Sulphur-containing Metal Complexes. Part 14.[1] Reactions of Carbene Anions with Carbon Disulphide or Carbon Diselenide

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The deprotonated aminocarbene complex $[\mathrm{Cr(CO)_5\{C(NH)Ph\}}]^-$, when treated successively with CS_2 and $[\mathrm{Et_3O}][\mathrm{BF_4}]$, affords the thiocarbene complex $[\mathrm{Cr(CO)_5\{C(SEt)Ph\}}]$. Similar reactions with the carbene complex $[\mathrm{(OC)_5Mn\text{-}Mn(CO)_4\{C(NH_2)Ph\}}]$ give the nitrile complex $[\mathrm{(OC)_5Mn\text{-}Mn(CO)_4(NCPh)}]$. The carbene anion $[\mathrm{Cr(CO)_5\{C(OEt)CH_2\}}]^-$ gives the vinylcarbene derivatives $[\mathrm{Cr(CO)_5\{C(OEt)CHC(SEt)_2\}}]$ and $[\mathrm{\overline{Cr(CO)_4\{C(OEt)CHC(S}Et)SEt\}}]$. Carbon diselenide is less discriminating towards the nature of the anion, and the triselenocarbonate complex $[\mathrm{Cr(CO)_5\{SeC(SeEt)_2\}}]$ is formed from both carbene anions of chromium.

The similarity between organic esters and pentacarbonyl(α-ethoxybenzylidene)chromium complexes, where the $Cr(CO)_5$ moiety takes the part of the carbonyl oxygen atom, was noted by Moser and Fischer[2] when they observed that corresponding products could be isolated from certain reactions. For example, aminolysis with NH_3 results in substitution of the alkoxy-group, OR^1, by NH_2 in both RCO_2R^1 and $[\mathrm{Cr(CO)_5\{C(OR^1)R\}}]$. One would thus be led to assume that a similar comparison could be drawn between aminocarbene complexes and organic amides.

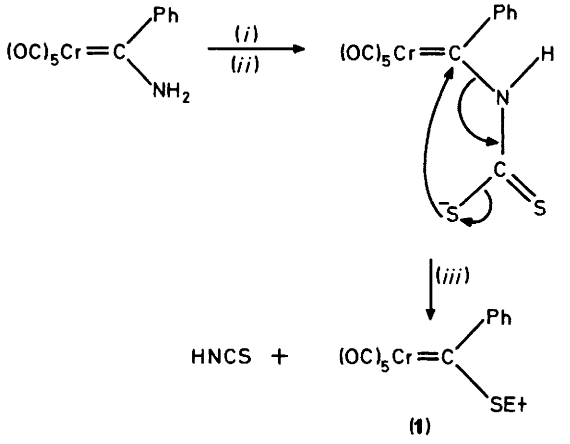
It is known that on consecutive reactions with bases and CS_2, amides yield thiocarboxylates and isothiocyanates.[3] Similar reactions were attempted, substituting the aminocarbene complexes $[\mathrm{Cr(CO)_5\{C(NHR)Ph\}}]$ (R = H or Me) for organic amides, and including $[\mathrm{(OC)_5Mn\text{-}Mn(CO)_4\{C(OEt)Ph\}}]$ to determine whether the analogy could be extended to include other metal units. By using CSe_2 instead of CS_2, this method would be suitable for preparing the relatively scarce selenocarbene complexes, and a product such as $[\mathrm{Cr(CO)_5\{C(SeEt)Ph\}}]$ could be envisaged upon further alkylation.

Reactions of carbanions with CS_2 are well known, and although CH acids normally afford 1,1-dithiolates according to reaction (1), we recently reported[4] a reaction of deprotonated co-ordinated 1,3-dithiane, $[\mathrm{Cr(CO)_5\{\overline{S(CH_2)_3SCH}\}}]^-$, with CS_2 which gave a dithiocarboxylate. The carbene anion $[\mathrm{Cr(CO)_5\{C(OEt)CH_2\}}]^-$ also contains a negative charge β to the chromium atom and its reactions with CS_2 and CSe_2 have now been investigated.

$$\mathrm{R\text{-}CH_2^- + CS_2 \longrightarrow R\text{-}CH_2C(S)S^- \xrightarrow{base} R\text{-}CH{=}CS_2^{2-}} \quad (1)$$

Results and Discussion

Reactions with CS_2.—The primary aminocarbene complex $[\mathrm{Cr(CO)_5\{C(NH_2)Ph\}}]$ was deprotonated with LiBu and then treated with CS_2 in tetrahydrofuran (thf) at −40 °C. After alkylation with $[\mathrm{Et_3O}][\mathrm{BF_4}]$ in CH_2Cl_2 at 0 °C, a product (**1**) that correlated with a thiocarboxylate, as mentioned above, was obtained. The same initial mechanism as suggested for the formation of the thiocarboxylate[3] is applicable to the formation of the thiocarbene complex (Scheme 1). There was, however, no further correspondence between aminocarbene complexes and organic amides. When the secondary aminocarbene complex $[\mathrm{Cr(CO)_5\{C(NHMe)Ph\}}]$ reacted under the same conditions to afford yellow crystals of (**2**) an apparently simple substitution of the amine proton took place and no net incorporation of CS_2 occurred [equation (2), reagents (*i*)—(*iii*) as in Scheme 1].



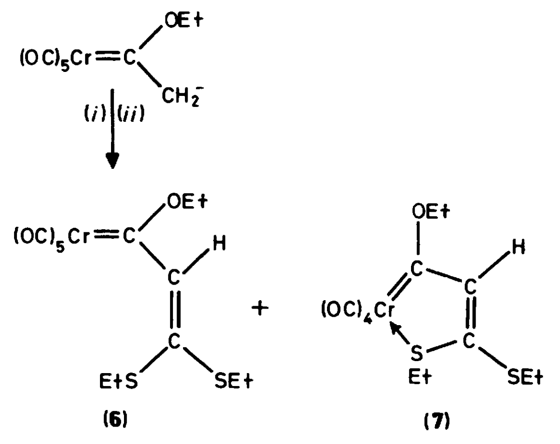
Scheme 1. (*i*) LiBu; (*ii*) CS_2; (*iii*) $[\mathrm{Et_3O}][\mathrm{BF_4}]$

$$\mathrm{(OC)_5Cr{=}C(NHMe)Ph \xrightarrow[(iii)]{(i),\,(ii)} \underset{(\mathbf{2})}{(OC)_5Cr{=}C\{N(Me)Et\}Ph}} \quad (2)$$

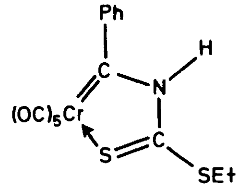
Inclusion of $[\mathrm{(OC)_5Mn\text{-}Mn(CO)_4\{C(NH_2)Ph\}}]$ (**4**) in the study led to a completely unexpected product (**5**), in which the aminocarbene ligand was replaced by (or converted into) a nitrile ligand and once again CS_2 did not seem to contribute to the final structure [equation (3), reagents (*i*)—(*iii*) as in Scheme 1]. The same product was prepared previously in low yield (3%) by the photochemical substitution of CO by PhCN.[5] To arrive at a nitrile ligand from the deprotonated carbene ligand =C(Ph)NHLi, a formal LiH abstraction is called for. Hydride abstractions have been rationalized by Ritchey *et al.*[6] for the formation of imines from amines, but a complete explanation for the appearance of complex (**5**) is not obvious. It should be mentioned that Fischer and Offhaus[7] previously obtained the acetonitrile complex $[\mathrm{(OC)_5Mn\text{-}Mn(CO)_4(NCMe)}]$ from the reaction of $[\mathrm{(OC)_5Mn\text{-}Mn(CO)_4\{C(OMe)Me\}}]$ and Me_2NNH_2. The nitrile probably forms by cleavage of the N–N bond in the aminocarbene complex $[\mathrm{(OC)_5Mn\text{-}Mn(CO)_4\{C(NHNMe_2)Me\}}]$.

$$\mathrm{\underset{(\mathbf{4})}{(OC)_5Mn\text{-}Mn(CO)_4{=}C(NH_2)Ph} \xrightarrow[(iii)]{(i),\,(ii)} \underset{(\mathbf{5})}{(OC)_5Mn\text{-}Mn(CO)_4(NCPh)}} \quad (3)$$

It is worth noting that in the preparation of the ethoxy-



Scheme 2. (*i*) CS_2; (*ii*) $[Et_3O][BF_4]$



(A)

phenylcarbene complex of manganese, $[(OC)_5Mn\text{-}Mn(CO)_4\{C(OEt)Ph\}]$ (3), the yield could be improved from 23%[7] to 65% by carrying out the alkylation step in CH_2Cl_2 instead of in water. The aminolysis of this compound, yielding the isolable aminocarbene complex (4), has for the first time been accomplished by reverting to diethyl ether, instead of hexane, as the solvent. In previous attempts hexane was used,[7] and aminolysis took place much more slowly. The product then decomposed before it could be isolated.

In complete contrast with the above, the alkoxycarbene complex $[Cr(CO)_5\{C(OEt)Me\}]$ lost a proton from the methyl group with LiBu, and the α anion thus generated reacted like an organic carbanion[8] with CS_2 and $[Et_3O][BF_4]$ (Scheme 2). Recent literature provides an additional example of this type in the reaction of CS_2 with the neutral complex $[Fe(\eta\text{-}C_5H_5)(PMe_3)_2\{C(OMe){=}CH_2\}]$ which produced a thermolabile complex that was methylated with MeI to give $[Fe(\eta\text{-}C_5H_5)(PMe_3)_2\{C(OMe)CH_2C(S)SMe\}]I$.[9]

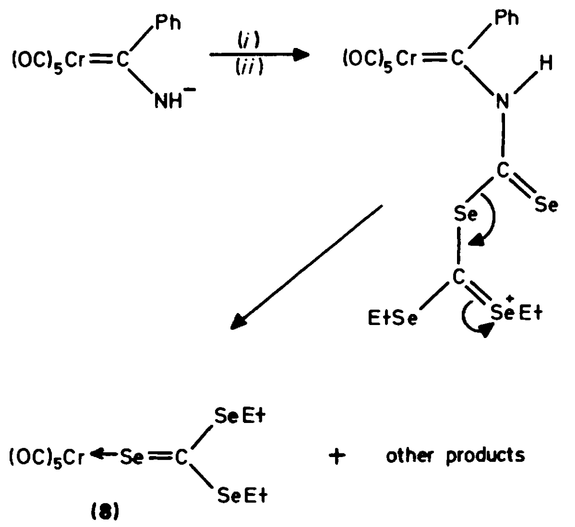
It was originally thought that the aminocarbene complexes discussed earlier should also be capable of chelating to yield the heterometallocyclic compound (A) but there is obviously not much resemblance between the reactions of C(carbene)–NH^- and C(carbene)–CH_2^- with CS_2; neither does the low yield of (6) and (7) suggest that they form from a main reaction route.

Reactions with CSe_2.—In its reactions, CSe_2 was much less discriminating towards the nature of the anion than CS_2 and the triselenocarbonate complex, $[Cr(CO)_5\{Se{=}C(SeEt)_2\}]$ (8), resulted from the reaction of both amino- and alkoxy-carbene anions with CSe_2.

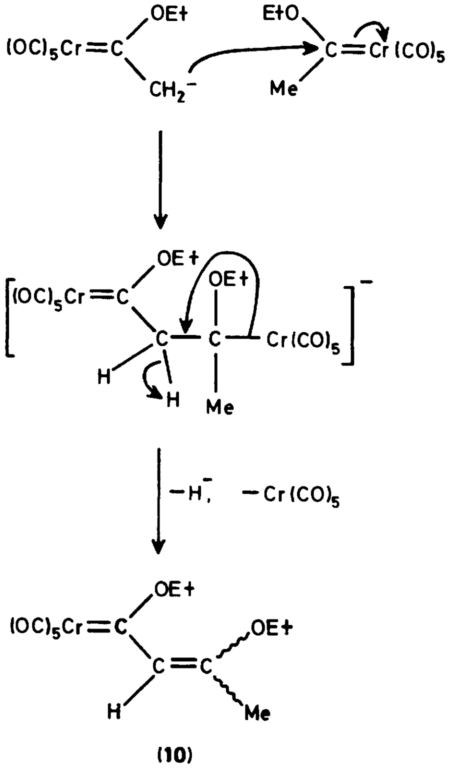
Upon treatment of $[Cr(CO)_5\{C(NH_2)Ph\}]$ with LiBu and CSe_2 in thf at −40 °C and subsequent alkylation with $[Et_3O][BF_4]$ in CH_2Cl_2 at 0 °C, two products appeared in high yield {equation (4): (*i*) LiBu; (*ii*) CSe_2; (*iii*) $[Et_3O][BF_4]$}. The working mechanism we present for the formation of complex (8) involves nucleophilic attack of the anionic centre on CSe_2, followed by the coupling of another CSe_2 unit after which a complete rearrangement takes place (Scheme 3). A similar mechanism was proposed when the same product resulted from the reaction of co-ordinated $S{=}C(Li)NMe_2$ with CSe_2 and $[Et_3O][BF_4]$.[10] An alternative possibility would be the coupling of two CSe_2 molecules, after having reacted with either the butyl or carbene anion, to form CSe_3^{2-}, similar to the formation of CS_3^{2-} when CS_2 reacts with base. Substitution of the carbene ligand with the triselenocarbonate would then, after alkylation, afford (8).

$$(OC)_5Cr{=}C(NH_2)Ph \xrightarrow[(iii)]{(i),\,(ii)}$$

$$\underset{(8)}{(OC)_5Cr{\leftarrow}Se{=}C(SeEt)_2} + \underset{(9)}{(OC)_5Cr{\leftarrow}Se{=}C(SeEt)Ph} \quad (4)$$



Scheme 3. (*i*) CSe_2; (*ii*) $[Et_3O][BF_4]$



(10)

Scheme 4.

Table. Physical and analytical data

Complex	Yield (g, %)	Colour	M.p. (θ_c/°C)	Analysis (%)[a] C	H	N, S, Se
(**1**) $[Cr(CO)_5\{C(SEt)Ph\}]$	1.03, 49	Red	*b*			
(**2**) $[Cr(CO)_5\{C[N(Me)Et]Ph\}]$	2.11, 44	Yellow	61—62	52.9	3.70	3.95
				(53.1)	(3.85)	(4.15)
(**3**) $[(OC)_5Mn–Mn(CO)_4\{C(OEt)Ph\}]$	3.32, 65	Orange	*c*			
(**4**) $[(OC)_5Mn–Mn(CO)_4\{C(NH_2)Ph\}]$	2.89, 95	Yellow	115	41.3	1.90	3.25
			(decomp.)	(41.15)	(1.50)	(3.00)
(**5**) $[(OC)_5Mn–Mn(CO)_4(NCPh)]$	1.08, 43	Yellow	*d*			
(**6**) $[Cr(CO)_5\{C(OEt)CHC(SEt)_2\}]$	0.15, 3	Orange	52—56	42.6	3.80	15.95
				(42.4)	(4.05)	(16.2)
(**7**) $[Cr(CO)_4\{C(OEt)CHC(SEt)SEt\}]$	0.26, 7	Red	Oil			
(**8**) $[Cr(CO)_5\{SeC(SeEt)_2\}]$	0.75, 30	Purple	52—54	24.2	2.15	47.25
				(24.05)	(2.00)	(47.45)
(**9**) $[Cr(CO)_5\{SeC(SeEt)Ph\}]$	0.61, 26	Purple	Oil			
(**10**) $[Cr(CO)_5\{C(OEt)CHC(OEt)Me\}]$	0.31, 3	Orange	41—44	46.6	4.30	
				(46.7)	(4.20)	

[a] Calculated values are given in parentheses. [b] U. Klabunde and E. O. Fischer, *J. Am. Chem. Soc.*, 1967, **89**, 7141. [c] Ref. 7. [d] Ref. 5.

The mechanism posed to rationalize the formation of (**9**), requires, as an intermediate, a selenocarbene complex analogous to the thiocarbene complex, (**1**). The next step involves a formal insertion of Se into the Cr–C(carbene) bond. Although no mention has been made in the literature of selenium insertions of this kind, sulphur insertion is well documented.[10,11]

In the reaction of the alkoxycarbene complex $[Cr(CO)_5\{C(OEt)Me\}]$ with consecutively LiBu, CSe_2, and $[Et_3O][BF_4]$, the triselenocarbonate complex, (**8**), was once again the main product. The formation of the minor vinylcarbene product, (**10**), from the reaction, involves nucleophilic attack of the α anion of the carbene complex on a second unreacted complex molecule. Another formal LiH abstraction would have to follow (Scheme 4). A comparable hydride abstraction has been used by Casey and Brunsvold[12] to interpret the reaction between a tungsten alkoxycarbene complex and the organolithium compound $LiCH=CH_2$.

Experimental

General.—All manipulations were carried out in an inert atmosphere (N_2) and solvents were dried and distilled under nitrogen before use. Published methods were followed for the preparation of $[Et_3O][BF_4]$,[13] $[Cr(CO)_5\{C(NH_2)Ph\}]$,[14] $[Cr(CO)_5\{C(NHMe)Ph\}]$,[14] and $[Cr(CO)_5\{C(OEt)Me\}]$.[15] Chemicals purchased from Strem, *viz.* CS_2, CSe_2, and $[Mn_2(CO)_{10}]$, were used without further purification. Column chromatography was done at −10 °C and silica gel (60 mesh, particle size 0.063—0.200 mm; Merck) was used as stationary phase.

Proton n.m.r. spectra were obtained on a Varian T60 spectrometer, using $CDCl_3$ as solvent and tetramethylsilane as internal standard. I.r. spectra were recorded on a Perkin-Elmer 297 spectrometer, calibrated with the polystyrene bands at 1 601 and 2 850 cm^{-1} and with hexane as solvent. Molecular-ion determinations were carred out on a Hitachi–Perkin-Elmer RMU-6H (60 eV, *ca.* 9.6×10^{-18} J) mass spectrometer. Elemental analyses were done by the Mikroanalytische Laboratory of Bonn.

Except for (**3**) and (**4**), the products reported were all prepared under the same reaction conditions. A detailed description is given for the preparation of complex (**1**). Physical and analytical data are presented in the Table. Yields were calculated on analytically pure compounds.

Preparations.—$[Cr(CO)_5\{C(SEt)Ph\}]$ (**1**). A solution of $[Cr(CO)_5\{C(NH_2)Ph\}]$ (1.81 g, 6.1 mmol) in thf (50 cm^3) was cooled to −40 °C and an equimolar amount of LiBu (1.8 mol dm^{-3}, 3.4 cm^3) added. After 5 min an equimolar amount of CS_2 (0.36 cm^3) was added, the reaction mixture warmed to room temperature and the solvent evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 (30 cm^3) and alkylated at 0 °C with a small excess of $[Et_3O][BF_4]$. The solvent was removed under reduced pressure and the product chromatographed with hexane–CH_2Cl_2 (10:1) as eluant. Physical and analytical data correlated with published results (Found: M^+, 342. $C_{14}H_{10}CrO_5S$ requires M^+, 342.3); $\nu_{max.}$(CO) 2 061m, 1 990w, 1 961s, and 1 949s cm^{-1}; δ (60 MHz) 1.10 (3 H, t, SCH_2CH_3), 2.70 (2 H, q, SCH_2CH_3), 6.6 (2 H, m, CPh), and 7.2 (3 H, m, CPh).

$[Cr(CO)_5\{C[N(Me)Et]Ph\}]$ (**2**). The complex $[Cr(CO)_5\{C(NHMe)Ph\}]$ (4.37 g, 14.0 mmol) was used as starting material and hexane–CH_2Cl_2 (5:2) as eluant in a similar procedure to the above (Found: M^+, 339. $C_{15}H_{13}CrNO_5$ requires M^+, 339.2); $\nu_{max.}$(CO) 2 058w, 1 969w, 1 931s, and 1 920 (sh) cm^{-1}; δ (60 MHz) 1.10 (3 H, t, NCH_2CH_3), 3.33 (2 H, q, NCH_2CH_3), 3.85 (3 H, s, NCH_3), 6.6 (2 H, m, CPh), and 7.2 (3 H, m, CPh).

$[(OC)_5Mn–Mn(CO)_4\{C(OEt)Ph\}]$ (**3**). The method described by Fischer and Offhaus[7] was slightly modified, using $[Mn_2(CO)_{10}]$ (3.90 g, 10 mmol) dissolved in diethyl ether (50 cm^3) as starting material. The solution was cooled to 0 °C and LiPh (1.5 mol dm^{-3}, 6.7 cm^3, 10 mmol) added. After 5 min the solvent was removed under reduced pressure, the residue dissolved in CH_2Cl_2 (30 cm^3) at 0 °C and alkylated with $[Et_3O][BF_4]$. The product was purified by column chromatography using hexane–ether (10:1) as eluant; $\nu_{max.}$(CO) 2 089m, 2 045w, 2 022s, 2 019 (sh), 1 992s, 1 968m, 1 957 (sh), and 1 950m cm^{-1} (ref. 5 reports only five i.r. bands).

$[(OC)_5Mn–Mn(CO)_4\{C(NH_2)Ph\}]$ (**4**). The complex $[(OC)_5Mn–Mn(CO)_4\{C(OEt)Ph\}]$ (3.1 g, 6.3 mmol) was dissolved in ether (50 cm^3) at room temperature and dry ammonia passed through the solution for 2 min. The solvent was evaporated under reduced pressure and the residue crystallized from hexane–ether (2:1) to yield $[(OC)_5Mn–Mn(CO)_4\{C(NH_2)Ph\}]$ as a yellow crystalline product (Found:

$M^+ - 4CO$, 355. $C_{16}H_7Mn_2NO_9$ requires $M^+ - 4CO$, 355.1); $\nu_{max.}$(CO) 2 082w, 2 018m, 1 983s, 1 972m, and 1 959m cm^{-1}; δ (60 MHz) 7.3 (5 H, m, CPh) and 8.2 (2 H, br s, NH_2).

$[(OC)_5Mn{-}Mn(CO)_4(NCPh)]$ (**5**). When $[(OC)_5Mn{-}Mn(CO)_4\{C(NH_2)Ph\}]$ (2.54 g, 5.44 mmol) was treated similarly to $[Cr(CO)_5\{C(NH_2)Ph\}]$ in the first experiment described, a dark yellow mixture afforded after chromatography a yellow crystalline product that was identified by comparison of its physical and spectral characteristics with literature data[7] (Found: M^+, 465. $C_{16}H_5Mn_2NO_9$ requires M^+, 465.1); $\nu_{max.}$(CO) 2 090w, 2 023m, 2 005m, 1 988 (sh), 1 983s, 1 961m, and 1 945m cm^{-1}.

Complexes $[Cr(CO)_5\{C(OEt)CHC(SEt)_2\}]$ (**6**) *and* $[Cr(CO)_4\{C(OEt)CHC(SEt)SEt\}]$ (**7**). Consecutive treatment of $[Cr(CO)_5\{C(OEt)Me\}]$ (2.98 g, 11.3 mmol) with LiBu, CS_2, and $[Et_3O][BF_4]$ yielded two products which were separated chromatographically, using hexane–CH_2Cl_2 (2:1) as eluant. Each product was further purified by chromatography with hexane–ether (5:1) as eluant, to yield (**6**) as orange crystals and (**7**) as a red oil. For (**6**) (Found: M^+, 396. $C_{14}H_{16}CrO_6S_2$ requires M^+, 396.4); $\nu_{max.}$(CO) 2 058m, 1 940s, and 1 938s cm^{-1}; δ (60 MHz) 1.3 (6 H, m, SCH_2CH_3), 1.67 (3 H, t, OCH_2CH_3), 3.0 (4 H, m, SCH_2CH_3), 4.95 (2 H, q, OCH_2CH_3), and 7.15 (1 H, s, CH). For (**7**) (Found: M^+, 368. $C_{13}H_{16}CrO_5S_2$ requires M^+, 368.4); $\nu_{max.}$(CO) 2 020m, 1 931m, 1 920s, and 1 881s cm^{-1}; δ (60 MHz) 1.4 (6 H, m, SCH_2CH_3), 1.63 (3 H, t, OCH_2CH_3), 3.1 (4 H, m, SCH_2CH_3), 4.97 (2 H, q, OCH_2CH_3), and 6.50 (1 H, s, CH).

$[Cr(CO)_5\{SeC(SeEt)_2\}]$ (**8**) *and* $[Cr(CO)_5\{SeC(SeEt)Ph\}]$ (**9**).—The complex $[Cr(CO)_5\{C(NH_2)Ph\}]$ (1.49 g, 5.01 mmol) was used as starting material with an equimolar amount of CSe_2 instead of CS_2; hexane–ether (10:1) was used as eluant in chromatography to produce (**8**), as a crystalline product, and (**9**) as an oil. Complex (**8**) was characterized by comparing its physical and spectral data with published values[10] (Found: M^+, 502. $C_{10}H_{10}CrO_5{}^{80}Se_3$ requires M^+, 502.2); $\nu_{max.}$(CO) 2 060m, 1 985w, 1 943s, and 1 929m cm^{-1}; δ (60 MHz) 1.63 (6 H, t, $SeCH_2CH_3$) and 3.55 (4 H, q, $SeCH_2CH_3$). For (**9**) (Found: M^+, 468. $C_{14}H_{10}CrO_5Se_2$ requires M^+, 468.2); $\nu_{max.}$(CO) 2 060m, 1 985w, 1 946s, and 1 930m cm^{-1}; δ (60 MHz) 1.55 (3 H, t, $SeCH_2CH_3$), 3.28 (2 H, q, $SeCH_2CH_3$), and 7.5 (5 H, m, CPh).

$[Cr(CO)_5\{C(OEt)CHC(OEt)Me\}]$ (**10**). The complex $[Cr(CO)_5\{C(OEt)Me\}]$ (3.88 g, 14.7 mmol) and CSe_2 (0.96 cm^3, 15 mmol) were used as starting materials. The two main products were separated by column chromatography with hexane–CH_2Cl_2 (5:1) as eluant and each product separately purified by chromatography, using hexane–ether (30:1) as eluant. Orange crystals of (**10**) and purple crystals of (**8**) were obtained. For (**10**) (Found: M^+, 334. $C_{13}H_{14}CrO_7$ requires M^+, 334.2); $\nu_{max.}$(CO) 2 055m, 1 941m, and 1 934s cm^{-1}; δ (60 MHz) 1.32 (3 H, t, OCH_2CH_3), 1.52 (3 H, t, $CrCOCH_2CH_3$), 2.07 (3 H, s, CCH_3), 3.93 (2 H, q, OCH_2CH_3), 4.87 (2 H, q, $CrCOCH_2CH_3$), and 6.92 (1 H, s, CH).

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