Sulphur-containing Metal Complexes. Part 9.[1] Synthesis of Trisubstituted Aminocarbene–Thioether Chelates of Chromium(0) and Tungsten(0)

Johanna C. Viljoen, Simon Lotz, Lorna Linford, and Helgard G. Raubenheimer *
Department of Chemistry, Rand Afrikaans University, Johannesburg 2000, South Africa

Several isocyanide–thioether complexes, *cis*-$[M(CNR)(CO)_4\{S(R^1)CH_2R^2\}]$ [M = Cr: R = Bu^t, $R^1R^2 = (CH_2)_3S$; R = R^1 = Ph, R^2 = SPh; R = cyclo-C_6H_{11} or CH_2Ph, $R^1R^2 = (CH_2)_3S$. M = W: R = Bu^t, $R^1R^2 = (CH_2)_3S$] were prepared by u.v. irradiation of the corresponding pentacarbonyl(isocyanide) complexes in the presence of the thioether compounds. Deprotonation of two of these, *cis*-$[M(CNBu^t)(CO)_4\{\overline{S(CH_2)_3SCH_2}\}]$ (M = Cr or W), with LiBu and addition of PEt_3, resulted (*via* consecutive carbonylation and isocyanide insertion into a metal–carbene bond) in the formation of the evasive trisubstituted aminocarbene–thioether chelates, *fac*-$[\underline{M(CO)_3\{C(NHBu^t)C(OEt){=}\overline{CS(CH_2)_3S}}\}(PEt_3)]$, upon alkylation with $[Et_3O][BF_4]$. Replacement of the phosphine by 1,3-dithiolane-2-thione under similar reaction conditions yielded, unexpectedly, the substitution products *cis*-$[Cr(CNR)(CO)_4\{S{=}\overline{CS(CH_2)_2S}\}]$ (R = Bu^t or Ph). When in addition, the isocyanide had been substituted for CO, the first saturated cyclic dithiocarbene complex of chromium, $[Cr(CO)_5\{\overline{CS(CH_2)_2S}\}]$, was formed.

Metallated thioacetals, for example 2-lithio-1,3-dithiane and bis(phenylthio)methyl-lithium, react with $[Cr(CO)_6]$ and $[W(CO)_6]$ to yield tetracarbonyl(alkoxycarbene–thioether) complexes, *cis*-$[\overline{M(CO)_4\{C(OEt)C(OR){=}C(SR^1)}R^2\}]$ [M = Cr or W, R = H or Et, R^1 = Me or Ph, R^2 = Me, Ph, or SPh, $R^1R^2 = (CH_2)_3S$] of chromium and tungsten after alkylation with $[Et_3O][BF_4]$.[2] Similarly, the reaction of the above-mentioned lithiated thioacetals with pentacarbonyl(phenyl isocyanide) complexes of the same metals give aminocarbene–thioether chelates, *cis*-$[\underline{M(CO)_4\{C(NHPh)C(OEt){=}\overline{CS(CH_2)_3S}}\}]$, upon alkylation.[1] The reactions are explained by the nucleophilic attack of the thioether anion on a carbonyl ligand, followed by a formal insertion of (co-ordinated) isocyanide into a metal–carbene bond. The proposed mechanism for the reaction is supported by the isolation of an alkylated intermediate, *cis*-$[M(CNPh)(CO)_4\{C(OEt)\overline{CHS(CH_2)_3S}\}]$.

The preparation of the *fac*-tricarbonyl(alkoxycarbene–thioether) complexes, *fac*-$[\overline{M(CO)_3\{C(OEt)C(OEt){=}C(SR^1)}R^2\}L]$ [M = Cr or W, R^1 = Me or Ph, R^2 = Me, Ph, or SPh, $R^1R^2 = (CH_2)_3S$] from pentacarbonyl(thioether)metal compounds in the presence of suitable π-acceptor ligands (L = phosphine, phosphite, or isocyanide) has been described.[3] The necessary pentacarbonyl(thioether) compounds, $[M(CO)_5\{S(R^1)CH_2R^2\}]$ are prepared by u.v. irradiation of the corresponding hexacarbonyl complex in the presence of the thioether ligand.

We were not successful in preparing trisubstituted aminocarbene–thioether chelates from *fac*-tricarbonyl(alkoxycarbene–thioether) complexes by aminolysis of the latter class of compounds.[1] Therefore, to prepare these sought after compounds and to establish whether the above-mentioned analogy between co-ordinated CO and CNR is also applicable to the consecutive double carbonylation process during the formation of the trisubstituted carbonyl chelates, the present study was undertaken.

$$[M(CNR)(CO)_5] + S(R^1)CH_2R^2 \xrightarrow{h\nu} \underset{(1)\text{—}(5)}{cis\text{-}[M(CNR)(CO)_4\{S(R^1)CH_2R^2\}]} + CO$$

(1) M = Cr, R = Bu^t, $R^1R^2 = (CH_2)_3S$
(2) M = W, R = Bu^t, $R^1R^2 = (CH_2)_3S$
(3) M = Cr, R = R^1 = Ph, R^2 = SPh
(4) M = Cr, R = cyclo-C_6H_{11}, $R^1R^2 = (CH_2)_3S$
(5) M = Cr, R = CH_2Ph, $R^1R^2 = (CH_2)_3S$

Scheme 1.

Results and Discussion

Several complexes of the type *cis*-$[M(CNR)(CO)_4\{S(R^1)CH_2R^2\}]$ (M = Cr or W) were prepared by u.v. irradiation of a tetrahydrofuran (thf) solution of the corresponding pentacarbonyl(isocyanide) complex[4] and thioether compound. Unstable yellow crystals [compounds (1), (2), and (5)] and oils [compounds (3) and (4)] were isolated after silica-gel column chromatography (hexane–CH_2Cl_2, 3 : 1) (Scheme 1). All these compounds decomposed slowly, even under nitrogen, at 20 °C. The new complexes, *cis*-$[M(CNR)(CO)_4\{S(R^1)CH_2R^2\}]$, were characterised by elemental analysis (the crystals; Table 1) and their i.r., ^1H n.m.r., and mass spectra. The oils were not analysed.

The i.r. spectra [Table 2(*a*)] of the isocyanide–thioether complexes (1)—(5) in the ν(CO) region consisted characteristically of four peaks of relative intensity medium, strong, very strong, medium. The expected number of resonances and correct relative intensities were observed in the ^1H n.m.r. spectra of the new compounds (Table 3). Mass spectra were obtained for all five isocyanide–thioether compounds. In each case a rearrangement ion $[M(CNR)(CO)_5]^+$, as well as the fragment ion $[S(R^1)CH_2R^2]^+$, were observed. In addition, the fragment ion $[Cr\overline{S(CH_2)_3SCH_2}]^+$ (m/e = 172) was present for complex (1) (Table 4).

Treatment of the isocyanide–thioether complexes (1) and

Table 1. Characterisation data for the new complexes [a]

Complex	Yield (%)	M.p. (°C)	Colour	Analysis [b] (%) C	H	S	Other	
(1)	45	90—93 (decomp.)	Yellow	42.35	4.45	17.30		
				(42.50)	(4.65)	(17.45)		
(2)	41	80—82	Yellow	31.35	3.30	12.70		
				(31.25)	(3.45)	(12.85)		
(3)	24	Oil	Yellow					
(4)	28	Oil	Yellow					
(5)	36	90—93 (decomp.)	Yellow	48.00	3.70	15.75		
				(47.85)	(3.75)	(15.95)		
(6)	24	110—112	Purple	49.00	7.15		2.75	6.15
				(49.10)	(7.10)		(2.75) (N)	(6.05) (P)
(7)	21	139—141	Purple	38.95	5.55		2.15	
				(39.05)	(5.65)		(2.15) (N)	
(8)	15, 9 [c]	97—99	Purple	46.80	6.45	12.40		
				(46.90)	(6.45)	(13.70)		
(9)	28	113—115	Dark red	37.35	3.50	24.45	3.55	
				(37.60)	(3.40)	(25.10)	(3.65) (N)	
(10)	24	112—114	Dark red	41.45	2.45	21.75		
				(41.70)	(2.25)	(23.85)		
(11)	2	96—97 (decomp.)	Orange	32.30	1.45		17.50	
				(32.45)	(1.35)		(17.55) (Cr)	

[a] Compounds (1)—(5) decomposed slowly, even under nitrogen, at −20 °C. Compounds (6)—(10) decomposed slowly, in solution under nitrogen, but were air-stable in crystalline form. [b] Calculated values are given in parentheses. [c] Yields, starting with compounds (4) and (5) respectively.

Table 2. Infrared data

(*a*) For the new tetracarbonyl complexes

Complex	ν(CO) [a]/cm^{-1} A_1^1	A_1^2	B_1	B_2	ν(CN) [b]/cm^{-1}
(1)	2 014m	1 929s	1 912vs	1 902m	2 130w
(2)	2 009m	1 924s	1 912vs	1 901m	2 117w
(3)	2 020m	1 945s	1 940vs	1 931m	2 070w
(4)	2 012m	1 927s	1 912vs	1 904m	2 139w
(5)	1 984m	1 943s	1 934vs	1 927m	2 077w
(9) [b]	2 020m	1 953s	1 925vs	1 899s	2 130w
(10) [b]	2 019m	1 957s	1 932vs	1 909s	2 112w

(*b*) For the new tricarbonyl complexes

Complex	ν(CO) [a]/cm^{-1}			ν(NH) [b]/cm^{-1}
(6)	1 919vs	1 847s	1 818vs	3 256w
(7)	1 927vs	1 847s	1 822vs	3 276w
(8)	1 940vs	1 882s	1 837vs	—

[a] Measured in hexane, except where stated otherwise. [b] Measured in CCl_4.

Table 3. Hydrogen-1 n.m.r. data * at room temperature for the new compounds

Complex	Chemical shift (τ)
(1)	6.30s (2 H, $\mathrm{SCH_2S}$), 7.17m (4 H, $\mathrm{SC}\mathit{H}_2\mathrm{CH_2}$), 7.77m (2 H, $\mathrm{SCH_2C}\mathit{H}_2$), 8.43s (9 H, $\mathrm{Bu^t}$)
(2)	6.10s (2 H, $\mathrm{SCH_2S}$), 7.03m (4 H, $\mathrm{SC}\mathit{H}_2\mathrm{CH_2}$), 7.80m (2 H, $\mathrm{SCH_2C}\mathit{H}_2$), 8.47s (9 H, $\mathrm{Bu^t}$)
(3)	2.65m (15 H, Ph), 5.62s (2 H, $\mathrm{CH_2}$)
(4)	6.57s (2 H, $\mathrm{SCH_2S}$), 7.23m (4 H, $\mathrm{SC}\mathit{H}_2\mathrm{CH_2}$), 7.77m (2 H, $\mathrm{SCH_2C}\mathit{H}_2$), 7.9—8.8m (11 H, $\mathrm{C_6H_{11}}$)
(5)	2.63m (5 H, Ph), 6.27s (2 H, $\mathrm{SCH_2S}$), 6.65m (2H, $\mathrm{CNCH_2}$), 7.18m (4 H, $\mathrm{SC}\mathit{H}_2\mathrm{CH_2}$), 7.95m ($\mathrm{SCH_2C}\mathit{H}_2$)
(6)	0.38br (1 H, NH), 6.20q (2 H, $\mathrm{OCH_2}$), 6.99m (4 H, $\mathrm{SCH_2}$), 7.68m (2 H, $\mathrm{SCH_2C}\mathit{H}_2$), 8.33s (9 H, $\mathrm{Bu^t}$), 8.65t (3 H, $\mathrm{OCH_2C}\mathit{H}_3$), 8.4—9.3m (15 H, $\mathrm{PEt_3}$)
(7)	0.58br (1 H, NH), 6.20q (2 H, $\mathrm{OCH_2}$), 6.70m (4 H, $\mathrm{SCH_2}$), 7.80m (2 H, $\mathrm{SCH_2C}\mathit{H}_2$), 8.38s (9 H, $\mathrm{Bu^t}$), 8.68t (3 H, $\mathrm{OCH_2C}\mathit{H}_3$), 8.9—9.3m (15 H, $\mathrm{PEt_3}$)
(8)	4.81q (2 H, $\mathrm{MCOCH_2}$), 5.94q (2 H, $\mathrm{CCOCH_2}$), 6.76m (4 H, $\mathrm{SCH_2}$), 7.44m (2 H, $\mathrm{SCH_2C}\mathit{H}_2$), 8.0—9.0m (15 H, $\mathrm{PEt_3}$), 8.19t (3 H, $\mathrm{MCOCH_2C}\mathit{H}_3$), 8.48t (3 H, $\mathrm{CCOCH_2C}\mathit{H}_3$)
(9)	6.05s (4 H, $\mathrm{SCH_2}$), 8.50s (9 H, $\mathrm{Bu^t}$)
(10)	2.62s (5 H, Ph), 6.02s (4 H, $\mathrm{SCH_2}$)
(11)	3.65s (4 H, $\mathrm{SCH_2}$)

* Measured in $CDCl_3$ relative to internal $SiMe_4$; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

(2) with LiBu and PEt_3, followed by alkylation with $[Et_3O][BF_4]$, produced the aminocarbene–thioether chelates (6) and (7) (Scheme 2). The isocyanide–thioether complexes (4) and (5) both yielded (8) after having lost a CNR moiety. The compositions of the three new tricarbonyl complexes (6)—(8) were established by elemental analysis (Table 1). Other physical data are collected in Tables 2—4.

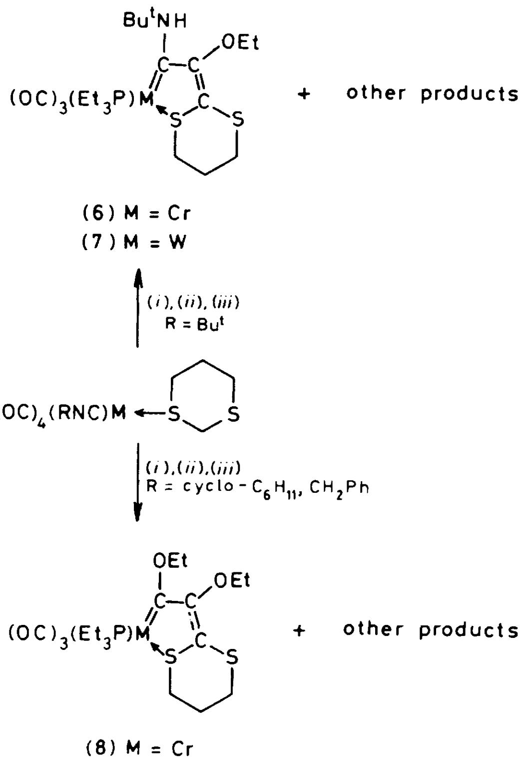
The trisubstituted complexes (6)—(8) showed three sharp, strong absorptions in the ν(CO) region [Table 2(*b*)]. The intensity of the centre band was characteristically somewhat weaker than that of the other two.[3] The ν(NH) frequencies (CCl_4 solutions) of the aminocarbene complexes (6) and (7) (3 256 and 3 276 cm^{-1} respectively) were very similar to the values obtained for the (*E*)-form of a series of aminocarbene compounds previously prepared in our laboratory.[1] The PEt_3 protons of the new complexes could not be assigned to individual peaks in their ^1H n.m.r. spectra due to the fact that they appeared together over a relatively small region (Table 3).

Molecular ions, M^+, were observed for the two tricarbonyl compounds (7) and (8) in the mass spectrometer. The fragment ion $[M - \mathrm{Bu^t} - \mathrm{H}]^+$ had the highest *m*/*e* value for the chelate (6).

Table 4. Mass spectrometric data for the new complexes [a]

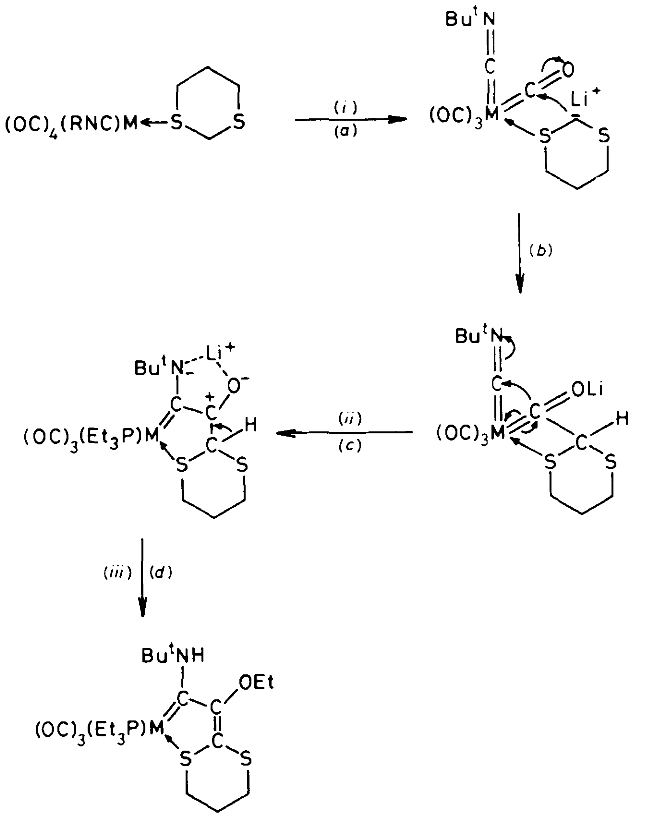
Complex	Max. *m/e* and other [b] *m/e*	Assignment	Calc. *m/e*
(1)	275	$[\mathrm{Cr(CNBu^t)(CO)_5)}]^+$	275.20
	172	$[\mathrm{CrS(CH_2)_3SCH_2}]^+$	172.24
(2)	407	$[\mathrm{W(CNBu^t)(CO)_5}]^+$	407.05
	120	$[\mathrm{S(CH_2)_3SCH_2}]^+$	120.24
(3)	295	$[\mathrm{Cr(CNPh)(CO)_5}]^+$	295.18
	232	$[\mathrm{CH_2(SPh)_2}]^+$	232.37
(4)	301	$[\mathrm{Cr(CNC_6H_{11})(CO)_5}]^+$	301.24
	120	$[\mathrm{S(CH_2)_3SCH_2}]^+$	120.24
(5)	309	$[\mathrm{Cr(CNCH_2Ph)(CO)_5}]^+$	309.21
	120	$[\mathrm{S(CH_2)_3SCH_2}]^+$	120.24
(6)	455	$[M - \mathrm{Bu^t} - \mathrm{H}]^+$	455.53
(7)	645	M^+	645.52
(8)	486	M^+	486.59
(9)	291	$[\mathrm{Cr(CNBu^t)(CO)_4(C{=}S)}]^+$	291.26
	275	$[\mathrm{Cr(CNBu^t)(CO)_5}]^+$	275.20
(10)	370	$[M - \mathrm{SH}]^+$	370.35
	295	$[\mathrm{Cr(CNPh)(CO)_5}]^+$	295.18
(11)	296	$[\mathrm{Cr(CO)_5\{CS(CH_2)_2S\}}]^+$	296.24

[a] Molecular ions are indicated by M^+. [b] Maximum *m/e* value for an ion containing the thioether ligand or a part thereof [compounds (1)—(5)] or thione ligand [(9) and (10)].



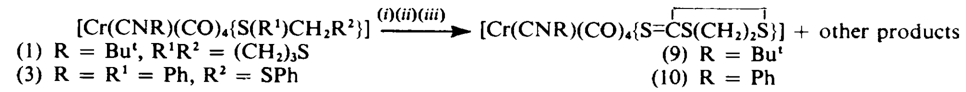
Scheme 2. (*i*) LiBu, hexane–thf; (*ii*) PEt$_3$, hexane–thf; (*iii*) $[\mathrm{Et_3O}][\mathrm{BF_4}]$, $\mathrm{CH_2Cl_2}$

The formation of the aminocarbene-donor complexes (6) and (7) can be explained by the steps in Scheme 3. The mechanism is comparable to the one proposed for the formation of the trisubstituted alkoxycarbene–thioether complexes mentioned above, which involves a double consecutive carbonylation.[2,3] The second carbonylation, however, is replaced [in step (*c*)] by an isocyanide insertion into a metal–carbene bond formed during step (*b*). In addition, the second activated proton α to the sulphur atoms is not removed or does not migrate to the neighbouring oxygen atom, but it is finally found on the more basic nitrogen atom [step (*d*)]. This mechanism is also comparable to the one proposed for the formation of a disubstituted aminocarbene–thioether chelate. The nucleophilic attack of an *unco-ordinated* deprotonated thioether compound on the carbonyl ligand *cis* to the isocyanide ligand in a pentacarbonyl isocyanide complex is also followed by the insertion of a co-ordinated isocyanide moiety into the metal–carbon bond.[1] During the formation of the same type of product previously obtained from pentacarbonyl thioether complexes, *fac*-$[\mathrm{M(CO)_3\{C(OEt)C(OEt){=}C(SR^1)R^2\}(PEt_3)}]$ (8), the isocyanide ligand was substituted for a carbonyl ligand. Although the substitution of isocyanide ligands by unco-ordinated carbon monoxide is known,[5] substitution of an isocyanide ligand by co-ordinated carbon monoxide has not been reported. The mechanism for this unexpected pathway is unknown. An analogous isocyanide substitution reaction was also observed during the synthesis of the aminocarbene compounds $[\mathrm{M\{C(NHPh)C(OEt){=}C(SR^1)R^2\}(CO)_4}]$, mentioned earlier.[1] It is well known that isocyanide complexes derived from the Group 6A carbonyls are not attacked on the isocyanide ligand(s) by organolithium compounds.[6] We have now shown this is also true for the internal nucleophilic attack by metallated co-ordinated thioacetals.



Scheme 3. M = Cr or W. (*i*) LiBu, hexane–thf; (*ii*) PEt$_3$, hexane–thf; (*iii*) $[\mathrm{Et_3O}][\mathrm{BF_4}]$, $\mathrm{CH_2Cl_2}$

When 1,3-dithiolane-2-thione was used in place of triethylphosphine as a π-acceptor ligand,[7] substitution of the thio-



$$[Cr(CNR)(CO)_4\{S(R^1)CH_2R^2\}] \xrightarrow{(i)(ii)(iii)} [Cr(CNR)(CO)_4\{S{=}CS(CH_2)_2S\}] + \text{other products}$$

(1) $R = Bu^t, R^1R^2 = (CH_2)_3S$
(3) $R = R^1 = Ph, R^2 = SPh$
(9) $R = Bu^t$
(10) $R = Ph$

Scheme 4. (*i*) LiBu, hexane–thf; (*ii*) $S{=}CS(CH_2)_3S$, hexane–thf; (*iii*) $[Et_3O][BF_4]$, CH_2Cl_2

ether ligand occurred, instead of chelate formation (Scheme 4).

The proposed structures of the two new isocyanide–thione complexes (9) and (10) were confirmed by spectroscopic measurements and by elemental analysis (Table 1).

The fact that the thione substituted the anionic chelate ring in *cis*-$[Cr\{C(NHBu^t)\{C(OLi){=}CS(CH_2)_3S\}(CO)_3(thf)\}]$ was surprising, since replacement of the ring in the neutral complex *cis*-$[Cr\{C(OEt)C(OEt){=}CS(CH_2)_3S\}(CO)_4]$ could not be achieved with any of the bidentate ligands used, even under drastic conditions.[8] Later it was found that a reaction of 1,3-dithiolane-2-thione with the postulated intermediate in the analogous cyclisation of $[Cr(CO)_5\{S(CH_2)_3SCH_2\}]$, *cis*-$[Cr(CO)_3\{C(OLi)C(OLi){=}CS(CH_2)_3S\}(thf)]$, yielded a blue, unstable compound which decomposed into the dithiocarbene complex $[Cr(CO)_5\{CS(CH_2)_2S\}]$ (11), at room temperature. The mechanism for this reaction, which also includes the replacement of a chelate ring, is not known. Due to the low yield in which (11) was formed this is not a viable synthetic route for the carbene preparation. It is, nevertheless, interesting that the desulphurisation occurred and, furthermore, compound (11) represents the only saturated cyclic dithiocarbene complex of chromium known.[9]

The i.r. spectra of the isocyanide–thione compounds in the ν(CO) region exhibited the pattern normally observed for tetracarbonyl complexes [Table 2(*a*)] with relative intensities medium, strong, very strong, strong. A comparison with the i.r. spectra of the isocyanide–thioether complexes showed that the three lower energy peaks for the thioether complexes occurred in a narrower region than the comparable peaks of the thione compounds. The expected number of resonances and correct relative intensities were observed in the ^1H n.m.r. spectra for the compounds (9)—(11) (Table 3). The rearrangement ion $[M(CNR)(CO)_5]^+$ was again observed in the mass spectra of the two thione compounds. The maximum *m/e* value for (9) corresponds to $[Cr(CNBu^t)(CO)_4(C{=}S)]^+$ (*m/e* = 291) and that of (10) to $[M - SH]^+$ (*m/e* = 370).

Experimental

General procedures have been discussed previously.[2,3] The starting materials $[M(CNR)(CO)_5]$ (R = Bu^t, Ph, cyclo-C_6H_{11}, or CH_2Ph) were prepared according to published procedures.[4]

Preparation of the cis-(*Tetracarbonyl*)(*isocyanide*)(*thioether*)-*metal*(0) *Complexes*, (1)—(5).—The synthesis of *cis*-(t-butyl isocyanide)(tetracarbonyl)(1,3-dithiane-*S*)chromium(0) (1) is described as a typical example.

A stirred solution of $[Cr(CNBu^t)(CO)_5]$ (2.67 g, 9.7 mmol) and 1,3-dithiane (1.16 g, 9.7 mmol) in thf (200 cm^3) was irradiated with u.v. light for 4 h. The solvent was removed *in vacuo* and the residue chromatographed on a silica-gel column (−10 °C) with hexane–CH_2Cl_2 (3 : 1) as eluant. The main yellow band was collected and the solution was evaporated under reduced pressure to afford 1.60 g (45%) of the compound (1). The other thioether complexes (2)—(5) were prepared similarly.

Synthesis of the fac-(*Carbene-thioether*)(*triethylphosphine*)-*metal*(0) *Chelates*, (6)—(8).—The method described here for the preparation of the tricarbonyl complex (6) is representative of the general procedure followed for all the reactions of the isocyanide–thioether complexes.

fac-*Tricarbonyl*[2-*ethoxy*-2-(1′,3′-*dithian*-2′-*ylidene*)-1-t-*butylaminoethylidene*-C′,S′](*triethylphosphine*)*chromium*(0), (6). To a stirred solution of *cis*-$[Cr(CNBu^t)(CO)_4\{S(CH_2)_3SCH_2\}]$ (1) (1.1 g, 3 mmol) in thf at −60 °C, was added 1.5 mol dm^{-3} LiBu (0.55 cm^3, 3.3 mmol, 10% excess). After 5 min, 67% PEt_3 in isopropyl alcohol (0.53 cm^3, 3.3 mmol) was added dropwise. The mixture was stirred for 1 h at −60 °C and then the mixture was allowed to attain room temperature. The solvent was evaporated under reduced pressure and the residue was dissolved in CH_2Cl_2. After alkylation with $[Et_3O][BF_4]$, the resulting mixture was filtered through SiO_2. The solvent (CH_2Cl_2) was removed under reduced pressure and the residue chromatographed on a silica column (−10 °C) using hexane–CH_2Cl_2 (1 : 1) as eluant. The slow-moving purple band was collected from the top of the column, and eluted with CH_2Cl_2 through a filter. The product was recrystallised twice from hexane–diethyl ether solutions (−30 °C) to afford analytically pure purple *crystals* of compound (6).

Isolation of the cis-(*Tetracarbonyl*)(*isocyanide*)(*thione*)-*chromium*(0) *Complexes*, (9) *and* (10).—Starting with the isocyanide complexes (1) and (3), the method described above for the preparation of compound (6) was used with 1,3-dithiolane-2-thione instead of PEt_3. The red compounds formed were purified chromatographically (SiO_2, −10 °C) using hexane–CH_2Cl_2 (1 : 1) as eluant. Finally, compounds (9) and (10) were crystallised as dark red *crystals* from hexane–diethyl ether solutions (−30 °C).

Isolation of the Carbene $[Cr(CO)_5\{CS(CH_2)_2S\}]$ (11).—The pentacarbonyl(thioether)chromium complex $[Cr(CO)_5\{S(CH_2)_3SCH_2\}]$ [2] was used in the conversion described above for the preparation of compound (6); but 1,3-dithiolane-2-thione replaced PEt_3. A blue product was observed by t.l.c. (hexane–CH_2Cl_2, 1 : 1) before alkylation. The product obtained from a SiO_2 column (eluant, hexane–CH_2Cl_2, 1 : 1) at −20 °C was unstable and decomposed completely into the stable carbene complex (11) [ν(CO) (hexane) 2 060w and 1 953vs cm^{-1}].

Acknowledgements

We thank the C.S.I.R. for financial assistance.

References

1 Part 8, S. Lotz, H. G. Raubenheimer, J. C. Viljoen, and H. W. Viljoen, *S. Afr. J. Chem.*, 1983, **36**, 13.
2 H. G. Raubenheimer, S. Lotz, H. W. Viljoen, and A. A. Chalmers, *J. Organomet. Chem.*, 1978, **152**, 73.

3 H. G. Raubenheimer, S. Lotz, H. E. Swanepoel, H. W. Viljoen, and J. C. Rautenbach, *J. Chem. Soc., Dalton Trans.*, 1979, 1701.
4 M. O. Albers, N. J. Coville, T. V. Ashworth, E. Singleton, and H. E. Swanepoel, *J. Organomet. Chem.*, 1980, **199**, 55.
5 Y. Yamamoto and H. Yamazaki, *J. Organomet. Chem.*, 1977, **137**, C31; *Inorg. Chem.*, 1978, **17**, 3111; W. E. Carroll, M. Green, A. M. R. Galas, M. Murray, T. W. Turney, A. J. Welch, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1980, 80.
6 J. A. Connor and E. M. Jones, *J. Chem. Soc., Dalton Trans.*, 1973, 2119.
7 H. G. Raubenheimer, J. C. Viljoen, S. Lotz, A. Lombard, and G. J. Kruger, *J. Chem. Soc., Chem. Commun.*, 1981, 750.
8 J. C. Viljoen, Ph.D. Thesis, Rand Afrikaans University, South Africa, 1983.
9 R. J. Angelici, F. B. McCormick, and R. A. Pickering in 'Fundamental Research in Organometallic Chemistry,' eds. M. Tsutsui, Y. Ishii, and H. Yaozeng, Van Nostrand-Reinhold, New York, 1982, p. 347.

Received 27*th June* 1983; *Paper* 3/1107