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Reactions of cyclomanganated complexes with carbon disulfide: routes to η^2-aryldithiocarboxylate-$Mn(CO)_4$ complexes and to the trithiocarbonate complex $(\mu_3\text{-}CS_3)_2Mn_4(CO)_{16}$

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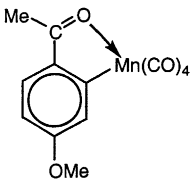
Abstract

Reaction of cyclomanganated aryl ketones with CS_2 proceeds with insertion into the Mn–C bond to give η^2-dithiocarboxylato–$Mn(CO)_4$ compounds. With other cyclomanganated substrates such as that from $Ph_3P{=}S$ and also with $Mn_2(CO)_{10}$, CS_2 gives $(\mu_3\text{-}CS_3)_2Mn_4(CO)_{16}$ with bridging trithiocarbonate ligands.

Keywords: Manganese; Cyclomanganates; Carbon disulfide; Insertion; Aryl dithiocarboxylate; Trithiocarbonate

1. Introduction

There is now a well-developed chemistry of cyclomanganated complexes [1]. These compounds are readily formed from aromatic and heteroaromatic ketones [2], from substrates with imine or amine donor groups [3], from triphenyl-phosphine or -arsine chalcogenides [4], and from chalcones [5] to give, for example, compounds **1**–**3**.



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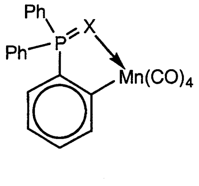
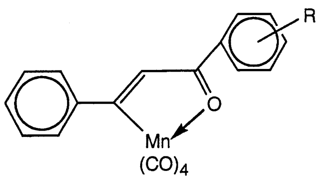


(**2a**) X = NPh
(**2b**) X = S
(**2c**) X = Se



(**3**)
(**3a**) R = 3,4,5-(OMe)$_3$

The Mn–C bond of these species is a site of reactivity, and combination with alkenes [6], alkynes [7], organoisocyanates [8], sulfur dioxide [9] or mercuric chloride [10] have all been shown to generate novel derivatives. For many of these reactions the first step in the process is undoubtedly insertion of the substrate into the Mn–C bond, followed by rearrangement with or without demanganation.

Another molecule that is known to insert into M–C bonds (as well as into M–H, M–O, M–P or M–S bonds) is CS_2 [11]. This generally leads to the formation of bidentate dithiocarboxylate complexes (e.g.

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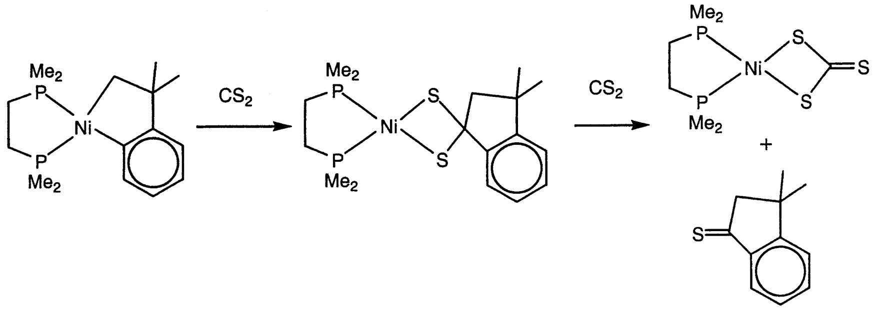
$MeCS_2Mn(CO)_4$ from $MeMn(CO)_5$ [12]), although monodentate species sometimes form (e.g. $PtCl(SC(S)H)(PPh_3)_2$ from $Pt(H)(Cl)(PPh_3)_2$ [13]. The only previous investigation involving cyclometallated substrates that we are aware of is the reaction of a nickel complex to give, initially, a *gem*-dithiolate complex which reacted further to give a η^2-trithiocarbonate complex and a thioketone (Eq. (1)) [14].



(1)

We now report the reactions of CS_2 with a range of cyclomanganated complexes.

2. Experimental

2.1. General

All manipulations were carried out in an oxygen-free N_2 atmosphere with dried solvents in standard Schlenk equipment or on a standard vacuum line. Orthomanganated substrates were prepared by published methods [2–5], while CS_2 was purified by trap-to-trap distillation on the vacuum line.

2.2. Instrumentation

Infrared spectra were recorded on a Digilab FTS-40 FTIR spectrophotometer. NMR spectroscopy was performed using a Bruker DRX400 Avance in $CDCl_3$; assignments were based on standard 2D experiments. Routine electrospray mass spectra (ESMS) were obtained on a VG Platform II spectrometer operating under standard conditions in MeOH. Na[OMe] was added as an ionisation aid [15]. Elemental analysis was performed by the Campbell Microanalytical Laboratory, University of Otago. Melting points were measured on a Reichart Thermopan melting point apparatus and are uncorrected.

2.3. Reactions

2.3.1. Reaction of η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese with CS_2

The cyclomanganated ketone **1** (133 mg, 0.42 mmol) was placed in a thick-walled glass ampoule (ca. 20 ml capacity). This was attached to a vacuum line, evacuated, and CS_2 (ca. 10 ml) was distilled in. The ampoule was sealed under vacuum and transferred to a Carius tube where it was heated at 85 °C for 24 h. When the cooled ampoule was stored at −20 °C for 72 h orange crystals formed. The ampoule was opened and the crystals were collected, and characterised as η^2-(2-acetyl-5-methoxyphenyldithiocarboxylato)tetracarbonylmanganese, **4**, (91 mg, 55%). M.p. 116 °C. Anal. Found: C, 44.2; H, 2.3. Calc. for $C_{14}H_9MnO_6S_2$: C, 42.9; H, 2.3%. IR: ν(CO) (CH_2Cl_2) 2093 (m), 2016 (vs), 2002 (vs),1963 (s) cm^{-1}; ^{1}H-NMR: δ 7.59 (1H, d, $3J_{H-H} = 8.6$ Hz, H3), 7.02 (1H, dd, $3J_{H-H} = 8.5$ Hz, $4J_{H-H} = 2.2$ Hz, H4), 6.95 (1H, d, $4J_{H-H} = 2.1$ Hz, H6), 3.92 (3H, s, OCH_3), 2.59 (3H, s, $C(O)CH_3$). ^{13}C-NMR: δ 199.2 (C7), 161.9 (C5), 149.2 (C1), 131.2 (C3), 129.6 (C2), 116.1 (C4), 113.0 (C6), 56.2 (OCH_3), 29.6 ($C(O)CH_3$); ESMS: (MeOH with added Na[OMe], cone voltage 20 V), *m/z* 423 (33%) $[M+OMe]^-$; 395 (100%) $[M+OMe-CO]^-$; 363 (48%) $[M-H-CO]^-$; 589 (28%) $[2M-Mn(CO)_5]^-$. This compound was also characterised by an X-ray crystal structure determination; see below.

2.3.2. Reaction of η^2-(2-benzoylphenyl)tetracarbonylmanganese with CS_2

Cyclomanganated benzophenone (190 mg, 0.55 mmol) was reacted with CS_2 (ca. 10 ml) in a sealed ampoule at 85 °C for 24 h, following the same procedure as above. The cooled ampoule was opened and the excess CS_2 removed under vacuum. The residue was chromatographed on an alumina column, with diethyl ether: petroleum spirits (1:1). The first fraction eluted gave a dark orange oil which did not crystallise. This was characterised as η^2-(2-benzoyl-phenyldithiocarboxylato)tetracarbonylmanganese, **5**, (156 mg, 67%). IR: ν(CO) (CH_2Cl_2) 2093 (m), 2019 (vs), 2007 (vs), 1964 (s) cm^{-1}; ^{1}H-NMR: δ 7.86–7.43 (m, Ar–*H*). ^{13}C NMR: δ 196.9 (–*C*OPh), 145.4 (*C*–CS_2), 137.6–125.7 (other Ar); ESMS: (MeOH with added Na[OMe], cone voltage 10 V), *m*/*z* 455 (40%) $[M+OMe]^-$; 427 (100%) $[M+OMe-CO]^-$; 653 (78%) $[2M-Mn(CO)_5]^-$.

2.3.3. Reaction of η^2-(2-acetylthien-3-yl)tetracarbonylmanganese with CS_2

The cyclomanganated thiophene derivative (112 mg, 0.38 mmol) was reacted with CS_2 (ca. 10 ml) in a sealed ampoule at 85 °C for 24 h, as above. Excess CS_2 was removed and the residue recrystallised from dichloromethane: petroleum spirits at −20 °C. Dark yellow rods of η^2-(2-acetyl-thien-3-yl-dithiocarboxylato)tetracarbonylmanganese, **6**, were obtained (114 mg, 80%). M.p. 108 °C (dec.). Anal. Found: C, 36.1; H, 1.4. Calc. for $C_{11}H_5MnO_5S_3$: C, 35.9; H, 1.4%. IR: ν(CO) (CH_2Cl_2) 2093 (m), 2016 (vs, br),1966 (s) cm^{-1}; ^{1}H NMR: δ 7.45 (1H, d, $^3J_{H-H}=5.0$ Hz, Ar–*H*), 7.24 (1H, d, $^3J_{H-H}=5.0$ Hz, Ar–*H*), 2.66 (3H, s, –C(O)C*H*$_3$). ^{13}C NMR: δ 191.4 (–*C(*O)CH_3), 150.4 (Ar), 140.0 (Ar), 129.8 (Ar–H), 128.4 (Ar–H), 30.0 (–C(O)*C*H_3). ESMS: (MeOH with added Na[OMe], cone voltage 10 V), *m*/*z* 399 (68%) $[M+OMe]^-$; 371 (74%) $[M+OMe-CO]^-$; 339, (16%) $[M-CO-H]^-$; 541 (100%) $[2M-Mn(CO)_5]^-$.

2.3.4. Reaction of η^2-[(2-diphenylthiophosphinyl)-phenyl]tetracarbonylmanganese with CS_2

Cyclomanganated triphenylphosphine sulfide (**2b**) (125 mg, 0.31 mmol) was reacted with CS_2 as above. ^{31}P-NMR and ESMS on the crude reaction mixture showed the presence of the starting material **2b** and Ph_3PS. Excess CS_2 was removed and the residue recrystallised from CH_2Cl_2: Et_2O at −20 °C. A small yield of orange blocks were obtained, identified as $(\mu_3\text{-}CS_3)_2Mn_4(CO)_{16}$ (**7**). M.p. > 115 °C (dec.). Anal. Found: C, 23.5; H, 0.0. Calc. for $C_{18}Mn_4O_{16}S_6$: C, 24.5; H, 0.0%. IR: ν(CO) (CH_2Cl_2) 2091 (s), 2049 (m), 2009 (vs, br), 1979 (m), 1965 (m) cm^{-1}; ESMS: (MeCN, cone voltage 10 V), *m*/*z* 717 (100%) $[M-Mn(CO)_4]^-$; 689 (27%) $[M-Mn(CO)_4-CO]^-$; 661, (8%) $[M-Mn(CO)_4-2CO]^-$. The characterisation was confirmed by an X-ray crystal structure analysis; see below.

Similar reactions of orthomanganated triphenylphosphine selenide (**2c**), orthomanganated triphenylphosphine phenylimine (**2a**) and the orthomanganted chalcone (**3a**), also gave low yields of $(\mu_3\text{-}CS_3)_2Mn_4(CO)_{16}$ as the only carbonyl-containing product.

2.3.5. Reaction of dimanganese decacarbonyl with CS_2

$Mn_2(CO)_{10}$ (517 mg, 1.33 mmol) was reacted with CS_2 in a sealed ampoule at 110 °C for 24 h. The unopened ampoule was stored at −20 °C for 48 h, to give crystals of the crude product. These were collected by filtration and chromatographed on silica gel plates, eluting with CH_2Cl_2:petroleum spirits (1:1) to give as the major product $(\mu_3\text{-}CS_3)_2Mn_4(CO)_{16}$, **7**, (217 mg, 39%). Spectroscopic data was identical to that given in Section 2.3.4.

2.4. X-ray crystallography

For compound **7** unit cell parameters and intensity data were collected using a Siemens SMART CCD diffractometer, using standard collection procedures, with monochromatic Mo–K_α X-rays (0.71073 Å), while for **4** a Siemens P4 four-circle diffractometer was used. Corrections for absorption and other effects were carried out with SADABS [16]. All other calculations used the SHELX-97 programs [17]. The structures were solved by direct methods, and developed routinely with refinement based on F^2. All non-hydrogen atoms were assigned anisotropic temperature factors, and hydrogen atoms were included in calculated positions.

2.4.1. Crystal data for η^2-(2-acetyl-5-methoxyphenyl-dithiocarboxylato)tetracarbonylmanganese (4)

$C_{14}H_9MnO_6S_2$, M_r 392.27, orthorhombic, *Pnma*, $a=22.878(8)$, $b=7.005(3)$, $c=9.973(6)$ Å, $V=1598.1(14)$ Å^3, $D_{calc}=1.630$ g cm^{-3}, $Z=4$, $F(000)=792$, μ(Mo–K_α) 1.113 mm^{-1}, T_{max} 0.262, T_{min} 0.238, crystal size $0.66\times0.17\times0.04$ mm^3. *T* 168 K.

A total of 1999 reflections, 1364 unique (R_{int} 0.0407) was collected $2<\theta<24°$. Final R_1 0.0415 [data with $I>2\sigma(I)$], 0.0767 (all data), wR_2 0.0863, GoF 1.014, final Δe +0.37/−0.35.

The structure is illustrated in Fig. 1, while selected bond parameters are listed in the caption.

2.4.2. Crystal data for $(\mu_3\text{-}CS_3)_2Mn_4(CO)_{16}$ (7)

$C_{18}Mn_4O_{16}S_6$, M_r 884.30, triclinic, $P\bar{1}$, $a=7.010(3)$, $b=8.410(4)$, $c=13.674(6)$ Å, $\alpha=83.40(1)$, $\beta=80.04(1)$, $\gamma=74.21(1)°$, $V=762.1(5)$ Å^3, $D_{calc}=1.927$ g cm^{-3}, $Z=1$, $F(000)=432$, μ(Mo–K_α) 2.099 mm^{-1}, T_{max} 1.00, T_{min} 0.76, crystal size $0.26\times0.16\times0.05$ mm^3. *T* 168 K.

A total of 9436 reflections, 3016 unique (R_{int} 0.0333) was collected $2<\theta<26.5°$. Final R_1 0.0309 [data with $I>2\sigma(I)$], wR_2 0.0702, GoF 0.954, final Δe +0.63/−0.50. The structure is illustrated in Fig. 2, with selected bond parameters in the caption.

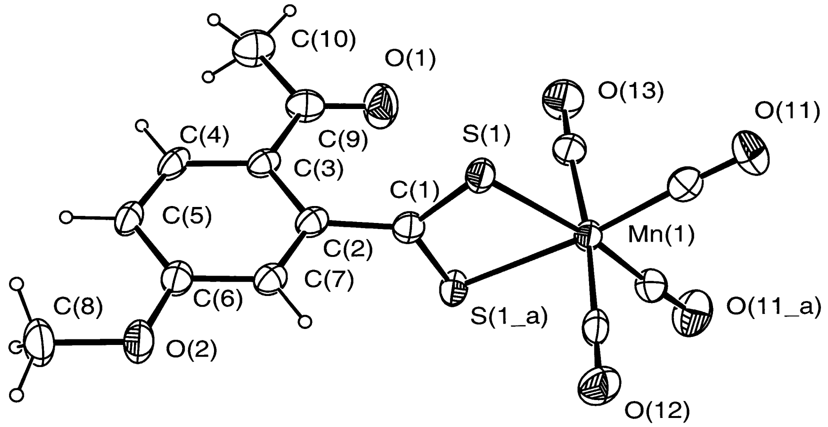


Fig. 1. The structure of η^2-(2-acetyl-5-methoxyphenyldithiocarboxylato)tetracarbonylmanganese (**4**). Bond parameters include: Mn(1)–S(1) 2.381(1), S(1)–C(1) 1.676(3), Mn(1)–C(11) 1.815(5), Mn(1)–C(12) 1.869(7) Å; S(1)–Mn(1)–S(1′) 72.73(6)°, Mn(1)–S(1)–C(1) 86.2(2)°, S(1)–C(1)–S(1′) 114.7(3)°.

3. Results and discussion

The reaction of the cyclometallated acetophenone **1** with $\mathrm{CS_2}$ at 85 °C for 24 h gave a reasonable yield of the dithiocarboxylate complex $(\eta^2\text{-}\mathrm{MeOC_6H_4CS_2})\mathrm{Mn(CO)_4}$ (**4**), which crystallised on cooling the reaction mixture. The temperature of reaction was critical; below 80 °C little change took place while above 90 °C extensive decomposition occurred.

The new complex **4** showed in the IR spectrum a characteristic νCO pattern for a *cis*-$\mathrm{L_2Mn(CO)_4}$ species, with a shift of around 10 $\mathrm{cm^{-1}}$ to higher frequencies compared with the starting complex **1**. The ^{1}H- and ^{13}C-NMR spectra were consistent with the dithiocarboxylate structure. Similarly the electrospray mass spectrum, with Na[OMe] added as an ionisation aid [15], gave expected peaks arising from both $\mathrm{OMe^-}$ addition and $\mathrm{H^+}$ abstraction from **4**. However, the spectroscopic data did not completely distinguish between the η^2-$\mathrm{RCS_2}$ bonding pattern as in **4**, and an alternative which has an η^1-$\mathrm{RCS_2}$ with the >C=O of the acetyl group still coordinated, as in **8**. Therefore, a single crystal X-ray determination was carried out to distinguish between the two possibilities.

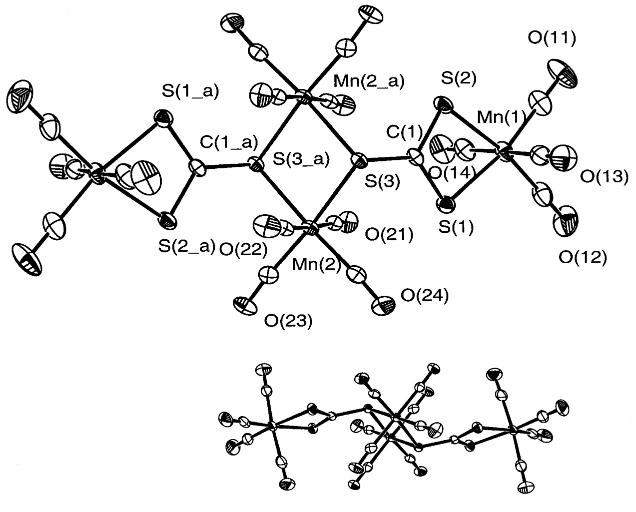


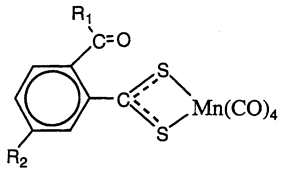
Fig. 2. The structure of $(\mu_3\text{-}\mathrm{CS_3})_2\mathrm{Mn_4(CO)_{16}}$ (**7**). Bond parameters include: Mn(1)–S(1) 2.3866(11), Mn(1)–S(2) 2.3971(13), Mn(2)–S(3) 2.4035(13), C(1)–S(1) 1.691(3), C(1)–S(2) 1.699(3), C(1)–S(3), 1.763(3) Å; S(1)–Mn(1)–S(2) 73.18(3)°, Mn(2)–S(3)–Mn(2′) 100.18(3)°, S(3)–Mn(2)–S(3′) 79.82(3)°, Mn(1)–S(1)–C(1) 86.41(10)°, S(1)–C(1)–S(2) 114.52(16)°, S(1)–C(1)–S(3) 122.84(16), S(2)–C(1)–S(3) 122.53(16)°. The inset is a side view emphasising the Z-shape of the molecule.

The structure is illustrated in Fig. 1. It shows that structure **4** is adopted, with the $\mathrm{Mn(CO)_4}$ group attached to the organic ligand by a symmetrical η^2-$\mathrm{RCS_2}$ linkage. The $\mathrm{CS_2}$ group is orthogonal to the aryl plane of the rest of the ligand, and the C=O group is uncoordinated. As expected, the Mn–CO distances of the two CO ligands *trans* to each other are significantly longer than the Mn-CO bonds *trans* to the dithiocarboxylate ligand.

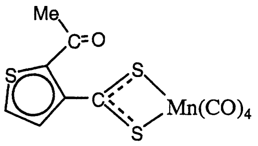
The corresponding reactions of orthomanganated benzophenone, and the orthomanganated 2-acetylthiophene complex, with $\mathrm{CS_2}$ under the same conditions produced the equivalent dithiocarboxylate complexes **5** and **6** respectively. This suggests that for manganated aryl ketones the conversion of the C,O-bonded R ligand to a $\mathrm{RCS_2}$ ligand is general.

A suggested pathway to **4**–**6** in these reactions involves initial insertion of $\mathrm{CS_2}$ into the Mn–C bond to give a S,O-bonded ligand with a seven-membered chelate ring, as in **8**. Displacement of the O-donor by the second sulfur atom would give the final product. This pathway is consistent with reactions of orthomanganated complexes involving other unsaturated molecules.

Although compounds **4**–**6** are new examples, other dithiocarboxylate complexes of $\mathrm{Mn(CO)_4}$ are established, having been prepared previously by insertion of $\mathrm{CS_2}$ into the Mn–C bond of $\mathrm{RMn(CO)_5}$ compounds



(**4**) $R_1 = Me$ $R_2 = OMe$
(**5**) $R_1 = Ph$ $R_2 = H$



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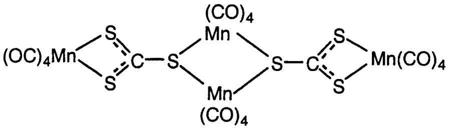

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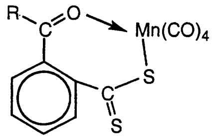

(**8**)

[12]. This earlier method, however, gave much lower yields (1–17%) than those found in the present study for the cyclomanganated substrates (55–80%). There appear to be only two instances of the direct reaction of dithiocarboxylate anions with either $BrMn(CO)_5$ or $[Mn(CO)_5(MeCN)]^+$ to give related species [18]. Therefore the reaction of CS_2 with orthomanganated aryl ketones may provide a useful route to dithiocarboxylates, especially those with functional groups that would interfere with the other syntheses.

The reaction of CS_2 with orthomanganated triphenyl phosphine sulfide, **2b**, was also investigated. This gave no evidence for the formation of a dithiocarboxylate, with the only new carbonyl-containing product being dark-yellow crystals isolated in low yield. Spectroscopic and analytical data were inconclusive, so an X-ray structure determination was carried out. This showed the product to be **7** as illustrated in Fig. 2. The centrosymmetric molecule consists of two η^3-trithiocarbonate anions, each with two of the sulfur atoms chelating to a $Mn(CO)_4$ group, while the third acts as a bridging atom between two other $Mn(CO)_4$ groups. The CS_3^{2-} groups are planar, with shorter C–S bonds to the chelating S atoms (1.695 Å) than to the bridging one (1.763 Å). The pyramidality at the bridging S atom induces a Z shape to the molecule (see inset to Fig. 2). The overall molecule is a combination of two common motifs — $(\eta^2\text{-}RCS_2)Mn(CO)_4$ as in the dithiocarboxylates discussed above [12,18] and related species [19], and a $(\mu\text{-}SR)_2Mn_2(CO)_8$ unit which is well-known for manganese carbonyl thiolates [20].

Also related to compound **7** are the $[(\eta^2\text{-}CS_3)Mn(CO)_4]^-$ and $(CO)_5Mn(\eta3\text{-}CS_3)Mn(CO)_4$ complexes found by Benson et al in reactions of $[Mn(CO)_5]^-$ with CS_2 [21].

Compound **7** does not appear to have been reported before, but the isomorphous Re analogue was isolated from the reaction of $F_3CRe(CO)_5$ with CS_2 [12,22].

The route to **7** is not clear. It seemed possible that the third S atom might have come from the orthomanganated $Ph_3P{=}S$, but this was discounted when **7** was also the product (albeit in low yield) when using the corresponding orthomanganated $Ph_3P{=}Se$ (**2c**); ESMS of the crude reaction mixture showed no traces of a dithioselenocarbonate analogue of **7** which would have been expected if atom transfer from the phosphine chalcogenide was involved.

Similarly $Ph_3P{=}NPh$ (**2a**) and chalcone (**3**) gave low yields of **7** when they were reacted with CS_2 under the same conditions.

To find a more rational synthesis of **7**, $Mn_2(CO)_{10}$ was reacted with CS_2. Although a higher temperature was needed (110 °C) the isolated yield of **7** was reasonable, 39%. It seems that formation of CS_3^{2-} ligands can readily arise from a formal redox disproportionation of CS_2 in reactions of a variety of manganese [21] (or rhenium [22] or nickel [14]) compounds.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 194981 and 194982 for compounds **4** and **7**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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