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Some insertion reactions of the Mn–C bond of cyclomanganated triphenylphosphine chalcogenides [1]

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Abstract

The complex $Ph_2P(\overline{S)C_6H_4Mn}(CO)_4$ (**1b**) reacts with alkenes CH_2=CH–R (R = COOMe, CN, C(O)Me) in refluxing MeCN or MeOH to give substituted derivatives of Ph_3P=S with a CH_2CH_2R group introduced in the *ortho* position of one phenyl ring. Other species are also formed including 3-cyano-4-(2-diphenylthiophosphinyl)phenyl)-2-buten-2-amine (characterised by an X-ray structure determination) from the reaction of **1b** with CH_2=CHCN in MeCN. In contrast, reaction with alkynes $C_2(COOMe)_2$ or $C_2H(COOMe)$ allowed isolation of the new seven-membered metallocycle arising from insertion of the alkyne into the Mn–C bond of **1b**. All three $Ph_2P(\overline{E)C_6H_4Mn}(CO)_4$ (E = O, S, Se) readily insert SO_2; a structure determination of the product with E = Se shows a six-membered metallocyclic ring which incorporates five different elements. © 1998 Elsevier Science S.A.

Keywords: Insertion reactions; Cyclomanganated triphenylphosphine chalcogenides; Metallocyclic ring

1. Introduction

We have recently described orthomanganated complexes of type **1** derived from triphenylphosphine chalcogenides [1]. These contain a Mn–C(sp^2) bond of the type which has been shown to be a reactive site for reactions of alkenes, alkynes and other unsaturated species with cyclomanganated compounds derived from aryl ketones [2,3a,3b,3c,3d,3e,3f,3g,3h], from α, β-unsaturated ketones [2,4a,4b] and from triphenylphosphite [5a,5b]. These reactions give new compounds via specific activation at the metallated carbon atom, and most are assumed to occur via initial insertion of the unsaturated substrate into the Mn–C bond, although only in the cases of the reactions of orthomanganated triphenylphosphite with alkynes [5a,5b], and the reactions of orthomanganated aryl ketones with SO_2 [6], have the initial insertion products been isolated. More usually further reactions occur, leading ultimately to organic products with loss of the manganese.

Complexes **1** have the organic ligand attached firmly to the manganese via the chalcogen atom, as shown for example by the reaction of **1b** with $P(OMe)_3$ in which up to two CO ligands are displaced rather than the S-donor atom [1]. These are therefore potential substrates for examining insertion reactions in more detail since the resulting compounds should retain the ligand coordinated to the metal. The reactions are of additional interest since they provide a route to *ortho*-functionalised compounds that could not be prepared readily from the free ligand.

This present paper describes reactions of the orthomanganated complexes **1** with alkenes, alkynes and

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[1] Dedicated to Professor Peter M. Maitlis on the occasion of his 65th birthday.

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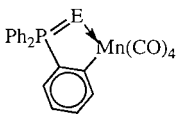
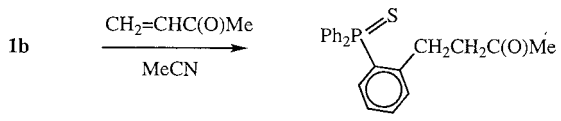
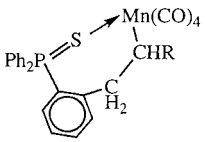
with SO_2. Most of the chemistry is developed with the sulfide **1b**, since this is the example which can be most efficiently prepared [1].



1a E = O
1b E = S
1c E = Se



(**2**)



3a R = C(O)Me
3b R = COOMe
3c R = CN

2. Experimental details

Instrumental methods have been described previously [1]. Reactions were performed under an atmosphere of dry nitrogen but subsequent work-up was carried out without precautions to exclude air. The orthomanganated triphenylphosphine chalcogenides were prepared as described elsewhere [1]. Preparative layer chromatography (PLC) was performed on 20 × 20 cm glass plates coated with Merck Kieselgel 60 silica gel. Petroleum spirits refers to a 60–80°C fraction. Electrospray mass spectra were recorded on a Fisons VG Platform II instrument, using $MeCN/H_2O$ (1:1) as mobile phase while high-resolution EI mass spectra were recorded on a VG 70-SE mass spectrometer.

2.1. Reactions of alkenes with orthomanganated triphenylphosphine chalcogenides

General procedure for thermally promoted coupling reactions of alkenes with orthomanganated triphenylphosphine chalcogenides: The orthomanganated chalcogenide (~0.22 mmol) and alkene (~0.3 mmol) were dissolved in the solvent (20 mL) and the solution was degassed. The mixture was refluxed under nitrogen for periods ranging from 2 h to several days, with the extent of reaction being monitored by t.l.c. At the completion of reaction the solvent was removed under vacuum and the residue chromatographed. Only major bands were extracted and products are reported in order of increasing polarity.

2.1.1. Reactions of orthomanganated triphenylphosphine sulfide with butenone

2.1.1.1. In acetonitrile. $Ph_2P(\overline{S)C_6H_4Mn}(CO)_4$ (**1b**) (100 mg, 0.218 mmol) and butenone (0.025 mL, 0.300 mmol) were refluxed in acetonitrile for 2 h. The residue was chromatographed (PLC, CH_2Cl_2) to give: (i) $Ph_3P{=}S$ (8 mg, 12%); (ii) 4-[(2-diphenylthiophosphinyl)phenyl]butan-2-one (**2**) (48 mg, 61%) as a colourless oil which crystallised from $CHCl_3$/pentane as colourless crystals, m.p. 126–127°C. Anal. found: C, 72.15; H, 5.63; $C_{22}H_{21}OPS$ calcd.: C, 72.51; H, 5.81%. ^{1}H NMR (300.13 MHz) ($CDCl_3$): δ 7.77 (m, 4H, Ar–H), 7.48 (m, 7H, Ar–H), 7.30 (m, 1H, Ar–H), 7.10 (m, 1H, H-5′), 6.92 (m, 1H, H-6′), 3.03 (t, ^3J = 7.8 Hz, 2H, H-4), 2.73 (t, ^3J = 7.8 Hz, 2H, H-3), 2.02 (s, 3H, H-1). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 208.1 (s, C-2), 145.9 (s, $^2J_{PC}$ = 9.1 Hz, C-2′), 133.1 (d, $^2J_{PC}$ = 12.0 Hz, C-6′), 132.8 (s, $^1J_{PC}$ = 84.3 Hz, C-1″), 132.3 (d, $^2J_{PC}$ = 10.6 Hz, C-2″, C-6″), 132.0 (d, $^4J_{PC}$ = 2.1 Hz, C-4′), 131.9 (s, $^1J_{PC}$ = 85.0 Hz, C-1′), 131.7 (d, $^4J_{PC}$ = 1.9 Hz, C-4″), 131.6 (d, $^3J_{PC}$ = 10.2 Hz, C-3′), 128.7 (d, $^3J_{PC}$ = 12.5 Hz, C-3″, C-5″), 125.9 (d, $^3J_{PC}$ = 12.7 Hz, C-5′), 45.2 (t, C-3), 29.8 (q, C-1), 28.6 (t, $^3J_{PC}$ = 6.2 Hz, C-4). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 42.1. GCMS: m/z 364 (M^+).

2.1.1.2. In methanol. The orthomanganated sulfide **1b** (100 mg, 0.218 mmol) and butenone (0.025 mL, 0.300 mmol) were refluxed in methanol for 5.5 h. The residue was chromatographed (PLC, CH_2Cl_2) to give: (i) $Ph_3P{=}S$ (18 mg, 28%); (ii) 4-[(2-diphenylthiophosphinyl)phenyl]butan-2-one (**2**) (43 mg, 54%).

2.1.1.3. In benzene. The same reaction in benzene for 72 h gave: (i) $Ph_3P{=}S$ (25 mg, 38%); (ii) 4-[(2-diphenylthiophosphinyl)phenyl]butan-2-one (**2**) (10 mg, 13%).

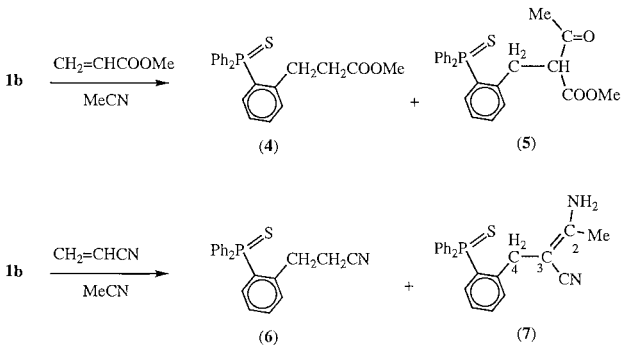
2.1.1.4. In carbon tetrachloride. The orthomanganated $Ph_3P{=}S$ **1b** (111 mg, 0.241 mmol) and butenone (0.028 mL, 0.338 mmol) were refluxed in carbon tetrachloride for 24 h. The residue was chromatographed (PLC, CH_2Cl_2) to give: (i) $Ph_3P{=}S$ (20 mg, 28%); (ii) 4-[(2-diphenylthiophosphinyl)phenyl]butan-2-one (**2**) (15 mg, 17%).

2.1.2. Reactions of orthomanganated triphenylphosphine sulfide with methyl acrylate

2.1.2.1. In acetonitrile. $Ph_2P(\overline{S)C_6H_4Mn}(CO)_4$ (**1b**) (101 mg, 0.219 mmol) and methyl acrylate (0.040 mL, 0.444 mmol) were refluxed in acetonitrile for 3 h. The residue was chromatographed (PLC, CH_2Cl_2) to give: (i) $Ph_3P{=}S$ (5 mg, 8%); (ii) methyl 3-[(2-diphenylthiophosphinyl)phenyl]propanoate (**4**) (10 mg, 12%) as a colourless oil which crystallised from ether/pentane as colourless crystals, m.p. 98–99°C. Anal. found: C, 68.86; H, 5.78; $C_{22}H_{21}O_2PS$ calcd.: C, 68.93; H, 5.56%. ^{1}H NMR (300.13 MHz) ($CDCl_3$): δ 7.78 (m, 4H, Ar–H), 7.48 (m, 7H, Ar–H), 7.34 (m, 1H, Ar–H), 7.12 (m, 1H, H-5′), 6.93 (m, 1H, H-6′), 3.60 (s, 3H, 1-OCH_3), 3.13 (t, ^3J = 7.8 Hz, 2H, H-3), 2.58 (t, ^3J = 7.8 Hz, 2H, H-2). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 173.3 (s, C-1), 145.3 (s, $^2J_{PC}$ = 9.5 Hz, C-2′), 133.1 (d, $^2J_{PC}$ = 12.0 Hz, C-6′), 132.8 (s, $^1J_{PC}$ = 84.1 Hz, C-1″), 132.4 (d, $^2J_{PC}$ = 10.6 Hz, C-2″, C-6″), 132.0 (d, $^4J_{PC}$ = 2.2 Hz, C-4′), 132.1 (s, $^1J_{PC}$ = 85.1 Hz, C-1′), 131.7 (d, $^4J_{PC}$ = 2.1 Hz, C-4″), 131.3 (d, $^3J_{PC}$ = 10.0 Hz, C-3′), 128.6 (d, $^3J_{PC}$ = 12.5 Hz, C-3″, C-5″), 126.0 (d, $^3J_{PC}$ = 12.4 Hz, C-5′), 51.6 (q, 1-OCH_3), 35.1 (t, C-2), 29.3 (t, $^3J_{PC}$ = 5.9 Hz, C-3). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 42.0; (iii) methyl 2-acetyl-3-[(2-diphenylthiophosphinyl)phenyl]propanoate (**5**) (54 mg, 58%) as a colourless oil which crystallised from ether/pentane as chunky colourless crystals, m.p. 117–119°C. HRMS Found: M^+, 422.1101; $C_{24}H_{23}O_3PS$ calcd.: M, 422.1106. ^{1}H NMR (300.13 MHz) ($CDCl_3$): δ 7.75 (m, 4H, Ar–H), 7.45 (m, 7H, Ar–H), 7.29 (m, 1H, Ar–H), 7.12 (m, 1H, H-5′), 6.90 (m, 1H, H-6′), 4.35 (m, 1H, H-2), 3.63 (s, 3H, 1-OCH_3), 3.42 (m, 1H, H-3), 3.18 (m, 1H, H-3), 2.14 (s, 3H, 2-$COCH_3$). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 202.9 (s, 2-$COCH_3$), 169.6 (s, C-1), 142.9 (s, $^2J_{PC}$ = 9.0 Hz, C-2′), 133.5 (d, $^2J_{PC}$ = 11.8 Hz, C-6′), 132.5 (s, $^1J_{PC}$ = 84.1 Hz, C-1′ or C-1″ or C-1‴), 132.5 (s, $^1J_{PC}$ = 84.5 Hz, C-1′ or C-1″ or C-1‴), 132.4–131.8 (d, C-2″, C-2‴, C-3′, C-4′, C-6″, C-6‴), 132.1 (s, $^1J_{PC}$ = 84.2 Hz, C-1′ or C-1″ or C-1‴), 128.8 (d, $^3J_{PC}$ = 12.6 Hz, C-3″, C-5″ or C-3‴, C-5‴), 128.7 (d, $^3J_{PC}$ = 12.3 Hz, C-3″, C-5″ or C-3‴, C-5‴), 126.6 (d, $^3J_{PC}$ = 12.5 Hz, C-5′), 60 (d, C-2), 52.3 (q, 1-OCH_3), 32.2 (t, $^3J_{PC}$ = 5.8 Hz, C-3), 30.2 (q, 2-$COCH_3$). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 41.9.

2.1.2.2. In methanol. The orthomanganated sulfide **1b** (101 mg, 0.219 mmol) and methyl acrylate (0.028 mL, 0.311 mmol) were refluxed in methanol for 3.5 h. The residue was chromatographed (PLC, CH_2Cl_2) to give: (i) $Ph_3P{=}S$ (33 mg, 52%); (ii) methyl 3-[(2-diphenylthiophosphinyl)phenyl]propanoate (**4**) (26 mg, 31%).

2.1.2.3. In methanol under carbon monoxide. The same reaction as in Section 2.1.2.2 was carried out under a static CO atmosphere for 3.5 h. The residue was chromatographed (PLC, CH_2Cl_2) to give: (i) $Ph_3P{=}S$ (52%); (ii) methyl 3-[(2-diphenylthiophosphinyl)phenyl]propanoate (**4**) (30%).



2.1.3. Reactions of orthomanganated triphenylphosphine sulfide with acrylonitrile

2.1.3.1. In acetonitrile. $Ph_2P(\overline{S)C_6H_4Mn}(CO)_4$ (**1b**) (101 mg, 0.220 mmol) and acrylonitrile (0.020 mL, 0.304 mmol) were refluxed in acetonitrile for 2 h. The residue was chromatographed (PLC, CH_2Cl_2) to give: (i) $Ph_3P{=}S$ (4 mg, 6%); (ii) 3-[(2-diphenylthiophosphinyl)phenyl]propanenitrile (**6**) (34 mg, 44%) as a colourless oil which crystallised from $CHCl_3$/pentane as colourless plates, m.p. 150–151°C. HRMS found: M^+, 347.0892; $C_{21}H_{18}NPS$ calcd.: M, 347.0898. ^{1}H NMR (300.13 MHz) ($CDCl_3$): δ 7.75 (m, 4H, Ar–H), 7.51 (m, 8H, Ar–H), 7.18 (m, 1H, H-5′), 6.90 (m, 1H, H-6′), 3.13 (t, ^3J = 7.3 Hz, 2H, H-3), 2.72 (t, ^3J = 7.3 Hz, 2H, H-2). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 142.5 (s, $^2J_{PC}$ = 9.2 Hz, C-2′), 133.3 (d, $^2J_{PC}$ = 11.7 Hz, C-6′), 132.4 (s, $^1J_{PC}$ = 84.4 Hz, C-1′), 132.3 (s, $^1J_{PC}$ = 84.6 Hz, C-1″), 132.3 (d, $^2J_{PC}$ = 10.6 Hz, C-2″, C-6″), 132.2 (d, $^3J_{PC}$ = 10.4 Hz, C-3′), 132.0 (d, C-4′), 132.0 (d, $^4J_{PC}$ = 2.2 Hz, C-4″), 128.8 (d, $^3J_{PC}$ = 12.6 Hz, C-3″, C-5″), 127.0 (d, $^3J_{PC}$ = 12.5 Hz, C-5′), 119 (s, C-1), 29.9 (t, $^3J_{PC}$ = 6.1 Hz, C-3), 18.6 (t, C-2). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 41.8; (iii) 3-cyano-4-(2-diphenylthiophosphinyl)phenyl)-2-buten-2-amine **7** as a colourless oil which crystallised from ether/pentane as white crystals, m.p. 203–206°C. Anal. found: C, 69.73; H, 5.17; N, 6.90%; $C_{23}H_{21}N_2PS$ calcd.: C, 71.11; H, 5.45; N 7.22%. ^{1}H NMR (400.13 MHz) ($CDCl_3$): δ 7.80 (m, 4H, Ar–H), 7.68 (m, 1H, Ar–H), 7.50 (m, 7H, Ar–H), 7.13 (m, 1H, H-5′), 6.84 (m, 1H, H-6′), 5.01 (s, br, 2H, NH_2), 3.52 (s, 2H, CH_2), 2.03 (s, 3H, CH_3). ^{13}C NMR (100.61 MHz) ($CDCl_3$): δ 156.4 (s, C-3), 143.6 (s, $^2J_{PC}$ = 9.4 Hz, C-2′), 132.3 (d, $^2J_{PC}$ = 10.7 Hz, C-2″, C-6″), 132.0 (d, $^4J_{PC}$ = 2.4 Hz, C-4″), 132.0 (d, C-4′), 131.5(s, $^1J_{PC}$ = 84.7 Hz, C-1″),

131.4 (s, $^1J_{PC}$ = 85.2 Hz, C-1′), 130.1 (d, $^3J_{PC}$ = 9.9 Hz, C-3′), 128.9 (d, $^3J_{PC}$ = 12.6 Hz, C-3″, C-5″), 126.5 (d, $^3J_{PC}$ = 12.4 Hz, C-5′), 125.1 (s, CN), 75.0 (s, C-2), 32.3 (t, C-4), 20.6 (q, C-1). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 42.4. ESMS: m/z 406 $(M + NH_4)^+$, 389 $(M + H)^+$. The compound **7** was further characterised by an X-ray crystallography study (see below).

2.1.3.2. In methanol. Complex **1b** (101 mg, 0.219 mmol) and acrylonitrile (0.020 mL, 0.304 mmol) were refluxed in methanol for 2 h. The residue was chromatographed (PLC, CH_2Cl_2) to give: (i) $Ph_3P{=}S$ (31 mg, 48%); (ii) 3-[(2-diphenylthiophosphinyl)phenyl]propanenitrile (6) (26 mg, 34%).

2.1.4. Attempted Li_2PdCl_4-promoted coupling reactions of alkenes with orthomanganated triphenylphosphine sulfide

2.1.4.1. Reaction with butenone in acetonitrile. $PdCl_2$ (77 mg, 0.435 mmol) and LiCl (77 mg, 1.81 mmol) were stirred in dry acetonitrile (20 mL) for 2 h to solubilise the $PdCl_2$ as Li_2PdCl_4. Compound **1b** (200 mg, 0.433 mmol) and methyl vinyl ketone (0.050 mL, 0.601 mmol) were added and the mixture refluxed for 17 h. Upon reaction the solution turned black with the precipitation of palladium metal. The mixture was filtered to remove metal, the filtrate passed through a short silica column and the solvent evaporated under reduced pressure. The residue was chromatographed (PLC, CH_2Cl_2) to give $Ph_3P{=}S$ (8 mg, 6%) but no major product.

2.1.4.2. Reaction with methyl vinyl ketone in methanol. Similarly $PdCl_2$ (39 mg, 0.220 mmol) and LiCl (40 mg, 0.934 mmol) were stirred in dry methanol (20 mL) and treated with **1b** (101 mg, 0.219 mmol) and methyl vinyl ketone (0.025 mL, 0.300 mmol). The mixture was stirred at ambient temperature for 60 h, by which time t.l.c. showed the presence of the orthomanganated compound and $Ph_3P{=}S$. The mixture was refluxed for 3 h. T.l.c. showed no major organic products except $Ph_3P{=}S$ so the reaction was abandoned.

2.2. Coupling reactions of alkynes with orthomanganated triphenylphosphine sulfide

2.2.1. Reaction of orthomanganated triphenylphosphine sulfide with dimethyl acetylenedicarboxylate in benzene

$Ph_2P(S)C_6H_4Mn(CO)_4$ (**1b**) (109 mg, 0.237 mmol) and dimethyl acetylenedicarboxylate (0.044 mL, 0.358 mmol) were refluxed in benzene for 3.5 h. The residue was chromatographed (PLC, 1:4 petroleum spirit/ethyl acetate) to give: (i) $Ph_3P{=}S$ (12 mg, 17%); (ii) a yellow oil which consisted of a mixture of (by integration of proton methoxy singlets): 94% 1,2-di(methoxycarbonyl)-2-[(2-diphenylthiophosphinyl)phenyl]ethenyl-tetracarbonylmanganese (**8a**) which crystallised from $CHCl_3$/pentane as yellow crystals (81 mg, 57%), m.p. 164–167°C. Anal. found: C, 55.92; H, 3.06; $C_{28}H_{20}O_8PSMn$ calcd.: C, 55.82; H, 3.35%. IR ($CHCl_3$): ν(CO) 2081(m), 2001(vs, br), 1959(s) cm^{-1}. ^{1}H NMR (300.13 MHz) ($CDCl_3$): δ 7.85–7.26 (m, 13H, Ar–H), 7.05 (m, 1H, Ar–H), 3.58 (s, 3H, 1-OCH_3), 3.42 (s, 3H, 4-OCH_3). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 215.6 (s, br, CO), 212.8 (s, br, $^3J_{PC}$ = 6.5 Hz, CO), 211.5 (s, br, CO), 210.3 (s, br, CO), 191.3 (s, C-2), 179.7 (s, C-1), 162.0 (s, C-4), 146.3 (s, $^2J_{PC}$ = 7.6 Hz, C-2′), 135.1 (s, C-3), 135.0 (d, J_{PC} = 10.6 Hz), 133.3 (d, J_{PC} = 9.4 Hz), 132.8 (d), 132.5 (d), 132.4 (d), 132.3 (d), 131.8 (d, J_{PC} = 11.1 Hz), 129.0 (d, J_{PC} = 12.1 Hz), 128.3 (d, J_{PC} = 13.7 Hz), 127.9 (s, $^1J_{PC}$ = 84.1 Hz), 127.8 (s, $^1J_{PC}$ = 85.5 Hz), 127.6 (d, J_{PC} = 12.8 Hz), 127.0 (s, $^1J_{PC}$ = 86.1 Hz), 51.5 (q, 4-OCH_3), 50.0 (q, 1-OCH_3). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 46.0. ESMS: m/z 620 $(M + NH_4)^+$, 603 $(M + H)^+$; 6% of an unidentified orange crystalline solid which crystallised from $CHCl_3$/pentane as small orange rosettes (5 mg, 3% based on a molecular mass of 716). IR ($CHCl_3$): ν(CO) 2027(s), 1942(s), 1918(s) cm^{-1}. ^{1}H NMR (300.13 MHz) ($CDCl_3$): δ 7.83–7.16 (m, 14H, Ar–H), 4.00 (s, 3H, –OCH_3), 3.80 (s, 3H, –OCH_3), 3.52 (s, 3H, –OCH_3), 3.16 (s, 3H, –OCH_3). ESMS: m/z 775 $(M + NH_4 + CH_3CN)^+$, 734 $(M + NH_4)^+$, 717 $(M + H)^+$.

The reaction was repeated with an excess of dimethyl acetylenedicarboxylate, but the results were not significantly altered. Similarly a longer reaction time did not enhance the yield of the orange compound.

2.2.2. Reaction of η^2-(C,S)-[(2-diphenylthiophosphinyl)phenyl]dicarbonylbis(trimethylphosphite)manganese with dimethyl acetylenedicarboxylate in benzene

The substituted complex $Ph_2P(S)C_6H_4Mn(CO)_2[P(OMe)_3]_2$ (112 mg, 0.172 mmol) and dimethyl acetylenedicarboxylate (0.056 mL, 0.416 mmol) were refluxed in benzene for 3 h. The residue was chromatographed (PLC, CH_2Cl_2) to give: (i) $Ph_3P{=}S$ (6 mg, 10%); (ii) unreacted starting complex (11 mg, 9%); (iii) E-1,2-di(methoxycarbonyl)-2-[(2-diphenylthiophosphinyl)phenyl]ethenyldicarbonylbis(trimethylphosphite)-manganese (**8b**) (41 mg, 30%) which crystallised from $CHCl_3$/pentane as yellow crystals, m.p. 179–182°C. IR ($CHCl_3$): ν(CO) 1950(s), 1870(s). ^{1}H NMR (300.13 MHz) ($CDCl_3$): δ 7.70–7.10 (m, 4H, Ar–H), 3.64 (m, 18H, $P(OCH_3)_3$), 3.42 (s, 3H, –$COOCH_3$), 3.19 (s, 3H, –$COOCH_3$). ^{31}P NMR (36.23

MHz) ($CDCl_3$): δ 176.5, 175.7, 42.9. ESMS: m/z 812 $(M + NH_4)^+$, 795 $(M + H)^+$.

2.2.3. Reaction of orthomanganated triphenylphosphine sulfide with methyl propiolate in benzene

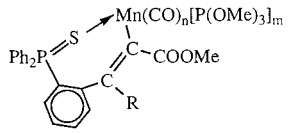
Methyl propiolate (0.030 mL, 0.337 mmol) and **1b** (102 mg, 0.222 mmol) were refluxed in benzene for 3.5 h. The residue was chromatographed (PLC, CH_2Cl_2) to give: (i) $Ph_3P{=}S$ (7 mg, 11%); (ii) Z-1-methoxycarbonyl-2-[(2-diphenylthiophosphinyl)phenyl]-ethenyltetracarbonylmanganese (**8c**) (49 mg, 41%) as a yellow oil. IR ($CHCl_3$): ν(CO) 2077(m), 1997(vs, br), 1989(vs, br), 1947(s) cm^{-1}. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 7.72–7.48 (m, 12H, Ar–H), 7.37 (s, 1H, H-3), 7.22 (m, 1H, H-5′), 6.99 (m, 1H, H-6′), 3.45 (s, 3H, 1-OCH_3). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 217.3 (s, br, C≡O), 213.7 (s, br, C≡O), 212.7 (s, br, 2 × C≡O), 179.1 (s, C-2), 165.6 (s, C-1), 147.1 (s, $^2J_{PC} = 8.1$ Hz, C-2′), 142.5 (d, C-3), 132.7–131.6 (d, C-4′, C-6′, C-2″, C-4″, C-6″), 128.9 (d, $^3J_{PC} = 12.2$ Hz, C-3″, C-5″), 128.8 (d, C-3′), 128.3 (s, $^1J_{PC} = 84.8$ Hz, C-1″), 126.7 (d, $^3J_{PC} = 12.5$ Hz, C-5′), 125.8 (s, $^1J_{PC} = 85.0$ Hz, C-1′), 50.7 (q, 1-OCH_3). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 45.2. ESMS: m/z 562 $(M + NH_4)^+$, 545 $(M + H)^+$, 517 $(M + H-CO)^+$; (iii) methyl E-3-[(2-diphenylthiophosphinyl)phenyl]prop-2-enoate (**10**) (11 mg, 13%) as a colourless oil. HRMS found: M^+, 378.0843; $C_{22}H_{19}O_2PS$ calcd.: M, 378.0843. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 8.25 (d, $^3J = 15.7$ Hz, 1H, H-3), 7.84 (m, 4H, Ar–H), 7.50 (m, 8H, Ar–H), 7.30 (m, 1H, H-5′), 7.16 (m, 1H, H-6′), 6.08 (d, $^3J = 15.7$ Hz, 1H, H-2), 3.64 (s, 3H, 1-OCH_3). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 166.4 (s, C-1), 143.2 (d, $^3J_{PC} = 7.0$ Hz, C-3), 138.4 (s, $^2J_{PC} = 7.4$ Hz, C-2′), 133.4 (s, $^1J_{PC} = 82.9$ Hz, C-1′), 133.1 (d, $^2J_{PC} = 10.9$ Hz, C-6′), 132.5 (d, $^2J_{PC} = 10.6$ Hz, C-2″, C-6″), 132.1 (s, $^1J_{PC} = 84.8$ Hz, C-1″), 132.0 (d, $^4J_{PC} = 2.0$ Hz, C-4′), 131.9 (d, $^4J_{PC} = 2.1$ Hz, C-4″), 129.1 (d, $^3J_{PC} = 12.3$ Hz, C-5′), 128.6 (d, $^3J_{PC} = 12.5$ Hz, C-3″, C-5″), 128.6 (d, C-3′), 120.0 (d, C-2), 51.6 (q, 1-OCH_3). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 41.4. GCMS: m/z 378 (M^+), 319 $(M-COOCH_3)^+$.

2.3. Unsuccessful coupling reactions with alkynes

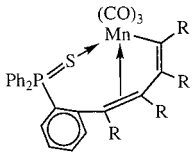
No new species were isolated from the following reactions of $Ph_2P(\overline{S)C_6H_4Mn}(CO)_4$:

1. with Ph_2C_2 in refluxing benzene, petroleum spirit or acetonitrile;
2. with 3-butyn-1-ol in refluxing benzene;
3. with 2-methyl-3-butyn-2-ol in refluxing benzene
4. with C_2H_2 in refluxing petroleum spirit;
5. with trimethylsilylacetylene in refluxing benzene;
6. with 2-methyl-1-buten-3-yne in refluxing acetonitrile.

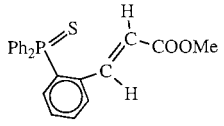
2.4. Sulfur dioxide insertion reactions of orthomanganated triphenylphosphine chalcogenides



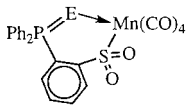
8a R = COOMe n = 4 m = 0
8b R = COOMe n = 2 m = 2
8c R = H n = 4 m = 0



9 R = COOMe



10



11a E = O
11b E = S
11c E = Se

2.4.1. Reaction of orthomanganated triphenylphosphine sulfide with sulfur dioxide

2.4.1.1. Thermally induced. $Ph_2P(\overline{S)C_6H_4Mn}(CO)_4$ **1b** (300 mg, 0.651 mmol) was placed in an ampoule and degassed. Liquid SO_2, which had been degassed by two cycles of freeze–pump–thawing was condensed into the ampoule using standard vacuum line techniques. The ampoule was sealed and placed in a Carius tube maintained at 52°C for 18 h. The ampoule was opened and, after the excess SO_2 had evaporated, the residue was extracted with dichloromethane and filtered. An infrared spectrum showed complete conversion to the SO_2 insertion product η^2-(S,S)-[(2-diphenylthiophosphinyl)phenylsulfonyl]tetracarbonylmanganese (**11b**) by the absence of the peaks at 2072(m), 1993(vs, br), 1978(vs, br), 1933(s) cm^{-1} and the appearance of peaks at higher frequency. Vapour diffusion of pentane into a saturated dichloromethane solution of **11b** gave small yellow crystals (304 mg, 89%), m.p. 119–121°C. Anal. found: C, 49.85; H, 2.61; $C_{22}H_{14}O_6S_2MnP$ calcd.: C, 50.39; H 2.69%. IR ($CHCl_3$): ν(CO) 2101(m), 2030(s), 2014(s), 1986(s) cm^{-1}. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 8.40 (m, 1H, H-6), 7.78 (m, 1H, H-5), 7.63–7.48 (m, 10H, Ar–H), 7.39 (m, 1H, H-4), 6.90 (m, 1H, H-3). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 212.6 (s, br, C≡O), 212.1 (s, br, C≡O), 208.1 (s, br, 2 × C≡O), 157.2 (s, $^2J_{PC} = 8.2$ Hz, C-1), 134.0 (d, C-5), 133.9 (d, C-3), 133.3 (d, C-4′), 133.0 (d, $^2J_{PC} = 10.7$ Hz, C-2′, C-6′), 129.7 (d, $^3J_{PC} = 12.1$ Hz, C-4), 129.0 (d, $^3J_{PC} = 13.5$ Hz, C-3′, C-5′), 127.9 (s, $^1J_{PC} = 90.1$ Hz, C-1′), 126.1 (d, $^3J_{PC} = 8.1$ Hz, C-6), 124.2 (s, $^1J_{PC} = 80.6$ Hz, C-2). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 34.6. ESMS: 547

$(M + Na)^+$, 542 $(M + NH_4)^+$, 538 $(M + H–CO + CH_3CN)^+$, 525 $(M + H)^+$, 497 $(M + H–CO)^+$.

2.4.1.2. Photochemically induced. Orthomanganated $Ph_3P{=}S$ (107 mg, 0.232 mmol) was sealed in an ampoule with SO_2 (~10 mL) and placed under a UV lamp for 18 h at ambient temperature. An infrared spectrum of the residue showed complete conversion to the SO_2 insertion product **11b** (106 mg, 87%).

2.4.2. Reaction of orthomanganated triphenylphosphine selenide with sulfur dioxide

Similarly, $Ph_2P(\overline{Se})C_6H_4\overline{Mn}(CO)_4$ (**1c**) (252 mg, 0.496 mmol) was treated with SO_2 (~10 mL) and left to react for 18 h at 52°C. An infrared spectrum showed the complete conversion to the SO_2 insertion product, η^2-(S,Se)-[(2-diphenylselenophosphinyl)phenylsulfonyl]tetracarbonylmanganese (**11c**). Vapour diffusion of pentane into a saturated dichloromethane solution gave small yellow crystals (238 mg, 84%), m.p. 133–135°C. Anal. found: C, 45.96; H, 2.19%; $C_{22}H_{14}O_6SMnPSe$ calcd.: C, 46.25; H 2.47%. IR ($CHCl_3$): υ(CO) 2096(m), 2026(s), 2009(s), 1982(s) cm^{-1}. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 8.40 (m, 1H, H-6), 7.78 (m, 1H, H-5), 7.62–7.52 (m, 10H, Ar–H), 7.39 (m, 1H, H-4), 6.90 (m, 1H, H-3). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 157.8 (s, $^2J_{PC} = 9.1$ Hz, C-1), 134.0 (d, C-5), 133.5 (d, C-3), 133.4 (d, $^2J_{PC} = 10.8$ Hz, C-2′, C-6′), 133.2 (d, $^4J_{PC} = 2.6$ Hz, C-4′), 129.6 (d, $^3J_{PC} = 11.4$ Hz, C-4), 129.0 (d, $^3J_{PC} = 13.6$ Hz, C-3′, C-5′), 126.9 (s, $^1J_{PC} = 82.0$ Hz, C-1′), 126.9 (d, $^3J_{PC} = 8.3$ Hz, C-6), 123.6 (s, $^1J_{PC} = 73.4$ Hz, C-2). ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 15.6. ESMS: 590 $(M + NH_4)^+$, 573 $(M + H)^+$, 545 $(M + H–CO)^+$. This compound was further characterised by an X-ray crystal structure determination (see below).

2.4.3. Reaction of orthomanganated triphenylphosphine oxide with sulfur dioxide

$Ph_2P(\overline{O})C_6H_4\overline{Mn}(CO)_4$ (**1a**) (273 mg, 0.614 mmol) was treated with SO_2 (~10 mL) and left to react for 18 h at 52°C. An orange oil which failed to crystallise was obtained, and was tentatively assigned as consisting of: (i) η^2-(S,O)-[(2-diphenylphosphinyl)phenylsulfonyl]tetracarbonyl-manganese, (**11a**) ESMS: 522 $(M + H–CO + CH_3CN)^+$, 509 $(M + H)^+$, 481 $(M + H–CO)^+$ and (ii) an unidentified product with ESMS: 800 $(M + H–CO + CH_3CN)^+$, 787 $(M + H)^+$, 759 $(M + H–CO)^+$.

Combined IR ($CHCl_3$): υ(CO) 2109(m)*, 2044(vs)*, 2036(vs)*, 2010(s)* 1978(s), 1959(vs), 1930(vs) cm^{-1}. Combined ^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 44.4*, 41.9. The peaks indicated by an asterisk are tentatively assigned to **11a**.

2.5. X-ray crystal structure determinations

2.5.1. 3-cyano-4-(2-diphenylthiophosphinyl)phenyl)-2-buten-2-amine (7)

White crystals were obtained from ether/pentane. The unit cell dimensions and intensity data were obtained on a Siemens SMART CCD diffractometer. The data collection nominally covered over a hemisphere of reciprocal space, by a combination of three sets of exposures; each set had a different ϕ angle for the crystal and each exposure covered 0.3° in ω. The crystal to detector distance was 5.0 cm. The data sets were corrected empirically for absorption using SADABS.

The structure was solved by direct methods and developed routinely. In the final cycles of least-squares refinement based on F^2 against all data (SHELXL-96 [7a,7b,7c]), all non-hydrogen atoms were treated anisotropically and hydrogen atoms were included in their calculated positions, except for the NH_2 hydrogen atoms of the two independent molecules which were located as the four highest residual peaks in a penultimate difference map, and were included in the final refinement with fixed U_{iso} values, but with unconstrained coordinates.

Crystal data: $C_{23}H_{21}N_2PS$, M_r 388.45, triclinic, space group $P\bar{1}$, $a = 12.3771(3)$, $b = 13.4731(3)$, $c = 14.4548(3)$ Å, $\alpha = 96.924(1)$, $\beta = 107.937(1)$, $\gamma = 109.478(1)°$, $U = 2094.01(7)$ Å^3, $D_{calc} = 1.232$ g cm^{-3}, $Z = 4$, $F(000)$ 816, μ(Mo Kα) = 0.24 mm^{-1}. Crystal size $0.37 \times 0.32 \times 0.21$ mm^3. A total of 20291 reflections were collected at 203 K in the range $1.6 < \theta < 28.2°$, corresponding to 9214 unique data ($R_{int} = 0.027$, $T_{max, min}$ 0.9623, 0.7857.

The refinement converged with $R_1 = 0.0442$ [for 7100 data with $I > 2\sigma(I)$], $R_1 = 0.0667$, wR_2 0.1096, GoF 1.043 (all data). The largest features in a final difference map were $+0.279/-0.330$ e Å^{-3}. Coordinates are listed in Table 1 and the structure of one of the independent molecules is illustrated in Fig. 1, with selected bond parameters given in Table 2.

2.5.2. 1,2-di(methoxycarbonyl)-2-[(2-diphenylthiophosphinyl)phenyl]ethenyl-tetracarbonylmanganese (8a) and [(2-diphenylselenophosphinyl)phenyl-sulfonyl]tetracarbonyl-manganese (11c)

For both of these compounds only poor quality determinations were possible. For **11c** only mediocre quality crystals were obtained by slow diffusion of pentane into a concentrated solution in $CHCl_3$, whereas for **8a** the crystals appeared to be of reasonable quality but the refinement gave poor R indices, possibly because of twinning problems. Both structure analyses confirmed the atom connectivity and the gross features of the molecules concerned, but only the crystal data is pre-

Table 1
Atomic coordinates and equivalent isotropic displacement parameters for **7**

	x	*y*	*z*	*U*(eq)
P(1)	0.2860(1)	0.4914(1)	0.7236(1)	0.034(1)
S(1)	0.1288(1)	0.4496(1)	0.7437(1)	0.049(1)
C(11)	0.3314(2)	0.7468(1)	0.7771(1)	0.035(1)
C(12)	0.2938(2)	0.8262(1)	0.8303(2)	0.035(1)
C(13)	0.3646(2)	0.9393(2)	0.8505(2)	0.039(1)
C(14)	0.1934(2)	0.7953(2)	0.8567(2)	0.046(1)
C(15)	0.1548(3)	0.8753(2)	0.9061(2)	0.066(1)
N(11)	0.4224(2)	1.0303(1)	0.8658(2)	0.056(1)
N(12)	0.1213(2)	0.6903(2)	0.8408(2)	0.069(1)
C(111)	0.4127(2)	0.5992(1)	0.8271(1)	0.030(1)
C(112)	0.5008(2)	0.5711(2)	0.8936(1)	0.035(1)
C(113)	0.5961(2)	0.6477(2)	0.9763(2)	0.041(1)
C(114)	0.6048(2)	0.7537(2)	0.9938(2)	0.043(1)
C(115)	0.5181(2)	0.7825(2)	0.9290(2)	0.038(1)
C(116)	0.4207(2)	0.7073(1)	0.8454(1)	0.031(1)
C(121)	0.3325(2)	0.3771(2)	0.7105(2)	0.041(1)
C(122)	0.2712(2)	0.2833(2)	0.7345(2)	0.054(1)
C(123)	0.3062(3)	0.1950(2)	0.7253(2)	0.073(1)
C(124)	0.4007(3)	0.2009(2)	0.6941(2)	0.078(1)
C(125)	0.4631(3)	0.2939(3)	0.6706(2)	0.079(1)
C(126)	0.4283(3)	0.3823(2)	0.6778(2)	0.063(1)
C(131)	0.2840(2)	0.5416(2)	0.6123(1)	0.037(1)
C(132)	0.3931(2)	0.6120(2)	0.6074(2)	0.050(1)
C(133)	0.3910(3)	0.6551(2)	0.5252(2)	0.068(1)
C(134)	0.2805(3)	0.6280(3)	0.4476(2)	0.075(1)
C(135)	0.1727(3)	0.5579(3)	0.4503(2)	0.070(1)
C(136)	0.1731(2)	0.5142(2)	0.5325(2)	0.050(1)
P(2)	0.7591(1)	1.0069(1)	0.6933(1)	0.032(1)
S(2)	0.5927(1)	0.9883(1)	0.6879(1)	0.045(1)
C(21)	0.8257(2)	1.2610(1)	0.7751(1)	0.032(1)
C(22)	0.7938(2)	1.3388(1)	0.8367(1)	0.032(1)
C(23)	0.8472(2)	1.4514(2)	0.8431(1)	0.037(1)
C(24)	0.7149(2)	1.3056(2)	0.8857(2)	0.037(1)
C(25)	0.6857(2)	1.3836(2)	0.9473(2)	0.050(1)
N(21)	0.8890(2)	1.5425(1)	0.8465(2)	0.055(1)
N(22)	0.6600(2)	1.1999(1)	0.8831(2)	0.048(1)
C(211)	0.8845(2)	1.0979(1)	0.8083(1)	0.030(1)
C(212)	0.9657(2)	1.0583(2)	0.8680(1)	0.036(1)
C(213)	1.0630(2)	1.1252(2)	0.9550(2)	0.039(1)
C(214)	1.0809(2)	1.2332(2)	0.9839(2)	0.041(1)
C(215)	1.0020(2)	1.2733(2)	0.9258(1)	0.036(1)
C(216)	0.9037(2)	1.2083(1)	0.8373(1)	0.030(1)
C(221)	.7995(2)	1.0611(1)	0.5940(1)	0.035(1)
C(222)	0.7086(2)	1.0550(2)	0.5063(2)	0.048(1)
C(223)	0.7407(2)	1.0957(2)	0.4307(2)	0.061(1)
C(224)	0.8617(2)	1.1432(2)	0.4415(2)	0.063(1)
C(225)	0.9534(2)	1.1504(2)	0.5289(2)	0.065(1)
C(226)	0.9229(2)	1.1096(2)	0.6051(2)	0.052(1)
C(231)	0.7720(2)	0.8757(2)	0.6837(2)	0.038(1)
C(232)	0.7286(2)	0.8094(2)	0.7422(2)	0.044(1)
C(233)	0.7355(2)	0.7084(2)	0.7364(2)	0.054(1)
C(234)	0.7824(3)	0.6719(2)	0.6710(2)	0.070(1)
C(235)	0.8225(3)	0.7355(2)	0.6113(3)	0.087(1)
C(236)	0.8187(3)	0.8381(2)	0.6179(2)	0.063(1)

sented here since the detailed bond parameters cannot be taken as being reliable. Intensity data was obtained on a Nicolet XRD P3 four-circle diffractometer with monochromated Mo Kα X-rays (λ 0.7107 Å) at 130 K. The structures were solved by direct methods

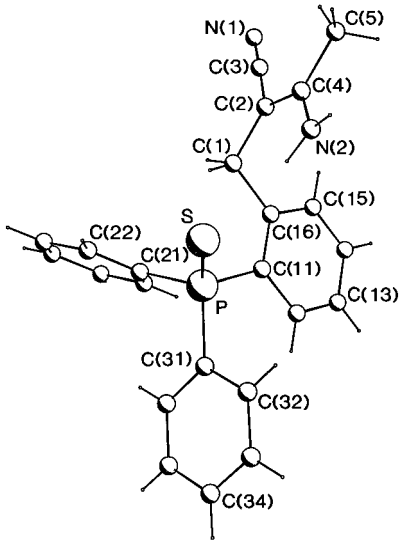


Fig. 1. The structure of one of the independent molecules of the enamine **7**. The labelling scheme for each molecule is generated by adding 1 or 2 appropriately; for example N(1) becomes N(11) for molecule 1 and N(21) for molecule 2.

(SHELXS-86 [7b]) and the refinement was based on F^2 (SHELXL-93 [7b]).

Crystal data for ***8a***: $C_{28}H_{20}MnO_8PS.CHCl_3$, M_r = 721.78, triclinic, space group $P\bar{1}$, $a = 10.810(3)$, $b = 11.831(4)$, $c = 14.347(7)$ Å, $\alpha = 67.67(4)$, $\beta = 91.19(1)$, $\gamma = 87.08°$, $V = 1695(1)$ Å^3, $D_{calc} = 1.414$ g cm^{-3}, for $Z = 2$; 4379 unique reflections, $4° < 2\theta < 55°$, 3306 with $I > 2\sigma(I)$. Best refinement gave $R_1 = 0.1234$ (2σ data); $R_1 = 0.1391$, w$R_2 = 0.3588$, GoF 1.035 (all data). Attempted refinement in P1 was equally unsuccessful. The structure is illustrated in Fig. 2.

Crystal data for ***11c***: $C_{22}H_{14}MnO_6PSSe$, M_r = 571.26, monoclinic, space group $P2_1/c$, $a = 13.09(3)$,

Table 2
Selected bond parameters for the enamine compound **7**

Bond (Å)	Molecule 1	Molecule 2
P–S	1.9604(7)	1.9649(7)
C(1)–C(16	1.525(2)	1.524(2)
C(2)–C(4)	1.359(2)	1.366(2)
C(4)–N(2)	1.343(2)	1.347(2)
C(1)–C(2)	1.518(2)	1.521(2)
C(2)–C(3)	1.421(2)	1.417(2)
C(3)–N(1)	1.148(2)	1.150(2)
C(4)–C(5)	1.506(2)	1.502(2)
Angle (°)	**Molecule 1**	**Molecule 2**
S–P–C(11)	112.94(7)	114.91(7)
S–P–C(31)	114.26(7)	109.30(7)
C(1)–C(2)–C(3)	118.4(2)	118.7(2)
C(2)–C(3)–N(1)	179.1(2)	178.7(2)
C(2)–C(4)–C(5)	122.9(2)	122.6(2)
S–P–C(21)	111.68(7)	114.72(7)
C(16)–C(1)–C(2)	115.6(2)	114.2(2)
C(1)–C(2)–C(4)	123.6(2)	123.3(2)
C(2)–C(4)–N(2)	122.1(2)	121.7(2)

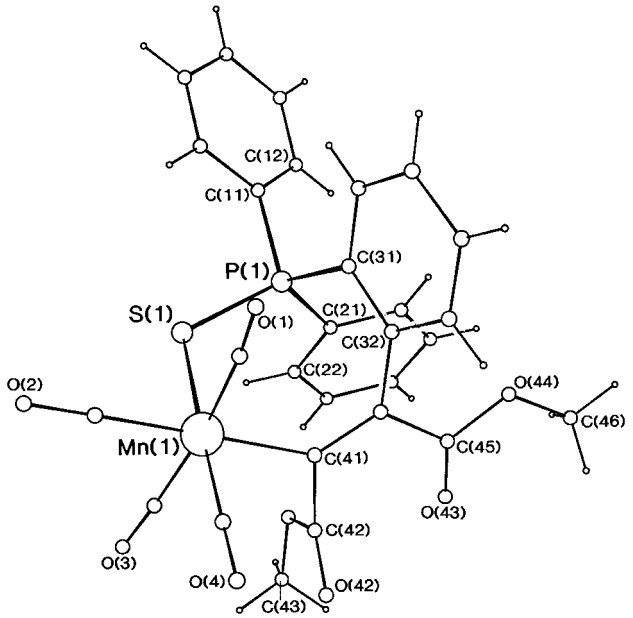


Fig. 2. The structure of **8a**, from insertion of $C_2(COOMe)_2$ into the Mn–C bond of $Ph_2P(\overline{S)C_6H_4Mn}(CO)_4$

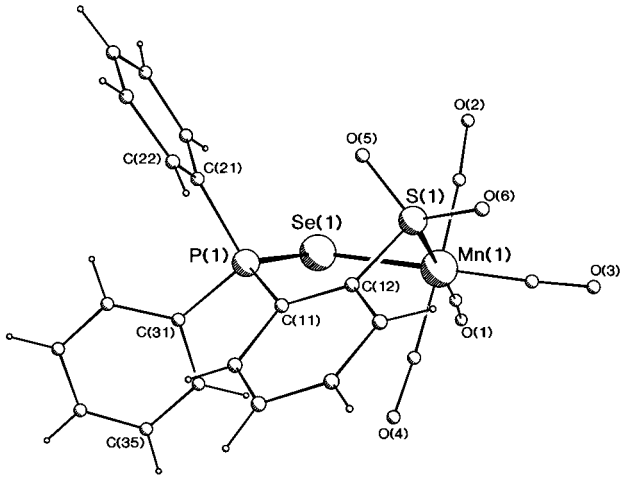


Fig. 3. The structure of **11c**, from insertion of SO_2 into the Mn–C bond of $Ph_2P(\overline{Se)C_6H_4Mn}(CO)_4$

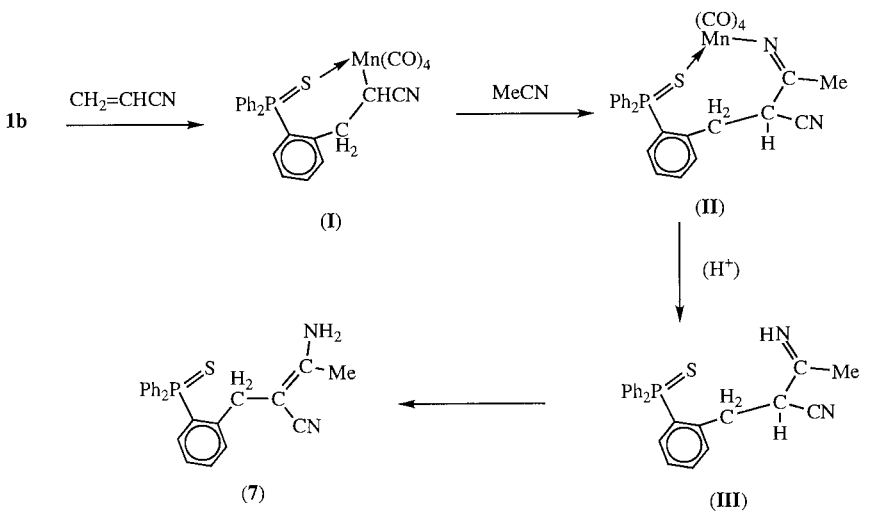
$b = 9.163(13)$, $c = 18.36(12)$ Å, $\beta = 94.2(3)°$, $V = 2196(16)$ Å^3, $D_{calc} = 1.728$ g cm^{-3}, $Z = 4$; 2024 unique reflections, $4° < 2\theta < 45°$, 1106 with $I > 2\sigma(I)$. Best refinement gave $R_1 = 0.1003$ (2σ data), $wR_2 = 0.2987$, GoF = 1.063 (all data). The structure is illustrated in Fig. 3.

3. Results and Discussion

*3.1. Reactions of $Ph_2P(\overline{S)C_6H_4Mn}(CO)_4$ (**1b**) with alkenes.*

When **1b** is refluxed in MeCN with butenone (methyl vinyl ketone) for 2 h, the major product is **2**, in which a butanone group has substituted for Mn at the *ortho* position of one of the phenyl rings of $Ph_3P{=}S$. The same reaction in MeOH gave essentially the same result, but in the non-polar solvents CCl_4 or C_6H_6 much lower yields of **2** were found. In all of these systems the only other significant product was $Ph_3P{=}S$ formed by demetallation of **1b**. Based on suggested mechanisms in related coupling reactions [3a,3b,3c,3d,3e,3f,3g,3h], the formation of **2** presumably involves insertion of the alkene into the Mn–C bond of **1b**, followed by demetallation of the intermediate species **3a**. The origin of the proton involved in such demetallations has been investigated by Cambie et al. [3d]. There was no sign of the unsaturated butenone compound that would result from β-elimination from **3a** but this process is perhaps precluded by the conformational restrictions imposed by the chelate ring.

The corresponding reaction of **1b** with methyl propenoate (methyl acrylate) gave only 12% of the



Scheme 1.

analogous coupled product **4** in MeCN, with the major product being **5**. This second species is envisaged as forming from a double insertion sequence. Initial insertion of the alkene would give **3b**, which then undergoes insertion of MeCN into the new Mn–C bond. Protio-demetallation generates the imine of **5** which would be hydrolysed to the final product **5** on work-up. Such products have been previously observed in similar coupling reactions of orthomanganated aryl ketones [8], and a similar process is encountered in the reaction with acrylonitrile discussed below. The sequence of insertion is specific; there was no indication of MeCN insertion into the $Mn–C_{aryl}$ bond of **1b**, only into the $Mn–C_{(sp3)}$ bond subsequent to alkene insertion. As expected, no **5** was formed when the reaction was carried out in MeOH, only **4** was isolated in 31% yield. When the reaction was performed in MeOH under an atmosphere of CO, the yield of **4** was unchanged and no product arising from a CO insertion was identified.

With acrylonitrile in MeCN, **1b** gave the expected coupled product **6** in 44% yield (34% in MeOH), and also gave a second species which ESMS showed to have a mass of 41 amu greater than that of **6**, indicating the inclusion of a molecule of MeCN. An unambiguous characterisation was not possible on the spectroscopic evidence so an X-ray crystal structure determination was carried out which showed that this second product is the cyano-enamine **7** (Fig. 1). A possible route to this species is outlined in Scheme 1. The first step will be the insertion of the C=C bond of acrylonitrile into the Mn–C bond to give the intermediate **I**, which then undergoes insertion of MeCN into the new Mn–C bond, giving intermediate **II**. Protio-demetallation would then give the primary imine **III**, which generates the final amine product **7** with a 1,3-H migration driven by the shift of the double bond into conjugation with the cyano group. Enamines are usually the less stable form in enamine-imine tautomerism, but the cyano groups are known to alter the stability balance [9].

There are two crystallographically independent molecules of **7** in the unit cell, but these do not differ in other than conformation—the major difference is in the dihedral angle between the plane of the $–CH_2C(CN)C(Me)NH_2$ group and the plane of the ring it is attached to, 72° and 88° respectively for molecule 1 and 2. The structure confirms the expected *trans* arrangement of the CN and NH_2 groups about the double bond. In each molecule the NH_2 group is orientated so that one N–H is directed towards the S atom, indicating at least a weak H-bond.

For all of these reactions the manganese is displaced during the reaction, but the first-formed species following insertion, **3**, are obviously long-lived enough to undergo subsequent insertion of MeCN in some cases. However it is not obvious why the butenone intermediate **3a** did not add MeCN to any significant extent, nor is the lack of insertion of CO by **3b** readily explained. These complicating secondary reactions can be avoided by using MeOH instead of MeCN as solvent, although demetallation of the starting material to produce $Ph_3P=S$ is a more significant competing process in MeOH.

Coupling reactions between orthomanganated aryl ketones and alkenes are promoted by Pd(II) [3a,3b,3c,3d,3e,3f,3g,3h]. The reaction of **1b** with butenone was therefore examined in MeCN and in MeOH with Li_2PdCl_4 present. However no tractable products were found.

*3.2. Reactions of $Ph_2P(\overline{S})C_6H_4\overline{Mn}(CO)_4$ (**1b**) with alkynes*

When the alkyne $C_2(COOMe)_2$ (DMAD) was reacted with **1b** under reflux in benzene, the major product was that expected on insertion, namely the seven-membered metallocycle **8a**. This was unambiguously identified by X-ray methods, Fig. 2, though the determination was of rather poor quality. Nevertheless, overall features are clear, showing that the seven-membered metallocyclic ring is in a strongly-puckered boat configuration similar to that in the analogous product from orthomanganated $P(OPh)_3$ [5a,5b].

A minor product from the **1b**/DMAD reaction corresponded to the addition of two moles of DMAD to, and the loss of one mole of CO from, **1b**. This was indicated by the ES mass spectrum, by the NMR spectrum which showed four inequivalent COOMe groups, and by the characteristic $Mn(CO)_3$-group pattern in the carbonyl-stretching region of the infrared spectrum. It appears that there has been a double insertion of DMAD to give a nine-membered metallocyclic ring which twists to allow one of the C=C bonds to displace a CO ligand from the manganese, as in **9**. Analogous species arising from double alkyne insertion are known for Pd [10a,10b,10c], and a related compound was tentatively identified from the reaction of DMAD with orthomanganated $P(OPh)_3$ [5a,5b]. The spectroscopic properties fit this assignment, but unfortunately no suitable crystals could be obtained for confirmation by X-ray methods. It is clear that the route to this minor product is not just a step-wise process, since longer reaction times with excess DMAD did not enhance the yield.

In an attempt to obtain an example of type **9** which would give X-ray quality crystals the reaction was carried between the substituted complex $Ph_2P(\overline{S})C_6H_4\overline{Mn}(CO)_2[P(OMe)_3]_2$ and DMAD. This gave the mono-insertion product **8b**, but no sign of the corresponding di-insertion compound.

With **1b** and methyl propiolate a moderate yield of the mono-inserted product **8c** was obtained, although some demetallation occurred to produce significant

amounts of the *ortho*-substituted compound **10**. As is usual in these reactions, the insertion of the unsymmetrical alkyne occurs regiospecifically, with the bulky substituent adjacent to the manganese atom [3a,3b,3c,3d,3e,3f,3g,3h,11].

Only for DMAD and methyl propiolate were insertion reactions observed. No new species could be isolated from reactions of a range of other alkynes (see Section 2) with **1b** under different conditions.

3.3. Reactions of $Ph_2P(\overline{E)C_6H_4Mn}(CO)_4$ (*1*) with SO_2.

Another reaction which is facile for orthomanganated compounds is SO_2 insertion [6]. When **1b** and liquid SO_2 were reacted either thermally at 52°C, or photochemically, essentially quantitative yields of the new metallocycle **11b** were obtained. The corresponding Se analogue **11c** was equally accessible from **1c**, and a similar species **11a** was probably formed from the orthomanganated oxide **1a**, although it could not be separated from another species which ESMS indicated incorporated two moles of $Ph_3P{=}O$. However the shift of the ν(CO) bands to higher frequencies, and the ^{31}P NMR shift to 44 ppm from 64 ppm in the precursor, are fully in accord with those for the sulfur and selenium analogues so **11a** is undoubtedly the corresponding compound.

The new species **11** represent a unique series of metallocyclic compounds, so the structure of the Se analogue **11c** was determined by X-ray crystallography. The molecule is illustrated in Fig. 3. The six-membered metallocyclic ring incorporates five different elements —Mn, Se, S, P and C, with the ligand bound to the manganese via the S and Se atoms. In contrast to the planar five-membered ring in the precursor **1c**, the six-membered ring has an envelope conformation, with the S(1) atom folded out of the least-squares plane through the remaining atoms of the ring. In the related compound formed by SO_2 insertion into the Mn–C bond of an orthomanganated acetophenone, the corresponding six-membered ring was less puckered, with the Mn atom folded out of the plane of the other atoms [6]. Obviously a marked increase in flexibility of the chelate ring accompanies expansion from five- to six-membered. The rather poor quality of the crystal structure determination precludes any more detailed discussion of the bond parameters.

4. Conclusion

The orthomanganated triphenylphosphine chalcogenides show similar reactivity to that established for orthomanganated aryl ketones, but there are significant differences. Coupling reactions with alkenes are best thermally-promoted rather than Pd(II)-promoted so give aryl-alkanes rather than the aryl-alkenes (or cyclised species) found for the ketone derivatives. Only a limited range of alkynes react, and the first-formed insertion product is isolable in contrast to the ketone species where subsequent reactions ensue. In this instance there is a closer parallel with the reactions of orthometallated triphenylphosphite. The SO_2 insertion reaction proceeds efficiently to give stable species.

The chemistry reported here therefore provides an interesting comparison with earlier systems. The reactions allow specific addition of a variety of groups in the *ortho* position of one aryl ring of the $Ph_3P{=}X$ ligands, providing compounds that would be difficult to prepare by other routes. They may therefore find application in the synthesis of novel ligands

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