Sulphur-containing Metal Complexes. Part 4.[1] Preparation of *fac*-Trisubstituted Carbonyl Complexes of Chromium(0) and Tungsten(0) containing a Phosphine, Phosphite, or Isocyanide Ligand in Addition to a Chelate Ring with Carbene Carbon and Sulphur Donor Atoms †

By **Helgard G. Raubenheimer,* Simon Lotz, Hester E. Swanepoel, Hendrik W. Viljoen, and Johanna C. Rautenbach**, Department of Chemistry, Rand Afrikaans University, Johannesburg 2000, South Africa

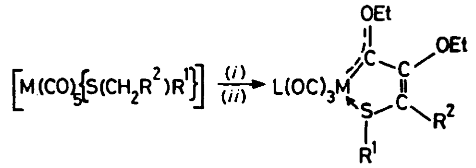
The reaction of LiBu with pentacarbonyl(thioether) complexes of chromium and tungsten [M(CO)$_5$S(CH$_2$R^2)R^1], in the presence of or prior to the addition of a π-acid ligand L, followed by alkylation, produces a series of trisubstituted carbonyl complexes of the type *fac*-[M(CO)$_3$L{C(OEt)C(OEt)=C(SR^1)R^2}]. A proposed mechanism involving a double consecutive carbonylation is substantiated by the formation of a *cis*-tetracarbonyl(aminocarbenethio)-chelate as a by-product during one of the reactions in which L = CNBu^t.

ALTHOUGH the chemistry of trisubstituted carbonyl complexes of the general types [M(CO)$_3$L$^1_3$] and [M(CO)$_3$L$^1_2$L^2] (M = Group 6 metal) is well known,[2] remarkably few reports of such compounds containing three different donor atoms [M(CO)$_3$L^{1}L^{2}L^3] are available.[3] Our concern with sulphur-donor complexes[4] led to a method for the synthesis of disubstituted (carbenethio)metal carbonyl species of the Group 6 metals from pentacarbonyl(thioether) compounds by treatment with LiBu.[1] In the proposed mechanism for this reaction, a double carbonylation and the generation of a solvent-occupied co-ordination site on the metal were invoked. The solvent molecule is substituted during alkylation ([OEt$_3$][BF$_4$]) by intermolecular carbonyl transfer. In principle, therefore, it seemed possible to replace the solvent molecule with a Lewis base before alkylation, thus affording neutral chiral *fac*-trisubstituted carbonyl complexes after alkylation.

To verify this possibility, to obtain more information on the compounds produced, and to study the structural consequences of introducing different ligands, we have investigated a series of reactions using different pentacarbonyl(thioether) complexes and a variety of unidentate ligands. A preliminary account of the new reaction type has appeared.[5]

RESULTS AND DISCUSSION

Synthetic Aspects.—When a cold (—80 °C) tetrahydrofuran ((thf)–hexane (1 : 10) solution of a pentacarbonyl(thioether) metal complex containing two protons α to the co-ordinated sulphur atom [M(CO)$_5${S(CH$_2$R^2)R^1}] (M = Cr or W) was treated in the presence of a π-acceptor ligand with 2 mol equivalents of LiBu, a dark red mixture resulted on warming to room temperature. After alkylation with Meerwein's reagent [OEt$_3$][BF$_4$], the listed purple compounds (1)—(12) (Scheme 1) were isolated. Improved yields ($\geqslant$15%) of the chelate compounds containing a phosphite ligand were obtained by adding this ligand after the excess of LiBu had been removed by washing with hexane. This observation is in accordance with our previous suggestion, that, in the absence of a suitable ligand, carbonyl transfer takes place only during the alkylation step. Ligands such as amines and cyanides did not co-ordinate and only the disubstituted carbenethio-chelates were formed. In the presence of SEt$_2$, SPh$_2$, and AsPh$_3$, the synthesis afforded trisubstituted unstable complexes in low yields which could not be isolated in pure form. The tungsten analogues of complexes (1), (2), and (7) were also very unstable.



(1) R^1 = R^2 = Ph, M = Cr, L = CNBu^t
(2) R^1 = R^2 = Ph, M = Cr, L = P(OMe)$_3$
(3) R^1 = R^2 = Ph, M = Cr, L = PMe$_3$
(4) R^1 = R^2 = Ph, M = W, L = PMe$_3$
(5) R^{1}R^2 = (CH$_2$)$_3$S, M = Cr, L = CNBu^t
(6) R^{1}R^2 = (CH$_2$)$_3$S, M = W, L = CNBu^t
(7) R^{1}R^2 = (CH$_2$)$_3$S, M = Cr, L = P(OMe)$_3$
(8) R^{1}R^2 = (CH$_2$)$_3$S, M = Cr, L = P(OPh)$_3$
(9) R^{1}R^2 = (CH$_2$)$_3$S, M = Cr, L = PPh$_3$
(10) R^{1}R^2 = (CH$_2$)$_3$S, M = Cr, L = PMe$_3$
(11) R^{1}R^2 = (CH$_2$)$_3$S, M = W, L = PMe$_3$
(12) R^{1}R^2 = CH$_2$SCH$_2$S, M = Cr, L = P(OMe)$_3$

SCHEME 1 (*i*) LiBu and L, thf–hexane; (*ii*) [OEt$_3$][BF$_4$], CH$_2$Cl$_2$

The proposed structure type of the new complexes *fac*-[M(CO)$_3$L{C(OEt)C(OEt)=C(SR^1)R^2}] was established on the basis of elemental analysis, mass-spectrometric molecular-mass measurement, spectroscopic data, and a single-crystal *X*-ray diffraction study of compound (5).[6] The ^{13}C n.m.r. spectra of the new complexes could not be measured owing to their low solubility.

The ring-closure reactions take place at a much slower rate for the tungsten compounds compared to their chromium analogues and during the normal synthesis of the isocyanide-containing compound (6) a stable orange-yellow by-product was isolated in low (7%) yield. It

---

† No reprints available.

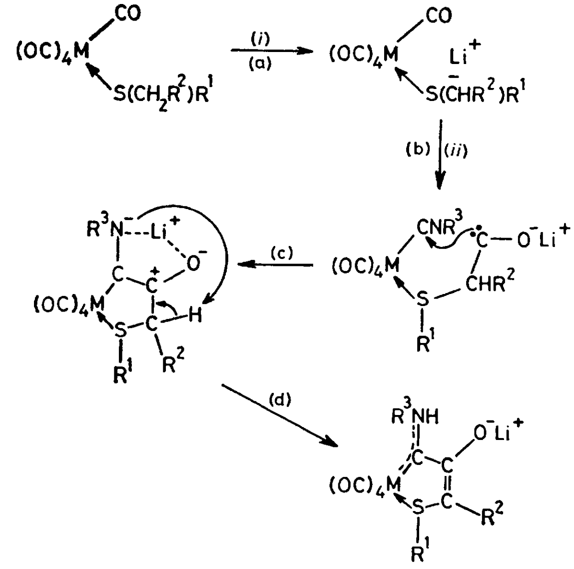
TABLE 1

Percentage yields, melting points, and analytical data (calculated values in parentheses) for some new tetra- and tricarbonylmetal(0) chelate complexes

Complex *	Yield (%)	M.p. (θ_c/°C)	Analysis (%) C	H	S	Other	
(1)	65	72—73	61.1	5.6		2.6 (N)	
			(61.0)	(5.5)		(2.6)	
(2)	27	129—132	52.3	5.1		5.4 (P)	
			(52.4)	(5.1)		(5.4)	
(3)	63	110—112	57.4	5.6		6.2 (P)	
			(57.2)	(5.6)		(5.9)	
(4)	*ca.* 15	Oil					
(5)	58	92—93	47.9	5.6	14.2	3.1 (N)	11.4 (Cr)
			(47.9)	(5.6)	(14.2)	(3.1)	(11.5)
(6)	35	105—108	36.8	4.6	11.1	2.4 (N)	
			(37.0)	(4.3)	(11.0)	(2.4)	
(7)	20	78—79	39.3	5.2		6.3 (P)	10.6 (Cr)
			(39.0)	(5.1)		(6.3)	(10.6)
(8)	15	53—54	54.7	5.0	9.0	4.2 (P)	
			(54.9)	(4.8)	(9.4)	(4.6)	
(9)	45	133—135	59.0	5.0		5.1 (P)	
			(59.0)	(5.0)		(4.9)	
(10)	30	119—120	43.3	5.7		7.3 (P)	11.3 (Cr)
			(43.2)	(5.7)		(7.0)	(11.7)
(11)	12	124—125	33.4	4.4		5.3 (P)	
			(33.4)	(4.4)		(5.4)	
(12)	30	90—91	36.8	4.6	11.1	2.4 (N)	
			(37.1)	(4.3)	(11.0)	(2.4)	
(13)	7	111—113	34.6	3.9	11.8		
			(34.6)	(3.8)	(11.5)		

* Complexes (1)—(12) are dark purple, (13) is orange-yellow.

proved to be the heterometallocyclic complex [13 : $R^1R^2 = (CH_2)_3S$]. Although we have found that it cannot be done *via* the standard aminolysis procedure,[7] the formation of this compound shows that aminocarbenethio-chelates containing bulky groups on the nitrogen atom can be prepared. The formation of the aminocarbene compound (13) can be explained on the basis of steps (a)—(d) in Scheme 2.



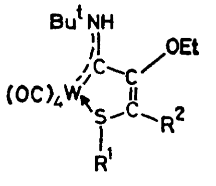
SCHEME 2 M = W, $R^1R^2 = (CH_2)_3S$. (*i*) LiBu, thf–hexane; (*ii*) R^3NC ($R^3 = Bu^t$)

In contrast to step (c) which involves a nucleophilic attack of a carbene carbon atom on a neighbouring co-ordinated isocyanide ligand, the formation of the main trisubstituted products (1)—(12) involves an attack on a *cis* co-ordinated carbonyl group similar to the mechanism which accounts for the disubstituted carbonyl chelates.[1] In the present case, however, one of the ligands L occupies the CO-vacated co-ordination position and no intermolecular carbonyl transfer is necessary during the alkylation step.

A report giving preparative details and structural studies on another product (now believed to be *cis*-$[Cr(CO)_4(CNBu^t)\{C(OEt)Bu\}]$) obtained during the synthesis of compounds (1) and (5) will appear later.

All the new compounds are slightly soluble in non-polar organic solvents such as hexane and more soluble in methylene chloride and acetone. Although the crystals are stable, decomposition takes place in solution even under nitrogen.

Spectroscopic Data.—All the tricarbonyl complexes reported have C_1 symmetry and show sharp strong absorptions (hexane solutions) in the i.r. region 1 838—1 958 cm^{-1} (Table 2) which are attributable to ν(C–O) ($A' + A' + A''$). The intensity of the centre band is characteristically somewhat weaker than that of the other two. Although the frequencies for the complexes (1), (2), and (3) indicate a σ(donor) : π(acceptor) ratio for the ligands L which follows the order $CNCMe_3 <$



(13) $R^1R^2 = (CH_2)_3S$

TABLE 2

Infrared and electronic spectral data (cm^{-1}) for *fac*-tricarbonyl compounds [a]

Complex	ν(CO)			Electronic	
(1) [b]	1 958	1 909	1 860	18 332	32 051
(2)	1 956	1 901	1 846	19 011	31 949
(3)	1 950	1 894	1 838	17 936	31 643
(4)	1 959	1 897	1 845	18 202	31 250
(5) [b]	1 948	1 892	1 858	18 116	32 050
(6) [b]	1 944	1 888	1 853	19 011	30 675
(7)	1 954	1 890	1 847	19 231	32 051
(8)	1 954	1 896	1 851	19 920	34 890
(9)	1 942	1 884	1 840	18 658	31 950
(10)	1 940	1 884	1 840	18 208	31 596
(11)	1 947	1 880	1 838	18 438	31 356
(12)	1 953	1 880	1 843	19 048	31 847

[a] For solutions in hexane. [b] ν(NC) at 2 120 cm^{-1}.

$P(OMe)_3 < PMe_3$, the same result is not obvious for the comparable complexes (5), (7), and (10). For the three isocyanide complexes ν(C–N) occurs at 2 210 cm^{-1}. The ν(C–O) band pattern of the aminocarbenethiochelate (13) consists of three peaks of relative intensity medium, strong, very strong, and strong all of which are observed at lower frequencies than those for *cis*-$[W(CO)_4\{C(OEt)C(OEt)=C(SR^1)R^2\}]$ [$R^1R^2 = (CH_2)_3S$],[1] indicating once again that aminocarbene ligands transfer more negative charge on to the metal than alkoxycarbene ligands.[8,9] The position of ν(N–H) in (13) at 3 240 cm^{-1} (CCl_4) is very similar to the value obtained for the N–H stretching mode for the *anti* form of the complex *cis*-$[Cr(CO)_4\{C(NHEt)C(OEt)=CS(CH_2)_3S\}]$ (3 278 cm^{-1}) recently prepared in this laboratory.[7]

TABLE 3

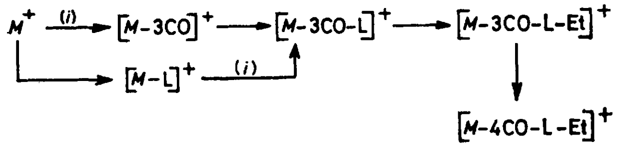
Hydrogen-1 n.m.r. data (τ) [a] for the complexes (1)—(12)

Complex No.	Complex L	C(carbene)-OCH_2	$COCH_2$	C(carbene)-OCH_2CH_3	$COCH_2CH_3$	Ph	L
(1)	$CNCMe_3$	4.79 (q)	6.08 (q)	8.31 (t)	8.75 (t)	2.79 (m)	8.75 (s)
(2)	$P(OMe)_3$	4.83 (q)	6.27 (q)	8.34 (t)	8.85 (t)	2.74 (d)	6.37 (d) [b]
(3)	PMe_3	4.90 (q)	6.12 (q)	8.33 (t)	8.75 (t)	2.79 (m)	8.65 (d) [c]
(4)	PMe_3	5.18 (q)	6.14 (q)	8.34 (t)	8.80 (t)	2.76 (m)	8.52 (d) [d]
(5)	$CNBu^t$ [e]	4.93 (q)	6.10 (q)	8.37 (t)	8.80 (t)		8.60 (s)
(6)	$CNBu^t$	5.14 (q)	6.07 (q)	8.40 (t)	8.80 (t)		8.57 (s)
(7)	$P(OMe)_3$	5.00 (q)	6.28 (q)	8.49 (t)	8.73 (t)		6.49 (d) [f]
(8)	$P(OPh)_3$	5.07 (q)	6.19 (q)	8.54 (t)	8.70 (t)	2.84 (m)	
(9)	PPh_3	5.18 (q)	6.15 (q)	8.46 (t)	8.74 (t)	2.54 (m)	
(10)	PMe_3 [g]	4.93 (q)	6.25 (q)	8.43 (t)			
(11)	PMe_3 [h]	5.19 (q)	6.07 (q)	8.48 (t)	8.75 (t)		8.58 (d) [i]
(12)	$P(OMe)_3$	4.88 (q)	6.05 (q)	8.37 (t)	8.69 (t)		6.43 (d) [j]

[a] Relative to internal $SiMe_4$, for solutions in $CDCl_3$; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Correct number of protons in each case established by integration. [b] *J*(PH) 10.8 Hz. [c] *J*(PH) 7.6 Hz. [d] *J*(PH) 8.0 Hz. [e] The $S(CH_2)_3S$ signals appear for compounds (5)—(11) as two multiplets at τ 6.93—7.00 and 7.63—7.70. [f] *J*(PH) 9.0 Hz. [g] The peaks from PMe_3 and $COCH_2CH_3$ overlap and an assignment is not possible. [h] Other resonance: SCH_2SCH_2S, τ 5.83 (s). [i] *J*(PH) 8.0 Hz. [j] *J*(PH) 10.8 Hz.

The ligands used in forming the tricarbonyl chelates do not differ drastically from the carbon monoxide molecule in their bonding characteristics. This is illustrated by the small difference between the observed frequencies for electronic absorption in the former compounds (Table 2) and the values reported for the comparable disubstituted chelates.[1] All the ^1H n.m.r. spectra (Table 3) show the normal resonances for the carbenethio-chelate ring [1] and the complexed unidentate ligands.

In the mass spectra for all the new chelates except (8) and (9) molecular ions *M* were observed. These also revealed that the initial fragmentation of the chromium complexes takes place according to Scheme 3. The main decomposition involves the stepwise loss of three carbonyl groups followed by a breaking of the metal–ligand (L) bond. According to the alternative route, the metal–ligand (L) bond is broken first and then the three carbonyl groups are lost to give the most abundant ions $[Cr\{C(OEt)C(OEt)=C(SR^1)R^2\}]^+$. In the case of the tungsten tricarbonyl chelates, two or three carbonyl groups are lost simultaneously. The main initial fragmentation of the aminocarbene compound (13) corresponds to the consecutive loss of four carbonyl ligands.



SCHEME 3 (*i*) Stepwise

EXPERIMENTAL

Microanalyses were by F. Pascher and E. Pascher, Bonn. Infrared spectra were obtained using a Perkin-Elmer 257 and n.m.r. spectra with a Varian T60 spectrometer relative to internal $SiMe_4$. Mass spectra were recorded on a Hitachi–Perkin-Elmer RMU-6H operating at 70 eV * ionizing potential, and electronic spectra on a Shimadzu double-beam spectrophotometer. M.p.s were measured using a Kofler hot-stage apparatus and are uncorrected. All the experiments were carried out under nitrogen and the solvents used were freshly dried and distilled under nitrogen. Analytical and spectroscopic data for the new complexes (1)—(12) are given in Tables 1—3. Some physical data for compound (13) are reported below.

---

* Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

Preparation of the Complexes fac-$[M(CO)_3L\{C(OEt)C(OEt)=C(SR^1)R^2\}]$.— fac-*Tricarbonyl*[*ethoxy*(α-*ethoxy*-β-*phenylthiostyryl*)*carbene*-CS](*t-butyl isocyanide*)*chromium*(0) (1). The complex $[Cr(CO)_5\{S(CH_2Ph)Ph\}]$ [1] (3.9 g, 10 mmol) in 150 cm^3 of a cooled (−80 °C) solution of thf–hexane (1 : 10) was mixed with t-butyl isocyanide (0.9 cm^3, 15 mmol). Butyl-lithium (20 mmol in hexane) was added dropwise and during 1.5 h of stirring the temperature of the mixture was allowed to rise to room temperature. The solvent was decanted from the dark red viscous residue which was washed with pentane and stripped of solvent *in vacuo*. After alkylation with $[OEt_3][BF_4]$ (4.0 g, 20 mmol) in CH_2Cl_2 (−10 °C), the solvent was removed under reduced pressure and the residue chromatographed on SiO_2 (−10 °C) with CH_2Cl_2–hexane (1 : 2) as eluant. The purple zone was stripped of solvent and again chromatographed with diethyl ether–hexane (1 : 4) to afford after recrystallisation (diethyl ether–pentane; −30 °C) 1.8 g (3.7 mmol, 65%) of (1) as purple air-stable *crystals*.

All the other complexes with L = $CNBu^t$, PMe_3, or PPh_3 were prepared by a similar method. The compounds (2), (7), (8), and (12) containing the phosphite ligands $P(OMe)_3$ and $P(OPh)_3$ were obtained after a slight modification of the above procedure. The ligands were added only just before the alkylation step.

Isolation of the Complex cis-$[W(CO)_4\{C(NHBu^t)C(OEt)=CS(CH_2)_3S\}]$ (13).—During the synthesis of the tungsten complex (6) an orange-yellow zone was obtained from the first SiO_2 column prior to elution of the main purple zone. Removal of the solvent mixture under reduced pressure and recrystallisation of the residue from hexane (−30 °C) yielded complex (13) as needle-like orange-yellow *crystals*. The yield, m.p., and analytical data are given in Table 1. ν(CO) (hexane) at 2 025m, 1 950w, 1 899vs, and 1 870s cm^{-1}; ν(NH) (CCl_4) at 3 240br cm^{-1}. Bands in electronic spectrum at 31 950 and 21 650 cm^{-1}. Mass spectrum: *m/e* 555 (*M*), 527 (*M* − CO), 499 (*M* − 2CO), 471 (*M* − 3CO), and 443 (*M* − 4CO). Hydrogen-1 n.m.r. spectrum: τ 0.33 (br, NH, 1 H), 6.07 (q, OCH_2, 2 H), 6.83 (m, SCH_2, 4 H), 7.57 (m, SCH_2CH_2, 2 H), 8.35 (s, Bu^t, 9 H), and 8.63 (t, OCH_2CH_3, 3 H).

We thank the Council for Scientific and Industrial Research for support.

[8/2136 *Received*, 11*th December*, 1978]

REFERENCES

[1] Part 3, H. G. Raubenheimer, S. Lotz, H. W. Viljoen, and A. A. Chalmers, *J. Organometallic Chem.*, 1978, **152**, 73.

[2] G. R. Dobson, I. W. Stolz, and R. K. Sheline, *Adv. Inorg. Chem. Radiochem.*, 1966, **8**, 1.

[3] H. Brunner and W. A. Herrmann, *Chem. Ber.*, 1972, **105**, 770.

[4] H. G. Raubenheimer, J. C. A. Boeyens, and S. Lotz, *J. Organometallic Chem.*, 1976, **112**, 145.

[5] H. G. Raubenheimer, S. Lotz, J. Coetzer, and G. Kruger, *J.C.S. Chem. Comm.*, 1977, 494.

[6] G. J. Kruger, J. Coetzer, H. G. Raubenheimer, and S. Lotz, *J. Organometallic Chem.*, 1977, **142**, 249.

[7] H. G. Raubenheimer, S. Lotz, and H. W. Viljoen, unpublished work.

[8] M. Y. Darensbourg and D. J. Darensbourg, *Inorg. Chem.*, 1970, **9**, 32.

[9] T. F. Block and R. F. Fenske, *J. Organometallic Chem.*, 1977, **139**, 235.