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SULPHUR-CONTAINING METAL COMPLEXES

III *. TETRACARBONYL(CARBENE—THIO) COMPLEXES OF CHROMIUM(0) AND TUNGSTEN(0)

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Summary

Reactions of α-lithiated sulphides with $(CO)_6Cr$ and $(CO)_6W$ followed by alkylation with $(Et_3O)BF_4$ give the new series of neutral carbene-thiometal chelates of general formulae *cis*-$(CO)_4\underline{MC(OEt)[C(OH)=C(S}R^1)R^2]$ (I) and *cis*-$(CO)_4\underline{MC(OEt)[C(OEt)=C(S}R^1)R^2]$ (II). This route probably involves carbonyl insertion into a metal—carbene bond. Complexes of type II can also be prepared by treatment of pentacarbonyl(thio)metal complexes, $(CO)_5MS(CH_2R^2)R^1$, with BuLi, and subsequent alkylation. It is suggested that the second method proceeds via the generation of an anion α to a coordinated sulphur atom followed by a double (*cis-cis*) carbonylation.

Introduction

Although the formation of organometallic chelates has received much attention in recent years, with *ortho*-metallation reactions particularly well studied [2], metallocyclic compounds containing both carbene-carbon and heteroatom donor atoms are rare [3,4]. We now report on two methods for the preparation of group VI metalcarbonyl chelates in which bonding to the metals takes place via carbene carbon and sulphur donor atoms. Sulphides of the general formula $S(CH_2R^2)R^1$ are used as starting materials for the synthesis of the complexes *cis*-$(CO)_4\underline{MC(OEt)[C(OR)C(S}R^1)R^2]$ (M = Cr, W; R = H, Et). Below we describe the results for the cases in which R^1 = Me, Ph, R^2 = Ph, SPh, and $R^1R^2 = (CH_2)_3S$. Final confirmation of the structure of one of the latter compounds has come

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* For Part II, see ref. 1.

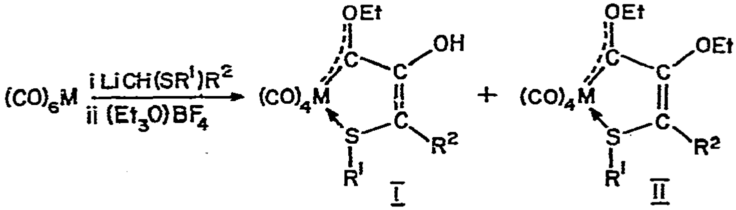
from a single-crystal X-ray study [1,5]. This study prompted us also to continue our work on pentacarbonyl(thio)metal complexes [6], some of which are used in the preparation of the carbene—thio chelates above, and we now also report on their synthesis and properties.

Results and discussion

Synthesis of carbene-thio chelates

Usually treatment of $(CO)_6Cr$ with LiR (R = organic group) affords the compounds $(CO)_5CrC(OLi)R$, which can be further alkylated by established procedures [7]. However, when $LiCH(SR^1)R^2$ was added to $(CO)_6M$ (M = Cr, W) in THF/hexane (1 : 10) solution according to Scheme 1, the mixture became darker and a brick-red precipitate formed, which could be alkylated to yield, after column chromatography, the chelate complexes I and II shown in the scheme. Interestingly, the complexes with $R^1 = CH_3$, Ph and R^2 = Ph could only be generated by this procedure if the lithium reagent had been synthesized from the appropriate sulphide and a BuLi · TMEDA (tetramethylethylenediamine) complex [8]. For M = W, the enol complexes I (except in the case where $R^1R^2 = (CH_2)_2S$) were even relatively unstable under nitrogen, and therefore not characterised. When two equivalents of both BuLi and oxonium salt were used during the preparation of the complexes, II was formed exclusively, in ca 12—15% higher yields than before. The complex $(CO)_5MC(OEt)Bu$ [9], formed from unreacted BuLi, $(CO)_6M$ and $(Et_3O)BF_4$, was also obtained in a low concentration in each case.

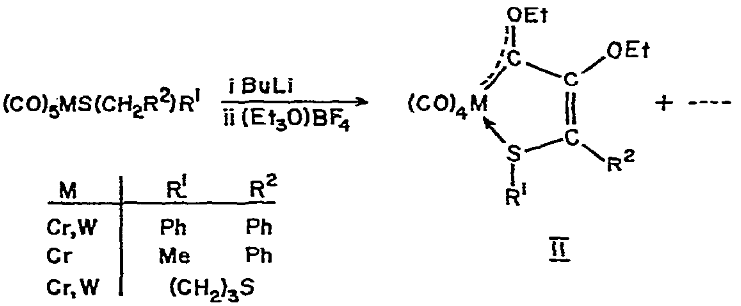
SCHEME 1



R^1	R^2	M I	M II
Me	Ph	Cr	Cr,W
Ph	Ph	Cr	Cr,W
Ph	SPh	Cr	Cr,W
$(CH_2)_3S$		Cr,W	Cr,W

During a preliminary study of the reactions of the complexes *cis*-$(CO)_4CrC(OEt)[C(OEt)C(SR^1)R^2]$ (R^1 = Me; R^2 = Ph; $R^1R^2 = (CH_2)_3S$), we found that reaction with hydrogen bromide yielded the pentacarbonyl(thio) complexes $(CO)_5CrS(CH_2R^2)R^1$ by a novel double decarbonylation reaction. In virtually the reverse of this reaction, treatment of pentacarbonyl(thio)metal complexes with the strong base BuLi, followed by similar alkylation as before (Scheme 2), gave red solutions from which the desired chelates were isolated by chromatography. This not only provided a second route to the disubstituted carbonyl

SCHEME 2



M	R1	R2
Cr,W	Ph	Ph
Cr	Me	Ph
Cr,W	$(CH_2)_3S$	

II

complexes but also led to a method for the preparation of *fac*-trisubstituted compounds [10]. It is not clear why the Bu-carbene complex $(CO)_5MC(OEt)Bu$ was again formed (albeit in very low yields) in this method. Yields obtained for the complexes II from the second method were somewhat lower than in those from the first procedure, and although the expected enol complexes I (compare

TABLE 1

YIELDS AND ANALYTICAL DATA FOR THE COMPLEXES $(CO)_4MC(OEt)[C(OH)C(SR^1)R^2]$ (I) AND $(CO)_4MC(OEt)[C(OEt)C(SR^1)R^2]$ (II)

Compound	M	R1	R2	M.p. (°C)	Yield (%) [a]	Analysis: Found (calcd.) (%)				
						C	H	M	O	S
Ia	Cr	Me	Ph	110—112	10	50.01 (49.75)	3.74 (3.65)			8.28 (8.28)
Ib	Cr	Ph	Ph	132—134	14	56.27 (56.25)	3.74 (3.60)	11.39 (11.60)	21.48 (21.41)	7.07 (7.15)
Ic	Cr	Ph	SPh	114—115	12	52.46 (52.49)	3.41 (3.36)			13.30 (13.35)
Id	Cr	$(CH_2)_3S$		114—116	11	38.69 (39.12)	3.45 (3.28)	14.06 (14.11)	26.41 (26.07)	17.10 (17.40)
Ie	W	$(CH_2)_3S$		118—119	8	28.91 (28.81)	2.51 (2.42)	37.10 (36.76)	19.37 (19.19)	12.79 (12.82)
IIa	Cr	Me	Ph	Oil [b]	20(6)	52.85 (52.17)	4.68 (4.38)			7.54 (7.74)
IIb	W	Me	Ph	Oil [b]	ca. 10					
IIc	Cr	Ph	Ph	101—102	22(14)	57.81 (57.98)	4.27 (4.23)	10.76 (10.91)	20.47 (20.15)	6.65 (6.73)
IId	W	Ph	Ph	Oil [b]	ca. 15(10)					
IIe	Cr	Ph	SPh	Oil	21	54.41 (54.32)	3.86 (3.90)			12.72 (12.60)
IIf	W	Ph	SPh	94—95	16	43.26 (43.20)	3.25 (3.15)			9.89 (10.03)
IIg	Cr	$(CH_2)_3S$		44—46	26(15)	42.84 (42.41)	4.24 (4.06)			16.24 (16.17)
IIh	W	$(CH_2)_3S$		54—56	15(10)	32.13 (31.83)	3.14 (3.05)	34.80 (34.80)	18.31 (18.17)	11.90 (12.14)

[a] Yields obtained according to the second method (see Experimental section) are in brackets. Compounds I and II with the same metal and substituents were obtained during the same synthesis. [b] These oils, although completely characterized by IR, NMR and mass spectra are fairly unstable and could not be obtained analitically pure.

TABLE 2

ANALYTICAL DATA FOR PENTACARBONYL(THIO) COMPLEXES [a]

Compound	M.p. (°C)	Analysis: Found (calcd.) (%)				
		C	H	Cr	O	S
$(CO)_5CrS(CH_2Ph)_2$	97—98	56.55 (56.20)	3.45 (3.47)	12.50 (12.80)	19.48 (19.70)	7.88 (7.89)
$(CO)_5CrS(CH_2Ph)Ph$	70—72	55.23 (55.10)	3.13 (3.08)	13.27 (13.25)		
$(CO)_5Cr\overline{S(CH_2)_3S}CH_2$	40—41	34.60 (34.61)	2.58 (2.58)	16.70 (16.65)		20.22 (20.53)
$(CO)_5CrSPh_2$	oil [b]					
$(CO)_5W\overline{S(CH_2)_3S}CH_2$	73—74	24.38 (24.34)	1.84 (1.83)			14.34 (14.44)

[a] For other pentacarbonyl(thio) complexes, compare references 6 and 21. [b] This unstable compound has not been analysed.

Scheme 1) were again shown to be present by thin layer chromatography, they were not isolated because the yields were too low.

The products, melting points, and yields are summarised in Table 1. Compounds obtained as red crystals are air-stable, but the oils decompose slowly, even at —30°C under nitrogen. Generally, the enol complexes I have higher melting points than their dialkylated counterparts II, which may be due to the observed intermolecular hydrogen bonding for the latter complexes in the solid state [1]. All the products are very soluble in more polar organic solvents such as $CHCl_3$, CH_2Cl_2 and ether, but somewhat less soluble in hexane. Table 1 shows that the yields obtained are dependent upon the groups R^1 and R^2 on the parent sulphide. Comparable reactions did not occur when the sulphides with R^1 = CH_2Ph, R^2 = Ph and R^1 = Ph, R^2 = Me, respectively, were used to prepare the organolithium starting reagents (Scheme 1) or thio complexes (Scheme 2).

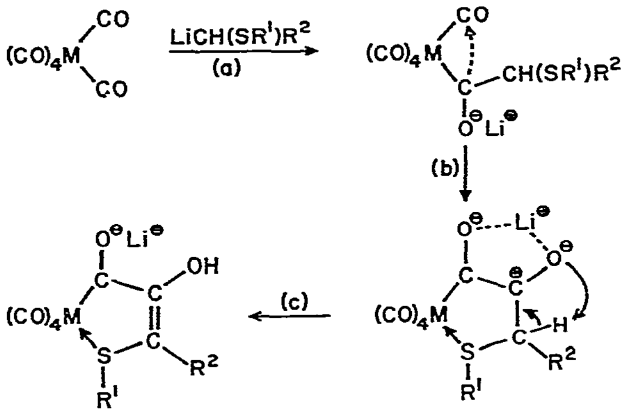
A few pentacarbonyl(thio)chromium(0) complexes, were prepared by UV irradiation [11] and isolated by column chromatography (Table 2). The tungsten thio complexes are generally more unstable than their chromium analogues and only $(CO)_5W\overline{S(CH_3)_3S}CH_2$ is described.

Reaction mechanisms

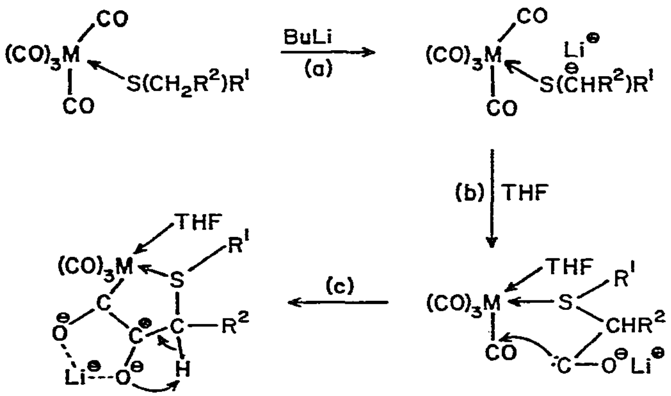
The mechanism (Scheme 3), we propose as a working hypothesis for the first synthesis, has not yet been substantiated by a mechanistic study. In this mechanism, the first intermediate is formed (step (a)) by a "Fischer-type" attack [12] on a terminal CO and then a five-membered ring is generated via a reaction step (b) which involves migration of the carbene group to a *cis*-coordinated carbonyl ligand (carbonyl insertion [13]) and the occupation of the vacated coordination site by an available and promoting sulphur-donor atom of the ligand. Some reasonable intramolecular migrations then lead to the carbene lithium salt (step (c)), which can be alkylated to give the product I. The complex II is obtained similarly after one of the intermediates has lost a proton due to a further reaction with $LiCH(SR^1)R^2$ or unreacted BuLi before alkylation.

A possible route to the chelate complexes by the second method (vide supra) is outlined in Scheme 4. In step (a) the BuLi generates an anion α to a coordi-

SCHEME 3



SCHEME 4



nated sulphur atom of the thio complex. This is followed by a carbonyl abstraction (step (b)), comparable to the formation of the unstable carbene, $Me_3SiC(O)Li$, from Me_3SiLi and carbon monoxide [14]. A THF (tetrahydrofuran) solvent molecule takes up the vacant coordination position. The second carbonylation involves a nucleophilic attack of a carbene carbon on a *cis* coordinated carbonyl group (step (c)), to form the last intermediate in the scheme, which can be stabilized by a rearrangement similar to that proposed before (step (c), Scheme 3). During this cyclisation, another proton is abstracted by BuLi to give mainly a dilithium salt. Only during alkylation is the solvent molecule replaced by a CO ligand transferred from one of the carbonyl complexes present in the mixture. These assumptions are supported not only by the fact that *fac*-trisubstituted carbonyl complexes were obtained when a series of π-acid ligands were added to the reagent thio complexes $(CO)_5MS(CH_2R^2)R^1$ together with the BuLi, but also by the observation that tricarbonyl complexes containing ligands (such as $P(OMe)_3$) which are reactive towards BuLi, could still be obtained when these ligands were added after the BuLi had finished reacting completely and the excess thereof been removed [15]. Somewhat disturbing, however, were the findings that (a) no reaction took place between the lithium salt obtained before alkylation (presumably $(CO)_4MC(OLi)[C(OLi)C(SR^1)R^2]$, M = Cr) and Cp_2TiCl_2 [16] and (b) yields could not be increased by bubbling CO through the solution during the final alkylation step. Result (b) may be explained on the basis that the proposed carbonyl transfer is not a rate determining step in the process.

Infrared and electronic spectra of the chelates and pentacarbonyl—thio complexes

As expected for C_s symmetry, four CO vibrations were observed for the new tetracarbonyl (carbene—thio) complexes of the type $(CO)_4ML_1L_2$. When assigning the bands in Table 3 however, we chose to regard the local symmetry of the carbonyl groups in these complexes as pseudo-C_{2v}, for which the normal modes of vibration are known [17]. Not only are the position and relative intensities of the four bands comparable to the reported (C_{2v} symmetry) spectra for non-chelated tetracarbonyl(carbene—phosphine) complexes in the same solvent [18], they also show the solvent dependence previously discussed by Poilblanc and Bigorgne [19] (who chose another designation scheme according to which our B_1 [17] becomes B_2 and vica versa) for complexes of the type $(CO)_4ML_1L_1$. The fact that Brunner and Herrmann [20] found a different intensity pattern to ours for complexes of the type $(CO)_4ML_1L_2$, is therefore probably due to the more polar solvent ($CHCl_3$) used by them. Two main regions of electronic absorption were observed for each of the tetracarbonyl complexes, viz. a well-defined band at ca. 20,000 cm^{-1}, and a broad band (which might consist of more than one maximum) at ca. 31,000 cm^{-1} (Table 3). The lower frequency absorption, which has no counterpart in the spectra of the free ligands, and is probably due to a *d*—*d* transition [22], is influenced to a small extent (variations of $<8\%$ occur) by the substituents R^1 and R^2 on the bidentate carbene—thio ligand. Changing the central metal from Cr to W, leads to a $\leqslant 5\%$ increase in this frequency. More important is the $>20\%$ decrease in absorption frequency observed when a CO ligand in a pentacarbonyl—sulphide complex (vide infra) is replaced

TABLE 3

INFRARED AND ELECTRONIC SPECTROSCOPIC DATA [a]

Compound	$\nu(CO)$ [b] (cm^{-1})				ν (electronic) (cm^{-1})	
	A_1^1	A_1^2	B_1	B_2		
Ia	2039s	1948s	1936vs	1890s	31 348	19 268
Ib	2032s	1948s	1934vs	1886s	30 120	18 975
Ic	2020s	1948s	1932vs	1885s	29 673	18 939
Id	2032s	1942(sh)	1929vs	1888s	30 488	19 417
Ie	2035s	1938s	1930vs	1880s	29 070	19 763
IIa	2035s	1938s	1925vs	1887s	31 949	19 418
IIb	2038s	1942s	1918vs	1881s	32 053	20 405
IIc	2028s	1944s	1929vs	1886s	31 545	19 194
IId	2030s	1940s	1930vs	1887s	32 051	20 202
IIe	2030s	1942s	1928vs	1885s	30 395	19 048
IIf	2035s	1937s	1928vs	1885s	29 761	19 801
IIg	2032s	1945(sh)	1929vs	1888s	30 303	19 380
IIh	2040s	1948s	1920vs	1888s	30 488	20 202

[a] Measured in hexane; s, strong; sh, shoulder; vs, very strong. [b] Assignments based on pseudo-C_{2v} symmetry and phases of symmetry as defined by Braterman [17].

TABLE 4

SPECTROSCOPIC DATA[a] FOR PENTACARBONYL(THIO) COMPLEXES

Complex	Infrared ν(CO) (cm^{-1})				Electronic ν(cm^{-1})		
$(CO)_5CrS(CH_2Ph)_2$	2082m (A_1^1)	1988w (B)	1945[b] vs (E)	1936(sh) (A_1^2)	32 050	31 152	25 253
$(CO)_5CrS(CH_2Ph)Ph$	2083m	1986w	1945[c] vs	1932(sh)	33 113	32 468	24 876
$(CO)_5CrS(CH_2Ph)Me$[d]	2070m	1985w	1944vs	1937(sh)			
$(CO)_5CrSPh_2$	2080m	1988w	1948vs	1935(sh)	33 340	32 787	24 691
$(CO)_5CrS(CH_2)_3SCH_2$	2078m	1984w	1940vs	1936(sh)	32 051	31 250	26 042
$(CO)_5WS(CH_2)_3SCH_2$	2078m	1978w	1941vs	1936(sh)	32 573	31 950	17 170

[a] Measured in hexane; m, medium; w, weak; vs, very strong; sh, shoulder. [b] Average of 1942 and 1948 values. [c] Average of 1943 and 1947 values. [d] Ref. 21.

during the formation of one of the heterometallocyclic tetracarbonyl complexes under discussion. This can be rationalized qualitatively in terms of the now well-known MO-diagrams for octahedral complexes [23], when an intermediate situation, between the extreme cases with and without metal to ligand π-bonding, is approached. The spectroscopic data for the pentacarbonyl(thio)chromium complexes (Table 4) are consistent with previous results [6], and establish the fact that the σ(donor)/π(acceptor) ratio falls between that for phosphine and amine monodentate ligands not only for dialkylsulphide ligands but also for alkyl-aryl and diaryl sulphides. With the relatively bulky thio ligands $S(CH_2Ph)Ph$ and $S(CH_2Ph)_2$, a splitting of the E band in the IR spectrum occurs [24].

NMR spectra

All the expected well resolved signals in the ^1H NMR spectra of the new complexes are in accord with the given structures, and are assigned in Tables 5 and 6. The electron loss on co-ordination of the thio ligands in the pentacarbonyl complexes is clearly seen on comparing the appropriate τ-values with the chemical shifts observed for the free ligands. It is interesting that two well-defined chemical shifts can be assigned to the different phenyl protons in the complex $(CO)_5CrS(CH_2Ph)Ph$, whereas the signals are not distinguishable in the free ligand.

The ^{13}C NMR data for selected products are listed in Table 7. The chelate compounds manifest themselves in these spectra by large low-field carbene carbon chemical shifts of 295—330 ppm (relative to TMS), which is comparable to the value reported for an unsubstituted vinylcarbene [25]. Even though the signals for the *cis* carbonyl ligands in the chromium (ca. 216 ppm) and tungsten (ca. 200 ppm) complexes are respectively constant and comparable to reported values for mono- and disubstituted carbonyl complexes [26,27], the ^{13}C chemical shifts for the *trans* carbonyl groups, both in the chromium (232 ppm) and tungsten (214 ppm) chelate complexes, are shifted downfield compared to *trans* carbonyl groups in both pentacarbonyl and tetracarbonyl complexes such as

TABLE 5

PROTON NMR CHEMICAL SHIFTS (τ REL TO TMS)[a] FOR THE COMPLEXES I AND II IN $CDCl_3$

Complex	$C_{carb}O\underline{CH_2}$	$CO\underline{CH_2}$	$C\underline{OH}$	$C_{carb}OCH_2\underline{CH_3}$	$COCH_2\underline{CH_3}$	$C\underline{Ph}$	$S\underline{Ph}$
Ia[b]	4.77q		3.47s	8.27t		2.75	
Ib	4.82q		3.10s	8.31t		2.82m	
Ic	4.81q		3.23s	8.25t			2.72m
Id[c]	4.88q		3.79s	8.32t			
Ie[d]	5.08q		3.58s	8.39t			
IIa[e]	4.82q	6.26q		8.31t	8.83t	2.60m	
IIb[f]	5.03q	6.27q		8.36t	8.75t	2.65m	
IIc	4.86q	6.19q		8.34t	8.82t	2.85m	
IId	5.12q	6.22q		8.33t	8.83t	2.80m	
IIe	4.90q	5.91q		8.31t	8.58t		2.87m
IIf	5.08q	5.90q		8.33t	8.56t		2.76m
IIg[g]	4.94q	6.10q		8.37t	8.80t		
IIh[h]	5.54q	6.10q		8.42t	8.71t		

[a] Abbreviations: s, singlet; t, triplet; q, quartet; m, multiplet. The expected number of protons corresponding to each signal was indicated by integration. [b] Others: 7.59s ($S\underline{Me}$). [c] Others: 7.53m ($SCH_2\underline{CH_2}$); 6.89q ($S\underline{CH_2}$). [d] Others: 7.59m ($SCH_2\underline{CH_2}$); 6.85q ($S\underline{CH_2}$). [e] Others: 7.66s ($S\underline{Me}$). [f] Others: 7.41s ($S\underline{Me}$). [g] Others: 7.59m ($SCH_2\underline{CH_2}$) 6.85m ($S\underline{CH_2}$). [h] Others: 7.60m ($SCH_2\underline{CH_2}$) 6.80m ($S\underline{CH_2}$).

TABLE 6

PROTON NMR SPECTRA OF THIO COMPLEXES AND FREE LIGANDS[a]

Compound	$\tau(\underline{CH_2}Ph)$	$\tau(CH_2\underline{Ph})$	$\tau(\underline{Ph})$	$\tau(S\underline{CH_2}S)$	$\tau(S\underline{CH_2}CH_2)$	$\tau(SCH_2\underline{CH_2})$
$S(CH_2Ph)_2$	6.48s	2.80m				
$(CO)_5CrS(CH_2Ph)_2$	6.19s	2.73m				
$S(CH_2Ph)Ph$	6.13s	2.77m				
$(CO)_5CrS(CH_2Ph)Ph$	5.87s	2.81m	2.64m			
SPh_2			2.92m			
$(CO)_5CrSPh_2$			2.83m			
$\overline{S(CH_2)_3S\check{C}}H_2$				6.26s	7.25m	7.90m
$(CO)_5Cr\overline{S(CH_2)_3S\check{C}}H_2$				6.24s	7.15m	7.77m
$(CO)_5W\overline{S(CH_2)_3S\check{C}}H_2$				6.06s	7.02m	7.77m

[a] $CDCl_3$ solutions. τ values relative to internal TMS. Abreviations as in Table 4. The correct number of protons is present in each case.

$(CO)_5CrC(OEt)Me$ (226 ppm) and $(CO)_4W(Ph_2P(CH_2)_2PPh_2)$ (204.6 ppm).

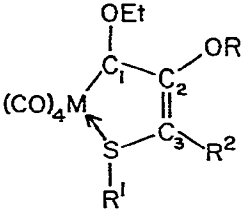
The signals corresponding to *cis* and *trans* carbonyl groups in the pentacarbonyl thiochromium complexes (*cis*: 215; *trans*: 222 ppm) are insensitive to changes in the alkyl or aryl groups on the coordinating sulphur atom.

Mass spectra

Except for compound Ic, which decomposed in the mass spectrometer, parent molecular ions, M^+, were observed for all the tetracarbonyl complexes $(CO)_4\underline{MC(OEt)[C(OR)C(S}R^1)R^2]$ (R = H, Et). The compounds exhibit metastable supported decompositions due to initial CO and Et· losses. The fragmenta-

TABLE 7

^{13}C NMR CHEMICAL SHIFTS[a] FOR PENTACARBONYL(THIO) COMPLEXES AND FOR THE COMPOUNDS

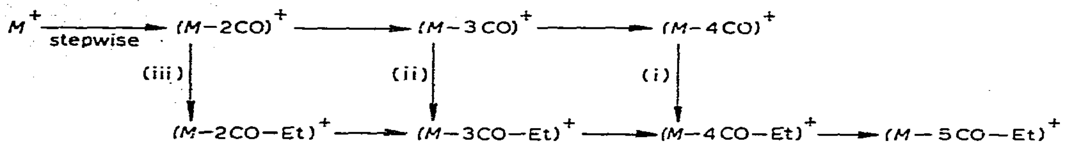


Compound	C_1	C_2	C_3	CO-groups	
				cis	*trans*
$(CO)_5CrS(Et)_2$ [b]				216	222
$(CO)_5CrS(CH_2Ph)Ph$				215	222
$(CO)_5Cr\overline{S(CH_2)_3S\check{C}}H_2$				215	222
$(CO)_5W\overline{S(CH_2)_3S\check{C}}H_2$				197	204
Ib	321	163	138	216	230, 232
Id	313	161	139	217	230, 232
Ie	295	167	156	200	211, 214
IIc	330	166	148	217	230, 232
IIg	312	161	138	216	230, 231

[a] Measured in $(CD_3)_2CO$, ppm from TMS. [b] Ref. 6.

SCHEME 5

INITIAL FRAGMENTATION ROUTES FOR THE COMPLEXES $(CO)_4MC(OEt)[C(OR)C(SR^1)R^2]$, M



Route	Complex
(i)	All Cr-complexes, IId
(ii)	Ie, IIf, IIh
(iii)	IIb

tion pattern is determined by the central metal, M and, for M = W, by the groups R^1 and R^2 as explained in Scheme 5. For all the chromium complexes, the ion $(M - 4\ CO)^+$ is the most abundant, whereas for the tungsten complexes the ions $(M - 3\ CO - Et)^+$ (IIb, IIf, IIh), $(M - 4\ CO - Et)^+$ (IId) and $(M - 5\ CO - Et)^+$ (Ie) appear with the highest intensity. At present we are investigating the different, and more complicated, fragmentation paths followed by the ions $(M - 5\ CO - Et)^+$. All the pentacarbonylthio complexes first loose the five carbonyl ligands before undergoing further fragmentation.

Experimental

General

All preparations and manipulations were carried out under purified nitrogen. Solvents were carefully dried and freshly distilled under nitrogen before use. Commercially available ligands and metalhexacarbonyls were used without purification.

Microanalysis were performed by F. Pascher and E. Pascher, Microanalitical Laboratory, Bonn. Infrared spectra were obtained with a Perkin—Elmer Model 257 and calibrated against polystyrene film. The ^1H NMR spectra were recorded in $CDCl_3$ with the Varian HA100 at 100 MHz or Varian T60 operating at 60 MHz relative to internal TMS and ^{13}C NMR with a Varian CFT-20. Chemical shifts in the latter case were measured by reference to the $(CD_3)_2CO$ solvent but are reported relative to TMS by use of the relation $\delta(TMS) = \delta((CD_3)_2CO) + 29.2$. Mass spectra were recorded on a Hitachi Perkin—Elmer RMU-6H (70 eV) instrument and electronic spectra on a calibrated Shimadzu double beam spectrophotometer. Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. An Engelhard-Hanovia mercury vapour lamp, enclosed in a water-cooled quartz jacket during irradiation, was used for photochemical reactions.

Synthesis of pentacarbonyl(thio)metal complexes

Pentacarbonyl(benzylphenylthio)chromium(0). This synthesis is described as a typical example. A stirred solution of 2.2 g (10 mmol) $(CO)_6Cr$ and 2.0 g (10 mmol) $S(CH_2Ph)Ph$ in 20 ml THF was irradiated for 2 h at room temperature.

The solvent was then removed in vacuo and the residue chromatographed on a silica gel column. Elution with hexane (—10°C) gave firstly unreacted hexacarbonyl and secondly, a yellow zone which was concentrated and stripped of solvent under vacuum. Recrystallization from ether/hexane (—30°C) yielded 2.98 g (76%) yellow crystals of the air stable product.

Other pentacarbonyl complexes were prepared analogously.

Synthesis of tetracarbonyl(carbene—thio)metal chelates

Two methods were used for the preparation of these complexes, illustrated by representative details below: *cis*-[(Ethoxy)-(1-phenylmercapto-2-hydroxystyryl)-carbene-C,S]tetracarbonylchromium(0) Ib, and *cis*-[(ethoxy)-(1-phenylmercapto-2-ethoxy-styryl)-carbene-C,S]tetracarbonylchromium(0) IIc.

Method A. To a stirred solution of 2.0 g (10 mmol) $S(CH_2Ph)Ph$ in 50 ml hexane at —20°C, 12 mmol of BuLi · TMEDA complex [8] in 15 ml hexane was added dropwise, the mixture stirred for an additional 2 h and then added to 2.2 g (10 mmol) $(CO)_6Cr$ in 100 ml THF/hexane (1 : 10). During 1 h of stirring, the temperature of the mixture was allowed to rise to room temperature. The supernatent liquid was then decanted and the dark red viscous residue washed thrice with 20 ml hexane and stripped of solvent under vacuum. After alkylation with 2.0 g (10 mmol) $(Et_3O)BF_4$ in CH_2Cl_2 (—10°C), the solvent was evaporated under reduced pressure and the residue chromatographed on SiO_2 (—10°C) with CH_2Cl_2/hexane (1 : 1) as the eluant. The faster moving red band afforded, after recrystallization from ether/hexane at —30°C, 1.04 g (22% based on $(CO)_6Cr$) of $(CO)_4\underline{CrC(OEt)[C(OEt)C(S}Ph)Ph]$ IIc as air-stable dark red crystals.

The second red fraction gave, after crystallization from ether/hexane, 0.64 g (14%) of red crystals $(CO)_4\underline{CrC(OEt)[C(OH)C(S}Ph)Ph]$ Ib. The same procedure as above was followed with the other appropriate sulphides. For $\overline{S(CH_2)_3SCH_2}$ and $S(Ph)CH_2SPh$ it was not necessary to use TMEDA, and THF was used as solvent for the lithiation [28]. Fluorosil columns were used to separate the tungsten compounds.

Method B. To a cooled (—40°C) solution of 3.92 g (10 mmol) $(CO)_5CrS(CH_2Ph)Ph$ in 100 ml ether/hexane (1 : 10), 10 mmol BuLi in hexane was added dropwise. Stirring was continued for 3 h, during which the temperature was increased to 22°C. Subsequent work-up was as in Method A. Chromatography furnished consecutively $(CO)_5CrC(OEt)Bu$ [9] (in low yield), unreacted thio complex, complex IIc, which was recrystallized as above to give 0.62 g (14% based on $(CO)_5CrS(CH_2Ph)Ph$), and complex Ib in a very low yield.

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