Reactions of Di(1-cyclohepta-2,4,6-trienyl)sulfane, $S(C_7H_7)_2$, with Derivatives of the Hexacarbonyls, $M(CO)_6$ (M = Cr, Mo, W)

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*Dedicated to Professor Martin Jansen on the Occasion of his 60*th Birthday

Abstract. Mononuclear carbonylmetal complexes of chromium, molybdenum and tungsten containing the sulfane $S(C_7H_7)_2$ (**1**) have been obtained starting from precursors such as the THF-stabilized pentacarbonylmetal fragments, $[M(CO)_5](thf)$, the acetonitrile intermediates $M(CO)_{6-x}(CH_3CN)_x$ (x = 1, 2, 3) (M = Cr, Mo, W) or the η^4-norbornadiene complexes $M(CO)_4(C_7H_8)$ (M = Cr, Mo). In addition to the pentacarbonyls, $M(CO)_5[S(C_7H_7)_2]$ (M = Cr (**2a**), Mo (**2b**), W (**2c**)) which contain **1** unchanged as a two-electron sulfane ligand with two pending cyclohepta-2,4,6-trienyl substituents, isomeric complexes $M(CO)_5[S(CH_2Ph)(C_7H_7)]$ (M = Cr (**3a**), W (**3c**)) were obtained at higher temperatures (40−50 °C) in which one of the two organic groups has been transformed into a benzyl substituent. In the tetracarbonyls, *cis*-$M(CO)_4[S(C_7H_7)(\eta^2\text{-}C_7H_7)]$ (M = Mo (**4b**), W (**4c**)), the ligand **1** serves as an olefinic sulfane four-electron chelate ligand. The reaction of either $Mo(CO)_6$ or (mesitylene)$Mo(CO)_3$ with $S(C_7H_7)_2$ (**1**) in boiling THF leads to the sulfur-free ditropyl complex $Mo(CO)_3[(\eta^6\text{-}C_7H_7)\text{-}C_7H_7]$ (**5b**, two isomers). The ^1H and ^{13}C NMR spectra of the new complexes **2**−**4** reveal various dynamic processes including pyramidal inversion of the sulfur atom and [1,7]-sigmatropic shifts at the C_7H_7 ring. The molecular structures of **2c**, **3a**, **4b** and **4c** have been determined by X-ray crystallography.

Keywords: Chromium; Molybdenum; Tungsten; Sulfane complexes; NMR spectra; Crystal structures

Umsetzungen von Di(1-cyclohepta-2,4,6-trienyl)sulfan, $S(C_7H_7)_2$, mit Derivaten der Hexacarbonyle, $M(CO)_6$ (M = Cr, Mo, W)

Inhaltsübersicht. Einkernige Carbonylmetall-Komplexe des Chroms, Molybdäns und Wolframs mit dem Sulfan $S(C_7H_7)_2$ (**1**) wurden ausgehend von Vorstufen wie den THF-stabilisierten Pentacarbonylmetall-Fragmenten, $[M(CO)_5](thf)$, den Acetonitril-Zwischenstufen, $M(CO)_{6-x}(CH_3CN)_x$ (x = 1, 2, 3) (M = Cr, Mo, W) oder den η^4-Norbornadien-Komplexen, $M(CO)_4(C_7H_8)$ (M = Cr, Mo) dargestellt. Neben den Pentacarbonylen, $M(CO)_5[S(C_7H_7)_2]$ (M = Cr (**2a**), Mo (**2b**), W (**2c**)), die **1** in unveränderter Form als Zweielektronen-Sulfanliganden mit zwei frei beweglichen Cyclohepta-2,4,6-trienyl-Substituenten enthalten, entstanden bei höherer Temperatur (40−50 °C) isomere Komplexe $M(CO)_5[S(CH_2Ph)(C_7H_7)]$ (M = Cr (**3a**), W (**3c**)), in denen eine der beiden Organylgruppen als Benzyl-Substituent vorliegt. In den Tetracarbonylen, *cis*-$M(CO)_4[S(C_7H_7)(\eta^2\text{-}C_7H_7)]$ (M = Mo (**4b**), W (**4c**)) fungiert das olefinische Sulfan **1** als Vierelektronen-Chelatligand. Die Reaktion von $Mo(CO)_6$ oder (mesitylen)$Mo(CO)_3$ mit $S(C_7H_7)_2$ (**1**) in siedendem THF führte zum schwefelfreien Ditropyl-Komplex, $Mo(CO)_3[(\eta^6\text{-}C_7H_7)\text{-}C_7H_7]$ (**5b**, zwei Isomere). Die ^1H- und ^{13}C-NMR-Spektren der neuen Komplexe **2**−**4** lassen verschiedene dynamische Prozesse erkennen, darunter pyramidale Inversion am Schwefelatom und [1,7]-sigmatrope Verschiebungen am C_7H_7-Ring. Die Molekülstrukturen von **2c, 3a, 4b** und **4c** im Kristall wurden anhand von Röntgenstrukturanalysen bestimmt.

Introduction

Mononuclear derivatives of the hexacarbonyl metals, $M(CO)_6$ (M = Cr, Mo, W), with the olefinic phosphane ligand, tri(1-cyclohepta-2,4,6-trienyl) phosphane, $P(C_7H_7)_3$, have been characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy [1]. The stepwise formation of pentacarbonyls, $M(CO)_5[P(C_7H_7)_3]$, tetracarbonyls, *cis*-$M(CO)_4[P(C_7H_7)_2(\eta^2\text{-}C_7H_7)]$, tricarbonyls, *fac*-$M(CO)_3[P(C_7H_7)_2(\eta^4\text{-}C_7H_7)]$ (M = Cr, Mo, W) and of a dicarbonyl, *cis*-$Cr(CO)_2[P(C_7H_7)(\eta^2\text{-}C_7H_7)(\eta^4\text{-}C_7H_7)]$, has led to complexes in which the phosphane ligand $[P(C_7H_7)_3]$ may progressively act as a two-, four-, six- or eight-electron ligand, although its basic structure remains intact.

The corresponding reactions with the olefinic sulfane, di(1-cyclohepta-2,4,6-trienyl)sulfane, $S(C_7H_7)_2$ (**1**), are more limited in scope due to the lower thermal stability and photosensitivity of the thioether **1** [2]. For example, the photoinduced reaction of $Mn_2(CO)_{10}$ with **1** produces the thiolato-bridged dimer, $[Mn(CO)_4(\mu_2\text{-}SC_7H_7)]_2$ [3], and complete disintegration of **1** has been observed in the reaction of the photo-generated fragment $[CpMn(CO)_2]$ with **1** to give decomposition products such as $[CpMn(CO)_2]_2(\mu_2\text{-}L)$ (L = S and SO) [3]. Nevertheless, $S(C_7H_7)_2$ (**1**) may

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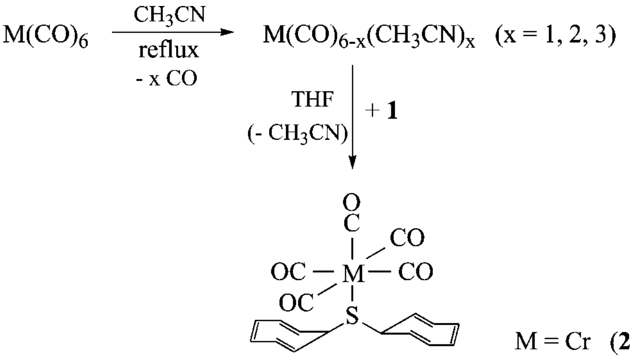
also be incorporated into carbonylmetal complexes as an intact ligand.

In the present study, we describe three types of Group 6 carbonylmetal complexes: the pentacarbonyls $M(CO)_5[S(C_7H_7)_2]$ (**2**, M = Cr (**2a**), Mo (**2b**) and W (**2c**)) with an intact di(1-cyclohepta-2,4,6-trienyl)sulfane ligand, the pentacarbonyls $M(CO)_5[S(CH_2Ph)(C_7H_7)]$ (**3**, M = Cr (**3a**), W (**3c**)) containing a partially rearranged sulfane ligand, and the *cis*-tetracarbonyls *cis*-$M(CO)_4[S(C_7H_7)(\eta^2\text{-}C_7H_7)]$ (**4**, M = Mo (**4b**), W (**4c**)) involving a chelating sulfane as a four-electron ligand. The molecular structures of **2c**, **3a**, **4b** and **4c** were confirmed by X-ray crystallography.



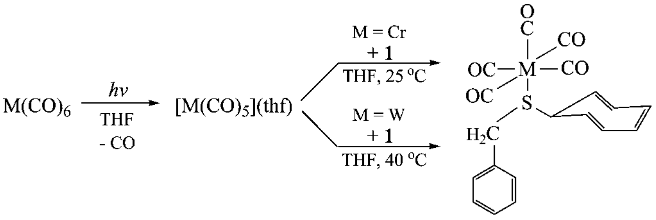
M = Cr (**2a**)
Mo (**2b**)
W (**2c**)

Synthesis and Spectroscopy

A reliable route to monosubstituted derivatives of the hexacarbonyl metals, $M(CO)_6$, which contain **1** as an unchanged two-electron ligand, involves the acetonitrile precursor $M(CO)_5(CH_3CN)$ (M = Cr, Mo, W). Although up to 3 CO ligands are stepwise replaced from $M(CO)_6$ in boiling acetonitrile to give $M(CO)_{6-x}(CH_3CN)_x$ (x = 1, 2, 3) [4,5], the reaction can be terminated when the pentacarbonyl is the dominant product in the mixture (after evolution of ca. 1.1 equivalent of CO).

The initial complexes (**2a**,**c**) may react further under isomerization of one 1-cyclohepta-2,4,6-trienyl to a benzyl substituent to give **3a**,**c**. In the case of M = Mo and W, the tetracarbonyls **4b**,**c** are formed together with **2b**,**c**. Therefore, **2b**,**c** were isolated from the reaction mixtures by column chromatography on silica.

The tungsten complex **2c** is also conveniently prepared *via* the 1:1 reaction of the photo-generated intermediate, $[W(CO)_5](thf)$, with the sulfane, $S(C_7H_7)_2$ (**1**), in THF solution at room temperature. If the reaction is carried out at 40−50 °C, the benzyl complex $W(CO)_5[S(CH_2Ph)(C_7H_7)]$ (**3c**) is obtained directly. The corresponding photo-induced reaction of $Cr(CO)_6$ with **1** gives **3a** even at room temperature.



M = Cr (**3a**)
W (**3c**)

The benzyl complexes **3a** and **3c** are clearly formed by thermal isomerization of **2a** and **2c**, respectively.

Table 1 Spectroscopic data of the di(1-cyclohepta-2,4,6-trienyl)sulfane complexes **2a**−**c**

	$S(C_7H_7)_2$ (**1**) [3]	$Cr(CO)_5[S(C_7H_7)_2]$ (**2a**) (orange)	$Mo(CO)_5[S(C_7H_7)_2]$ (**2b**) (dark-yellow)	$W(CO)_5[S(C_7H_7)_2]$ (**2c**) (light-yellow)
^1H NMR ($CDCl_3$)				
$\delta(H^1)$	3.61t (2H)	3.89t (2H)	3.92t (2H)	4.02t (2H)
$\delta(H^2, H^7)$	5.48m (4H)	5.52dd (4H)	5.55m (4H)	5.54m (4H)
$\delta(H^3, H^6)$	6.22dt (4H)	6.38m (4H)	6.38m (4H)	6.41m (4H)
$\delta(H^4, H^5)$	6.58t (4H)	6.68s (4H)	6.70t (4H)	6.69t (4H)
^{13}C NMR ($CDCl_3$)				
$\delta(C^1)$	41.6	47.6	48.0	49.7
$\delta(C^2, C^7)$	124.7	121.3	121.9	121.8
$\delta(C^3, C^6)$	126.4	128.7	128.6	128.9
$\delta(C^4, C^5)$	131.2	132.0	131.8	131.9
δ(CO) (cis) [a]		215.2	204.7	197.3 [129.0] [b]
δ(CO) (trans)		221.3	211.5	199.5 [155.8] [b]
IR: ν(CO) [cm^{-1}] [c] (pentane)		2075(w), 1951(s), 1941(m), 1928(m)	2075(w),1954(s), 1945(s), 1933(s)	2073(w), 1945(s), 1937(s), 1931(sh)

[a] The complexes **2a-c** consistently show two ^{13}C NMR signals for the 5 CO ligands, the stronger peak corresponding to the 4 CO ligands *cis* to the sulfur ligand appears at higher field, cf. $Cr(CO)_6$ 213.9, $Mo(CO)_6$ 201.0, $W(CO)_6$ 191.1.
[b] Coupling constant, $^1J(^{183}W, ^{13}C)$ [Hz].
[c] Intensities: s strong, m medium, w weak, sh shoulder.

Table 2 Spectroscopic data of the (1-cyclohepta-2,4,6-trienyl)-benzyl-sulfane complexes **3a** and **3c**

	$Cr(CO)_5[S(CH_2Ph)(C_7H_7)]$ (**3a**)	$W(CO)_5[S(CH_2Ph)(C_7H_7)]$ (**3c**)
^1H NMR ($CDCl_3$)		
δ(H^1)	4.16t (1H)	4.36t (1H)
δ(H^2, H^7)	5.69dd (2H)	5.72dd (2H)
δ(H^3, H^6)	6.43m (2H)	6.50m (2H)
δ(H^4, H^5)	6.71dd (2H)	6.74dd (2H)
δ(CH_2)	3.88s (2H)	4.08s (2H)
δ(Ph)	7.18-7.30m (5H)	7.20-7.31m (5H)
^{13}C NMR ($CDCl_3$)		
δ(C^1)	51.0	53.2
δ(C^2, C^7)	121.6	121.9
δ(C^3, C^6)	129.5	129.6
δ(C^4, C^5)	132.0	132.1
δ(CH_2)	43.3	45.5
δ(Ph) [a]	128.2(p), 128.7(m), 129.6(o), 134.6(i)	128.3(p), 128.8(m), 129.7(o), 134.4(i)
δ(CO) (cis)	214.9	197.0 [129.3] [b]
δ(CO) (trans)	221.3	199.9
IR: n(CO) [cm^{-1}] [c] (pentane)	2068(w), 1945(s) / 1939(s) / 1930(m) [d]	2073(w), 1941(s) / 1935(s) / 1929(s) [d]

[a] The tentative assignments of the o- and m-carbon signals correspond to that in the ^{13}C NMR spectrum of dibenzyl sulfide, cf. http://www.aist.go.jp

[b] Coupling constant, $^1J(^{183}W, ^{13}C)$ [Hz].

[c] Intensities: s strong, m medium, w weak; cf. $Cr(CO)_6$ 1987 cm^{-1}, $W(CO)_6$ 1984 cm^{-1}.

[d] Broad absorption.

The characteristic spectroscopic data of the pentacarbonyl complexes **2a**−**c** and **3a**,**c** at room temperature are collected in Tables 1 and 2. Compared with the uncoordinated sulfane, $S(C_7H_7)_2$ (**1**), the ^1H and ^{13}C NMR patterns of the freely pending cyclohepta-2,4,6-trienyl substituents appear to be essentially unchanged, only the signals of the protons H^1 and of the carbon atoms C^1 (connected with the sulfur atom) are slightly shifted to higher frequencies, the effect being more pronounced in the cases of **3a**,**c** than of **2a**−**c**. The assignment of the benzyl and cyclohepta-2,4,6-trienyl ^{13}C NMR signals of **3a**,**c** (Fig. 1) is based on 2D $^{13}C/^1H$ HETCOR experiments. The pentacarbonylmetal structure is evident from the two ^{13}C carbonyl NMR signals in the range of $\delta = 195-225$; the signal of lower intensity (due to the CO group *trans* to the sulfane ligand) is observed at higher frequency relative to the main signal (due to the four CO groups *cis* to the sulfane). At a first glance, the NMR spectra of the complexes of type **2** and **3**, measured at room temperature, seem to indicate a rigid S−M coordination and the absence of fast fluxional processes. However, if pyramidal inversion of the sulfur atom is slow, all pairs of olefinic CH units in **2** should be diastereotopic, and in **3**, the benzylic CH_2 hydrogen atoms should also be diastereotopic as well as the olefinic CH units. Since these features are not observed, it must be concluded that inversion of the coordinated sulfur atom occurs fast when compared with the NMR time scale. Furthermore, when the ^1H NMR spectrum of **2c** was measured at elevated temperatures (Fig. 2), the ^1H resonances became broad, and this indicates another dynamic process related to sigmatropic shifts at the cycloheptatrienyl ring. At low temperature, the pyramidal inversion is slowed down and most of the expected splittings in the ^1H and ^{13}C NMR spectra are observed, as shown for the example of **2c** in Figure 2. The ^{13}C NMR spectra of **2c** (Fig. 3), measured at room temperature and below, are also in support of either fast or slow inversion at the sulfur atom. At low temperature, the benzylic $^1H(CH_2)$ NMR signal of **3c** is split, showing the characteristic pattern of an AB spin system ($^2J(^1H,^1H)$ = 12.0 Hz), and from the coalescense of the signals at 230 K, the activation energy of the barrier to inversion of the sulfur atom can be evaluated [6] as $\Delta G^{\#} = 46.5 \pm 1$ $kJmol^{-1}$. This value is in the range described in numerous studies carried out by other groups, in particular by *Abel* et al. [7−11].

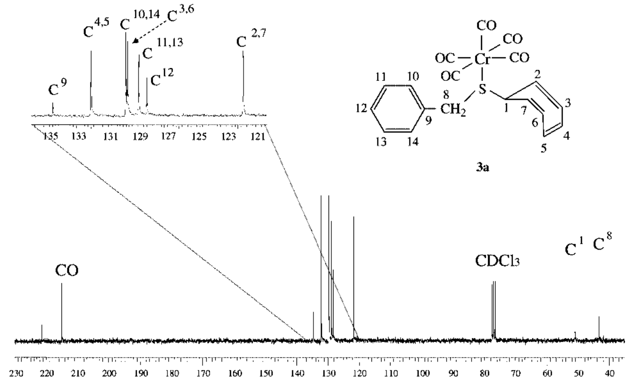


Fig. 1 ^{13}C NMR spectrum of $Cr(CO)_5[S(CH_2Ph)(C_7H_7)]$ (**3a**) at room temperature.

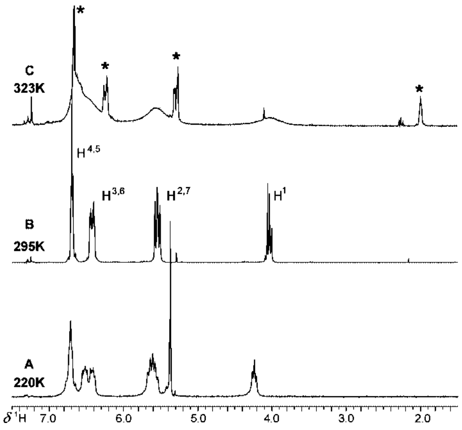


Fig. 2 250 MHz ^1H NMR spectra of $W(CO)_5[S(C_7H_7)_2]$ (**2c**) at various temperatures. **A** (220 K): The ^1H NMR signals for $H^{2,7}$ start to split, and the signals for $H^{3,6}$ are split due to chemical non-equivalence. **B** (room temperature): The ^1H NMR spectrum looks deceptively simple. **C** (323 K): Broadening of all ^1H NMR signals is observed indicating dynamic processes; the sharp signals are the result of decomposition and can arise from the formation of C_7H_7-C_7H_7.

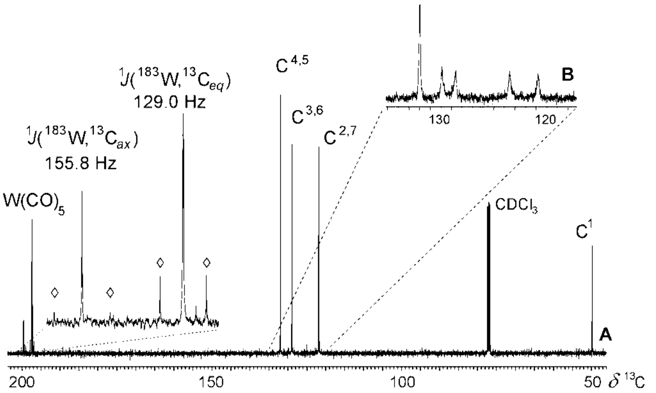
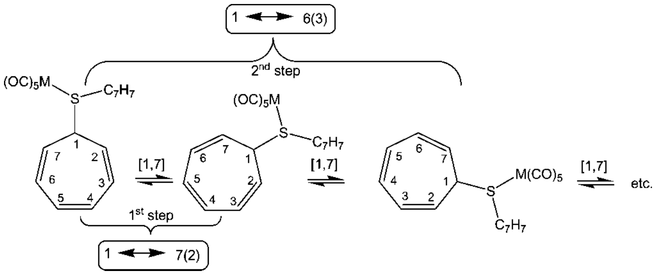


Fig. 3 125.8 MHz $^{13}C\{^1H\}$ NMR spectra of $W(CO)_5[S(C_7H_7)_2]$ (**2c**) at room temperature (**A**) and at 230 K (**B**). The spectrum in **A** looks deceptively simple and ^{183}W satellites are visible for the $^{13}C(CO)$ NMR signals, as marked in the expansion. In **B**, the ^{13}C NMR signals for carbon atoms $C^{2,7}$, $C^{3,6}$ are split and that for $C^{4,5}$ is broad at low temperature because of chemical non-equivalence, when the pyramidal inversion of the sulfur atom becomes slow.

The [1,7]-sigmatropic rearrangement [12−14] indicated by the high-temperature NMR spectrum of **2c** (Fig. 2) is clearly visualized by the results of two-dimensional (2D) $^1H/^1H$ EXSY NMR experiments [15], (Fig. 4).



The first and the second step of the [1,7]-sigmatropic movement of the sulfur-containing group around the C_7H_7 ring can be observed. The appearance of the cross peaks (Fig. 4) in the contour plot (with the same phase as the diagonal peaks), depending in their intensities on the respective mixing times, indicates the exchange, and the rate constant for the [1,7]-sigmatropic shift can be evaluated [16] by integration of the cross peaks as $k = 4.5 \pm 0.5\ s^{-1}$. Interestingly, in the free ligand **1**, this process takes place much more slowly, since 1D magnetization transfer $^1H/^1H$ experiments did not show effects of exchange. The exchange is also slow in $PhS(C_7H_7)$, the S-phenyl derivative of **1**, for which a value of $k = 6.5\ s^{-1}$ has been determined at 100 °C [17].

The IR spectra of **2a−c** and **3a,c** (in pentane solution) show the typical pentacarbonyl metal structure with 4 absorptions (Table 1 and 2), and the molecular size of the isomeric chromium complexes **2a** and **3a** was also confirmed by observation of the respective molecular ion (m/e = 406) in the field-desorption mass spectra (FD-MS).

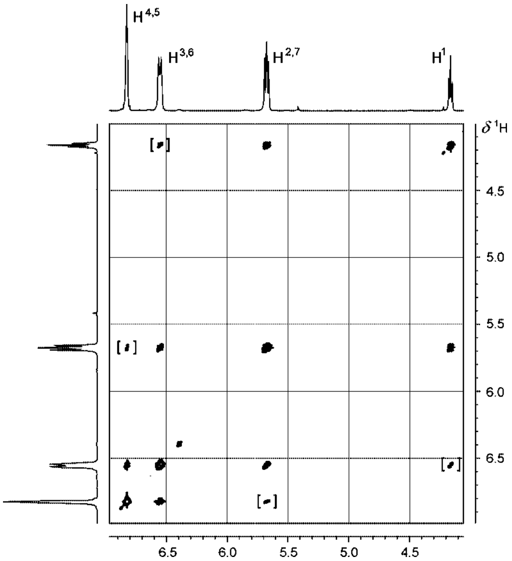
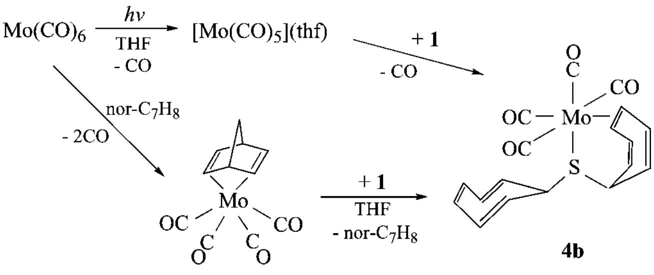


Fig. 4 Contour plot of the 250 MHz 2D $^1H/^1H$ EXSY spectrum, measured for $W(CO)_5[S(C_7H_7)_2]$ (**2c**) at room temperature using a mixing time of 0.2 s. The off-diagonal cross peaks indicate the exchange via [1,7]-sigmatropic rearrangements, the more intensive ones corresponding to fast [1,7]-migration of the sulfur around the seven-membered ring. The marked off-diagonal cross peaks with lower intensities arise from two subsequent migrations of the same type. A mixing time of 0.1 s leads to suppression of these cross peaks, whereas a mixing time of 0.5 s shows additional cross peaks for the third and further rearrangements.

Whereas the photo-generated intermediates $[M(CO)_5](thf)$ (M = Cr, W) react with $S(C_7H_7)_2$ (**1**) in THF solution to give pentacarbonylmetal complexes (**2c** and **3a**,**c**), the corresponding molybdenum precursor $[Mo(CO)_5](thf)$ leads immediately to the tetracarbonyl chelate complex, *cis*-$Mo(CO)_4[S(C_7H_7)(\eta^2-C_7H_7)]$ (**4b**), which is also accessible *via* the norbornadiene intermediate $Mo(CO)_4(\eta^4-C_7H_8)$ [18].



The analogous tungsten complex, $W(CO)_4[S(C_7H_7)(\eta^2-C_7H_7)]$ (**4c**), was obtained (together with a minor amount of **2c**) from the reaction of the mixture of acetonitrile precursors, $W(CO)_{6-x}(CH_3CN)_x$ (x = 1, 2, 3), with $S(C_7H_7)_2$ (**1**). Attempts to prepare the tetracarbonyl chelate complex of chromium (**4a**) were not successful. Both $[Cr(CO)_5](thf)$ and $Cr(CO)_4(\eta^4-C_7H_8)$ [18] gave **3a**, and irradiation of **2a** resulted in photo-induced decomposition instead of CO substitution.

Table 3 Spectroscopic data of the chelate complexes **4b** and **4c**

	$Mo(CO)_4[S(C_7H_7)(\eta^2\text{-}C_7H_7)]$ (**4b**) 25 °C	$W(CO)_4[S(C_7H_7)(\eta^2\text{-}C_7H_7)]$ (**4c**) 25 °C	 -20 °C
^1H NMR ($CDCl_3$)			
$\delta(H^1)$	3.89t [7.9] (1H)	3.92t (1H)	4.01t (1H)
$\delta(H^{1'})$	4.82t [8.1] (1H)	4.94t (1H)	4.96t (2H)
$\delta(H^{4'}, H^{5'})$	5.60m (2H)	5.38br (2H)	5.34m (2H)
3 multiplet groups	5.60m (4H) 6.47m (2H) 6.67m (4H)	5.59m (4H) 6.48m (2H) 6.68m (4H)	5.68-5.46m (4H) 6.59-6.49m (2H) 6.80-6.62m (4H)
^{13}C NMR ($CDCl_3$)			
$\delta(C^1)$	42.6	43.7	43.2
$\delta(C^{1'})$	47.3	48.2	47.9
$\delta(C^{4'}, C^{5'})$	84.6	77.2; 76.2	76.8; 76.0
Remaining 10 signals	(partially broadened)	(partially broadened)	132.68; 132.65; 131.8; 131.0; 130.0; 129.7; 126.1; 124.8; 123.7; 120.8
$\delta(CO)$	213.8; 213.5	203.6 [166.1] [a)] 203.3 [168.1]	203.8; 203.3; 202.1; 198.8
IR: $\nu(CO)$ [cm^{-1}] [b)] (pentane)	2034(m), 1945(s), 1931(s), 1898(s)	2032(m), 1942(s), 1927(s), 1896(s)	

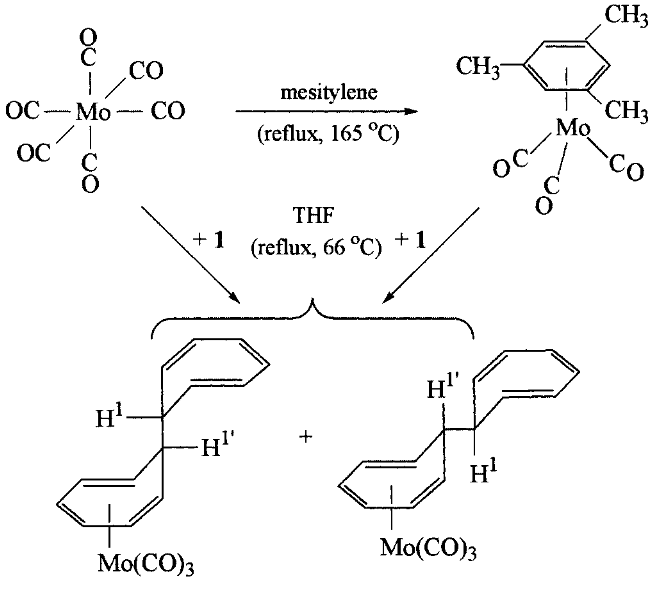
[a)] Coupling constant, $^1J(^{183}W, ^{13}C)$ [Hz].

[b)] Intensities: s strong, m medium.

The spectroscopic data for the tetracarbonyl chelate complexes **4b** and **4c** are given in Table 3. The assignment of ^1H and ^{13}C NMR signals is based on 2D $^1H/^{13}C$ HETCOR experiments, intensity data and comparison with the related tetracarbonyl chelate complexes of the phosphane, $M(CO)_4[P(C_7H_7)_2(\eta^2\text{-}C_7H_7)]$ (M = Cr, Mo, W) [1]. In the ^1H NMR spectra of **4b** and **4c**, the expected presence of 14 protons of the sulfane ligand was confirmed, although only the pseudotriplets of H^1 and $H^{1'}$ have been unequivocally assigned; the signal of proton $H^{1'}$ of the coordinated C_7H_7 substituent undergoes a larger shift to higher frequencies than that of the freely-pending substituent (H^1), if compared to the chemical shift of H^1 in the uncoordinated thioether **1** ($\delta(H^1) = 3.61$, cf. Table 1). The complex dynamic situation in the compounds **4b** and **4c** becomes apparent by the broadened ^{13}C NMR signals (at room temperature) of the sulfane ligand and by the observation of only two $^{13}C(CO)$ signals in equal intensity which, in the case of **4c**, are accompanied by ^{183}W satellites due to $^{183}W\text{-}^{13}C$ spin-spin coupling. In addition to the dynamic processes described for the complexes **2** and **3** (*vide supra*) it is conceivable that a third process is also involved, namely the exchange between the η^2-coordinated and the pending C_7H_7 groups. This was not investigated in detail. However, at -20 °C, the ^{13}C NMR spectrum of **4c** shows 18 sharp signals for all individual carbon atoms, i.e. 14 signals for the sulfane ligand and 4 $^{13}C(CO)$ signals of equal intensity. The ^1H and ^{13}C NMR signals of the coordinated double bond ($H^{4',5'}$ and $C^{4',5'}$) are shifted to low frequencies as a result of π-complexation, as compared with the corresponding signals of freely pending C_7H_7 rings in both **4b,c** and in **1**. The IR spectra of **4b** and **4c** (in pentane solution) reveal the characteristic *cis*-tetracarbonylmetal pattern with 4 $\nu(CO)$ absorptions (Table 3).

In the series of carbonylmolybdenum complexes, an attempt was made to prepare a tricarbonyl complex containing a η^6-coordinated sulfane ligand, i.e. the unknown sulfane complexes $Mo(CO)_3[(\eta^6\text{-}C_7H_7)S(C_7H_7)]$ or $S[(\eta^6\text{-}C_7H_7)Mo(CO)_3]_2$, related to the phosphane compound $P[(\eta^6\text{-}C_7H_7)Mo(CO)_3]_3$ [19].

However, if either $Mo(CO)_6$ or (mesitylene)$Mo(CO)_3$ were heated in refluxing THF solution in the presence of $S(C_7H_7)_2$ (**1**), loss of sulfur and formation of the ditropyl complex **5b** was observed. The mixture of *endo*-hydrogen and *exo*-hydrogen (H^1 and $H^{1'}$, resp.) isomers of **5b** can be separated by thin-layer chromatography (TLC). The *endo*-



5b - *endo*(H^1) **5b** - *exo*(H^1)

form had been obtained previously [20] from $Mo(CO)_6$ and ditropyl.

Studies on the dinuclear, ditropyl-bridged complexes, $[Mo(CO)_3]_2[\mu\text{-}(\eta^6\text{-}C_7H_7)_2]$ (*endo* and *exo* isomers) are also reported in the literature [20,21].

X-Ray Crystal Structure Analyses

The molecular structures of the two pentacarbonylmetal sulfane complexes $Cr(CO)_5[S(CH_2Ph)(C_7H_7)]$ (**3a**) and $W(CO)_5[S(C_7H_7)_2]$ (**2c**) are presented in Figures 5 and 6. Bond distances are given in Table 4, bond angles and a few characteristic dihedral angles are collected in Table 5.

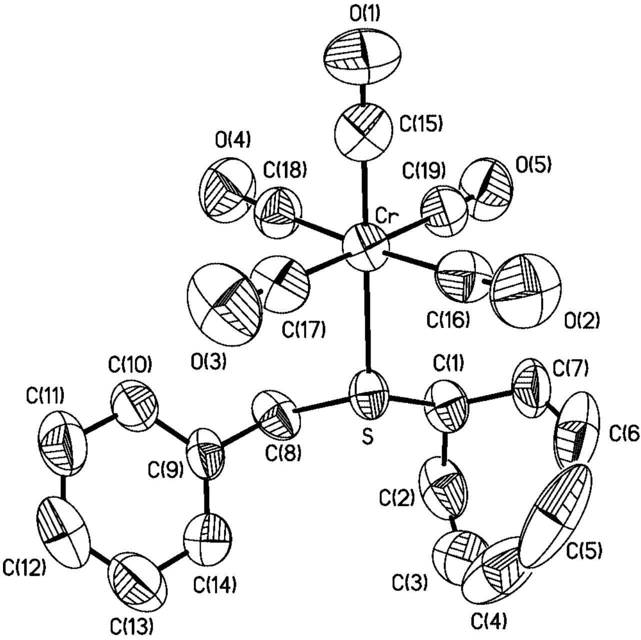


Fig. 5 Molecular structure (50% probability ellipsoids) of $Cr(CO)_5[S(CH_2Ph)(C_7H_7)]$ (**3a**)

In both **3a** and **2c** the pseudo-octahedral coordination sphere of the metal contains a monodentate sulfane donor ligand. The distance between the metal and the CO ligand *trans* to sulfur (M-C(15)) is reduced by 5−7 pm as compared with the average bond lengths between the metal and the four *cis*-carbonyl ligands. This structural "trans-influence" of the sulfur-coordinated ligand is generally observed in pentacarbonylchromium complexes, unless the ligand itself is a π-acceptor (like, e.g., SO_2 [22]). For comparison, Table 6 gives the metal carbonyl distances in $[Cr(CO)_5]$- and $[W(CO)_5]$ complexes with sulfur-containing ligands, together with the metal-sulfur bond lengths. In line with the special role of the *trans*-carbonyl group, the shortened M−C(15) bond length (184.0(7) pm in **3a**, 197.3(4) pm in **2c**) is associated with a significantly lengthened C(15)−O(1) bond (116.7(7) pm in **3a**, 116.3(5) pm in **2c**), as compared with the C−O bond distances of the four *cis*-carbonyl ligands (av. 113.7(7) pm in **3a**, av. 113.8(5) pm in **2c**), and the angle M−C(15)−O(1) (178.4(6)° in **3a**, 178.6(4)° in **2c**) is

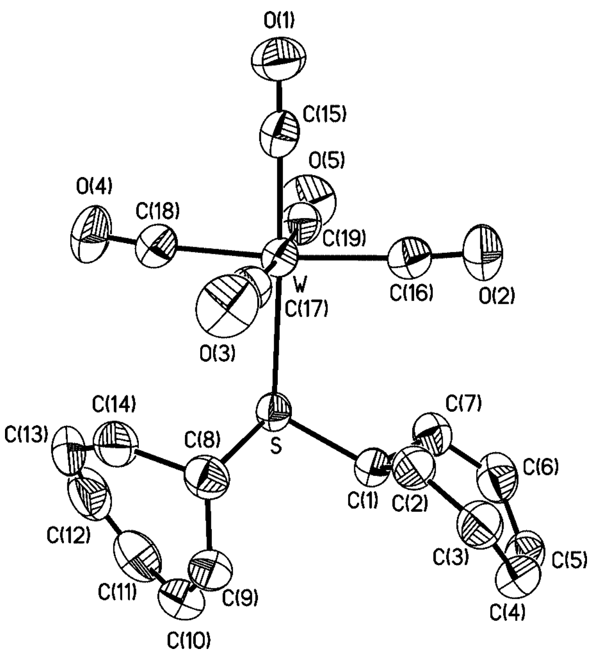


Fig. 6 Molecular structure (50% probability ellipsoids) of $W(CO)_5[S(C_7H_7)_2]$ (**2c**)

Table 4 Bond distances /pm in the pentacarbonylmetal sulfane complexes **3a** (M = Cr) and **2c** (M = W)

	$Cr(CO)_5[S(CH_2Ph)(C_7H_7)]$ (**3a**)	$W(CO)_5[S(C_7H_7)_2]$ (**2c**)
M-S	242.68(16)	257.32(10)
M-C(15)	184.0(7)	197.3(4)
M-C(16)	189.6(7)	204.7(4)
M-C(17)	189.3(7)	203.8(4)
M-C(18)	188.4(7)	204.0(4)
M-C(19)	190.6(7)	203.3(5)
S-C(1)	186.3(5)	182.6(4)
S-C(8)	183.1(6)	187.3(4)
O(1)-C(15)	116.7(7)	116.3(5)
O(2)-C(16)	112.9(7)	113.6(5)
O(3)-C(17)	113.9(7)	114.1(5)
O(4)-C(18)	115.0(7)	113.8(5)
O(5)-C(19)	113.1(7)	113.6(6)
C(1)-C(2)	147.7(9)	149.5(6)
C(1)-C(7)	146.8(9)	150.0(5)
C(2)-C(3)	132.6(12)	133.5(6)
C(3)-C(4)	137.1(16)	142.5(8)
C(4)-C(5)	134.9(17)	133.3(8)
C(5)-C(6)	145.8(16)	145.6(8)
C(6)-C(7)	128.4(11)	133.3(6)
C(8)-C(9)	150.6(7) [a]	131.5(7)
C(8)-C(14)		150.2(6)
C(9)-C(10)	137.6(8) [a]	149.9(6)
C(9)-C(14)	136.5(8) [a]	
C(10)-C(11)	138.8(9) [a]	140.9(8)
C(11)-C(12)	136.0(10) [a]	131.6(8)
C(12)-C(13)	136.5(10) [a]	142.4(9)
C(13)-C(14)	138.8(9) [a]	135.2(8)

[a] Benzyl substituent.

Table 5 Angles /° in the pentacarbonylmetal sulfane complexes **3a** (M = Cr) and **2c** (M = W)

	$Cr(CO)_5[S(CH_2Ph)(C_7H_7)]$ (**3a**)	$W(CO)_5[S(C_7H_7)_2]$ (**2c**)
C(15)-M-C(16)	89.2(3)	87.92(16)
C(15)-M-C(17)	89.0(3)	87.65(16)
C(15)-M-C(18)	87.5(3)	88.80(16)
C(15)-M-C(19)	90.4(3)	89.80(17)
C(16)-M-C(17)	90.6(3)	94.53(18)
C(16)-M-C(18)	176.3(3)	172.84(16)
C(16)-M-C(19)	89.9(3)	88.61(18)
C(17)-M-C(18)	90.9(3)	91.69(16)
C(17)-M-C(19)	179.2(3)	175.88(15)
C(18)-M-C(19)	88.5(3)	85.02(17)
C(15)-M-S	175.5(2)	177.55(11)
C(16)-M-S	87.84(19)	94.23(11)
C(17)-M-S	87.6(2)	91.00(11)
C(18)-M-S	95.6(2)	89.20(11)
C(19)-M-S	93.0(2)	91.44(12)
C(1)-S-M	112.8(2)	112.71(12)
C(8)-S-M	111.2(2)	108.35(13)
C(1)-S-C(8)	98.4(3)	98.31(18)
S-C(1)-C(2)	111.1(4)	115.0(3)
S-C(1)-C(7)	110.0(4)	111.1(3)
C(2)-C(1)-C(7)	110.0(6)	108.7(3)
C(1)-C(2)-C(3)	123.9(8)	119.8(4)
C(2)-C(3)-C(4)	127.5(10)	125.1(5)
C(3)-C(4)-C(5)	128.5(12)	125.9(5)
C(4)-C(5)-C(6)	121.6(11)	126.4(4)
C(5)-C(6)-C(7)	128.5(9)	124.4(5)
C(6)-C(7)-C(1)	125.5(7)	119.7(4)
S-C(8)-C(9)	110.2(4) [a]	111.3(3)
S-C(8)-C(14)	109.0(3)	
C(9)-C(8)-C(14)	111.0(4)	
C(8)-C(9)-C(10)	120.4(6) [a]	126.0(4)
C(8)-C(9)-C(14)	120.4(5) [a]	
C(10)-C(9)-C(14)	119.2(6) [a]	
C(9)-C(10)-C(11)	119.9(6) [a]	127.3(4)
C(10)-C(11)-C(12)	119.9(7) [a]	127.1(6)
C(11)-C(12)-C(13)	121.1(7) [a]	126.7(6)
C(12)-C(13)-C(14)	118.6(7) [a]	127.3(5)
C(13)-C(14)-C(9)	121.3(7) [a]	
C(13)-C(14)-C(8)	124.2(5)	
M-C(15)-O(1)	178.4(6)	178.6(4)
M-C(16)-O(2)	176.1(6)	175.1(4)
M-C(17)-O(3)	176.7(6)	177.4(4)
M-C(18)-O(4)	177.5(6)	174.4(3)
M-C(19)-O(5)	177.7(6)	
	175.1(4)	
Dihedral angles [b]		
α	α_1 45.3 (ax)	α_1 56.4 (eq) α_8 42.8 (ax)
β	β_1 22.6	β_1 26.8 β_8 21.5
C(1)SC(8)/MS	145.1	147.5
C(16)MC(17)/C(18)MC(19)	3.4	4.3

[a] Benzyl substituent.
[b] cf. Fig. 7. The numbering (α_1, β_1 and α_8, β_8) refers to the cyclohepta-2,4,6-trienyl ring containing the carbon atoms C(1) or C(8), respectively.

Table 6 Metal-sulfur and metal-carbonyl bond distances in $[Cr(CO)_5]$- and $[W(CO)_5]$ complexes with sulfur-containing ligands

$Cr(CO)_5[L]$	Cr-S	Cr-CO (*trans*)	Cr-CO (*cis*)	Ref.
L = SO_2 (A)	219.2(6)	187.3(17)	av. 189.7(13)	[22]
(B)	218.3(6)	190.0(17)	av. 190.0(15)	
$S(=O)[CH_2CH]_2$ [a]	233.1	185.8(5)	av. 190.9(3)	[23]
$S=CMe_2$ [b]	237.7(4)	183.5	av. 189.8	[24]
S=C(Ph)Fc	241.2(1)			[25]
$S=C(S)Pet_3$	238.9(4)	178(2)	av. 186(2)	[26]
$S=N\text{-}NMe_2$	238.6(1)	184.6(2)	av. 190.3(5)	[27]
$S=N\text{-}NPh_2$	235.7(2)	184.8(7)	av. 190.0(9)	[27]
$S(Ph)N(CH_2Ph)_2$ (A)	240.9(2)	181.2(7)	av. 187.1(8)	[28]
(B)	239.6(2)	181.6(10)	av. 186.3(11)	
$S(Ph)NCy_2$	244.5(1)	183.0(4)	av. 188.5(5)	[29]
	244.1(2)	184.4(4)	av. 188.8(4)	
$S(CH_2Ph)(C_7H_7)$	242.68(16)	184.0(7)	av. 189.5(7)	[A]
$S(CH_2Ph)(Et)$	245.8(2)	185.9(7)	av. 187.9(10)	[30]
$S[CMe_2]_2CO$ [c]	242.41(5)	185.7(2)	av. 191.2(1)	[31]
$S=C[OCMe_2]_2$ [d]	243.8(1)	184.1(4)	av. 191.2(4)	[32]
$S(H)(^tBu)$	243.9(2)	182.8(8)	av. 192.3(8)	[33]
$S=PMe_3$	251.0(2)	181.5(8)	av. 190.0(4)	[34]
$S=C[N(Me)CH_2]_2$ [e]	251.0(3)	182.7(10)	av. 188.5(12)	[35]
$S(SnMe_3)_2$	252.2(3)	180(1)	av. 190(2)	[36]
cf.				
$\{Cr(CO)_5[SH]\}^-$ $\{Na(2.2.1\text{-crypt})\}^+$	247.3(2)	189.8(5)	av. 190.5(5)	[37]
$\{Cr(CO)_5[S^tBu]\}^-$ $\{PPN\}^+$	247.9(1)	182.4(4)	av. 188.1(6)	[38]
$\{[Cr(CO)_5]_2[S^tBu]\}^-$	250.9(1)	183.4(5)	av. 189.2(5)	[38]
$\{PPN\}^+$	251.8(1)	182.2(6)	av. 188.9(5)	

$W(CO)_5[L]$	W-S	W-CO (*trans*)	W-CO (*cis*)	Ref.
L = S=C(H)Ph [f]	247.9(3)	200(1)		[39]
S=CH-C(Ph)=C(OEt)Ph	250.8(5)			[40]
$S_4(NH)_4$	252.5(2)	197(1)	av. 203(1)	[41]
S=CC(Ph)C(Ph)SS	252.8(6)			[42]
$S[N(SiMe_3)BMe]_2NH$ [g]	253.3(2)	196.5	201.7-205.6	[43]
S=C(OH)Me	254.8(2)	200.4(18)	av. 206.3(17)	[44]
$S_3(CHMe)_3$ [h]	255.3(6)	192(3)	av. 197(3)	[45]
	255.3(7)	187(3)	av. 202(3)	
$S(CH_2)_2N(H)C(O)CH_2$ [i]	255.1(14)	200.0(18)	av. 204.3(17)	[46]
$S(CH_2)_2N(H)C(S)CH_2$ [j]	255.6(8)	195(2)	av. 204.5	[47]
$S(CH_3)[C(SMe)\text{-}PPh_2Me]$	255.5(2)	197.2(9)	av. 203.4(9)	[48]
$S=C(N(H)(CH_2)_2S)$ [k]	256(0.6)	197(2)	av. 202.5(20)	[49]
$S=C[CHCH]_2NH$ [l]	256.8(2)	196.0(6)	av. 203.7(9)	[50]
$S=C(NH_2)N(H)N=CMe_2$ [m]	256.8(2)	197.6(8)	av. 203.7(9)	[51]
$\{S\text{-}C(S)OEt\}^-$ [n] $\{PPh_4\}^+$	257.1(3)	194.5(13)	av. 204.5(14)	[52]
$S(^tBu)(CH_2S^tBu)$	257.1(5)	196.5(13)	av. 203.0(14)	[53]
$S(C_7H_7)_2$	257.32(10)	197.3(4)	av. 204.0(5)	[A]
$S\text{-}CH(Ph)(PMe_3)$ [o]	257.9(2)	196.1(6)		[39]
$S(^tBu)Sb(S^tBu)_2$	259.6(2)	195.3(6)	av. 201.9(7)	[54]
$S=C[N(Me)CH_2]_2$ [e]	261.7(2)	195.6(6)	av. 203.1(8)	[35]
$S(GeMe_3)_2$	262.2(5)	194(2)	av. 204(2)	[36]

[A] This work.
[a] 2,5-Dihydrothiophene-1-oxide; [b] thioacetone; [c] 2,2,4,4-tetramethyl-3-thietanone; [d] 4,4,5,5-tetramethyl-1,3-dioxolan-2-thione; [e] N,N'-dimethyl-imidazolidine-2-thione; [f] thiobenzaldehyde; [g] 3,5-dimethyl-2,6-bis(trimethylsilyl)-1-thia-2,4,6-triaza-3,5-diborinane; [h] 2,4,6-trimethyl-1,3,5-trithian; [i] thiomorpholin-3-one; [j] thiomorpholin-3-thione; [k] thiazolidine-2-thione; [l] pyridine-2(1H)thione; [m] acetone-thiosemicarbazone; [n] xanthate; [o] (α-trimethylphosphonio)benzyl thiolate.

slightly larger than the average value for the four *cis*-carbonyl ligands (av. 175.5° in **3a**, 177.0° in **2c**). The four *cis*-carbonyl ligands and the metal are essentially coplanar; the dihedral angles, e.g. C(16)MC(17)/C(18)MC(19) (3.4° in **3a**, 4.3° in **2c**), are small.

According to Table 6, Cr−S distances between 218 and 253 pm have been reported for $[Cr(CO)_5]$ complexes with various sulfur-containing ligands. The Cr−S bond length determined for $Cr(CO)_5[S(CH_2Ph)(C_7H_7)]$ (**3a**) (242.68(16) pm) falls into the typical range (240−246 pm) of $[Cr(CO)_5]$

compounds with amino sulfanes, $S(Ph)NR_2$ (R = CH_2Ph [28], C_6H_{11} [29]), thioalcohols (^tBuSH [33]) and thioethers ($S(CH_2Ph)Et$ [30]), cf. Table 6. In a similar manner, the W−S bond length in $W(CO)_5[S(C_7H_7)_2]$ (**2c**) (257.32(10) pm) is almost identical with that in the thioether complex, $W(CO)_5[S(^tBu)(CH_2S^tBu)]$ (257.1(5) pm [53]). In general, the W−S distances in $[W(CO)_5]$ complexes of sulfur-containing ligands are observed in the range of 247−262 pm, cf. Table 6.

The 1-cyclohepta-2,4,6-trienyl substituent in the crystals of **3a** carries the sulfur atom in an axial position. In **2c** only one C_7H_7 substituent has the axial conformation, the other assumes the (more spherical) equatorial conformation with larger dihedral angles α and β, as defined in Figure 7. In the uncoordinated sulfane **1**, both C_7H_7 substituents are axial [3]. It can be assumed that the axial or equatorial conformation of the 1-cyclohepta-2,4,6-trienyl substituents in the crystal are determined by the steric situation in the lattice. There is only a very small difference in energy (0.9 $kJmol^{-1}$) between the axial and equatorial isomers of C_7H_7-SH, with the axial isomers being slightly more stable, according to calculations on the B3LYP/6-311+G(d,p) level of theory [Gaussian 03 program package].

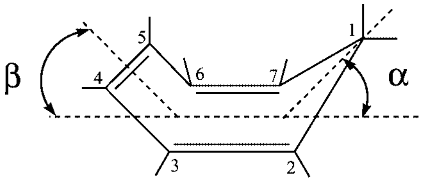


Fig. 7 Conformation of the 1-cyclohepta-2,4,6-trienyl substituent

The isostructural *cis*-tetracarbonyl complexes $M(CO)_4[S(C_7H_7)(\eta^2\text{-}C_7H_7)]$ (M = Mo (**4b**) and W (**4c**)) crystallize in the monoclinic space group $P2_1/c$. The unit cell which contains 4 molecules is slightly (*ca.* 1%) smaller in the case of **4c**, i.e. the tungsten-containing complex molecules **4c** are marginally more compact than their molybdenum analogues **4b**. The molecular geometry of the tungsten complex **4c** with the numbering scheme is presented in Fig. 8; the bond distances and angles are collected in Tables 7 and 8, respectively.

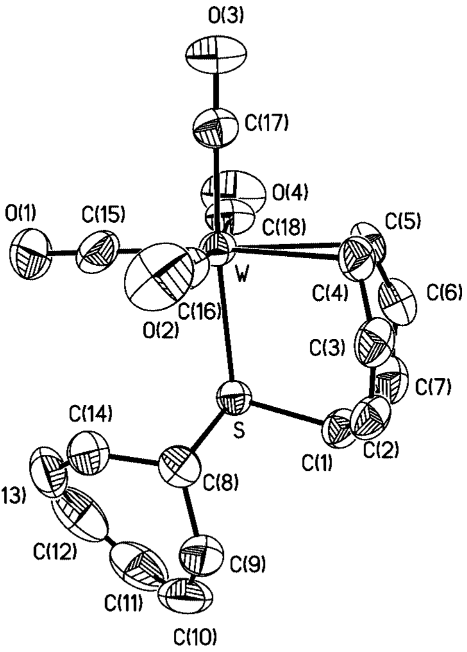


Fig. 8 Molecular structure (50% probability ellipsoids) of $W(CO)_4[S(C_7H_7)(\eta^2\text{-}C_7H_7)]$ (**4c**)

Table 7 Bond distances /pm in $M(CO)_4[S(C_7H_7)(\eta^2\text{-}C_7H_7)]$ (M = Mo (**4b**) and W (**4c**))

	M = Mo (**4b**)	M = W (**4c**)
M-S	253.8(3)	252.85(11)
M-C(4)	250.2(10)	246.0(5)
M-C(5)	248.6(10)	247.0(5)
M-C(15)	196.1(13)	199.1(6)
M-C(16)	203.2(14)	202.8(5)
M-C(17)	195.6(12)	195.7(5)
M-C(18)	201.6(13)	202.1(5)
O(1)-C(15)	115.7(12)	113.0(7)
O(2)-C(16)	115.1(13)	113.4(6)
O(3)-C(17)	115.2(12)	116.3(6)
O(4)-C(18)	114.3(13)	114.8(7)
S-C(1)	186.2(10)	185.2(5)
S-C(8)	186.5(10)	186.0(5)
C(1)-C(2)	149.0(15)	148.8(7)
C(1)-C(7)	148.8(14)	151.2(7)
C(2)-C(3)	132.1(15)	130.6(7)
C(3)-C(4)	143.5(15)	146.7(7)
C(4)-C(5)	138.8(15)	138.6(8)
C(5)-C(6)	143.4(15)	145.8(8)
C(6)-C(7)	133.4(15)	131.7(8)
C(8)-C(9)	149.5(16)	147.5(7)
C(8)-C(14)	148.9(14)	148.2(7)
C(9)-C(10)	126.0(18)	133.8(10)
C(10)-C(11)	145.0(2)	142.3(11)
C(11)-C(12)	134.0(2)	134.1(11)
C(12)-C(13)	143.0(19)	143.8(10)
C(13)-C(14)	132.8(16)	131.7(8)

The pseudo-octahedral coordination sphere of **4b**,**c** contains two types of CO ligands, on the one hand the CO groups *trans* to the sulfur (C(17)−O(3)) and to the coordinated double bond (C(15)−O(1)), on the other hand the CO groups *cis* to the ligand positions (C(16)−O(2) and C(18)−O(4)). The distance between the metal and the "*trans*" carbonyl ligands is significantly shortened as a result of the structural "trans-influence", and the angle M−C−O is close to linearity (*ca.* 179°). The two "*cis*" carbonyl ligands (M−C *ca.* 202 pm, M−C−O *ca.* 174°) include an angle C(16)−M−C(18) of 169.4(5)° (**4b**) or 169.5(2)° (**4c**). The three CO ligands in the equatorial plane (which is defined by the metal and the carbon atoms C(4), C(5), C(15), C(16), C(18)) are slightly pushed upwards by the sulfane ligand towards the *trans*-carbonyl, C(17)−O(3).

Compared with the free molecule $S(C_7H_7)_2$ (**1**), the bidentate sulfane ligand in **4b**,**c** has undergone only small

Table 8 Angles /° in $M(CO)_4[S(C_7H_7)(\eta^2\text{-}C_7H_7)]$ (M = Mo (**4b**) and W (**4c**))

	M = Mo (**4b**)	M = W (**4c**)
C(4)-M-S	84.8(3)	86.22(13)
C(5)-M-S	85.9(3)	84.63(13)
C(4)-M-C(5)	32.3(4)	32.66(18)
C(4)-M-C(15)	165.3(5)	161.1(2)
C(4)-M-C(16)	78.4(4)	76.8(2)
C(4)-M-C(17)	90.5(4)	89.66(19)
C(4)-M-C(18)	109.5(4)	111.4(2)
C(5)-M-C(15)	162.2(5)	166.0(2)
C(5)-M-C(16)	110.6(4)	109.4(2)
C(5)-M-C(17)	90.7(4)	89.9(2)
C(5)-M-C(18)	77.2(4)	78.9(2)
C(15)-M-C(16)	87.2(5)	84.5(2)
C(15)-M-C(17)	91.2(5)	92.3(2)
C(15)-M-C(18)	85.2(5)	87.6(2)
C(16)-M-C(17)	85.0(4)	88.7(2)
C(16)-M-C(18)	169.4(5)	169.5(2)
C(17)-M-C(18)	87.9(4)	84.82(19)
C(15)-M-S	93.1(3)	92.80(17)
C(16)-M-S	93.1(3)	94.01(15)
C(17)-M-S	175.2(3)	174.43(16)
C(18)-M-S	94.6(3)	93.19(14)
C(1)-S-C(8)	99.6(5)	99.1(2)
C(1)-S-M	106.8(4)	107.86(16)
C(8)-S-M	109.1(3)	109.05(16)
S-C(1)-C(2)	107.4(7)	112.6(3)
S-C(1)-C(7)	112.2(7)	106.7(3)
C(2)-C(1)-C(7)	113.4(9)	112.1(4)
C(1)-C(2)-C(3)	124.0(11)	124.8(5)
C(2)-C(3)-C(4)	127.8(12)	127.1(5)
C(3)-C(4)-C(5)	123.8(12)	125.0(5)
M-C(4)-C(5)	73.2(6)	74.1(3)
M-C(4)-C(3)	114.7(7)	114.1(3)
C(4)-C(5)-C(6)	127.5(11)	125.1(5)
M-C(5)-C(4)	74.5(6)	73.3(3)
M-C(5)-C(6)	113.6(7)	114.7(3)
C(5)-C(6)-C(7)	126.5(11)	127.9(5)
C(1)-C(7)-C(6)	123.5(11)	123.3(5)
S-C(8)-C(9)	111.1(8)	112.3(4)
S-C(8)-C(14)	108.5(8)	108.8(3)
C(9)-C(8)-C(14)	109.7(9)	111.0(4)
C(8)-C(9)-C(10)	128.8(14)	125.6(6)
C(9)-C(10)-C(11)	125.9(14)	125.9(6)
C(10)-C(11)-C(12)	125.3(14)	126.5(7)
C(11)-C(12)-C(13)	126.9(15)	126.3(7)
C(12)-C(13)-C(14)	126.2(13)	126.9(6)
C(8)-C(14)-C(13)	125.9(11)	125.3(5)
M-C(15)-O(1)	179.1(12)	179.5(7)
M-C(16)-O(2)	173.7(12)	174.5(5)
M-C(17)-O(3)	179.1(11)	178.1(5)
M-C(18)-O(4)	174.7(11)	174.0(5)
Dihedral angles [a]		
α_1	45.6 (ax)	46.1 (ax)
β_1	23.2	23.0
α_8	41.7 (ax)	44.6 (ax)
β_8	22.8	21.8
C(1)SC(8)/MS	151.4	150.8
C(4)MC(5)/MC(15,16,18)	4.3	4.8
O(1)C(15)MC(4,5)/MS	85.7	85.5
O(1)C(15)MC(4,5)/MC(17)O(3)	90	88.6

[a] cf. Fig. 7. The numbering (α_1, β_1 and α_8, β_8) refers to the cyclohepta-2,4,6-trienyl ring containing the carbon atoms C(1) or C(8), respectively.

distortions. Both C_7H_7 ring substituents retain the axial conformation as in **1**, although the coordinated C_7H_7 substituent (C(1)−C(7)) is marginally more bent (cf. Fig. 7 and Table 8). The axial conformation is required for π-complexation *via* the C(4),C(5) double bond, which is lengthened by 5−6 pm as a result of π-interaction with the metal (C(4),C(5) 133.0(3) pm in **1**, 138.8(15) and 138.6(8) pm in **4b** and **4c**, respectively). The distances S−C(1) and S−C(8) and the angle C(1)−S−C(8) are nearly unchanged if compared with uncoordinated $S(C_7H_7)_2$ (**1**) (S−C(1) 184.43(18) pm, C(1)−S−C(8) 100.71(12)° [3]). The distance W−S is shorter in the tetracarbonyl **4c** than in the (precursor) pentacarbonyl **2c** (252.85(11) versus 257.32(10) pm), but the dihedral angles between the W−S bond and the C(1)WC(8) plane are very similar (147.5° in **2c**, 150.8° in **4c**).

Experimental

The syntheses and all manipulations were routinely carried out under argon; the solvents (THF, CH_3CN, CH_2Cl_2) were dried and saturated with argon. Standard procedures were used to prepare the starting complexes, $M(CO)_{6-x}(CH_3CN)_x$ (M = Cr, Mo, W; x = 1, 2, 3) [4,5], (norbornadiene)$M(CO)_4$ (M = Cr, Mo) [18] and (mesitylene)$Mo(CO)_3$ [55]. The ligand $S(C_7H_7)_2$ (**1**) was obtained [3] from tropylium bromide, C_7H_7Br [56], and H_2S.

Photo-induced decarbonylation of the hexacarbonyls $M(CO)_6$ in dilute THF solution to give the labile, solvent-stabilized pentacarbonyls, $[M(CO)_5](thf)$, was accomplished using the high-pressure mercury arc Hanovia (700 W).

Instrumentation: IR: Perkin Elmer 983 G (pentane). ^1H and ^{13}C NMR: Bruker ARX 250 ($CDCl_3$, reference signal $\delta(^1H)$ 7.24 (residual protons) and $\delta(^{13}C)$ 77.0).
FD-MS: Varian, MAT 311A.

X-Ray crystallography: Siemens P4 (Mo-K_α radiation, λ = 71.073 pm, graphite monochromator). Structure solution and refinement with the program package SHELXTL-PLUS V.5.1. The crystallographic data and the structure refinement details are collected in Table 9.

Syntheses

$Cr(CO)_5[S(C_7H_7)_2]$ (**2a**) and $Mo(CO)_5[S(C_7H_7)_2]$ (**2b**)
A tetrahydrofuran (THF) solution (10 ml) containing 214 mg (1 mmol) $S(C_7H_7)_2$ (**1**) was slowly added to an orange THF solution (50 ml) which contained ca. 1 mmol $M(CO)_{6-x}(CH_3CN)_x$ (x = 1, 2, 3), previously prepared by refluxing 1 mmol $M(CO)_6$ (M = Cr or Mo) in acetonitrile until 1.1 equivalents of CO had evolved. The reaction mixture was stirred at room temperature overnight. Then the solvent THF was removed under vacuum, the residue dissolved in pentane and filtered through cellulose filter flocks. The pentane filtrate was concentrated and cooled to −28 °C in a refrigerator, where slow crystallization occured.
$Cr(CO)_5[S(C_7H_7)_2]$, orange crystals, yield 155 mg (38.2 %), m.p. (dec.) above 77 °C, FD-MS: m/e 406 (M^+).
$Mo(CO)_5[S(C_7H_7)_2]$, dark-yellow crystals, yield 175 mg (38.9 %), m.p. (dec.) above 70 °C.

$W(CO)_5[S(C_7H_7)_2]$ (**2c**) and $W(CO)_5[S(CH_2Ph)(C_7H_7)]$ (**3c**)
A solution of 352 mg (1 mmol) $W(CO)_6$ in 100 ml of THF was irradiated for 7 h with a high-pressure mercury arc (Hanovia, 700W), until the intense ν(CO) band of the educt (1974 cm^{-1}) had

Table 9 Crystallographic data and structure refinement details

	$W(CO)_5[S(C_7H_7)_2]$ **(2c)**	$Cr(CO)_5[S(PhCH_2)(C_7H_7)]$ **(3a)**	$M(CO)_4[S(C_7H_7)(\eta^2\text{-}C_7H_7)]$	
			M = Mo (**4b**)	M = W (**4c**)
Empirical formula	$C_{19}H_{14}WO_5S$	$C_{19}H_{14}CrO_5S$	$C_{18}H_{14}MoO_4S$	$C_{18}H_{14}WO_4S$
Molecular mass / (g·mole^{-1})	538.21	406.36	422.29	510.20
Temperature / K	296(2)	293(2)	293(2)	293(2)
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$	$P2_1/c$	$P2_1/c$
Unit cell dimensions:				
a / pm	920.49(16)	1885.66(15)	1602.0(2)	1596.44(19)
b / pm	983.4(2)	1638.79(12)	942.3(3)	938.41(6)
c / pm	1200.27(15)	1459.06(11)	1195.5(2)	1193.44(10)
α / °	69.868(13)	90	90	90
β / °	70.009(10)	121.061(5)	102.011(9)	102.316(7)
γ / °	89.151(15)	90	90	90
Volume / (10^6 pm^3)	952.1(3)	3862.3(5)	1765.2(6)	1746.8(3)
Z	2	8	4	4
Density (calc.) / (Mg·m^{-3})	1.877	1.301	1.589	1.940
Absorption coefficient / mm^{-1}	6.201	0.716	0.879	6.750
F(000)	516	1552	848	976
Crystal dimensions / mm	0.22 × 0.17 × 0.12	0.18 × 0.15 × 0.12	0.15 × 0.14 × 0.04	0.25 × 0.18 × 0.10
Theta range / θ	1.94 to 25.00°	2.49 to 25.00°	2.52 to 24.99°	2.53 to 25.00°
Index ranges	$-10<h<1$, $-10<k<10$, $-14<l<13$	$-1<h<22$, $-1<k<19$, $-17<l<15$	$-17<h<17$, $-1<k<11$, $-1<l<12$	$-18<h<18$, $-11<k<1$, $-14<l<1$
Reflections collected	3609	3949	3074	3987
Independent reflections	3043 [R(int) = 0.0311]	3342 [R(int) = 0.0366]	2314 [R(int) = 0.0673]	3056 [R(int) = 0.0400]
Completeness to θ	91.0 %	98.6 %	74.6 %	99.5 %
Absorption correction	Empirical	Empirical	Empirical	Empirical
Max. and min. transmission	0.6969 and 0.4165	0.5917 and 0.5266	0.3507 and 0.2716	0.3379 and 0.2227
Refinement method	Full-matrix least-squares on F2	Full-matrix least-squares on F2	Full-matrix least-squares on F2	Full-matrix least-squares on F2
Data / restraints / parameters	3043 / 0 / 236	3342 / 0 / 235	2314 / 0 / 217	3056 / 0 / 218
Goodness-of-fit on F2	1.079	0.963	0.998	1.052
Final R indices [I > 2σ (I)]	R1 = 0.0184, wR2 = 0.0468	R1 = 0.0594, wR2 = 0.1382	R1 = 0.0632, wR2 = 0.1296	R1 = 0.0251, wR2 = 0.0659
R indices (all data)	R1 = 0.0201, wR2 = 0.0478	R1 = 0.1187, wR2 = 0.1745	R1 = 0.1253, wR2 = 0.1587	R1 = 0.0293, wR2 = 0.0685
Extinction coefficient	0.0097(4)			0.0029(2)
Largest diff. peak and hole / (10^{-6} e·pm^{-3})	0.781 and -0.803	0.421 and -0.314	1.074 and -0.816	1.617 and -1.148

become weak. Then 214 mg (1 mmol) $S(C_7H_7)_2$ (**1**) were added to the yellow THF solution and the reaction mixture stirred for 1 day at room temperature. The orange-brown THF solution was concentrated and purified by column chromatography on silica (elution with pentane/THF (10:1)). The product **2c** was obtained as light-yellow crystals, m.p. 55 °C (beginning decomposition). Yield 310 mg (57.6 %).

If the reaction mixture containing $[W(CO)_5](thf)$ and **1** is stirred for 1 day at 40 °C (instead at room temperature) and worked up in an analogous manner, the product is **3c**. Yellow crystals, m.p. (dec.) 55 °C. Yield 268 mg (49.8 %).

$Cr(CO)_5[S(CH_2Ph)(C_7H_7)]$ (**3a**)

a) The THF solution (100 ml) of 220 mg (1 mmol) $Cr(CO)_6$ was irradiated until the ν(CO) absorption in the IR spectra (1980 cm^{-1}) had almost disappeared (ca. 6 h). Then 214 mg (1 mmol) $S(C_7H_7)_2$ (**1**) were added and the dark orange-red solution of $[Cr(CO)_5](thf)$ was stirred at 25 °C for 2 days. The solvent THF was evaporated and the concentrated solution (ca. 1−2 ml) given on top of a chromatography column containing silica in pentane. Elution with pentane/THF (10:1) produced a solution from which yellow-green crystals of **3a** were obtained after concentration and cooling to −28 °C. M.p. 65 °C (beginning decomposition). Yield 187 mg (46.1 %). FD-MS: m/e 406 (M$^+$).

b) 214 mg (1 mmol) $S(C_7H_7)_2$ (**1**) were added to the solution of 256 mg (1 mmol) $Cr(CO)_4(\eta^4\text{-}nor\text{-}C_7H_8)$ in 30 ml of THF, and the reaction solution stirred for 2 days at ambient temperature. The solvent was removed under vacuum, the residue dissolved in pentane and the solution filtered over filter flocks. The filtrate was concentrated and cooled to −28 °C. Yellow-green crystals, yield 165 mg (40.6 %).

c) A solution of 203 mg (0.5 mmol) **2a** in 20 ml of THF was stirred at 60 °C for 5 h, then concentrated to 1−2 ml and subjected by column chromatography. Elution with pentane/THF (10:1) and crystallization gave yellow-green **3a**, yield 115 mg (56.7 %).

$W(CO)_5[S(CH_2Ph)(C_7H_7)]$ (**3c**)

A solution of 269 mg (0.5 mmol) $W(CO)_5[S(C_7H_7)_2]$ (**2c**) in 20 ml of THF was kept at 50 °C for 5 h. The isomerized complex **3c** was isolated by concentrating the dark orange solution and chromatographic purification. Yellow crystals, yield 142 mg (52.8 %).

$Mo(CO)_4[S(C_7H_7)(\eta^2\text{-}C_7H_7)]$ (**4b**)

a) A solution of 264 mg (1 mmol) $Mo(CO)_6$ in 100 ml of THF was irradiated with the UV lamp, until the strong ν(CO) band (1980 cm^{-1}) had nearly disappeared (3−5 h), and then stirred in the presence of 214 mg (1 mmol) $S(C_7H_7)_2$ (**1**) for 20 h at 25 °C. The solvent THF was removed under high vacuum, the residue dissolved in diethyl ether and the solution filtered over filter flocks. The filtrate was concentrated and cooled to −28 °C. Yellow crystals of **4b** were slowly formed, m.p. 80 °C (beginning decomp.), total decomp. at 95 °C. Yield 146 mg (34.6 %). FD-MS: m/e 424 (M$^+$).

b) A THF solution (30 ml) containing both 300 mg (1 mmol) $Mo(CO)_4(\eta^4\text{-}nor\text{-}C_7H_8)$ and 214 mg (1 mmol) $S(C_7H_7)_2$ (**1**) was stirred for 2 days at room temperature. Then the solvent was evaporated (together with *nor*-C_7H_8) under high vacuum and the residue dissolved in diethyl ether. Filtration over cellulose filter flocks and subsequent concentration to 1−2 ml gave a clear yellow solution from which yellow crystals were formed over night at -28 °C. Yield 175 mg (41.3 %).

$W(CO)_4[S(C_7H_7)(\eta^2\text{-}C_7H_7)]$ (**4c**)
A THF solution (10 ml) containing 214 mg (1 mmol) $S(C_7H_7)_2$ (**1**) was slowly added to an orange-red THF solution (50 ml) of $W(CO)_{6-x}(CH_3CN)_x$ (x = 1, 2, 3). The combined solution was stirred for 1 day. The dark-brown mixture was concentrated to 1−2 ml and then separated by column chromatography over silica (in pentane). An orange zone was eluted using pentane/THF (10:1), from which yellow-orange crystals could be obtained, m.p. 105 °C (decomp. 105−112 °C). Yield 215 mg (42.2 %). FD-MS: m/e 510 (M^+).

$Mo(CO)_3[(\eta^6\text{-}C_7H_7)\text{-}C_7H_7]$ (**5b**)
An equimolar mixture of $Mo(CO)_6$ (264 mg, 1 mmol) and $S(C_7H_7)_2$ (**1**) (214 mg, 1 mmol) in 50 ml of THF was heated under reflux for 1 day. The solvent THF was evaporated and replaced by diethyl ether, Et_2O. The etheral solution was concentrated to 2 ml and chromatographed over silica. Elution with pentane/THF (10:1) and crystallization gave a mixture of orange crystals, m.p. 131 °C (cf. 117−119 °C [7]). FD-MS: m/e 364 (M^+); IR (pentane): ν(CO) 1997(s), 1934(s), 1910(s) cm^{-1}.
Separation by TLC gave 85 mg (23.4 %) **5b**-*endo* and 37 mg (10.2 %) **5b**-*exo*.
5b-*endo*: ^1H NMR ($CDCl_3$): free ring: $\delta(H) = 0.79$m (H^1, *endo*), 5.04m (H^2, H^7), 6.11m (H^3, H^6), 6.53t (H^4, H^5); coordinated ring: $\delta(H') = 3.27$m ($H^{1'}$, *endo*), 3.98t ($H^{2'}$, $H^{7'}$), 4.92m ($H^{3'}$, $H^{6'}$), 5.92m ($H^{4'}$, $H^{5'}$).−^{13}C NMR ($CDCl_3$): free ring: $\delta(C) = 49.1$ (C^1), 122.4 (C^2, C^7), 126.3 (C^3, C^6), 130.7 (C^4, C^5); coordinated ring: $\delta(C') = 39.9$ ($C^{1'}$), 68.1 ($C^{2'}$, $C^{7'}$), 100.7 ($C^{3'}$, $C^{6'}$), 97.0 ($C^{4'}$, $C^{5'}$).
5b-*exo*: ^1H NMR ($CDCl_3$): free ring: $\delta(H) = 2.07$m (H^1, *exo*), 5.16m (H^2, H^7), 6.25m (H^3, H^6), 6.70t (H^4, H^5); coordinated ring: $\delta(H') = 2.42$m ($H^{1'}$, *exo*), 3.41t ($H^{2'}$, $H^{7'}$), 4.97m ($H^{3'}$, $H^{6'}$), 6.01m ($H^{4'}$, $H^{5'}$).−^{13}C NMR ($CDCl_3$): free ring: $\delta(C) = 43.0$ (C^1), 123.3 (C^2, C^7), 126.2 (C^3, C^6), 131.2 (C^4, C^5); coordinated ring: $\delta(C') = 39.4$ ($C^{1'}$), 62.6 ($C^{2'}$, $C^{7'}$), 100.3 ($C^{3'}$, $C^{6'}$), 97.4 ($C^{4'}$, $C^{5'}$).

Crystal structure analyses

All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms are in calculated positions. All hydrogen atoms were refined applying the riding model with fixed isotropic temperature factors. Crystallographic data (excluding structure factors) for the structures described in the present paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications, no. CCDC-241940 (**2c**), CCDC-241938 (**3a**), CCDC-248937 (**4b**) and CCDC-241939 (**4c**). Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. Code+(1223) 336-033; e-mail: deposit@chemcrys.cam.ac.uk).

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