

REACTIONS OF METAL CARBONYL COMPLEXES

IX *. THIOCARBONYL COMPLEXES OF CHROMIUM(0), MANGANESE(I) AND RHENIUM(I) **

I.S. BUTLER, N.J. COVILLE *** and D. COZAK ***

*Department of Chemistry, McGill University, 801 Sherbrooke St., West, Montreal,
 Quebec H3A 2K6 (Canada)*

(Received November 29th, 1976)

Summary

Reaction of $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{M}(\text{CO})_2(\text{THF})$ ($\text{M} = \text{Mn}$, $\text{R} = \text{H}$, Me ; $\text{M} = \text{Re}$, $\text{R} = \text{H}$), formed in situ by the UV irradiation of THF solutions of the corresponding tricarbonyl complexes, with CS_2/PPh_3 affords $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{M}(\text{CO})_2(\text{CS})$ and PPh_3S . Similar reactions of $(\eta^6\text{-C}_6\text{H}_5\text{R})\text{Cr}(\text{CO})_2(\text{THF})$ ($\text{R} = \text{H}$, CO_2Me) with CS_2 alone yield $(\eta^6\text{-C}_6\text{H}_5\text{R})\text{Cr}(\text{CO})_2(\text{CS})$; the fate of the other sulphur atom in the absence of a suitable sulphur-acceptor is unknown. This route to the monothiocarbonyl complexes is significantly faster than the existing method, but the yields are somewhat lower. The photochemical reactions of $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2(\text{CS})$ and $(\eta^6\text{-C}_6\text{H}_5\text{R})\text{Cr}(\text{CO})_2(\text{CS})$ with PPh_3 afford $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})(\text{CS})(\text{PPh}_3)$ and $(\eta^6\text{-C}_6\text{H}_5\text{R})\text{Cr}(\text{CO})(\text{CS})(\text{PPh}_3)$, respectively. The rhenium(I) complexes are the first examples of rhenium thiocarbonyls to be reported. The extended reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{THF})$ with CS_2 prior to addition of PPh_3 yields various products, among them $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$, $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CS})$, $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{PPh}_3)$, $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2]_2\text{CS}_2$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2]_2\text{CS}$. While the nature of the bridging in $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2]_2\text{CS}_2$ is open to question, that in $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2]_2\text{CS}$ probably involves the $\text{MnC}\equiv\text{SMn}$ linkage.

Introduction

Over the past ten years, various synthetic routes to transition metal thiocarbonyl complexes have been reported [2,3]. One of these involves the reaction

* For Part VIII, see Ref. 1.

** Taken in part from the Ph.D. Theses of N.J.C. (1973) and D.C. (1977), McGill University, Montreal, Quebec (Canada). Presented in part at the 58th National Meeting of the Chemical Institute of Canada, Toronto, Ontario, June 1975.

*** Present addresses: N.J.C., Dept. of Chemistry, University of Witwatersrand, Johannesburg (South Africa); D.C., Anorganisch-Chemisches Institut der Technische Universität München (West Germany).

of a metal carbonyl-olefin complex with CS₂ in the presence of PPh₃, and thiocarbonyls such as (η^5 -C₅H₅)Mn(CO)₂(CS) [4] and (η^6 -C₆H₅CO₂Me)Cr(CO)₂(CS) [5] have been prepared in this manner. The only drawback with this route is the necessity of preparing the carbonyl-olefin complexes from commercially available materials prior to reaction with CS₂/PPh₃. In the case of (η^5 -C₅H₅)Mn(CO)₂(CS), for example, this leads to about a 2-day period for its synthesis from (η^5 -C₅H₅)Mn(CO)₃ via (η^5 -C₅H₅)Mn(CO)₂(C₈H₁₄) [4]. Since the displacement of the weakly coordinated tetrahydrofuran (THF) ligand from (η^5 -C₅H₅)Mn(CO)₂(THF) by other ligands (L) is a well-known procedure for the facile synthesis of (η^5 -C₅H₅)Mn(CO)₂L derivatives [6], it occurred to us that the in situ formation of labile THF species such as (η^5 -C₅H₅)Mn(CO)₂(THF) and their subsequent reaction with CS₂/PPh₃ might be a convenient and faster route to certain thiocarbonyl complexes. This has proved to be true and, in this paper, we report the syntheses of (η^5 -C₅H₄R)M(CO)₂(CS) (M = Mn, R = H, Me; M = Re, R = H) and (η^6 -C₆H₅R)Cr(CO)₂(CS) (R = H, CO₂Me) by this method. The derivatives, (η^5 -C₅H₅)Re(CO)(CS)(PPh₃) and (η^6 -C₆H₅R)Cr(CO)(CS)(PPh₃), have also been prepared. The rhenium(I) complexes are the first examples of rhenium thiocarbonyls to be reported. Thiocarbonyl complexes are known for several other third-row transition metals: tungsten [7], osmium [8], iridium [9] and platinum [10].

Experimental

With the exception of (η^5 -C₅H₄R)Mn(CO)₃ (generous gifts from Ethyl Corporation Ltd.), the starting materials were prepared by the literature methods indicated: (η^5 -C₅H₅)Re(CO)₃ [11]; (η^6 -C₆H₅R)Cr(CO)₃ [12,13]. Triphenylphosphine (Aldrich Chemical Co.) was used without further purification. All solvents (Anachemia Chemical Ltd.) were refluxed under nitrogen over suitable drying agents prior to distillation, e.g., THF (LiAlH₄ * or sodium metal strips in the presence of benzophenone, 2 h) and CS₂ (Linde-3A molecular sieves, 2 h).

The preparative TLC separations were performed on precoated (silica gel) glass plates (20 × 20 cm, 1 mm thick; Analtech Inc.). For the analytical TLC separations, precoated (silica gel or alumina) plastic plates (3 × 7 cm; Eastman Kodak Co.) were used. Activating the plates at 130°C for 24 h had no effect on the separations achieved. Column chromatography was carried out on a long column (75 × 6 cm).

The IR spectra were recorded on either a Perkin-Elmer model 337 (coupled to a Texas Instruments Servo-Riter model II external recorder) or a model 521 grating spectrophotometer and were calibrated with CO gas and polystyrene film (accuracy ± 1 cm⁻¹). The ¹H NMR spectra were obtained on a Varian T-60 spectrometer (accuracy ± 0.1 Hz relative to TMS) **. The mass spectra were measured on an AEI MS-902 spectrometer operating at 70 eV. Melting points were recorded on a Gallenkamp apparatus and are uncorrected. Microanalyses were performed by either Chemalytic Inc. or Schwarzkopf Microanalytical Laboratory.

* Care should be taken when drying THF with LiAlH₄ as the presence of peroxides may cause an explosion [14].

** Carbon-13 NMR spectra have already been reported for several of the Group VIIB complexes described in this paper, see ref. 15.

TABLE 1

$\nu(\text{CO})$ STRETCHING MODES FOR THE STARTING MATERIALS AND THE MONOSUBSTITUTED THF DERIVATIVES IN THF SOLUTION

Complex	$\nu(\text{CO})$ (cm^{-1})		
$(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$	2017s (A_1)	1929s (E)	
$(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{THF})$	1925s (A')	1850s (A'')	
$(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_3$	2012s (A_1)	1926s (E)	
$(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2(\text{THF})$	1921s (A')	1846s (A'')	
$(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3$	2018s (A_1)	1922s (E)	
$(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2(\text{THF})$	1908s (A')	1836s (A'')	
$(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$	1965s (A_1)	1892s (E)	
$(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{THF})$	1825s (A')	1776s (A'')	
$(\eta^6\text{-C}_6\text{H}_5\text{CO}_2\text{Me})\text{Cr}(\text{CO})_3$	1980s (A_1)	1910s (E)	1730m ^a
$(\eta^6\text{-C}_6\text{H}_5\text{CO}_2\text{Me})\text{Cr}(\text{CO})_2(\text{THF})$	1938s (A')	1845s (A'')	1702m ^a
$(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2(\text{CS})$	1997s (A')	1935s (A'')	
$(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})(\text{CS})(\text{THF})$	1895s		

^a For the CO_2Me group.

All reactions and manipulations were carried out routinely under nitrogen. The two UV irradiation vessels used (capacities (180 and 1800 ml) were similar in design to that described by Strohmeier [16] and the quartz fingers were water cooled. The UV source was an Ace—Hanovia high-pressure, quartz mercury-vapour lamp (100 W, 366.0 nm).

Synthesis of $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{M}(\text{CO})_2(\text{CS})$ and $(\eta^6\text{-C}_6\text{H}_5\text{R})\text{Cr}(\text{CO})_2(\text{CS})$

General procedure. The irradiation vessel containing the appropriate tricarbonyl complex was connected to a solvent refluxing unit through a sidearm and THF solvent was allowed to distill directly over into the vessel. Once charged with solvent, the vessel was wrapped with aluminum foil and placed in an ice-water bath. The UV lamp was then switched on and the irradiation was started. The system was purged continuously with dry nitrogen; extensive decomposition occurred if this was not done. The progress of the reaction was followed by monitoring the disappearance of the A_1 $\nu(\text{CO})$ mode of the tricarbonyl complex and the appearance of the A'' $\nu(\text{CO})$ mode of the monosubstituted THF derivative in the IR spectra of the reaction mixture (Table 1) *. When the former peak had almost vanished and the latter peak appeared to have reached maximum intensity, the irradiation was stopped. A mixture of CS_2/PPh_3 ** or CS_2 alone (vide infra) was then syringed through a rubber septum cap into the reaction vessel. The ice-water bath was removed and the mixture was allowed to stand in the dark for a period of time with warm water (45–55°C) passing through the immersed quartz finger of the irradiation cell. A precipitate and/or darkening of the solution always occurred and the reaction was terminated when the A'' $\nu(\text{CO})$ mode of the THF derivative had disappeared completely. Specific details for each

* Tetrahydrofuran has a broad overtone or combination band in the IR at 1966 cm^{-1} which should not be confused with a $\nu(\text{CO})$ absorption. The local symmetries of the $\text{M}(\text{CO})_3$ and $\text{M}(\text{CO})_2\text{L}$ (L = THF, CS, etc.) moieties are C_{3v} and C_s , respectively.

** If the PPh_3 was not first dissolved in CS_2 , the monosubstituted triphenylphosphine derivative rather than the thiocarbonyl complex was formed.

of the reactions and the work-up procedures for the thiocarbonyl products are given below.

($\eta^5\text{-C}_5\text{H}_5$)Mn(CO)₂(CS). (η^5 -Cyclopentadienyl)tricarbonylmanganese(I) (0.33 g, 1.6 mmol) was dissolved in THF (150 ml) and the solution was irradiated until the 2017 cm⁻¹ IR band of the tricarbonyl had virtually vanished (~1 h). Triphenylphosphine (0.42 g, 1.6 mmol) dissolved in CS₂ (25 ml) was then added to the wine-red solution and the mixture was left standing in the dark for 1 h. The resulting dark-yellow solution was transferred to a 500-ml round-bottomed flask and the solvent was stripped off on a rotary evaporator*. The brown, oily gum which remained was dissolved in hexanes and passed through an alumina filter prepared in hexanes**. The yellow, acetone filtrate was evaporated to dryness under reduced pressure to give a yellow solid which was placed in an aluminum foil-wrapped sublimator and sublimed (25°C/0.001 Torr) onto a water-cooled probe (yield 0.16 g, 45%; m.p. 56°C (lit. [4], 52–53°C)). Anal. Found: C, 43.2; H, 2.20; S, 15.0. C₈H₅O₂SMn calcd.: C, 43.6; H, 2.29; S, 14.6%. Mol. wt.: found, 220 (mass spectrum); calcd. 220. ¹H NMR (CS₂ solution): 4.5 ppm (singlet, C₅H₅). IR (CS₂ solution): $\nu(\text{CO})$ 2000s (A'), 1949s (A''); $\nu(\text{CS})$ 1267s (A') cm⁻¹.

($\eta^5\text{-C}_5\text{H}_4\text{Me}$)Mn(CO)₂(CS). (η^5 -Methylcyclopentadienyl)tricarbonylmanganese(I) (1.41 g, 6.1 mmol) was dissolved in THF (1700 ml) and the solution was irradiated for ~1 h. To the resulting red solution, PPh₃ (1.57 g, 6.0 mmol) in CS₂ (50 ml) was added and the mixture was left standing overnight in the dark under nitrogen in the usual way. The THF solvent was removed on a rotary evaporator and hexanes (50 ml) was added to the residue. This solution was filtered through a Whatman No. 1 filter paper and the filtrate was reduced in volume on a rotary evaporator. The resulting oil was vacuum distilled (70°C/0.001 Torr) to afford the thiocarbonyl complex as a golden-yellow oil (yield 1.07 g, 75%). Mol. wt.; found, 234 (mass spectrum); calcd. 234. ¹H NMR (CS₂ solution): 1.9 (singlet, CH₃), 4.6 ppm (singlet, C₅H₄). IR (CS₂ solution): $\nu(\text{CO})$ 2000s (A'), 1949s (A''); $\nu(\text{CS})$ 1265s (A') cm⁻¹.

($\eta^5\text{-C}_5\text{H}_5$)Re(CO)₂(CS). A solution of the tricarbonyl complex, ($\eta^5\text{-C}_5\text{H}_5$)Re(CO)₃ (1.11 g, 3.3 mmol), in freshly distilled THF (1700 ml) was irradiated for ~2 h. Triphenylphosphine (0.87 g, 3.3 mmol) in CS₂ (50 ml) was then added to

* The solvent should be removed as much as possible at this stage without allowing the product to go completely dry as there is a danger of the pyrophoric material igniting. This comment also applies to the other reactions to be described later.

** This filtration procedure proved to be an effective way of eliminating organic residues, traces of oils and any unreacted ligands in many of the reactions described in this paper. A 150-ml, fritted disk, glass suction funnel was filled with activated alumina (70–80 g) mixed with a non-polar solvent such as hexanes, in much the same way as a chromatographic column is prepared. A Whatman No. 1 filter paper was placed on top of the alumina and any insoluble material present in the hexanes solution of the reaction product was filtered off. The coloured product was visibly absorbed at the top of the alumina and did not move when the filter was washed repeatedly with hexanes (1–2 l). This process eluted any organic compounds present. The filter was flushed until the washings did not contain any oils or ligands. This was checked by sampling the washings and developing the samples on iodine-stained TLC plates. The desired product was then eluted by passing acetone, CH₂Cl₂ or CH₃OH through the filter. If the elution proved too slow, suction was applied to the filter without any noticeable loss in separation efficiency. However, the solid decomposition material remaining on top of the filter was sometimes pyrophoric and ignited when suction was applied to the dried-up filter. Note that if traces of a polar solvent or too much oil were originally present, the filter became ineffective owing to either deactivation of the alumina or elution of the thiocarbonyl product with the oil phase.

the yellow reaction mixture. After standing for 1 h in the customary manner, the contents of the irradiation cell were transferred to a 2-l round-bottomed flask and the solvents were flash evaporated off. The brown gum remaining was taken up in CH_2Cl_2 (25 ml) and the solution was filtered through an alumina filter prepared in CH_2Cl_2 . The yellow thiocarbonyl product was eluted off the alumina filter with CH_2Cl_2 . The identities of the purple and red products which were eluted after the thiocarbonyl are unknown. The CH_2Cl_2 solvent was stripped off under reduced pressure and n-pentane (~ 100 ml) was added to the yellow oil remaining. After cooling in a dry ice/acetone bath, the brown decomposition product which had formed was filtered off and the n-pentane was removed gradually from the filtrate on a rotary evaporator until yellow crystals began to form. The solution was immediately cooled again to -78°C and the yellow crystals were filtered off. After drying in vacuo, the crystals were sublimed in an aluminum foil-wrapped sublimer at $60^\circ\text{C}/0.001$ Torr to afford the pure rhenium(I) monothiocarbonyl product (yield 0.4 g, 34%; m.p. $83-84^\circ\text{C}$). Anal. Found: C, 27.5; H, 1.53, S, 8.36. $\text{C}_5\text{H}_5\text{O}_2\text{SRe}$ calcd.: C, 27.3; H, 1.43; S, 9.10%. Mol. wt.: found, 352 (mass spectrum, ^{187}Re); calcd. 352. ^1H NMR (CS_2 solution): 5.4 ppm (singlet, C_5H_5). IR (CS_2 solution): $\nu(\text{CO})$ 1998s (A'), 1937s (A''); $\nu(\text{CS})$ 1277 (A') cm^{-1} .

$(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{CS})$. A THF solution (150 ml) of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ (0.3 g, 1.3 mmol) was irradiated in the usual manner for ~ 30 min *. Carbon disulphide (10 ml) was then added and the reaction mixture was left standing as described in the general procedure for 30 min **. Following passage through an alumina filter prepared in hexanes, the subsequent CH_3OH filtrate was concentrated under reduced pressure and then chromatographed on an alumina column using a 3/1 petroleum ether ($30-60^\circ\text{C}$)/ Et_2O mixture as eluent. The first yellow band eluted was the desired thiocarbonyl complex, while the second was unreacted $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$. Further purification by preparative TLC, followed by vacuum sublimation ($60^\circ\text{C}/0.001$ Torr) onto a dry-ice/acetone finger afforded the pure thiocarbonyl derivative (yield 0.064 g, 20%; m.p. 125°C (decomp.)). Anal. Found: C, 46.5; H, 2.38; S, 14.1; Cr, 22.4. $\text{C}_9\text{H}_6\text{O}_2\text{SCr}$ calcd.: C, 47.0; H, 2.63; S, 13.9; Cr, 22.6%. Mol. wt.: found, 230 (mass spectrum); calcd. 230. ^1H NMR (CS_2 solution): 5.4 ppm (singlet, C_6H_6). IR (CS_2 solution): $\nu(\text{CO})$ 1967s (A'), 1922s (A''); $\nu(\text{CS})$ 1220s (A') cm^{-1} .

$(\eta^6\text{-C}_6\text{H}_5\text{CO}_2\text{Me})\text{Cr}(\text{CO})_2(\text{CS})$. Following the normal method, $(\eta^6\text{-C}_6\text{H}_5\text{CO}_2\text{Me})\text{Cr}(\text{CO})_3$ (1.6 g, 5.9 mmol) dissolved in THF (1700 ml) was irradiated for ~ 15 min. At this stage, the 1981 cm^{-1} IR band of the tricarbonyl species was barely detectable. To the bright-red solution, CS_2 (10 ml) was added and the reaction mixture was allowed to stand as usual for 1 h. Isolation of the thiocarbonyl derivative as for $(\eta^5\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{CS})$ (except that the chromatography eluent was a 3/1 hexanes/ Et_2O mixture) afforded red-brown crystals of the complex (yield 0.26 g, 15% m.p. 81°C (lit. [17] 79°C)). Anal. Found: C, 45.8, H, 2.80; S, 11.5; Cr,

* Note that C_6H_6 has a strong overtone or combination band in the IR at 1953 cm^{-1} which should not be confused with the A_1 $\nu(\text{CO})$ mode of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ at 1965 cm^{-1} .

** Unlike the Group VIIB metal thiocarbonyls, the presence of PPh_3 was found not to be essential for the formation of the chromium thiocarbonyls described in this paper.

18.1. $C_{11}H_8O$ SCr calcd.: C, 45.8; H, 2.80; S, 11.1; Cr, 18.0%. Mol. wt.: found, 288 (mass spectrum); calcd, 288. 1H NMR (CS_2 solution: 3.8 (singlet, CH_3), 5.4 (multiplet, C_6H_5), 6.0 ppm (doublet, C_6H_5). IR (CS_2 solution): $\nu(CO)$ 1980s (A'), 1940s (A''), 1729m (CO_2Me); $\nu(CS)$ 1224s (A') cm^{-1} .

Isolation of PPh_3S

In a typical experiment, the discarded filtrates and solid residues from the synthesis of one of the Group VIIB metal carbonyl-thiocarbonyls were mixed together and the solvents were removed on a rotary evaporator. The black or brown residue remaining was washed thoroughly with C_6H_6 and the insoluble material was filtered off on a Whatman No. 1 filter paper. The volume of the filtrate was then reduced on a rotary evaporator to the point of crystallization. Addition of CH_3OH and cooling to dry-ice temperature caused light-brown crystals to precipitate from solution. These crystals were recovered by filtration and a second recrystallization was carried out in the same manner to afford white crystals of PPh_3S (m.p. $160^\circ C$ (lit. [18,19] $158^\circ C$)). Anal. Found: C, 73.4; H, 5.28. $C_{18}H_{15}PS$ calcd.: C, 73.4; H, 5.14%. Mol. wt.: found, 294 (mass spectrum); calcd. 294.

Synthesis of derivatives of the thiocarbonyl complexes

($\eta^5-C_5H_5$) $Re(CO)(CS)(PPh_3)$. As described above in the general procedure for the synthesis of the parent thiocarbonyl complexes, a THF solution (1700 ml) of ($\eta^5-C_5H_5$) $Re(CO)_2(CS)$ (0.50 g, 1.4 mmol) was irradiated until the IR-active $\nu(CO)$ modes of the starting material had ceased decreasing in intensity (~ 1 h). Triphenylphosphine (0.73 g, 2.8 mmol) was then added to the golden-yellow solution. After 30 min, the reaction mixture was transferred to a 2-l round-bottomed flask and the solvent was removed under reduced pressure. The oil remaining was introduced onto an alumina filter making sure that none of the product was left behind in the flask. This was achieved by washing the flask several times with warm hexanes until the washings were colourless. Since the product was not particularly soluble in hexanes, this process was accelerated by washing the flask with a minimal volume (1–10 ml) of CH_2Cl_2 and then adding a large excess of hexanes until the insoluble decomposition products precipitated out. These decomposition products were filtered off on the Whatman No. 1 filter paper located on top of the alumina. The desired complex was freed from the filter by passage of CH_2Cl_2 . The volume of the filtrate was reduced to a minimum under vacuum and n-pentane was added. On cooling the solution to $-78^\circ C$, the pale-yellow triphenylphosphine complex was precipitated. Further purification was achieved by preparative TLC using CS_2 as eluent (yield 0.1 g, 12%; m.p. $215-216^\circ C$). Anal. Found: C, 51.4; H, 3.48; Re, 31.3. $C_{25}H_{20}OPSRe$ calcd.: C, 51.3; H, 3.44; Re, 31.8%. Mol. wt.: found, 586 (mass spectrum, ^{187}Re); calcd. 586. 1H NMR (CS_2 solution): 4.8 (singlet, C_5H_5), 7.1 ppm (multiplet, C_6H_5). IR (CS_2 solution): $\nu(CO)$ 1914s; $\nu(CS)$ 1246s cm^{-1} .

($\eta^6-C_6H_6$) $Cr(CO)(CS)(PPh_3)$. This complex was prepared by irradiating a C_6H_6 solution (1700 ml) of ($\eta^6-C_6H_6$) $Cr(CO)_2(CS)$ (0.74 g, 3.2 mmol) and a stoichiometric amount of PPh_3 for 3 h, as described above in the general procedure. By replacing the C_6H_6 solvent from samples syringed from the reaction mixture

with CS₂ (in order to avoid confusion of the 1953 and 1808 cm⁻¹ IR bands of C₆H₆ with $\nu(\text{CO})$ modes), the progress of the reaction could be followed conveniently by IR spectroscopy. Following product work-up in the usual manner, the triphenylphosphine derivative was separated from any unreacted starting materials by preparative TLC on silica gel plates using CS₂ (or hexanes/Et₂O (3/1)) as eluent. An orange-brown complex was obtained (yield 0.28 g, 17%; m.p. 120–124°C). Mol. wt.; found, 464 (mass spectrum); calcd. 464. ¹H NMR (CS₂ solution): 5.3 (singlet, C₆H₆), 7.5 ppm (multiplet, C₆H₅). IR (CS₂ solution): $\nu(\text{CO})$ 1902s; $\nu(\text{CS})$ 1183s cm⁻¹.

($\eta^6\text{-C}_6\text{H}_5\text{CO}_2\text{Me}$)Cr(CO)(CS)(PPh₃). A solution of hexanes (1700 ml) containing ($\eta^6\text{-C}_6\text{H}_5\text{CO}_2\text{Me}$)Cr(CO)₂(CS) (0.47 g, 1.6 mmol) and a slight excess of PPh₃ was irradiated as usual for 2 h. The progress of the reaction was monitored by IR spectroscopy as above. The reaction mixture was filtered through a Whatman No. 1 filter paper and the yellow filtrate was placed on an alumina filter. A yellow band was absorbed onto the alumina and then washed thoroughly with hexanes. Addition of CH₃OH freed this band from the filter and the desired product was isolated from the CH₃OH filtrate by preparative TLC on silica gel plates using hexanes/CH₂Cl₂ (7/3) (or petroleum ether (30–60°C)/Et₂O (4/1)) mixtures as eluent (oily red liquid, yield ~20%). Mol. wt.: found, 522 (mass spectrum); calcd. 522. ¹H NMR (CS₂ solution): 4.8 ppm (singlet, CH₃). IR (neat liquid): $\nu(\text{CO})$ 1850s, 1721m (CO₂Me); $\nu(\text{CS})$ 1196 cm⁻¹.

The two chromium derivatives were characterized by the similarity of their spectroscopic properties to those of related complexes such as ($\eta^6\text{-C}_6\text{H}_5\text{CO}_2\text{Me}$)-Cr(CO)(CS)[P(OEt)₃] [17].

Reaction of ($\eta^5\text{-C}_5\text{H}_5$)Mn(CO)₂(THF) with CS₂

Exactly as described above for the synthesis of ($\eta^5\text{-C}_5\text{H}_5$)Mn(CO)₂(CS), a THF solution of the parent tricarbonyl complex was irradiated until the IR spectrum indicated complete reaction. Carbon disulphide (25 ml) was added to the wine-red solution and the mixture was allowed to stand overnight in the dark under nitrogen. Excess PPh₃ (1.87 g, 7.1 mmol) was then added to the solution. After 30 min, the solution was transferred to a 2-l round-bottomed flask in the following manner. Rubber septum caps were fitted onto the nitrogen outlet sidearm of the irradiation vessel and on the 24/40 joint of the 2-l flask. The vessels were connected by a length of stainless steel hypodermic needle tubing (1 m × 2 mm I.D.). A standard syringe needle was pushed through the septum cap on the large flask and acted as a nitrogen outlet. After flushing the flask with dry nitrogen for 30 min, the end of the stainless steel tubing was pushed below the level of the solution in the irradiation cell. By gently increasing the nitrogen pressure, the solution was transferred to the 2-l flask. Following solvent removal on a rotary evaporator, the black gum remaining was extracted with hexanes (solution A) and Me₂CO (solution B). Analytical TLC separations were performed on both solutions using alumina and silica gel plates and various mixtures of hexanes/CH₂Cl₂ as eluent. Preparative TLC was carried out using silica gel plates and a hexanes/CH₂Cl₂ (2/1) mixture. These plates showed only two bands for solution A and at least nine for solution B. The front-running, burgundy-red band for solution A was the major product (complex I) in this mixture. This band was followed by a much narrower violet band (complex II). For solution B, the front-

running, yellow band contained unreacted $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ and some $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CS})$ (identified by their IR and mass spectra). Another prominent band located in the middle of the plate was at the same position and had the same colour as complex I. The major component was a violet band at the origin of the plate which had the same IR spectrum as complex II. Some $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{PPh}_3)$ was also present.

The above experimental observations were completely reproducible (four separate reactions were carried out). However, when PPh_3 was omitted an additional green band (complex III) appeared on the plates. Complex III was isolated as a solid, but it decomposed into complexes I and II and $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CS})$ on standing (10 min) at room temperature. Therefore, care was taken not to vacuum evaporate solutions of this complex on a warm water bath. When dissolved in CH_2Cl_2 and exposed to air, the green colour of complex III changed to pale-red both when the solution was kept in the dark or exposed to room light. Infrared spectroscopy and analytical TLC showed that these solutions contained complexes I and II and also $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CS})$. In CH_2Cl_2 or CS_2 solutions under nitrogen, complex I was slowly transformed at room temperature into complex II and $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CS})$.

In an experiment where only a stoichiometric amount of CS_2 was added to the $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{THF})$ solution, complexes I, II and III were formed but a blue species (complex IV) was also noted on the TLC plates. This blue complex rapidly turned into the green complex III, as evidenced by the streaking blue band tailing off into the following green band.

Complex I. Mol. wt: found, 428 (mass spectrum). ^1H NMR (CS_2 solution): 4.7 ppm (singlet, C_5H_5). IR (CS_2 solution): $\nu(\text{CO})$ 2016vs, 1972s, 1927vs, 1874s; $\nu(\text{CS})$ 1201vw cm^{-1} . IR (hexanes solution): $\nu(\text{CO})$ 2024vs, 1976s, 1923vs, 1864s cm^{-1} .

Complex II. Mol. wt: found, 396 (mass spectrum). ^1H NMR (CS_2 solution): 4.7 ppm (singlet, C_5H_5). IR (CS_2 solution): $\nu(\text{CO})$ 2007vs, 1956vs, 1937s, 1923(sh); $\nu(\text{CS})$ 1048m cm^{-1} . These complexes were not obtained in sufficient quantities for elemental analyses to be carried out. Complexes III and IV could not be characterized even spectroscopically owing to their rapid decomposition.

Results and discussion

The in situ formation of $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Mn}(\text{CO})_2(\text{THF})$ ($\text{R} = \text{H}, \text{Me}$) during the UV irradiation of THF solutions of $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Mn}(\text{CO})_3$ has been known for some time [6]. However, the analogous reactions of $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3$ and $(\eta^6\text{-C}_6\text{H}_5\text{R})\text{Cr}(\text{CO})_3$ ($\text{R} = \text{H}, \text{CO}_2\text{Me}$) have apparently not been investigated previously. These reactions proceeded in a similar manner to those of the manganese complexes and, like $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Mn}(\text{CO})_2(\text{THF})$, the resulting THF derivatives decomposed when attempts were made to isolate them from solution. The $\text{M}(\text{CO})_2(\text{THF})$ moieties possess C_s local symmetry and so two strong $\nu(\text{CO})$ modes ($A' + A''$) were expected for each complex, as was observed (Table 1).

Treatment of the monosubstituted THF derivatives with CS_2/PPh_3 (or CS_2 alone in the case of the chromium species) afforded the monothiocarbonyl complexes. When PPh_3 was present, PPh_3S was also produced. For those reactions carried out in

the absence of PPh_3 , the fate of the remaining sulphur atom was not established. When mixtures of CS_2/PPh_3 were added to $(\eta^6\text{-C}_6\text{H}_5\text{R})\text{Cr}(\text{CO})_2(\text{THF})$, both $(\eta^6\text{-C}_6\text{H}_5\text{R})\text{Cr}(\text{CO})_2(\text{CS})$ and $(\eta^6\text{-C}_6\text{H}_5\text{R})\text{Cr}(\text{CO})_2(\text{PPh}_3)$ were formed, with the latter being the major product.

Although the synthesis of certain carbonyl-thiocarbonyls by the THF route is clearly a viable method, the yields of the complexes ($\sim 40\%$) were somewhat lower than those obtained by the analogous olefin route ($\sim 60\%$) [4,5]. This situation was partly offset, however, by the much shorter irradiation times required to produce the THF intermediates (0.5–1 h) compared to the *cis*-cyclooctene intermediates (1–24 h).

The IR and ^1H NMR data given in the Experimental Section for the previously unknown monothiocarbonyl derivatives, $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2(\text{CS})$ and $(\eta^6\text{-C}_6\text{H}_6)\text{-Cr}(\text{CO})_2(\text{CS})$, are in complete agreement with the proposed formulae. Furthermore, the mass spectral fragmentation patterns are strikingly similar to those already reported for $(\eta^5\text{-C}_5\text{H}_5\text{R})\text{Mn}(\text{CO})_2(\text{CS})$ [20,21]. A detailed analysis of the mass spectra of these and related thiocarbonyls will be presented elsewhere [22].

During the synthesis of $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2(\text{CS})$, there was IR and mass spectral evidence for the formation of a small amount of $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})(\text{CS})_2$ ($\nu(\text{CO})$ 1985s (A'); $\nu(\text{CS})$ 1325s (A'), 1245 (A'') cm^{-1} ; parent molecular ion at m/e 354 (^{187}Re)). This dithiocarbonyl complex is of particular interest because, in contrast to metal carbonyls, there are only four examples of multiple-CS attachment to a transition metal, viz., $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{L})(\text{CS})_2$ ($\text{L} = \text{CO}, \text{CS}, \text{C}_8\text{H}_{14}$) [4] and $\text{Ni}(\text{CS})_4$ [23].

The substitution reactions of $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2(\text{CS})$ and $(\eta^6\text{-C}_6\text{H}_5\text{R})\text{Cr}(\text{CO})_2(\text{CS})$ with PPh_3 were also investigated. Ultraviolet irradiation of a THF solution of the rhenium(I) complex afforded $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})(\text{CS})(\text{THF})$ which, upon addition of PPh_3 , gave $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})(\text{CS})(\text{PPh}_3)$. Similar reactions of the chromium(0) complexes in hydrocarbon solvents yielded $(\eta^6\text{-C}_6\text{H}_5\text{R})\text{Cr}(\text{CO})(\text{CS})(\text{PPh}_3)$. These substitution reactions parallel those already reported for other chromium thiocarbonyls [17] as well as $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CS})$ [4,24,25] and $\text{W}(\text{CO})_5(\text{CS})$ [26,27] in that CO was replaced preferentially to CS.

In the extended reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{THF})$ with CS_2 prior to addition of PPh_3 , several highly coloured species were produced but spectroscopic information could only be obtained for two of them, complexes I and II. In an earlier study on the reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{C}_8\text{H}_{14})$ with CS_2 alone, complexes possessing the same colours and spectroscopic properties as I and II were observed [4]. On the basis of IR and mass spectral data, it was suggested that complex II might possibly be a dimer. In this context, it is of interest that Nesmeyanov et al. [28] have recently isolated the stable bimetallic species $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2]_2\text{C}\equiv\text{CPhH}$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{C}\equiv\text{CPh}]_2$ from the reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{THF})$ with $\text{PhC}\equiv\text{CH}$. Furthermore, the thiocarbonyl-bridged species $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{NO})(\text{CS})]_2$ has been the subject of a recent communication [29], while the presence of numerous bimetallic ions in the mass spectra of $(\eta^5\text{-C}_5\text{H}_5\text{R})\text{Mn}(\text{CO})_2(\text{CS})$ has been established [30]. All of these results indicate that bimetallic formulations for complexes I and II would not be unprecedented.

Bearing in mind the IR, ^1H NMR and mass spectral data (Tables 2 and 3) for complexes I and II, the most likely formulae for these complexes are $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2]_2\text{CS}_2$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2]_2\text{CS}$, respectively. The $(\eta^5\text{-C}_5\text{H}_5)$

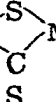
TABLE 2

PRINCIPAL FRAGMENTS IN THE MASS SPECTRUM OF COMPLEX I^a

<i>m/e</i>	Relative abundance	Assignment
428	15.0	(C ₅ H ₅) ₂ (CO) ₄ Mn ₂ (CS ₂) ⁺
396	0.1	(C ₅ H ₅) ₂ (CO) ₄ Mn ₂ (CS) ⁺
382	8.8	(C ₅ H ₅) ₂ (CO) ₄ Mn ₂ S ⁺
372	18.8	(C ₅ H ₅) ₂ (CO) ₂ Mn ₂ (CS ₂) ⁺
360	1.0	(C ₅ H ₅) ₂ (CO) ₂ Mn ₂ S ₂ ⁺
316	5.0	(C ₅ H ₅) ₂ Mn ₂ (CS ₂) ⁺
307	1.0	(C ₅ H ₅)(CO) ₂ Mn ₂ (CS ₂) ⁺
272	21.3	(C ₅ H ₅) ₂ Mn ₂ S ⁺
252	0.6	(C ₅ H ₅)(CO) ₂ Mn(CS ₂) ⁺
240	2.5	(C ₅ H ₅) ₂ Mn ₂ ⁺
220	12.5	(C ₅ H ₅)(CO) ₂ Mn(CS) ⁺
217	14.0	(C ₅ H ₅)(CO)Mn ₂ CH ₂ ⁺
215	13.0	(C ₅ H ₅)(CO)Mn ₂ C ⁺
207	14.0	(C ₅ H ₅)Mn ₂ S ⁺
196	0.3	(C ₅ H ₅)Mn(CS ₂) ⁺
170	8.8	(C ₃ H ₃)Mn(CS ₂) ⁺
164	27.5	(C ₅ H ₅)Mn(CS) ⁺
157	8.8	(C ₂ H ₂)Mn(CS ₂) ⁺
152	25.0	(C ₅ H ₅)MnS ⁺
149	8.8	(C ₅ H ₅)(CO)MnH ⁺
148	7.0	(C ₅ H ₅)(CO)Mn ⁺
147	10.0	(C ₅ H ₄)(CO)Mn ⁺
139	57.5	(CO) ₃ Mn ⁺
133	7.5	(C ₆ H ₆)Mn ⁺
128	3.8	H(CO)Mn(CS) ⁺
120	87.5	(C ₅ H ₅)Mn ⁺
115	8.8	(CO)MnS ⁺
55	100.0	Mn ⁺

^a Unassigned peaks (relative intensity) at *m/e* 414 (2.5), 398 (0.2), 327 (2.5), 249 (0.6).

resonance in the ¹H NMR spectrum of II is much broader than usual and may exhibit a doublet under higher resolution conditions. Also, the low energy of the ν(CS) mode (1048 cm⁻¹) would be in accord with the CS end-to-end bridged structure, (η⁵-C₅H₅)(CO)₂MnC≡SMn(CO)₂(η⁵-C₅H₅), which we favour for this product, i.e., similar to that proposed previously for (Diphos)₂(CO)WC≡SW(CO)₅ [31]. No definitive structure can be given for complex I at this stage. However, assuming a symmetric arrangement for the two (η⁵-C₅H₅)(CO)₂Mn moieties,

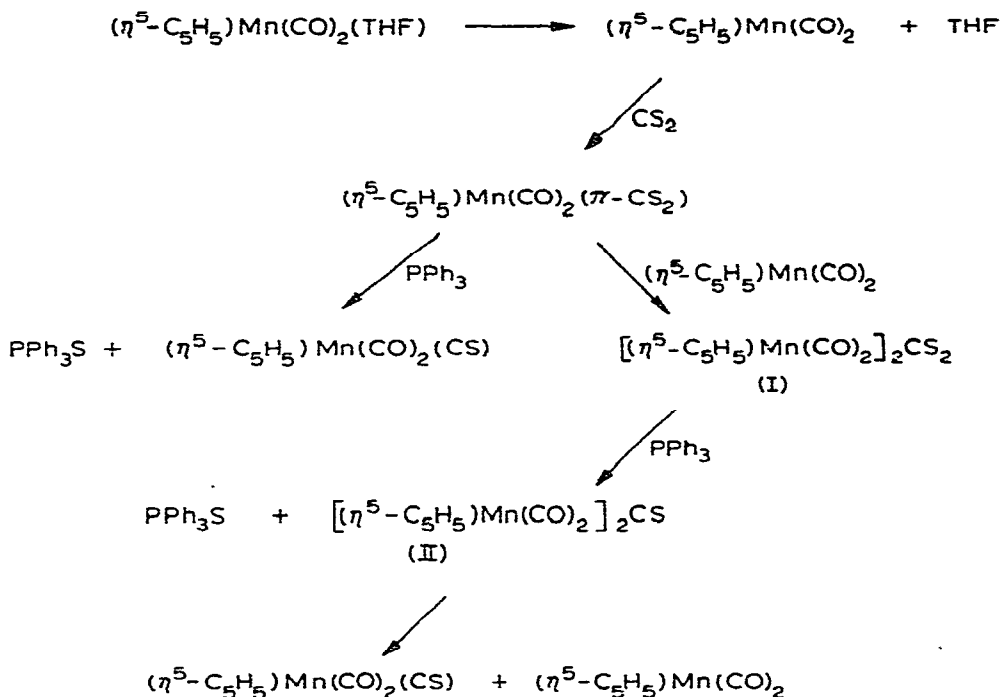
bridging of the type MnS=C=SMn or Mn  Mn would be plausible. Any other

form of bridging would either give rise to two (η⁵-C₅H₅) resonances in the ¹H NMR or would not satisfy the 18-electron rule, e.g., MnCSMn bridging analogous to that proposed recently for the closely related [(η⁵-C₅H₅)Fe(CO)₂]₂CS₂ species [32].

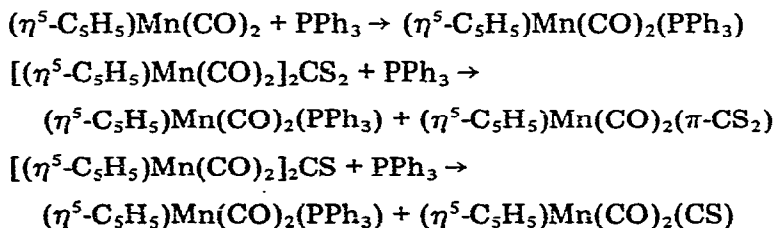
Several metastable transitions supportive of the proposed formulations for complexes I and II were observed in their mass spectra, e.g., [(C₅H₅)(CO)₂Mn]₂-CS₂⁺ (*m/e* 428) → (C₅H₅)(CO)₂Mn(CS)⁺ (*m/e* 220) (*m*^{*} 113.1) and (C₅H₅)(CO)-Mn(CS)Mn⁺ → MnS⁺ (*m/e* 87) (*m*^{*} 30.6). For both complexes, the structure of

the $(\text{C}_5\text{H}_5)(\text{CO})_2\text{Mn}(\text{CS})_2^+$ fragment (m/e 252) is probably similar to that of the $\pi\text{-CS}_2$ intermediate which is believed to play an important role in the synthesis of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CS})$ from $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{C}_8\text{H}_{14})$ and CS_2/PPh_3 [4].

The most probable steps involved in the formation of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CS})$ from $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{THF})$ and CS_2/PPh_3 are shown below. In contrast to the analogous reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{C}_8\text{H}_{14})$, strong THF absorptions in the IR at $\sim 1000\text{ cm}^{-1}$ masked any $\pi\text{-CS}_2$ absorptions present and so the existence of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\pi\text{-CS}_2)$ could not be confirmed. Whether or not complexes III and IV play a role in the overall mechanism is not clear.



The presence of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{PPh}_3)$ (identified by its IR spectrum in CS_2 solution: $\nu(\text{CO})$ 1932s, 1869s cm^{-1}) was probably due to the following reactions:



The mechanism of thiocarbonyl formation for the chromium reactions described here and those reported earlier [5] presumably involves rapid CS_2 coordination to the intermediate $(\eta^6\text{-C}_6\text{H}_5\text{R})\text{Cr}(\text{CO})_2$ species to give $(\eta^6\text{-C}_6\text{H}_5\text{R})\text{Cr}(\text{CO})_2(\pi\text{-CS}_2)$ followed by sulphur abstraction.

TABLE 3

PRINCIPAL FRAGMENTS IN THE MASS SPECTRUM OF COMPLEX II^a

<i>m/e</i>	Relative abundance	Assignment
295	0.1	(C ₅ H ₅) ₂ (CO) ₄ Mn ₂ (CS) ⁺
310	1.0	(C ₅ H ₅) ₂ (CO) ₂ Mn ₂ (CS) ⁺
328	0.2	(C ₅ H ₅) ₂ (CO) ₂ Mn ₂ S ⁺
324	0.2	(C ₅ H ₅) ₂ (CO) ₃ Mn ₂ ⁺
316	<<0.1	(C ₅ H ₅) ₂ Mn ₂ (CS ₂) ⁺
307	<0.1	(C ₅ H ₅)(CO)Mn ₂ (CS ₂) ⁺
284	4.0	(C ₅ H ₅) ₂ Mn ₂ (CS) ⁺
275	1.3	(C ₅ H ₅)(CO) ₂ Mn ₂ (CS) ⁺
268	0.1	(C ₅ H ₅) ₂ (CO)Mn ₂ ⁺
263	0.1	(C ₅ H ₅)(CO) ₂ Mn ₂ S ⁺
259	0.1	(C ₅ H ₅)(CO) ₃ Mn ₂ ⁺
252	0.1	(C ₅ H ₅)(CO) ₂ Mn(CS ₂) ⁺
247	0.3	(C ₅ H ₅)(CO)Mn ₂ (CS) ⁺
240	0.6	(C ₅ H ₅) ₂ Mn ₂ ⁺
231	0.6	(C ₅ H ₅)(CO) ₂ Mn ₂ ⁺
220	100.0	(C ₅ H ₅)(CO) ₂ Mn(CS) ⁺
219	0.1	(C ₅ H ₅)Mn ₂ (CS) ⁺
207	2.7	(C ₅ H ₅)Mn ₂ S ⁺
204	50.0	(C ₅ H ₅)(CO) ₃ Mn ⁺
192	4.0	(C ₅ H ₅)(CO)Mn(CS) ⁺
178	9.3	(C ₃ H ₃)(CO) ₃ Mn ⁺
176	10.0	(C ₅ H ₅)(CO) ₂ Mn ⁺
164	>100.0	(C ₅ H ₅)Mn(CS) ⁺
152	<0.1	(C ₅ H ₅)MnS ⁺
148	20.0	(C ₅ H ₅)(CO)Mn ⁺
142	0.1	Mn ₂ S ⁺
127	<0.1	(CO)Mn(CS) ⁺
120	>100.0	(C ₅ H ₅)Mn ⁺
115	1.3	(CO)MnS ⁺
99	8.0	Mn(CS) ⁺
87	1.3	MnS ⁺
55	100.0	Mn ⁺

^a Unassigned peaks (relative intensity) at *m/e* 301 (0.1), 269 (0.1), 254 (0.1), 250 (0.1), 244 (0.5), 234 (0.8), 134 (0.2), 130 (0.2), 129 (0.2), 128 (0.1).

Acknowledgements

This research was generously supported by the National Research Council of Canada and the Quebec Department of Education. The same two granting agencies and McGill University are thanked for the award of graduate scholarships to N.J.C. and D.C.

References

- 1 I.S. Butler and H.K. Spedjian, *Can. J. Chem.*, **54** (1976) 2833.
- 2 I.S. Butler and A.E. Fenster, *J. Organometal. Chem.*, **66** (1974) 161.
- 3 C.J. Curtis and M. Kubota, *Inorg. Chem.*, **13** (1974) 2277.
- 4 A.E. Fenster and I.S. Butler, *Inorg. Chem.*, **13** (1974) 915.
- 5 G. Simonneaux, A. Meyer and G. Jaouen, *J. Chem. Soc. Chem. Commun.*, (1975) 69 and ref. therein.
- 6 W. Strohmeier and H. Hellman, *Chem. Ber.*, **98** (1965) 1598.
- 7 B.D. Dombek and R.J. Angelici, *Inorg. Chem.*, in press.
- 8 K.E. Grundy, R.O. Harris and W.R. Roper, *J. Organometal. Chem.*, **90** (1975) C34.
- 9 M.J. Mays and F.P. Stefanini, *J. Chem. Soc. A*, (1971) 2747.

- 10 R.J. Angelici, J. Clardy, E.D. Dobrzynski and J.M. Lisey, *J. Amer. Chem. Soc.*, **97** (1975) 656.
- 11 M.L.H. Green and G. Wilkinson, *J. Chem. Soc.*, (1958) 4314.
- 12 B. Nicholls and M.C. Whiting, *J. Chem. Soc.*, (1959) 551.
- 13 M.D. Rausch, G.A. Moser, F.J. Zaiko and A.L. Lipman, Jr., *J. Organometal. Chem.*, **23** (1970) 185.
- 14 R.W. Parry, *Inorg. Synth.*, **XII** (1970) 317.
- 15 D. Cozak and I.S. Butler, *Spectrosc. Lett.*, **9** (1976) 673.
- 16 W. Strohmeier and P. Pföhler, *J. Organometal. Chem.*, **108** (1976) 393 and ref. therein.
- 17 G. Jaouen and R. Dabard, *J. Organometal. Chem.*, **72** (1974) 377; *Inorg. Synth.*, **XIX**, in press.
- 18 R.A. Zingaro, *Inorg. Chem.*, **2** (1963) 192.
- 19 R. Reynold-Carlson and D.W. Meek, *Inorg. Chem.*, **13** (1974) 1741.
- 20 A. Efraty, M.H.A. Huang and C.A. Weston, *Inorg. Chem.*, **14** (1975) 2796.
- 21 A.E. Fenster, Ph.D. Thesis, McGill University, Montreal, Quebec, Canada, 1972.
- 22 I.S. Butler, N.J. Coville, D. Cozak, A.E. Fenster, A. Garcia-Rodriguez and T. Sawai, to be published.
- 23 L.W. Yarbrough, G.V. Calder and J.G. Verkade, *J. Chem. Soc. Chem. Commun.*, (1973) 705.
- 24 N.J. Coville and I.S. Butler, *J. Organometal. Chem.*, **64** (1974) 101.
- 25 I.S. Butler and N.J. Coville, *J. Organometal. Chem.*, **80** (1974) 235.
- 26 B.D. Dombek and R.J. Angelici, *J. Amer. Chem. Soc.*, **96** (1974) 7568.
- 27 B.D. Dombek and R.J. Angelici, *Inorg. Chem.*, **15** (1976) 1089.
- 28 A.N. Nesmeyanov, G.G. Aleksandrov, A.B. Antonova, K.N. Anisimov, N.E. Kolobova and Y.T. Struchkov, *J. Organometal. Chem.*, **110** (1976) C36.
- 29 A. Efraty and R. Arneri, *J. Amer. Chem. Soc.*, **98** (1976) 639.
- 30 I.S. Butler and D. Cozak, to be published.
- 31 B.D. Dombek and R.J. Angelici, *Inorg. Chem.*, **15** (1976) 2397.
- 32 J.E. Ellis, R.W. Fennell and E.A. Flom, *Inorg. Chem.*, **15** (1976) 2031.