{e}	128.63 (9.3)^{f}	128.92	215.8 (27.5)^{e}	218.3 (8.3)^{e}	207.5 (8.3)^{e}
4	34.13	137.31 (38.4)^{d}	145.79 (31.4)^{e}	130.14	134.46	131.39	131.39 (9.6)^{e}	135.71 (41.5)^{d}	132.29 (13.4)^{e}	128.66 (9.1)^{f}	128.99	207.7 (30.3)^{e}	208.6 (5.5)^{e}	201.0 (5.5)^{e}

[a] Resonance peaks are singlets if no coupling constant are reported, those with coupling constants in parentheses are doublets.
[b] Carbon atoms are numbered as in Figs. 1 and 2.
[c] Chemically and magnetically equivalent.
[d] $^{1}J_{CP}$ coupling constant.
[e] $^{2}J_{CP}$ coupling constant.
[f] $^{3}J_{CP}$ coupling constant.
[g] CO(3), CO(4) and CO(5) are similarly shielded as CO(2).

Table 6
^{13}C-{^{1}H}-NMR chemical shifts (ppm)^{a} and coupling constants (Hz) for complexes **5**–**7**^{b}

	CH_3(6), CH_3(7)	C(11)	C(12)	C(13), C(24), C(26)	C(14)	C(15)	C(16)	C(21)	C(22)	C(23)	C(25)	C(31)	C(32,36)^{c}	C(33,35)^{c}	C(34)	CO(1)	CO(2)	CO(3 and 4)
PSS	17.30	136.16 (9.6)^{d}	143.78 (28.6)^{e}	126.75, 129.34, 133.35	129.34	125.34	133.35	136.16 (9.6)^{d}	143.78 (28.6)^{e}	126.75 (3.7)^{d}	125.34	135.46 (11.2)^{d}	134.32 (20.6)^{e}	128.64 (7.6)^{f}	128.93			
5	29.40, 18.71	138.48 (31.2)^{d}	146.17 (36.2)^{e}	129.65–130.97^{g}	132.67	130.97	129.38 (5.7)^{e}	132.87 (40.2)^{d}	143.17 (13.6)^{e}	128.56	125.35 (5.2)^{f}	137.07 (37.3)^{d}	133.27 (12.9)^{e}	129.00 (10.3)^{f}	129.05	227.0	228.0 (11.4)^{e}	217.1 (12.3)^{e}, 219.5 (13.5)^{d}
6	31.38, 18.36	137.88 (32.4)^{d}	145.00 (30.8)^{e}	130.23–30.48^{g}	133.96	130.77	131.08 (8.2)^{e}	132.60 (38.0)^{d}	143.11 (13.6)^{e}	128.87	125.16 (5.5)^{f}	136.94 (36.7)^{d}	133.41 (13.7)^{e}	128.92 (10.3)^{f}	129.17	216.2 (30.3)^{e}	218.3 (5.5)^{e}	206.3 (5.5)^{e}, 208.8 (8.3)^{d}
7	33.02, 18.82	138.88 (38.5)^{d}	146.01 (30.2)^{e}	130.41–131.00^{g}	134.07	131.05	131.04 (8.3)^{e}	132.31 (42.6)^{d}	143.26 (12.4)^{e}	129.07	125.20 (6.9)^{f}	136.90 (44.0)^{d}	133.46 (13.8)^{e}	129.15 (11.0)^{f}	129.42	207.8 (30.2)^{e}	208.8 (5.5)^{e}	200.1, 202.0 (5.5)^{e}

[a] Resonance peaks are singlets if no coupling constant are reported, those with coupling constants in parentheses are doublets.
[b] Carbon atoms are numbered as in Fig. 3.
[c] Chemically and magnetically equivalent.
[d] $^{1}J_{CP}$ coupling constant.
[e] $^{2}J_{CP}$ coupling constant.
[f] $^{3}J_{CP}$ coupling constant.
[g] Resonances can not be interpreted more precisely because of overlapping.

Table 7
^{31}P-{^{1}H} chemical shifts (ppm) and ^{31}P co-ordination shifts ($\Delta\delta = \Delta\delta_{\text{complex}} - \Delta\delta_{\text{ligand}}$)

	δ(P)	$\Delta\delta$(P)
PS	−18.1	
PSS	−22.0	
1	70.5	88.6
2	84.5	102.6
3	61.9	80.0
4	51.4	69.5
5	78.3	100.3
6	55.2	77.2
7	45.7	67.7

(**5**). This induces deviations also to the other angles. In compound **1** only slight deviations from ideal octahedral symmetry can be observed.

Structures of the Mo compounds **3** and **6** are closely similar to the structure of [Mo(CO)$_4$(P(Ph)$_2$(CH$_2$)$_2$SCH$_3$)] [6]. For example the P(1)–M(1)–S(1) angles are 3.2 and 2.6° smaller in **3** and **6**, due to the different steric restrictions of the ligand, and the other angles and bond distances show only insignificant differences. Similarly the structure of **1** is closely related to the crystal structure of [Cr(CO)$_5$PPh$_3$] [32].

3.3. Spectroscopic data

^{1}H- and ^{13}C-{^{1}H}-NMR spectra of the complexes **1**–**7** are consistent with the crystal structures and can be interpreted on grounds of spectra of free ligands, decoupling experiments and HSQC spectra. The assignments of the CO resonances are based on the ^{13}C-signal intensity ratios and on the magnitude of the phosphorus coupling constants. In the ^{13}C-{^{1}H}-NMR spectra of the ligands the assignments of the aromatic carbons are based on calculated values [36] and on the known spectra of triphenylphosphine. The ^{1}H resonance peaks of ligands are intepreted with help of decoupling experiments and HSQC spectra. The ^{1}H-, ^{13}C-{^{1}H}- and ^{31}P-{^{1}H}-NMR spectra are presented in Tables 4–7.

When complexes **2**–**7** are formed, the ^{1}H- and ^{13}C-NMR shielding of the –SCH$_3$ group decreases due to coordination of sulfur to metal center. The deshielding effect increases from Cr to Mo to W. In ^{1}H-NMR also some deshielding of the aromatic protons of thioanisole is observed due to coordination of sulfur atom.

In the ^{13}C-{^{1}H}-NMR spectra of the aromatic area, shielding of the phenyl ring carbons do not change remarkably due to coordination of the ligand. There are some changes due to phosphorus coordination in the sulfur uncoordinated thioanisyl ring of complexes **1** and **5**–**7**: shielding of the carbon directly bonded to phosphorus increases about 3.3–4.6 ppm (C(11) for complex **1** and C(21) for complexes **5**–**7**), there is slight increase in shielding of C(16) for **1** and C(26) for **5**–**7**, and the small deshielding of carbons C(13) and for **1** and C(23) and for **5**–**7**. The coordination of the sulfur causes increase of the aromatic carbon frequencies by 1–6 ppm compared to shifts of free ligands. However, the chemical shift of C(11) in complexes **2**–**4** do not change, and the shift of C(16) decreases a little in all complexes. The chemical shifts of the aromatic carbons are closely similar in Cr, Mo and W analogues.

The $^1J_{\text{CP}}$ coupling constants increase clearly due to coordination of phosphorus to the metal center. The $^2J_{\text{CP}}$ coupling constants of the thioanisyl uncoordinated from sulfur decrease due to phosphorus coordination, and $^3J_{\text{CP}}$ coupling constants C(15)–P for complex **1** and C(25)–P for **5**–**7** become observable. Contrasingly, the $^2J_{\text{CP}}$ coupling constants of the sulfur coordinated thioanisyl increase and no $^3J_{\text{CP}}$ coupling constants can be observed.

The shielding of carbonyl carbons increases in order Cr < Mo < W, together with the increasing number of electrons in the metal, which is consistent with previous results [4]. The spectrum of complex **1** exhibits two carbonyl signals due to the carbonyls oriented *trans* and *cis* to phosphorus (CO (1) and CO (2–5), respectively). Spectra of bidentate complexes **2**–**4** exhibit three signals indicating the presence of three types of carbonyl signals, one trans to phosphorus (CO (1)), one *trans* to sulfur (CO (2)) and one *cis* to both phosphorus and sulfur (CO (3) and (4)). The spectra of PSS complexes **5**–**7** are in agreement with crystal structures showing four inequivalent signals, one trans to P (CO (1)), one *trans* to metal bound S (CO (2)), one *cis* to both P and S (CO (3)), and one being otherwise equal to (CO (3)), but affected by a free –SCH$_3$ group spaced near to it (CO (4), see Fig. 3).

$^2J_{\text{CP}}$ coupling constants of phosphorus bound group 6 carbonyl complexes have been found to follow a trend: for chromium complexes $|J|_{cis} > |J|_{trans}$ and for molybdenum and tungsten complexes $|J|_{cis} < |J|_{trans}$ [4,37,38]. Spectra of complexes **1**–**7** are consistent with this trend. *Trans* to P coupling constants for Mo and W complexes (**3**, **4**, **6**, **7**) are in range 27.5–30.3 Hz, while *cis* to P coupling constants are in the range 5.5–8.3 Hz. For Cr complexes (**1**, **2**, **5**), no *trans* coupling to P can be observed, while *cis* couplings are in range 2.5–13.5 Hz. Sulfur does not seem to have any *trans* influence for the coupling constant of carbonyl group.

The signals in the ^{31}P-{^{1}H}-NMR spectra move to higher frequency on coordination to the metal center. These coordination shifts ($\Delta\delta$, Table 5) decrease in the order Cr > Mo > W. This agrees with the observation that high field shift of the ^{31}P resonance should be observed as one descends in a given periodic group [39]. Similar trend has been observed with tetracarbonyl phosphinothioformamide compounds [4,8]. Thus the

^{31}P chemical shift is 2–3 ppm higher for PS complex of each metal than for PSS complex.

The ^{31}P coordination shift difference between monosubstituted chromium complex **1** and chelated complex **2** is 14 ppm. The lower shielding of **2** can be explained in terms of chelate ring contributions. The typical ^{31}P deshielding in phosphorus bound bidentate complexes is about 25–32 ppm compared to the corresponding monodentate structures [39]. It seems that deshielding effect of phosphorus–sulfur chelate ring is smaller.

IR spectrum of **1** exhibits three CO-bands at 2062, 1983 and 1937 cm^{-1}, very much like [Cr(CO)$_5$PPh$_3$] (2066, 1988, 1942 cm^{-1}) [40]. IR spectra of tetracarbonyl complexes **2**–**7** exhibit four ν(CO) bands, as should be expected for *cis*-M(CO)$_4$ complexes [8]. Stretching frequencies are in the range 1869–2024 cm^{-1}, being closely the same ($\pm$5 cm^{-1}) for PS and PSS complexes slightly changing with metal ($\pm$15 cm^{-1}). No clear trend from metal to metal can be observed.

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