

Cyclomanganated derivatives of triphenylphosphine chalcogenides

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Abstract

Reaction of the triphenylphosphine chalcogenides $\text{Ph}_3\text{P}=\text{E}$ (E = O, S, Se) with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ at 70–90°C in hydrocarbon solvents gave the orthomanganated derivatives $(\text{OC})_4\text{MnC}_6\text{H}_4\text{P}(\text{E})\text{Ph}_2$ in 41% (E = O), 90% (E = S) or 22% (E = Se) yields. The different yields are rationalised in terms of the preferred angles of coordination at the E atom and the P=E bond stability. The new compounds were fully characterised, including X-ray crystal structure determinations for the examples with E = S and Se. $(\text{OC})_4\text{MnC}_6\text{H}_4\text{P}(\text{S})\text{Ph}_2$ reacted with $\text{P}(\text{OMe})_3$ to replace two of the CO ligands without disrupting the Mn–S bond; an X-ray structure determination shows the two phosphite ligands are *trans* to each other, and have little effect on the geometry of the rest of the molecule.

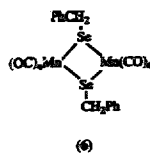
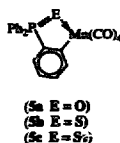
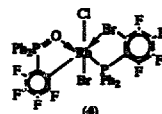
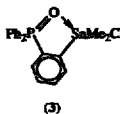
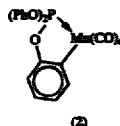
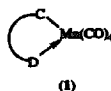
Keywords: Manganese; Cyclometallation; Crystal structure; Phosphine; Chalcogenide; Metallocycle

1. Introduction

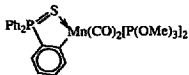
Many cyclometalated derivatives of type 1 incorporating a $\text{Mn}(\text{CO})_5$ fragment are now known, following from initial reports from Kaesz's group [1]. Substrates that are directly metalated by $\text{RMn}(\text{CO})_5$ (R = Me, PhCH_2 usually) include aromatic ketones [2,3], heteroaromatic ketones [3], azobenzenes [4], imines [5], amines [6], thioethers [7] and α,β -unsaturated ketones [8] (for an indirect route to these species see [9]), all of which give rise to five-membered metallocyclic rings. Many of these species are useful substrates in organic synthesis [10,11], as discussed in a recent review [12]. The direct cyclometallation of Ph_3P corresponding four-membered species [1,13], while $(\text{PhO})_2\text{P}$ gives 2 on reaction with $\text{RMn}(\text{CO})_5$ [1,14]. The generality of this reaction means that any substrate containing both a donor atom (such as O, N, S, P, etc.) and a $\text{C}(\text{sp}^2)\text{--H}$ in a position that allows formation of a five-membered ring on metalation should be regarded as suitable for cyclomanganation.

Potential substrates that meet these criteria are the well-known phosphine chalcogenides $\text{Ph}_3\text{P}=\text{X}$ (X = O, S, Se). These species are good ligands, acting through their chalcogen atoms, and they form a wide variety of coordination complexes [15,16]. However, there are few reports of cyclometalated compounds incorporating these compounds. The tin complex 3 [17] and an Rh

complex 4 (and its *cis* isomer) [18] are the only examples of this type for which structural data are published, and in each case the method of preparation was indirect. We have therefore examined the direct reactions of $\text{Ph}_3\text{P}=\text{X}$ (X = O, S, Se) with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ under the usual cyclometallation conditions.



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2. Experimental details

Instrumental methods have been described previously [11]. Reactions were performed under an atmosphere of dry nitrogen but subsequent work-up was carried out without precautions to exclude air. $\text{PhCH}_2\text{Mn}(\text{CO})_5$ was prepared by the standard method [19]. $\text{Ph}_3\text{P}=\text{O}$ was prepared from Ph_3P and H_2O_2 in acetone at room temperature, m.p. 151–153°C (lit. 152–153°C [20]), while $\text{Ph}_3\text{P}=\text{E}$ (E = S, Se) were obtained from the reaction of Ph_3P with elemental S or Se in refluxing toluene, $\text{Ph}_3\text{P}=\text{S}$ m.p. 162–164°C (lit. 162–164°C [20]), $\text{Ph}_3\text{P}=\text{Se}$ m.p. 186–188°C (lit. 187–188°C [20]). Chromatography was performed on $20 \times 20 \text{ cm}^2$ glass plates coated with Merck Kieselgel 60 silica gel. Petroleum spirits refers to a 60–80°C fraction.

2.1. Orthomanganation reactions

2.1.1. Orthomanganation of triphenylphosphine oxide

2.1.1.1. In petroleum spirit. Triphenylphosphine oxide (174 mg, 0.623 mmol) and $\text{PhCH}_2\text{Mn}(\text{CO})_5$ (187 mg, 0.653 mmol) were dissolved in petroleum spirit (AR, 40 ml) and the solution was degassed. After refluxing under nitrogen for 6 h, the petroleum spirit was removed under vacuum. The yellow/brown residue was dissolved in CH_2Cl_2 and chromatographed on silica gel plates with 1:3 v/v ethyl acetate/petroleum spirit as the eluant. A broad yellow/orange band of $\eta^2\text{-(C,O)-}[(2\text{-diphenylthiophosphinyl})\text{phenyl}]\text{-tetracarbonylmanganese (5a)}$, 114 mg, 41%, was collected as an orange oil which failed to crystallise. IR (CHCl_3): $\nu(\text{CO})$ 2080(m), 1991(vs, br), 1935(s) cm^{-1} ; (KBr disk): $\nu(\text{P}=\text{O})$ 1066(m) cm^{-1} . $^1\text{H NMR}$ (300.13 MHz) (CDCl_3): δ 8.02 (m, 1H, H-6), 7.72–7.35 (m, 10H, H-2', H-3', H-4', H-5', H-6'), 7.24 (m, 1H, H-5), 7.15 (m, 2H, H-3, H-4). $^{13}\text{C NMR}$ (75.47 MHz) (CDCl_3): δ 221.3 (s, br, C=O), 213.7 (s, $^3J_{\text{PC}} = 9.6 \text{ Hz}$, C=O), 213.0 (s, br, $2 \times \text{C} \equiv \text{O}$), 180.9 (s, $^2J_{\text{PC}} = 24.0 \text{ Hz}$, C-1), 142.1 (d, $^3J_{\text{PC}} = 16.2 \text{ Hz}$, C-6), 137.1 (s, $^1J_{\text{PC}} = 120.5 \text{ Hz}$, C-2), 133.0 (d, $^4J_{\text{PC}} = 1.9 \text{ Hz}$, C-4'), 132.0 (d, $^2J_{\text{PC}} = 10.6 \text{ Hz}$, C-2', C-6'), 131.4 (d, $^4J_{\text{PC}} = 2.7 \text{ Hz}$, C-5), 130.2 (s, $^1J_{\text{PC}} = 100.6 \text{ Hz}$, C-1'), 129.8 (d, $^2J_{\text{PC}} = 20.5 \text{ Hz}$, C-3), 129.0 (d, $^3J_{\text{PC}} = 12.1 \text{ Hz}$, C-3', C-5'), 123.9 (d, $^3J_{\text{PC}} = 13.2 \text{ Hz}$, C-4), $^{31}\text{P NMR}$ (36.23 MHz) (CDCl_3): δ 64.4.

2.1.1.2. In heptane. A similar reaction with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ (202 mg, 0.707 mmol) and triphenylphosphine oxide (171 mg, 0.615 mmol) under reflux in heptane over 80 min gave, after work-up, **5a** (90 mg, 33%).

2.1.2. Orthomanganation of triphenylphosphine sulfide

Similarly prepared from $\text{PhCH}_2\text{Mn}(\text{CO})_5$ (426 mg, 1.49 mmol) and triphenylphosphine sulfide (397 mg, 1.35 mmol) under reflux in heptane over 1.5 h was $\eta^2\text{-(C,S)-}[(2\text{-diphenylthiophosphinyl})\text{phenyl}]\text{-tetracarbonylmanganese (5b)}$, 557 mg, 90%, which recrystallised from CH_2Cl_2 /pentane (vapour diffusion) as yellow blocks, m.p. 163°C. Anal. Found: C, 57.86; H, 2.73. $\text{C}_{22}\text{H}_{14}\text{O}_4\text{MnPS}$ Calc.: C, 57.40; H, 3.07%. IR (CHCl_3): $\nu(\text{CO})$ 2072(m), 1993(vs), 1978(vs), 1933(s) cm^{-1} ; (KBr disk): $\nu(\text{P}=\text{S})$ 606(m) cm^{-1} . $^1\text{H NMR}$ (300.13 MHz) (CDCl_3): δ 8.07 (m, 1H, H-6), 7.61 (m, Ar-H), 7.48 (m, Ar-H), 7.27 (m, 1H, H-5), 7.08 (m, 2H, H-3, H-4). $^{13}\text{C NMR}$ (75.47 MHz) (CDCl_3): δ 219.9 (s, br, C=O), 215.3 (s, $^3J_{\text{PC}} = 17.5 \text{ Hz}$, C=O), 214.6 (s, br, $2 \times \text{C} \equiv \text{O}$), 179.7 (s, $^2J_{\text{PC}} = 38.9 \text{ Hz}$, C-1), 144.4 (d, $^3J_{\text{PC}} = 19.9 \text{ Hz}$, C-6), 141.6 (s, $^1J_{\text{PC}} = 106.7 \text{ Hz}$, C-2), 132.8 (d, $^4J_{\text{PC}} = 2.3 \text{ Hz}$, C-4'), 132.6 (d, $^2J_{\text{PC}} = 10.7 \text{ Hz}$, C-2', C-6'), 131.4 (d, $^4J_{\text{PC}} = 19.6 \text{ Hz}$, C-3), 130.5 (d, $^4J_{\text{PC}} = 3.0 \text{ Hz}$, C-5), 130.2 (s, $^1J_{\text{PC}} = 78.6 \text{ Hz}$, C-1'), 129.0 (d, $^3J_{\text{PC}} = 12.5 \text{ Hz}$, C-3', C-5'), 123.2 (d, $^3J_{\text{PC}} = 12.8 \text{ Hz}$, C-4). $^{31}\text{P NMR}$ (36.23 MHz) (CDCl_3): δ 66.6.

2.1.3. Orthomanganation of triphenylphosphine selenide

Following the same procedure, triphenylphosphine selenide (402 mg, 1.18 mmol) was treated with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ (383 mg, 1.34 mmol) and refluxed in petroleum spirit over 4 h. The residue was chromatographed to give the following products.

Band 1 was $\text{Mn}_2(\mu\text{-SeCH}_2\text{Ph})_2(\text{CO})_8$ (**6**), 56 mg, 14%, which crystallised from CH_2Cl_2 /pentane to yield red block-shaped crystals, m.p. dec. 150°C (lit. 156°C [21]). Anal. Found: C, 39.37; H, 1.96. $\text{C}_{22}\text{H}_{14}\text{O}_8\text{Mn}_2\text{Se}_2$ Calc.: C, 39.20; H, 2.09%. IR (CHCl_3): $\nu(\text{CO})$ 2062(m), 2006(vs), 1996(vs), 1967(s) cm^{-1} . $^1\text{H NMR}$ (300.13 MHz) (CDCl_3): δ 7.26 (m, 5H, Ar-H), 3.84 (s, 2H, CH_2). $^{13}\text{C NMR}$ (75.47 MHz) (CDCl_3): δ 139.0 (s, C-1), 128.9 (d, (C-2, C-6) or (C-3, C-5)), 128.8 (d, (C-2, C-6) or (C-3, C-5)), 127.7 (d, C-4), 26.9 (CH_2). EIMS: m/z 676 (M^+), 564 ($\text{M} - 4\text{CO}$) $^+$, 508 ($\text{M} - 6\text{CO}$) $^+$, 452 ($\text{M} - 8\text{CO}$) $^+$, 361 ($\text{M} - 8\text{CO} - \text{CH}_2\text{C}_6\text{H}_5$) $^+$, 91 ($\text{C}_6\text{H}_5\text{CO}$) $^+$.

Band 2 was *cis*- $\text{PhCH}_2\text{Mn}(\text{CO})_2\text{PPh}_3$, 98 mg, 16%, which crystallised from CHCl_3 /petroleum spirit as colourless plates, m.p. 156°C (lit. 155°C [22]). IR: (CHCl_3) $\nu(\text{CO})$ 2053(m), 1966(vs), 1937(s) cm^{-1} . $^1\text{H NMR}$ (300.13 MHz) (CDCl_3): δ 7.57–7.46 (m, 15H, Ar-H), 7.06 (m, 2H, Ar-H), 6.95 (m, 2H, Ar-H), 6.88

(*m*, 1H, Ar-H), 1.71 (*d*, $^3J_{\text{PH}} = 5.8$ Hz, 2H, CH₂). ^{31}P NMR (36.23 MHz) (CDCl₃): δ 61.1. ESMS: *m/z* 562 (M + H + CH₃CN)⁺, 521 (M + H)⁺, 470 (M + CH₃CN - CH₂C₆H₅)⁺, 429 (M - CH₂C₆H₅)⁺. EIMS: *m/z* 429 (M - CH₂C₆H₅)⁺, 401 (M - CH₂C₆H₅ - CO)⁺, 373 (M - CH₂C₆H₅ - 2CO)⁺, 345 (M - CH₂C₆H₅ - 3CO)⁺, 317 (M - CH₂C₆H₅ - 4CO)⁺, 318 (Ph₃PMn + H)⁺, 262 (Ph₃P)⁺.

Band 3 was η^2 -(C,Se)-[(2-diphenylselenophosphinyl)phenyl]tetracarbonylmanganese (**5c**), 134 mg, 22%, which crystallised from CHCl₃/petroleum spirit as yellow block-shaped crystals, m.p. 165–167 °C. Anal. Found: C, 52.32; H, 2.78%. IR (CHCl₃): $\nu(\text{CO})$ 2067(*m*), 1990(*vs*), 1973(*vs*), 1931(*s*) *cm*⁻¹; (KBr disk): $\nu(\text{P}=\text{Se})$ 549(*m*) *cm*⁻¹. ^1H NMR (300.13 MHz) (CDCl₃): δ 8.15 (*m*, 1H, H6), 7.63 (*m*, Ar-H), 7.49 (*m*, Ar-H), 7.26 (*m*, 1H, H-5), 7.06 (*m*, 2H, H-3, H-4). ^{13}C NMR (75.47 MHz) (CDCl₃): δ 220.5 (*s*, br, C=O), 216.0 (*s*, $^2J_{\text{PC}} = 15.8$ Hz, C=O), 215.0 (*s*, br, 2 × C=O), 180.0 (*s*, $^2J_{\text{PC}} = 43.1$ Hz, C-1), 145.4 (*d*, $^3J_{\text{PC}} = 21.2$ Hz, C-6), 141.7 (*s*, $^1J_{\text{PC}} = 99.4$ Hz, C-2), 132.8 (*d*, $^2J_{\text{PC}} = 10.8$ Hz, C-2', C-6'), 132.8 (*d*, C-4'), 132.0 (*d*, $^2J_{\text{PC}} = 18.7$ Hz, C-3), 130.1 (*d*, $^4J_{\text{PC}} = 3.4$ Hz, C-5), 129.2 (*s*, $^1J_{\text{PC}} = 71.0$ Hz, C-1'), 129.0 (*d*, $^3J_{\text{PC}} = 12.3$ Hz, C-3', C-5'), 123.0 (*d*, $^3J_{\text{PC}} = 12.1$ Hz, C-4). ^{31}P NMR (36.23 MHz) (CDCl₃): δ 52.2. EIMS: *m/e* 508 (M⁺), 424 (M - 3CO)⁺, 396 (M - 4CO)⁺, 342 (Ph₃PSe + H)⁺, 262 (Ph₃P)⁺.

Band 4 was unreacted triphenylphosphine selenide, 97 mg, 25%.

Table 2

Atomic coordinates and equivalent isotropic displacement parameters for (OC)₄Mn(C₆H₅P(S)Ph₂)(5b)

Atom	x	y	z	U _{eq}
Mn(1)	0.2395(1)	0.0913(1)	0.0658(1)	0.017(1)
P(1)	0.4208(1)	0.1198(1)	0.2377(1)	0.015(1)
S(1)	0.4194(1)	0.0122(1)	0.1485(1)	0.021(1)
C(1)	0.2415(2)	-0.0357(2)	0.0083(2)	0.024(1)
C(2)	0.1152(3)	0.1477(2)	-0.0023(2)	0.026(1)
C(3)	0.1065(2)	0.0444(2)	0.1348(1)	0.023(1)
C(4)	0.3774(2)	0.1699(2)	0.0122(1)	0.023(1)
O(1)	0.2369(2)	-0.1145(2)	-0.0280(1)	0.039(1)
O(2)	0.0391(2)	0.1834(2)	-0.0484(1)	0.041(1)
O(3)	0.0244(2)	0.0219(2)	0.1793(1)	0.038(1)
O(4)	0.4602(2)	0.2077(2)	-0.0201(1)	0.039(1)
C(11)	0.3173(2)	0.2346(2)	0.2091(1)	0.016(1)
C(12)	0.2377(2)	0.2288(2)	0.1390(1)	0.017(1)
C(13)	0.1551(2)	0.3217(2)	0.1244(1)	0.024(1)
C(14)	0.1524(2)	0.4106(2)	0.1749(2)	0.027(1)
C(15)	0.2346(2)	0.4138(2)	0.2429(2)	0.024(1)
C(16)	0.3180(2)	0.3255(2)	0.2600(1)	0.021(1)
C(21)	0.3522(2)	0.0623(2)	0.3275(1)	0.018(1)
C(22)	0.4273(3)	-0.0207(2)	0.3669(1)	0.025(1)
C(23)	0.3700(3)	-0.0662(2)	0.4349(2)	0.034(1)
C(24)	0.2451(3)	-0.0304(2)	0.4626(2)	0.034(1)
C(25)	0.1729(3)	0.0500(2)	0.4227(2)	0.031(1)
C(26)	0.2259(2)	0.0972(2)	0.3555(1)	0.024(1)
C(31)	0.5919(2)	0.1693(2)	0.2609(1)	0.016(1)
C(32)	0.6712(2)	0.2011(2)	0.1970(1)	0.025(1)
C(33)	0.8015(2)	0.2444(2)	0.2107(2)	0.031(1)
C(34)	0.8530(2)	0.2567(2)	0.2869(2)	0.028(1)
C(35)	0.7739(2)	0.2261(2)	0.3502(2)	0.027(1)
C(36)	0.6429(2)	0.1826(2)	0.3372(1)	0.021(1)

Table 1

Selected bond lengths (Å) and angles (deg) for the isomorphous complexes (OC)₄Mn(C₆H₅P(E)Ph₂)(5b, E = S; 5c, E = Se) and for (OC)₄[Mn(O)₃P]₂Mn(C₆H₅P(S)Ph₂)(7)

Parameter	Ph ₃ P=S complex 5b, E = S	Ph ₃ P=Se complex 5c, E = Se	(MeO) ₃ P substituted complex 7
P(1)–E(1)	1.996(1) ^a	2.154(1) ^a	1.993(2)
Mn(1)–E(1)	2.410(1)	2.514(1)	2.412(1)
Mn(1)–C(12)	2.081(2)	2.096(5)	2.078(4)
C(11)–C(12)	1.399(3)	1.410(6)	1.422(6)
P(1)–C(11)	1.782(2)	1.796(5)	1.787(5)
Mn–P(2)			2.228(1)
Mn–P(3)			2.227(1)
P(1)–E(1)–Mn(1)	99.64(3)	96.09(4)	99.59(6)
C(12)–Mn(1)–E(1)	89.60(6)	90.8(1)	88.3(1)
C(11)–C(12)–Mn(1)	122.1(2)	123.4(4)	123.5(3)
C(12)–C(11)–P(1)	119.1(2)	120.4(4)	116.7(3)
C(11)–P(1)–E(1)	108.42(8)	108.2(2)	108.4(2)
C(3)–Mn(1)–C(2)	90.0(1)	90.9(3)	86.9(2)
C(3)–Mn(1)–C(4)	168.0(1)	166.6(2)	
P(3)–Mn(1)–P(2)			175.79(6)

^a The P–E distances in the free ligands are 1.950(3) Å (Ph₃P=S [24]) and 2.112(1) Å (Ph₃P=Se [25]).

2.2. Preparation of η^2 -(C,S)-[(2-diphenylthiophosphinyl)phenyl]dicarbonyl-bis(trimethylphosphite)manganese (7)

The orthomanganated triphenylphosphine sulfide complex **5b** (201 mg, 0.436 mmol), and trimethylphosphite (0.26 ml, 2.20 mmol) were added to nitrogen-saturated heptane. The solution was refluxed for 5 h and the heptane was removed under vacuum. The yellow residue was chromatographed (PLC, 1:2 ethyl acetate/hexane) to give *trans*- η^2 -(C,S)-[(2-diphenylthiophosphinyl)phenyl]dicarbonyl-bis(trimethylphosphite)manganese (**7**) (250 mg, 88%) as a yellow solid which crystallised from CH₂Cl₂/pentane as yellow needles, m.p. 149–150 °C. Anal. Found: C, 47.96; H, 5.22%. C₂₆H₃₂O₈MnP₃S Calc.: C, 47.86; H, 4.94%. IR (CHCl₃): $\nu(\text{CO})$ 1933(*s*), 1855(*s*) *cm*⁻¹. ^1H NMR (300.13 MHz) (CDCl₃): δ 8.45 (*m*, 1H, H-6), 7.76–7.63 (*m*, Ar-H), 7.52–7.37 (*m*, Ar-H), 7.10 (*m*, 1H, H-3), 7.03 (*m*, 1H, H-5), 6.89 (*m*, 1H, H-4), 3.33 (*s*, $^3J_{\text{PH}} = 4.8$ Hz, 18H, POCH₃). ^{13}C NMR (75.47 MHz) (CDCl₃): δ 226.7 (*s*, $^2J_{\text{PC}} = 36.0$ Hz, C=O), 221.8 (*s*, unresolved J_{PC} , C=O), 195.5 (*s*, $^2J_{\text{PC}} = 48.5$ Hz, $^2J_{\text{PC}} = 33.2$ Hz, C-1), 145.7 (*d*, $^3J_{\text{PC}} = 21.9$ Hz, C-6), 140.4

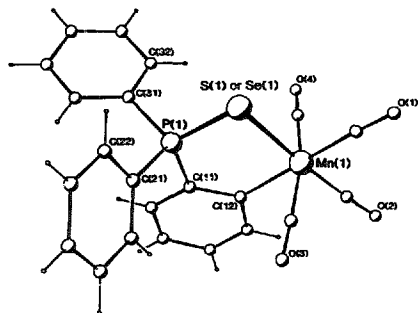


Fig. 1. The structures of $(OC)_2Mn(C_6H_4)P(E)Ph_2$ (**5b**, E = S; **5c**, E = Se). The molecules form isomorphous crystals.

(s, $^1J_{PC} = 107.8$ Hz, C-2), 133.3 (s, $^1J_{PC} = 77.5$ Hz, C-1'), 132.3 (d, $^2J_{PC} = 10.1$ Hz, C-2', C-6'), 131.3 (d, $^2J_{PC} = 2.4$ Hz, C-4'), 130.9 (d, $^2J_{PC} = 20.9$ Hz, C-3), 128.2 (d, $^2J_{PC} = 12.0$ Hz, C-3', C-5'), 127.5 (d, C-5), 120.8 (d, $^2J_{PC} = 12.7$ Hz, C-5'), 51.5 (q, $-P(OCH_3)_3$).

Table 3
Atomic coordinates and equivalent isotropic displacement parameters for $(OC)_2Mn(C_6H_4)P(Se)Ph_2$ (**5c**)

Atom	x	y	z	U_{eq}
Mn(1)	0.2368(1)	0.0932(1)	0.0634(1)	0.011(1)
Se(1)	0.4217(1)	0.0013(1)	0.1444(1)	0.013(1)
P(1)	0.4205(1)	0.1172(1)	0.2395(1)	0.009(1)
C(1)	0.2344(5)	-0.0297(5)	0.0034(3)	0.021(1)
C(2)	0.1140(5)	0.1539(5)	-0.0023(3)	0.021(1)
C(3)	0.1031(5)	0.0469(4)	0.1326(3)	0.016(1)
C(4)	0.3794(5)	0.1630(5)	0.0122(3)	0.019(1)
O(1)	0.2278(4)	-0.1078(3)	-0.0339(2)	0.030(1)
O(2)	0.0388(4)	0.1912(3)	-0.0471(2)	0.032(1)
O(3)	0.0220(4)	0.0226(3)	0.1781(2)	0.032(1)
O(4)	0.4658(4)	0.2074(3)	-0.0178(2)	0.031(1)
C(11)	0.3165(4)	0.2313(4)	0.2098(3)	0.009(1)
C(12)	0.2391(5)	0.2278(4)	0.1391(3)	0.011(1)
C(13)	0.1599(5)	0.3218(4)	0.1255(3)	0.016(1)
C(14)	0.1563(5)	0.4098(4)	0.1758(3)	0.020(1)
C(15)	0.2365(5)	0.4039(4)	0.2442(3)	0.018(1)
C(16)	0.3163(5)	0.3203(4)	0.2614(3)	0.014(1)
C(21)	0.3493(5)	0.0595(4)	0.3286(3)	0.011(1)
C(22)	0.4212(5)	-0.0227(4)	0.3678(3)	0.015(1)
C(23)	0.3657(6)	-0.0678(5)	0.4344(3)	0.028(1)
C(24)	0.2400(6)	-0.0338(5)	0.4629(3)	0.027(1)
C(25)	0.1668(6)	0.0460(5)	0.4230(3)	0.023(1)
C(26)	0.2210(5)	0.0937(4)	0.3562(3)	0.016(1)
C(31)	0.5918(5)	0.1674(4)	0.2662(3)	0.010(1)
C(32)	0.6736(5)	0.2008(4)	0.1996(3)	0.017(1)
C(33)	0.8029(5)	0.2449(5)	0.2132(3)	0.022(1)
C(34)	0.8522(5)	0.2566(4)	0.2889(3)	0.020(1)
C(35)	0.7722(5)	0.2233(4)	0.3520(3)	0.019(1)
C(36)	0.6432(5)	0.1803(4)	0.3386(3)	0.015(1)

^{31}P NMR (36.23 MHz) ($CDCl_3$): δ 177.7, 69.6. ESMS: m/z 694 (M + H + CH_3CN) $^+$, 653 (M + H) $^+$.

2.3. X-ray crystal structure determinations

For all three examples yellow crystals were obtained by slow diffusion of pentane into a concentrated solution in $CHCl_3$. Space group information and crystal quality were examined by preliminary precession photography. Intensity data were obtained on a Nicolet XRD P3 four-circle diffractometer with monochromated Mo K α X-rays ($\lambda = 0.7107$ Å) for **5b** and **7** or Cu K α ($\lambda = 1.5418$ Å) for **5c** at -143 °C. Absorption corrections were based on a series of Ψ scans. The structures were solved by direct methods (SHELXS-86 [23]) and the

Table 4
Atomic coordinates and equivalent isotropic displacement parameters for $(OC)_2(MeO)_2P(Se)_2Mn(C_6H_4)P(S)Ph_2$ (**7**)

Atom	x	y	z	U_{eq}
Mn(1)	-0.2782(1)	-0.5147(1)	-0.2033(1)	0.016(1)
P(1)	-0.3848(1)	-0.4791(1)	-0.0469(1)	0.018(1)
P(2)	-0.4416(2)	-0.6193(1)	-0.2175(1)	0.019(1)
P(3)	-0.1132(1)	-0.4131(1)	-0.1814(1)	0.018(1)
S(1)	-0.4653(1)	-0.4469(1)	-0.1346(1)	0.019(1)
C(1)	-0.3432(5)	-0.4598(3)	-0.2737(2)	0.019(1)
C(2)	-0.1442(6)	-0.5636(3)	-0.2554(2)	0.021(1)
C(3)	-0.6698(6)	-0.6699(4)	-0.1541(3)	0.036(1)
C(4)	-0.4221(8)	-0.7775(3)	-0.2557(3)	0.044(2)
C(5)	-0.6918(6)	-0.5424(3)	-0.2543(3)	0.031(1)
C(6)	-0.1056(7)	-0.2505(3)	-0.1665(3)	0.037(1)
C(7)	0.0187(7)	-0.3835(3)	-0.2958(3)	0.034(1)
C(8)	0.0943(6)	-0.4626(3)	-0.0949(3)	0.031(1)
O(1)	-0.3768(4)	-0.4277(2)	-0.3228(2)	0.029(1)
O(2)	-0.0593(4)	-0.5925(2)	-0.2923(2)	0.033(1)
O(3)	-0.5279(4)	-0.6546(2)	-0.1538(2)	0.025(1)
O(4)	-0.3585(4)	-0.6965(2)	-0.2503(2)	0.028(1)
O(5)	-0.5832(4)	-0.6078(2)	-0.2681(2)	0.026(1)
O(6)	-0.1914(4)	-0.3239(2)	-0.1833(2)	0.026(1)
O(7)	0.0369(4)	-0.4026(2)	-0.2274(2)	0.024(1)
O(8)	-0.0277(4)	-0.4072(2)	-0.1124(2)	0.024(1)
C(11)	-0.2577(5)	-0.5650(3)	-0.0571(2)	0.019(1)
C(12)	-0.2090(5)	-0.5827(3)	-0.1220(2)	0.017(1)
C(13)	-0.1095(6)	-0.6522(3)	-0.1260(2)	0.023(1)
C(14)	-0.0655(6)	-0.6983(3)	-0.0721(2)	0.026(1)
C(15)	-0.1164(6)	-0.6780(3)	-0.0096(2)	0.028(1)
C(16)	-0.2136(6)	-0.6120(3)	-0.0026(2)	0.024(1)
C(21)	-0.5441(6)	-0.5083(3)	0.0058(2)	0.020(1)
C(22)	-0.6161(6)	-0.4505(3)	0.0457(2)	0.026(1)
C(23)	-0.7493(6)	-0.4707(4)	0.0790(2)	0.033(1)
C(24)	-0.8084(6)	-0.5497(3)	0.0738(3)	0.031(1)
C(25)	-0.7375(6)	-0.6078(3)	0.0347(2)	0.030(1)
C(26)	-0.6049(6)	-0.5875(3)	0.0011(3)	0.028(1)
C(31)	-0.2962(6)	-0.3935(3)	-0.0041(2)	0.022(1)
C(32)	-0.3354(7)	-0.3132(3)	-0.0221(3)	0.031(1)
C(33)	-0.2887(8)	-0.2470(3)	0.0159(3)	0.041(2)
C(34)	-0.1999(7)	-0.2596(3)	0.0706(3)	0.038(1)
C(35)	-0.1552(8)	-0.3387(4)	0.0877(3)	0.040(2)
C(36)	-0.2045(7)	-0.4060(3)	0.0506(3)	0.035(1)

refinement was based on F^2 (SHELXL-93 [23]). All non-hydrogen atoms were treated anisotropically, with hydrogen atoms included in calculated positions.

2.3.1. η^2 -(C,S)-[(2-diphenylthiophosphinyl)phenyl]tetracarboxylmanganese (5b)

Crystal data: $C_{22}H_{14}MnO_4PS$, $M_r = 460.30$, monoclinic, space group $P2_1/c$, $a = 9.689(2)$, $b = 12.183(1)$, $c = 16.861(2)$ Å, $\beta = 91.19(1)^\circ$, $V = 1989.9(5)$ Å³, $D_{calc} = 1.536$ g cm⁻³, $Z = 4$, $F(000) = 936$, $\mu(Mo\ K\alpha) = 0.875$ mm⁻¹, $T_{max} = 0.692$, $T_{min} = 0.574$. A total of 3700 reflections was collected, $4^\circ < 2\theta < 50^\circ$, 3496 unique ($R_{int} = 0.0211$), 2908 with $I > 2\sigma(I)$. Final $R_1 = 0.0301$ (2σ data); $R_1 = 0.0419$, $wR_2 = 0.0708$, $Goof = 1.041$ (all data). Largest final feature 0.338 e Å⁻³. Table 1 gives selected bond parameters, Table 2 lists final positional parameters and Fig. 1 illustrates the molecule.

2.3.2. η^2 -(C,Se)-[(2-diphenylselenophosphinyl)phenyl]tetracarboxylmanganese (5c)

Crystal data: $C_{22}H_{14}MnO_4PSe$, $M_r = 507.20$, monoclinic, space group $P2_1/c$, $a = 9.653(2)$, $b = 12.293(2)$, $c = 16.990(3)$ Å, $\beta = 90.45(3)^\circ$, $V = 2016.0(6)$ Å³, $D_{calc} = 1.671$ g cm⁻³, $Z = 4$, $F(000) = 1008$, $\mu(Cu\ K\alpha) = 8.369$ mm⁻¹, $T_{max} = 0.745$, $T_{min} = 0.431$. A total of 2714 reflections was collected, $4^\circ < 2\theta < 110^\circ$, 2534 unique ($R_{int} = 0.0496$), 2141 with $I > 2\sigma(I)$. Final $R_1 = 0.0368$ (2σ data); $R_1 = 0.0436$, $wR_2 = 0.1067$, $Goof = 1.081$ (all data). Largest final feature -0.883 e Å⁻³. Table 3 lists final positional parameters, and the geometry is illustrated in Fig. 1.

2.3.3. η^2 -(C,S)-[(2-diphenylthiophosphinyl)phenyl]dicarbonyl-bis(trimethylphosphite)manganese (7)

Crystal data: $C_{26}H_{32}MnO_6P_3S$, $M_r = 652.43$, orthorhombic, space group $P2_12_12_1$, $a = 8.709(2)$, $b = 16.154(1)$, $c = 20.424(2)$ Å, $V = 2873.3(6)$ Å³, $D_{calc} = 1.508$ g cm⁻³, $Z = 4$, $F(000) = 1352$, $\mu(Mo\ K\alpha) = 0.746$ mm⁻¹, $T_{max} = 0.260$, $T_{min} = 0.237$. A total of 4269 unique reflections was collected, $4^\circ < 2\theta < 58^\circ$, 3415 with $I > 2\sigma(I)$. Final $R_1 = 0.0463$ (2σ data); $R_1 = 0.0680$, $wR_2 = 0.1057$, $Goof = 1.054$ (all data). A Flack absolute structure parameter of $-0.02(3)$ confirmed the refinement had been carried out with the correct polarity of the non-centric space group. Largest final feature 0.517 e Å⁻³. Table 1 gives selected bond parameters, Table 4 lists final positional parameters and Fig. 2 illustrates the molecule.

3. Results and discussion

3.1. Orthomanganation reactions

The reaction of all three $Ph_3P=X$ ($X = O, S, Se$) with $PhCH_2Mn(CO)_5$ gave the expected cyclometalated derivatives **5a–c**, although yields varied significantly. The most straightforward substrate was $Ph_3P=S$, which gave 90% yields of **5b** in refluxing heptane as yellow crystals after work-up. The corresponding reaction with $Ph_3P=O$ gave only 33% yields of **5a** in refluxing heptane, so milder conditions were explored (refluxing petroleum spirits 60–80°C) but gave only a slight improvement in yield (41%). In both cases compound **5a** could be isolated only as an orange oil that did not crystallise.

The reaction of $PhCH_2Mn(CO)_5$ with $Ph_3P=Se$ was more complex. The expected product **5c** was isolated as yellow crystals, but only in 22% yield. Other products identified were the known *cis*- $PhCH_2Mn(CO)_4(PPh_3)$ [22] together with $Mn_2(\mu-SeCH_2Ph)_2(CO)_8$ (**6**) which was identified spectroscopically and by a single-crystal X-ray analysis. The structure of **6**, prepared by an alternative route, has very recently been reported independently [21], so is not discussed further here. Clearly in this last reaction cleavage occurs of $Ph_3P=Se$ into Ph_3P (which then substitutes for a CO ligand on $PhCH_2Mn(CO)_5$) and Se (which inserts into the Mn–C bond of $PhCH_2Mn(CO)_5$ to give $PhCH_2SeMn(CO)_5$, subsequent dimerisation then generating **6**). Precedents for this process include the deliberate use of $Ph_3P=Se$ as a source of both Ph_3P and Se in the synthesis of iron and ruthenium clusters [26], and a report describing $Et_3P=Te$ as a source of soluble Te for preparing manganese compounds related to **6** [27].

The differing yields in the preparation of **5b** and **5c** can therefore be explained in terms of the stability of

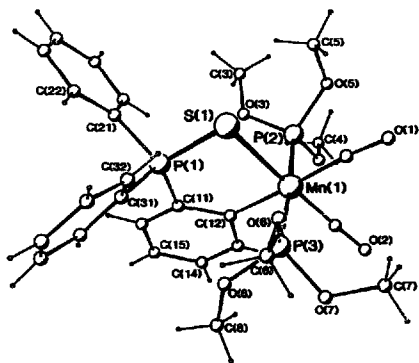


Fig. 2. The structure of the substituted complex $(OC)_2(MeO)_3P_1Mn(C_6H_4)PS(Ph)_2$ (**7**)

Table 5
Structural parameters for $\eta^1\text{-Ph}_3\text{P}=\text{X}$ complexes^a

	X = O	X = S	X = Se
Sample number ^b	94	9	5
Mean P–X (Å)	1.499	2.018	2.177
Mean P–X–Mn	156°	108°	100°
Range of P–X–Mn	130–180°	102–116°	98–103°
P–X in compound 5 (Å)	—	1.996	2.154
P–X–Mn in compound 5	—	99.6°	96.1°

^a Derived from the April 1996 release of the Cambridge Crystallographic Data Files [29].

^b For η^1 complexes only; four of the five $\text{Ph}_3\text{P}=\text{Se}$ examples are for gold derivatives so the figures may not be truly representative.

the P=E bond. The P=S bond is stable under the reaction conditions, but for $\text{Ph}_3\text{P}=\text{Se}$ the ready cleavage of the weaker P=Se bond [28] introduces competing products.

The reasons for the lower yields for **5a** from $\text{Ph}_3\text{P}=\text{O}$ are less obvious. Hard/soft acid/base ideas would suggest that the O atom of the phosphine oxide is presumably a poorer donor than the S of $\text{Ph}_3\text{P}=\text{S}$ to manganese(I), but this is not a limiting factor in the cyclomanganation of ketones which also involve O → Mn coordination and give high yields. A more reasonable explanation is revealed by a search of the Cambridge Crystallographic Data Files [29] for complexes in which $\text{Ph}_3\text{P}=\text{X}$ is coordinated in a mono-hapto mode, the results of which are summarised in Table 5. The key parameter is the P=E–M angle, which will reflect the preferred coordination geometry in these unconstrained complexes. For the S and Se examples this angle has a mean value of 108° and 100° respectively, which does not differ greatly from the values in the corresponding orthomanganated complexes **5b** and **5c** (99.6° and 96.1° respectively), as found in the crystal structure analyses reported below. However, for $\eta^1\text{-Ph}_3\text{P}=\text{O}$ complexes the mean value for the angle at the oxygen atom is 156°, with a range of 130–180°. The structure of the cyclomanganated complex **5a** has not been determined, but a P=O–Mn angle of ca. 115° can be estimated by extrapolation from the heavier analogues. This indicates that incorporation of the P=O group of $\text{Ph}_3\text{P}=\text{O}$ into a five-membered metallocyclic ring will induce a strained angle at the oxygen atom, and so will be a less favoured process. Why there should be such a disparity between the preferred angle of the oxide on the one hand and the sulfide or selenide on the other is not clear. Other distinctive features have been noted; for example, the P=O bond in $\text{R}_2\text{P}=\text{O}$ is less polar than the corresponding P=S or P=Se bonds [28], contrary to expectations based on electronegativities. A fully accepted theoretical model of P=E bonds in the free ligands is still not

available, with the latest proposals suggesting the phosphorus–oxygen linkage can even be regarded as a triple bond [28].

The complexes **5a–c** appear to be the first examples of direct cyclometalation of triphenylphosphine chalcogenides, and **5c** is the first orthomanganated complex incorporating a selenium donor atom. All three compounds can be handled in air as solids or in solution without decomposition and are readily soluble in organic solvents.

3.2. Spectroscopy

The carbonyl region infrared spectra of **5a–c** show the characteristic four-band pattern found for other orthomanganated species [12], although the two middle bands of **5a** are not resolved. There is the expected shift to lower frequencies from **5a** → **5b** → **5c**, paralleling the decrease in the electronegativity of the donor chalcogen atom.

There is a decrease in the $\nu(\text{P}=\text{E})$ stretching frequency going from the free ligands to the orthomanganated complexes. This is greatest for $\text{Ph}_3\text{P}=\text{O}$ (1190 to 1066 cm^{-1}), the difference of 124 cm^{-1} being similar to the drop in $\nu(\text{CO})$ found between free and orthometalated aromatic ketones [3,12]. It is much greater than the decrease of 40–60 cm^{-1} observed in $\eta^1\text{-Ph}_3\text{P}=\text{O}$ complexes of the 3d M^{2+} ions [16,30], possibly because of the more acute angle at oxygen in the cyclometalated example (cf. Table 5). The change is less for $\text{Ph}_3\text{P}=\text{S}$ (639 to 606 cm^{-1}), the difference of 33 cm^{-1} lying at the lower end of the range found for η^1 -metalated complexes involving higher oxidation state ions [15] but greater than the 9–15 cm^{-1} decrease in $\text{M}(\text{CO})_2(\text{SPPH}_2)$ ($\text{M} = \text{Cr}, \text{W}$) [31]. For $\text{Ph}_3\text{P}=\text{Se}$ (562 to 549 cm^{-1}) only a small change is observed, presumably reflecting the low sensitivity of the heavy selenium atom vibrations to coordination.

The ^{13}C NMR spectra of **5a–c** were straightforward. The three broad signals around δ 215 ppm of intensity 1:1:2 from lower to higher field can be assigned to the Mn–CO groups. Only the middle signal, which can be tentatively assigned to the carbonyl group *trans* to the aryl carbon, shows a small 1J coupling to the phosphorus atom. There is a W-type configuration between this C atom and the P atom, similar to that in other systems where long range coupling by conjugation has been found. This provides further support for the previous assignment of the CO NMR signals in orthomanganated complexes [12], which was based on the premise that the CO groups receiving the greatest back-bonding will give the highest ^{13}C chemical shifts [32]. The metalated aryl carbon atoms give rise to a ^{13}C signal around 180 ppm, about 50 ppm to lower field than the corresponding signal in the free ligand. This is fully in accord with observations for related compounds.

The ^{31}P NMR chemical shifts show deshielding when the ligand forms the complexes. The shifts are δ 29.0 \rightarrow 64.4 ($\Delta\delta$ 35.4) for the oxide **5a**, δ 43.3 \rightarrow 66.6 ($\Delta\delta$ 23.3) for the sulfide **5b** and δ 35.2 \rightarrow 52.2 ($\Delta\delta$ 17.0) for the selenide **5c**. There is little data in the literature for the effect on ^{31}P NMR of metalation of phosphine chalcogenides in monodentate complexes, although shifts are likely to be small because of the indirect link of the phosphorus atom to the metal. This is supported by the data for $\text{Ph}_3\text{P}=\text{E}$ adducts with HgCl_2 where shifts of less than 10 ppm were found [33]. The major contribution to $\Delta\delta$ in complexes **5a–c** probably arises from incorporation of the phosphorus atom into a five-membered chelate ring, which is known to provide a chemical shift of 21–33 ppm in addition to any shift induced by metalation [34]. The $\Delta\delta$ shifts of 17–35 ppm found for the cyclomanganated complexes fall broadly into the expected range, and parallel the approximately 11–30 ppm shifts found for $\text{Ph}_2\text{PCH}_2(\text{Ph})_2\text{P}=\text{E}$ chelated complexes containing $\text{M}(\text{CO})_5$ units ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) [35,36] or those of the same type of ligand with platinum or rhodium: [37].

One interesting comparison is between the orthomanganated phosphine oxide **5a**, and orthomanganated triphenylphosphite **2** [14]. Both examples have the same atoms in the five-membered chelate ring, with the P and O atoms interchanged. For **2** the ^{31}P signal has shifted by 67 ppm on cyclometalation, but this can be divided to give a $\Delta\delta$ value of 31 ppm for the component arising from incorporation of the phosphorus atom into a five-membered chelate ring. This is close to the value 35 ppm for **5a** which suggests the ring-forming effect on the ^{31}P chemical shift is not dependent on the position of the phosphorus atom in the ring.

3.3. X-ray structures of **5b** and **5c**

The orthomanganated complexes from $\text{Ph}_3\text{P}=\text{S}$ and $\text{Ph}_3\text{P}=\text{Se}$ form isomorphous crystals. Fig. 1 gives a view of individual molecules, which consist of a triphenylphosphine chalcogenide ligand bonded to a tetracarbonylmanganese unit in a chelating fashion via an E–Mn bond ($\text{E} = \text{S}$ or Se) and an Mn–C bond to an *ortho* carbon atom of one of the phenyl rings. The geometry at the Mn atom is close to octahedral. The five-membered metallocyclic ring is essentially planar, as with other orthomanganated compounds, although in these present examples complete delocalisation of electron density over the ring is precluded by the sp^3 phosphorus atom. This may explain why the Mn–C(12) bond lengths are longer than the range of 2.00–2.07 Å found in orthomanganated complexes where delocalisation is possible [12], although explanations based on the lower electronegativity of sulfur or selenium compared to the oxygen atoms which are the donor atoms in the other

examples are also possible. The inclusion of two larger atoms, namely P and S or Se, reduces the strain associated with the five-membered ring compared with cyclomanganated aryl ketones. The C(12)–Mn(1)–E bite angles of 89.60(6)° ($\text{E} = \text{S}$) or 90.8(1)° ($\text{E} = \text{Se}$) are essentially ideally octahedral, in contrast to the normal values of 78–80° for manganacyclic rings with only carbon and oxygen atoms. The angles at C(11) and C(12) are also closer to ideal trigonal values in **5b** and **5c** than in other examples. The only angles that deviate from ideal ones are those at the E atoms, 99.6° at S and 96.1° at Se, with the difference arising from the presence of the larger Se atom in **5c** which otherwise has the same geometry as **5b**. As discussed above, these are not very different from the 'natural' angle when these ligands bind in an unconstrained η^1 fashion (averages 108° and 100° respectively, Table 5) to a range of metal ions. The P=E bonds are slightly but significantly lengthened on coordination, by 0.046(4) Å when $\text{E} = \text{S}$ and by 0.042(2) Å when $\text{E} = \text{Se}$ (Table 1).

The CO ligands on the manganese atom adopt the normal pattern, with the two out-of-plane *trans* CO groups leaning towards the cyclometalated ring (C(3)–Mn(1)–C(4) ca. 167°). The shortest Mn–CO bond is opposite the chalcogen atom, the next shortest is *trans* to the C_{ortho} atom and the remaining two COs opposite each other are the most distant. This can be explained in terms of competition for d_{π} electron density [12].

3.4. Reaction of **5b** with $(\text{MeO})_3\text{P}$

The orthomanganated $\text{Ph}_3\text{P}=\text{S}$ complex **5b** was reacted with $(\text{MeO})_3\text{P}$ to see whether the S atom could be displaced. However, when **5b** and excess $(\text{MeO})_3\text{P}$ were heated at reflux in heptane the only product isolated, in high yield, was **7** in which the original metallocyclic ring remains intact and two of the CO groups have been substituted by the phosphite ligands. The appearance of $[\text{M} + \text{H}]^+$ and $[\text{M} + \text{H} + \text{MeCN}]^+$ peaks in the electrospray mass spectrum confirmed the molecular formula. There are two ^{31}P NMR signals, one at δ 69.6 which is barely moved from that in the parent **5b**, and the other at δ 177.7 which indicates that the two $(\text{MeO})_3\text{P}$ ligands are mutually *trans*. The two strong $\nu(\text{CO})$ bands in the infrared spectrum suggest that the carbonyl groups are *cis* to each other. Although the spectroscopic characterisation was strong, a single-crystal X-ray analysis was carried out. The structure of **7** is shown in Fig. 2, and selected bond parameters are compared with those of the unsubstituted **5b** in Table 1. Replacement of two COs by $(\text{MeO})_3\text{P}$ ligands has very little effect on the rest of the molecule. In particular, the metallocyclic ring shows no significant difference between the two molecules, except perhaps for a slight puckering away from planarity (biggest deviation

0.151 Å in **7** compared with 0.090 Å in **5b**). About the manganese atom the P(2)–Mn(1)–P(3) angle of 175.8° is closer to linear than the corresponding C(3)–Mn(1)–C(4) angle in **5b**, and the C(1)–Mn(1)–C(2) angle in **7** has closed by 3.1° to 86.9°. These small changes can be attributed to the steric bulk of the phosphite ligands. The remaining two Mn–CO distances are significantly shorter in **7** than in **5b**, the change arising because of less competition for π electrons from the metal. Overall, there is remarkably little effect on changing the coordination about the manganese atom.

The preparation of **7** illustrates the stability of the cyclometalated ring in **5b**. There was no indication that the Mn–S bond was cleaved in the presence of the phosphite ligands. η^1 -Aryl complexes of manganese carbonyl are stable, so a derivative in which the sulfur atom was displaced should be detectable. A two-step sequence in which the incoming ligand displaced the sulfur atom, which then displaced a CO ligand, cannot be excluded but seems less likely than direct exchange since no by-product with uncoordinated sulfur was seen, and the reaction conditions were those associated with dissociative replacement of CO ligands on manganese by Lewis bases. All the evidence indicates that the metallocyclic ring formed by $\text{Ph}_3\text{P}=\text{S}$ is very robust. This must arise through chelation because it is known that monodentate $\text{Ph}_3\text{P}=\text{S}$ ligands are very readily displaced, for example by CO or Ph_3P in derivatives such as $\text{M}(\text{CO})_5(\text{SPPH}_3)$ ($\text{M} = \text{Cr}, \text{W}$) [31].

4. Conclusion

It has been shown that $\text{R}_3\text{P}=\text{X}$ are suitable substrates for orthomanganation, and should form similar cyclometalated complexes with other metals such as Pd(II) or Rh(III). $\text{Ph}_3\text{P}=\text{S}$ is likely to be the most successful substrate because the Se analogue suffers from the fragility of the $\text{P}=\text{Se}$ bond, and $\text{Ph}_3\text{P}=\text{O}$ results in an unfavourable bond angle at oxygen when the $\text{P}=\text{O}$ group is incorporated into a five-membered metallocyclic ring.

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