

Orthomanganation of the iminophosphorane $\text{Ph}_3\text{P}=\text{NPh}$, and of triphenylarsine-oxide and -sulfide

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Abstract

Two novel types of cyclometallated rings are described. Orthomanganation of $\text{Ph}_3\text{P}=\text{NPh}$ gave $\text{Ph}_2\text{P}[\overline{\text{NPh}}]\text{C}_6\text{H}_4\text{Mn}(\text{CO})_4$, **5a**, containing an N,C-chelated five-membered ring, characterised by single crystal X-ray determinations of two distinct polymorphs. Solutions of **5a** are thermochroic. The rhenium analogue of **5a** was also prepared. Reaction of $\text{Ph}_3\text{As}=\text{X}$ ($\text{X}=\text{O}, \text{S}$) with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ gave the first examples of orthometallated triphenylarsine chalcogenides. The example with $\text{X}=\text{O}$ was characterised structurally. Attempted cyclomanganation of Ph_3As was unsuccessful, but gave (in low yield) a dimanganese complex containing $\mu\text{-AsPh}_2$ and $\mu\text{-}\eta^1, \eta^6\text{-benzyl}$ ligands. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Orthometallation; Manganese; Iminophosphorane; Triphenylarsine oxide; Triphenylarsinesulfide

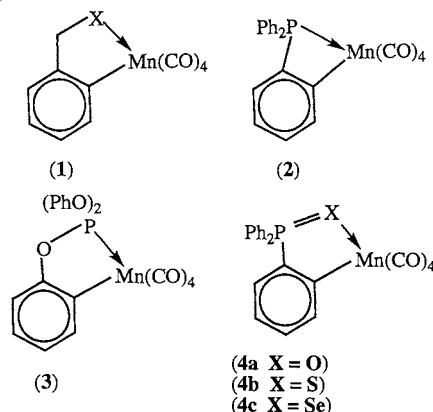
1. Introduction

Cyclometallation reactions involving manganese are now second only to those of palladium in the amount of study devoted to them. Reaction of $\text{RMn}(\text{CO})_5$ with a whole range of O-, N-, S- and P-donor aryl substrates gives stable derivatives of the type **1**, usually with a five-membered ring [1–3]. The manganese compounds derived from aromatic ketones are especially well-studied and have been shown to be of use in organic synthesis [1,4–6].

The cyclomanganation chemistry of phosphines has a long history. Kaesz's group [7] first showed that PPh_3 gave rise to the four-membered ring compound **2** together with other products arising from secondary reactions of **2**. Reaction with $(\text{PhO})_3\text{P}$ was more predictable, leading to good yields of the five-membered ring compound **3** [8]. The reactivity of **3** towards insertion reactions with alkynes has been studied in detail [9]. More recently we extended this work to the orthomanganation of triphenylphosphine chalcogenides $\text{Ph}_3\text{P}=\text{X}$,

($\text{X}=\text{O}, \text{S}, \text{Se}$) which gave stable derivatives **4** which showed interesting reactivity at the $\text{Mn}-\text{C}_{\text{aryl}}$ bond [10,11].

The present paper extends this previous work in two ways. Firstly we report the successful cyclometallation of the iminophosphorane $\text{Ph}_3\text{P}=\text{NPh}$, an example from a class of compound electronically analogous to the phosphine chalcogenides. Secondly, we describe the corresponding reactions of the triphenylarsenic oxide and sulfide, which also appear not to have been examined under cyclometallation conditions before.



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2. Experimental

2.1. General

All manipulations were carried out in an oxygen-free N_2 atmosphere with dried solvents in Schlenk equipment. $PhCH_2Mn(CO)_5$ was prepared by the standard method [12], and $PhCH_2Re(CO)_5$ analogously. $Ph_3P=NPh$ was produced from Ph_3P and PhN_3 , using the Staudinger reaction [13]. $Ph_3As=O$ (m.p. 192–195°C, lit. 189°C) was from H_2O_2 -oxidation of Ph_3As , while the corresponding sulfide was from $Ph_3As=O$ and CS_2 (m.p. 167–168°C, lit. 167–168°C) [14].

2.2. Instrumentation

Infrared spectra were recorded on a Digilab FTS-40 FTIR spectrophotometer. NMR spectroscopy was performed using a Bruker AC300P Multinuclear FT spectrometer. Electrospray mass spectra were collected using a VG Platform II instrument, usually in MeOH with added NaOMe for derivatisation [15]. Elemental analysis was performed by the Campbell Microanalytical Laboratory, University of Otago.

2.3. Reactions

2.3.1. Reaction of $Ph_3P=NPh$ with $PhCH_2Mn(CO)_5$

To a Schlenk flask was added $Ph_3P=NPh$ (0.300 g, 0.85 mmol), $PhCH_2Mn(CO)_5$ (0.283 g, 0.99 mmol) and heptane (35 ml), and the mixture was heated under reflux for 2 h. The solution became an intense purple colour, which changed to golden yellow on cooling. An IR spectrum showed the 2107 cm^{-1} band of the starting material had disappeared. The solvent was evaporated under vacuum to about a quarter volume and the solution was left at 0°C to give yellow crystals of the product **5a** (0.283 g, 64%). Found C 64.76, H 3.62, N 2.89%; $C_{28}H_{19}PNO_4Mn$ requires C 64.75, H 3.69, N 2.70%. IR $\nu(\text{CO})$: (petroleum spirits, cm^{-1}) 2069 (m), 1982 (vs, br), 1927(s). Raman (solid, cm^{-1}) $\nu(\text{CO})$: 2073(m), 2066(m), 1972(s), 1967(s), 1917(m) 1908(m). NMR (δ $CDCl_3$): $^1\text{H-NMR}$, 8.09–8.06, 7.59–7.30, 7.09–7.04, 6.93–6.82 (all m, Ar–H); $^{13}\text{C-NMR}$, 220.36 (s, CO), 215.17 (s, 2CO), 213.65 (s, CO), 180.62 (d, $J_{\text{pc}} = 25.6$ Hz, Mn–C), 151.56 (s), 142.63 (d, $J_{\text{pc}} = 16.0$ Hz), 139.61 (d, $J_{\text{pc}} = 135.5$ Hz), 133.18 (d, $J_{\text{pc}} = 9.7$ Hz), 138.49 (d, $J_{\text{pc}} = 2.0$ Hz), 130.79 (d, $J_{\text{pc}} = 22.4$ Hz), 130.76 (d, $J_{\text{pc}} = 3.0$ Hz), 129.61 (d, $J_{\text{pc}} = 2.0$ Hz), 129–128 (m), 123.58 (d, $J_{\text{pc}} = 14.2$ Hz), 122.90 (d, $J_{\text{pc}} = 2.0$ Hz); $^{31}\text{P-NMR}$, 44.3. ESMS (MeOH with NaOMe) m/z 550 $[M + \text{OMe}]^-$, 522 $[M + \text{OMe} - \text{CO}]^-$. The compound was fully characterised by X-ray crystal structure determinations on two different crystal forms (see below).

2.3.2. Reaction of $Ph_3P=NPh$ with $PhCH_2Re(CO)_5$

Similarly $Ph_3P=NPh$ (0.291 g, 0.83 mmol), $PhCH_2Re(CO)_5$ (0.345 g, 0.83 mmol) and petroleum spirits (100–130°C fraction, 40 ml) were heated under reflux until the 2127 cm^{-1} band of the starting material had disappeared (about 2 h). The solvent was evaporated under vacuum to about half volume and cooled to precipitate as a pale yellow powder the product **5b** (0.425 g, 88%). IR $\nu(\text{CO})$: (petroleum spirits, cm^{-1}) 2083 (m), 2015 (s), 1970 (vs), 1925(s). NMR (δ $CDCl_3$): $^1\text{H-NMR}$, 8.27–8.22, 7.72–7.58, 7.54–7.37, 7.21–7.12, 6.99–6.91 (all m, Ar–H); ^{13}C , 192.34 (s, CO), 192.11 (d, $J_{\text{pc}} = 4.6$ Hz, CO), 190.76 (s, 2CO), 169.36 (d, $J_{\text{pc}} = 26.1$ Hz, Re–C), 151.52 (d, $J_{\text{pc}} = 2.0$ Hz), 144.06 (d, $J_{\text{pc}} = 16.2$ Hz), 141.22 (d, $J_{\text{pc}} = 132.1$ Hz), 133.39 (d, $J_{\text{pc}} = 9.6$ Hz), 133.49 (d, $J_{\text{pc}} = 2.0$ Hz), 132.86 (d, $J_{\text{pc}} = 1.9$ Hz), 131.04 (d, $J_{\text{pc}} = 2.6$ Hz), 129.20 (d, $J_{\text{pc}} = 43.2$ Hz), 129.03 (d, $J_{\text{pc}} = 11.8$ Hz), 128.74 (s), 128.23 (d, $J_{\text{pc}} = 6.2$ Hz), 123.89 (d, $J_{\text{pc}} = 14.4$ Hz), 123.27 ($J_{\text{pc}} = 1.5\text{ Hz}$); $^{31}\text{P-NMR}$, 50.6. ESMS (MeOH with NaOMe) m/z 682 $[M + \text{OMe}]^-$, 654 $[M + \text{OMe} - \text{CO}]^-$.

2.3.3. Reaction of $Ph_3As=O$ with $PhCH_2Mn(CO)_5$

$Ph_3As=O$ (0.353 g, 1.095 mmol), $PhCH_2Mn(CO)_5$ (0.393 g, 1.37 mmol) and hexane (45 ml) were heated under reflux for 2h by which time an IR spectrum showed the 2107 cm^{-1} band of the starting material had disappeared. The solvent was evaporated under vacuum to about half volume and the solution was left at 0°C to give yellow crystals of orthomanganated $Ph_3As=O$, **6a** (0.182 g, 34%). IR $\nu(\text{CO})$: (petroleum spirits, cm^{-1}) 2075 (m), 1988 (vs, br), 1929(s). ESMS (MeOH with NaOMe) m/z 519 $[M + \text{OMe}]^-$. The compound was characterised fully by an X-ray crystal structure determination (see below).

2.3.4. Reaction of $Ph_3As=S$ with $PhCH_2Mn(CO)_5$

A directly analogous procedure with $Ph_3As=S$ (0.135 g, 0.40 mmol), $PhCH_2Mn(CO)_5$ (0.123 g, 0.43 mmol) and hexane (40 ml) for 2.5 h gave yellow/orange crystals of orthomanganated $Ph_3As=S$, **6b** (0.045 g, 22%). IR $\nu(\text{CO})$: (petroleum spirits, cm^{-1}) 2070 (m), 1984 (vs, br), 1927(s). ESMS (MeOH with NaOMe) m/z 535 $[M + \text{OMe}]^-$.

2.3.5. Reaction of Ph_3As with $PhCH_2Mn(CO)_5$

Ph_3As (0.100 g, 0.33 mmol) and $PhCH_2Mn(CO)_5$ (0.085 g, 0.30 mmol) were added to heptane (30 ml), and the mixture was heated under reflux for 2.5 h. A preliminary TLC indicated that at least 10 compounds were present, all in rather small amounts. A preparative scale separation on a silica plate gave incomplete resolution and only three compounds could be isolated in low yield and identified:

Table 1
Refined parameters for the structure of the *C2/c* form of orthomanganated $\text{Ph}_3\text{P}=\text{NPh}$, **5a**

Atom	x	y	z	U_{eq}
Mn(1)	0.0991(1)	0.1028(1)	0.1061(1)	0.030(1)
P(1)	0.1427(1)	-0.0159(1)	0.0642(1)	0.026(1)
N(1)	0.1111(1)	-0.0493(3)	0.0723(1)	0.026(1)
C(11)	0.1435(2)	0.0408(4)	0.1819(2)	0.042(1)
C(12)	0.0590(2)	0.0030(5)	0.0938(2)	0.043(1)
C(13)	0.0921(1)	0.2339(5)	0.1373(2)	0.040(1)
C(14)	0.0640(1)	0.1899(5)	0.0325(2)	0.037(1)
O(11)	0.1734(1)	0.0081(3)	0.2296(2)	0.077(1)
O(12)	0.0338(1)	-0.0557(3)	0.0874(2)	0.060(1)
O(13)	0.0879(1)	0.3207(4)	0.1577(2)	0.064(1)
O(14)	0.0438(1)	0.2532(3)	-0.0104(2)	0.060(1)
C(111)	0.0851(1)	-0.1653(4)	0.0446(2)	0.027(1)
C(112)	0.0956(2)	-0.2779(5)	0.0776(2)	0.046(1)
C(113)	0.0693(2)	-0.3878(5)	0.0518(3)	0.062(2)
C(114)	0.0324(2)	-0.3849(5)	-0.0081(3)	0.059(2)
C(115)	0.0217(2)	-0.2737(6)	-0.0414(2)	0.053(2)
C(116)	0.0476(1)	-0.1633(5)	-0.0157(2)	0.039(1)
C(121)	0.1181(1)	0.0065(4)	-0.0131(2)	0.027(1)
C(122)	0.1115(1)	0.1324(4)	-0.0356(2)	0.031(1)
C(123)	0.0914(1)	0.1536(4)	-0.0952(2)	0.040(1)
C(124)	0.0786(1)	0.0468(5)	-0.1325(2)	0.041(1)
C(125)	0.0843(1)	-0.0802(5)	-0.1116(2)	0.040(1)
C(126)	0.1039(1)	-0.1006(4)	-0.0522(2)	0.036(1)
C(131)	0.1833(1)	-0.1393(4)	0.0972(2)	0.025(1)
C(132)	0.1977(1)	-0.1794(4)	0.0707(2)	0.032(1)
C(133)	0.2297(1)	-0.2710(4)	0.0993(2)	0.043(1)
C(134)	0.2480(1)	-0.3199(4)	0.1550(2)	0.045(1)
C(135)	0.2351(1)	-0.2782(5)	0.1829(2)	0.044(1)
C(136)	0.2029(1)	-0.1879(4)	0.1541(2)	0.034(1)
C(141)	0.1657(1)	0.1372(4)	0.1033(2)	0.026(1)
C(142)	0.1994(1)	0.1915(4)	0.1142(2)	0.034(1)
C(143)	0.2147(1)	0.3146(5)	0.1416(2)	0.042(1)
C(144)	0.1959(2)	0.3814(5)	0.1570(2)	0.045(1)
C(145)	0.1629(1)	0.3261(4)	0.1469(2)	0.038(1)
C(146)	0.1461(1)	0.2018(4)	0.1195(2)	0.026(1)
Mn(2)	0.1934(1)	0.5334(1)	0.4430(1)	0.031(1)
P(2)	0.1045(1)	0.4586(1)	0.3140(1)	0.026(1)
N(2)	0.1511(1)	0.5050(3)	0.3490(1)	0.026(1)
C(21)	0.1781(1)	0.7110(5)	0.4250(2)	0.038(1)
C(22)	0.2376(1)	0.5550(5)	0.4494(2)	0.036(1)
C(23)	0.2278(1)	0.5637(4)	0.5225(2)	0.038(1)
C(24)	0.2001(1)	0.3529(5)	0.4558(2)	0.037(1)
O(21)	0.1683(1)	0.8198(3)	0.4131(2)	0.061(1)
O(22)	0.2667(1)	0.5685(3)	0.4565(1)	0.054(1)
O(23)	0.2504(1)	0.5827(4)	0.5736(1)	0.060(1)
O(24)	0.2029(1)	0.2405(3)	0.4635(1)	0.055(1)
C(211)	0.1616(1)	0.5444(4)	0.3155(2)	0.030(1)
C(212)	0.1512(2)	0.6699(5)	0.2906(2)	0.054(2)
C(213)	0.1623(2)	0.7088(6)	0.2597(3)	0.082(2)
C(214)	0.1840(2)	0.6262(7)	0.2541(2)	0.067(2)
C(215)	0.1950(2)	0.5038(6)	0.2795(2)	0.055(2)
C(216)	0.1835(1)	0.4626(5)	0.3099(2)	0.039(1)
C(221)	0.0925(1)	0.2932(4)	0.2829(2)	0.030(1)
C(222)	0.0520(1)	0.2490(5)	0.2354(2)	0.043(1)
C(223)	0.0448(2)	0.1201(5)	0.2132(2)	0.055(2)
C(224)	0.0776(1)	0.0360(5)	0.2382(2)	0.055(2)
C(225)	0.1176(2)	0.0779(5)	0.2852(2)	0.052(1)
C(226)	0.1248(2)	0.2054(4)	0.3076(2)	0.042(1)
C(231)	0.0644(1)	0.5615(4)	0.2503(2)	0.027(1)
C(232)	0.0447(1)	0.6603(4)	0.2549(2)	0.030(1)
C(233)	0.0172(1)	0.7473(4)	0.2077(2)	0.034(1)

Table 1 (Continued)

Atom	x	y	z	U_{eq}
C(234)	0.0098(1)	0.7386(4)	0.1557(2)	0.034(1)
C(235)	0.0294(1)	0.6421(4)	0.1508(2)	0.041(1)
C(236)	0.0564(1)	0.5530(4)	0.1973(2)	0.039(1)
C(241)	0.1026(1)	0.4667(4)	0.3705(2)	0.026(1)
C(242)	0.0660(1)	0.4415(4)	0.3576(2)	0.033(1)
C(243)	0.0656(1)	0.4503(4)	0.4022(2)	0.037(1)
C(244)	0.1025(2)	0.4840(4)	0.4601(2)	0.040(1)
C(245)	0.1389(1)	0.5080(4)	0.4733(2)	0.032(1)
C(246)	0.1405(1)	0.5015(4)	0.4288(2)	0.028(1)

1. From the fastest moving yellow band was isolated some orthomanganated $\text{Ph}_3\text{As}=\text{O}$, **6a**, identified by comparison with an authentic sample.
2. From a second yellow band was crystallised *cis*- $\text{PhCH}_2\text{Mn}(\text{CO})_4(\text{AsPh}_3)$, m.p. 130°C, IR $\nu(\text{CO})$: (petroleum spirits, cm^{-1}) 2055 (m), 1980 (m), 1969(s), 1938 (m). The compound was characterised by an X-ray crystal structure determination on a poor quality crystal (final R_1 0.12). The result confirmed the identity and overall geometry of the compound but the accuracy of the determination does not merit further discussion.
3. From a slower moving orange band was isolated a red crystalline product identified as $(\mu-\eta^1, \eta^6-\text{C}_6\text{H}_5\text{CH}_2)(\mu-\text{AsPh}_2)\text{Mn}_2(\text{CO})_6$, **7**, IR $\nu(\text{CO})$: (cm^{-1}) 2066 (m), 2018 (m), 1990 (m), 1979(s), 1949 (s). ESMS (MeOH with NaOMe) m/z 629 $[\text{M} + \text{OMe}]^-$. Full characterisation was by a single crystal X-ray determination (see below).

In an attempt to improve the specificity of the reaction, $\text{PhCH}_2\text{Mn}(\text{CO})_4(\text{AsPh}_3)$ was prepared separately using $[\text{Mn}(\text{CO})_4(\text{AsPh}_3)]^-$ (from $\text{Mn}_2(\text{CO})_8(\text{AsPh}_3)_2$ and Na/Hg amalgam) with PhCH_2Br , and this was then pyrolysed in refluxing heptane. Again a plethora of products resulted so the reaction was not investigated further.

2.4. X-ray crystallography

For the structure determinations of the *Cc* form of **5a**, and for **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). Corrections for absorption and other effects were carried out with SADABS [16]. For the *C2/c* version of **5a** and for **6a** data was collected on a Siemens P4 four-circle diffractometer using ω -scans, and was corrected for absorption using a Φ -scan method. Calculations used the SHELX97 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.

Table 2

Refined parameters for the structure of the *Cc* form of orthomanganated $\text{Ph}_3\text{P}=\text{NPh}$, **5a**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Mn(1)	0.8493(1)	0.1273(1)	0.9113(1)	0.032(1)
P(1)	0.8428(1)	0.3191(1)	0.9002(2)	0.027(1)
N(1)	0.8831(3)	0.2436(3)	0.9900(5)	0.027(1)
C(1)	0.9391(5)	0.1311(4)	0.8062(8)	0.043(2)
C(2)	0.9116(4)	0.0778(4)	1.0650(7)	0.043(2)
C(3)	0.8140(4)	0.0312(4)	0.8409(7)	0.046(2)
C(4)	0.7548(4)	0.1373(4)	1.0012(7)	0.036(2)
O(1)	0.9932(3)	0.1379(3)	0.7399(6)	0.068(2)
O(2)	0.9523(3)	0.0446(3)	1.1570(5)	0.063(1)
O(3)	0.7876(3)	−0.0291(3)	0.7950(5)	0.071(2)
O(4)	0.6966(3)	0.1448(4)	1.0532(5)	0.062(2)
C(11)	0.9291(3)	0.2529(3)	1.1318(6)	0.030(1)
C(12)	1.0124(3)	0.2727(3)	1.1473(6)	0.034(1)
C(13)	1.0584(3)	0.2754(4)	1.2841(6)	0.040(2)
C(14)	1.0227(4)	0.2586(4)	1.4085(6)	0.043(2)
C(15)	0.9389(4)	0.2399(4)	1.3951(6)	0.045(2)
C(16)	0.8930(3)	0.2368(4)	1.2588(5)	0.036(1)
C(21)	0.7670(4)	0.3744(3)	0.9891(6)	0.028(1)
C(22)	0.7883(4)	0.4067(3)	1.1268(6)	0.039(2)
C(23)	0.7303(4)	0.4479(4)	1.1961(6)	0.043(2)
C(24)	0.6514(4)	0.4562(4)	1.1305(7)	0.042(2)
C(25)	0.6294(4)	0.4249(4)	0.9932(7)	0.045(2)
C(26)	0.6858(3)	0.3828(3)	0.9214(6)	0.033(1)
C(31)	0.9175(3)	0.3932(3)	0.8585(6)	0.026(1)
C(32)	0.9780(4)	0.3671(4)	0.7772(7)	0.047(2)
C(33)	1.0381(4)	0.4202(5)	0.7428(7)	0.053(2)
C(34)	1.0388(4)	0.4981(4)	0.7877(7)	0.052(2)
C(35)	0.9798(4)	0.5253(4)	0.8688(7)	0.053(2)
C(36)	0.9195(4)	0.4724(4)	0.9050(6)	0.042(2)
C(41)	0.7944(3)	0.2746(4)	0.7331(6)	0.029(1)
C(42)	0.7621(3)	0.3224(4)	0.6147(6)	0.038(1)
C(43)	0.7220(4)	0.2862(4)	0.4886(6)	0.048(2)
C(44)	0.7173(4)	0.2025(4)	0.4866(6)	0.047(2)
C(45)	0.7503(3)	0.1568(4)	0.6027(6)	0.041(2)
C(46)	0.7908(3)	0.1902(3)	0.7332(6)	0.030(1)

2.4.1. Crystal data for the *C2/c* form of cyclomanganated $\text{Ph}_3\text{P}=\text{NPh}$, **5a**

$\text{C}_{28}\text{H}_{19}\text{MnNO}_4\text{P}$, *M_r* 519.35, monoclinic, *C2/c*, *a* = 44.03(3), *b* = 10.093(7), *c* = 30.50(2) Å, β = 133.47(2), *V* = 9835(11) Å³, *D*_{calc} = 1.403 g cm^{−3}, *Z* = 16, *F*(000) = 4256, μ(Mo–K_α) 0.637 mm^{−1}, *T*_{max} 0.823, *T*_{min} 0.743, crystal size 0.6 × 0.4 × 0.2 mm³, *T* 173 K.

A total of 9182 reflections, 6990 unique (*R*_{int} 0.0395) was collected 2° < θ < 24°. Final *R*₁ 0.0482 (4326 data with *I* = 2σ(*I*)), 0.1023 (all data), *wR*₂ 0.0931, *GoF* 1.042, final Δ*e* + 0.301. Refined coordinates are in Table 1, and selected bond parameters in Table 5.

2.4.2. Crystal data for the *Cc* form of cyclomanganated $\text{Ph}_3\text{P}=\text{NPh}$, **5a**

$\text{C}_{28}\text{H}_{19}\text{MnNO}_4\text{P}$, *M_r* 519.35, monoclinic, *Cc*, *a* = 16.3218(5), *b* = 16.5622(5), *c* = 9.1942(1) Å, β = 97.3780(1), *V* = 2464.8(1) Å³, *D*_{calc} = 1.400 g cm^{−3}, *Z* = 4, *F*(000) = 1064, μ(Mo–K_α) 0.635 mm^{−1}, *T*_{max} 1.162, *T*_{min} 0.729, crystal size 0.2 × 0.2 × 0.2 mm³, *T* 203 K.

A total of 7059 reflections, 5350 unique (*R*_{int} 0.0471) was collected 2° < θ < 26°. Final *R*₁ 0.0596 (3753 data with *I* = 2σ(*I*)), 0.0806 (all data), *wR*₂ 0.1061, *GoF* 1.221, final Δ*e* + 0.324. The penultimate refinement cycles suggested racemic twinning, which was included in the final refinement leading to a Flack *x* parameter of 0.225(35) [17]. Refined coordinates are in Table 2, and selected bond parameters in Table 5.

2.4.3. Crystal data for orthomanganated $\text{Ph}_3\text{As}=\text{O}$, **6a**

$\text{C}_{22}\text{H}_{14}\text{AsMnO}_5$, *M_r* 488.19, monoclinic, *P2₁/n*, *a* = 11.307(1), *b* = 14.460(2), *c* = 13.564(2) Å, β = 110.23(1), *V* = 2080.9(5) Å³, *D*_{calc} = 1.558 g cm^{−3}, *Z* = 4, *F*(000) = 976, μ(Mo–K_α) 2.242 mm^{−1}, *T*_{max} 0.823, *T*_{min} 0.743, crystal size 0.88 × 0.72 × 0.64 mm³, *T* 169 K.

A total of 3712 reflections, 3636 unique (*R*_{int} 0.0252) was collected 2° < θ < 25°. Final *R*₁ 0.0283 (2670 data with *I* = 2σ(*I*)), 0.0446 (all data), *wR*₂ 0.0532, *GoF* 1.015, final Δ*e* − 0.297. Refined coordinates are in Table 3, and selected bond parameters are in the caption to Fig. 2.

2.4.4. Crystal data for (μ-η¹,η⁶-C₆H₅CH₂)(μ-AsPh₂)-Mn₂(CO)₆, **7**

$\text{C}_{25}\text{H}_{17}\text{AsMn}_2\text{O}_6$, *M_r* 598.19, monoclinic, *P2₁/n*, *a* =

Table 3

Refined parameters for the structure of orthomanganated $\text{Ph}_3\text{As}=\text{O}$, **6a**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
As(1)	0.1857(1)	0.3462(1)	0.3732(1)	0.024(1)
Mn(1)	0.0070(1)	0.1845(1)	0.3976(1)	0.028(1)
C(1)	0.1510(3)	0.1349(2)	0.4936(3)	0.036(1)
O(1)	0.2376(2)	0.1073(2)	0.5574(2)	0.062(1)
C(2)	−0.0195(3)	0.0875(2)	0.3048(3)	0.039(1)
O(3)	−0.1434(2)	0.0957(2)	0.5081(2)	0.069(1)
C(3)	−0.0851(3)	0.1303(2)	0.4637(3)	0.044(1)
O(2)	−0.0359(2)	0.0256(2)	0.2500(2)	0.065(1)
C(4)	−0.1314(3)	0.2531(2)	0.3182(2)	0.034(1)
O(4)	−0.2153(2)	0.2975(2)	0.2721(2)	0.056(1)
O(11)	0.1089(2)	0.2498(1)	0.3156(1)	0.027(1)
C(11)	0.1305(2)	0.3664(2)	0.4876(2)	0.025(1)
C(12)	0.0510(3)	0.2967(2)	0.4999(2)	0.027(1)
C(13)	0.0119(3)	0.3091(2)	0.5865(2)	0.034(1)
C(14)	0.0489(3)	0.3837(2)	0.6528(3)	0.042(1)
C(15)	0.1262(3)	0.4510(2)	0.6370(3)	0.042(1)
C(16)	0.1683(3)	0.4423(2)	0.5539(2)	0.034(1)
C(21)	0.3646(2)	0.3300(2)	0.4211(2)	0.027(1)
C(22)	0.4300(3)	0.3100(2)	0.5255(2)	0.033(1)
C(23)	0.5580(3)	0.2954(2)	0.5584(3)	0.046(1)
C(24)	0.6209(3)	0.3022(2)	0.4882(3)	0.052(1)
C(25)	0.5569(3)	0.3222(2)	0.3849(3)	0.053(1)
C(26)	0.4289(3)	0.3366(2)	0.3506(2)	0.037(1)
C(31)	0.1455(3)	0.4440(2)	0.2725(2)	0.023(1)
C(32)	0.0297(3)	0.4417(2)	0.1926(2)	0.026(1)
C(33)	−0.0043(3)	0.5133(2)	0.1208(2)	0.031(1)
C(34)	0.0788(3)	0.5844(2)	0.1274(2)	0.034(1)
C(35)	0.1945(3)	0.5866(2)	0.2070(2)	0.035(1)
C(36)	0.2285(3)	0.5163(2)	0.2802(2)	0.032(1)

Table 4

Refined parameters for the structure of $(\mu\text{-}\eta^1, \eta^6\text{-C}_6\text{H}_5\text{CH}_2)(\mu\text{-AsPh}_2)\text{Mn}_2(\text{CO})_6$, **7**

Atom	x	y	z	U_{eq}
As(1)	0.2608(1)	0.1299(1)	0.6648(1)	0.021(1)
Mn(1)	0.3436(1)	0.0291(1)	0.7809(1)	0.026(1)
Mn(2)	0.3768(1)	0.2396(1)	0.6846(1)	0.023(1)
C(31)	0.2404(1)	0.0993(1)	0.5046(1)	0.026(1)
C(32)	0.1643(2)	0.0408(1)	0.4803(2)	0.036(1)
C(33)	0.1528(2)	0.0139(1)	0.3700(2)	0.044(1)
C(34)	0.2171(2)	0.0451(1)	0.2831(2)	0.042(1)
C(35)	0.2916(2)	0.1038(1)	0.3048(2)	0.039(1)
C(36)	0.3033(2)	0.1309(1)	0.4162(1)	0.031(1)
C(41)	0.0915(1)	0.1496(1)	0.6954(1)	0.026(1)
C(42)	0.0393(2)	0.1295(1)	0.7977(2)	0.033(1)
C(43)	-0.0795(2)	0.1467(1)	0.8194(2)	0.043(1)
C(44)	-0.1467(2)	0.1850(1)	0.7399(2)	0.059(1)
C(45)	-0.0962(2)	0.2050(1)	0.6379(2)	0.054(1)
C(46)	0.0225(2)	0.1872(1)	0.6156(2)	0.041(1)
C(11)	0.2014(2)	-0.0179(1)	0.7825(2)	0.038(1)
C(12)	0.3873(2)	-0.0158(1)	0.6474(2)	0.035(1)
C(13)	0.4182(2)	-0.0418(1)	0.8631(2)	0.039(1)
C(14)	0.3126(2)	0.0859(1)	0.9073(2)	0.036(1)
O(11)	0.1122(1)	-0.0488(1)	0.7832(2)	0.065(1)
O(12)	0.4155(2)	-0.0447(1)	0.5662(1)	0.060(1)
O(13)	0.4677(1)	-0.0865(1)	0.9127(1)	0.061(1)
O(14)	0.2928(1)	0.1219(1)	0.9842(1)	0.056(1)
C(21)	0.2860(2)	0.2826(1)	0.5775(2)	0.031(1)
C(22)	0.2720(2)	0.2724(1)	0.7875(2)	0.033(1)
O(21)	0.2258(1)	0.3116(1)	0.5109(1)	0.048(1)
O(22)	0.2061(1)	0.2953(1)	0.8528(1)	0.054(1)
C(1)	0.5180(2)	0.0835(1)	0.7792(2)	0.034(1)
C(2)	0.5212(1)	0.1602(1)	0.7402(1)	0.027(1)
C(3)	0.5290(1)	0.1772(1)	0.6216(1)	0.030(1)
C(4)	0.5380(1)	0.2494(1)	0.5834(2)	0.034(1)
C(5)	0.5329(2)	0.3079(1)	0.6615(2)	0.036(1)
C(6)	0.5191(2)	0.2926(1)	0.7773(2)	0.036(1)
C(7)	0.5143(1)	0.2194(1)	0.8163(2)	0.031(1)

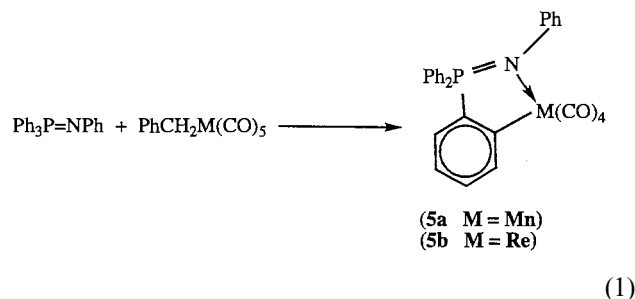
11.1750(3), $b = 18.3067(4)$, $c = 11.7205(3)$ Å, $\beta = 90.737(1)$, $V = 2397.6(1)$ Å³, $D_{\text{calc}} = 1.657$ g cm⁻³, $Z = 4$, $F(000) = 1192$, $\mu(\text{Mo-K}\alpha) 2.461$ mm⁻¹, $T_{\text{max}} 0.638$, $T_{\text{min}} 0.458$, crystal size $0.42 \times 0.40 \times 0.32$ mm³, $T 203$ K.

A total of 14266 reflections, 5509 unique ($R_{\text{int}} 0.0181$) was collected $2^\circ < \theta < 28^\circ$. Final $R_1 0.0208$ (4852 data with $I = 2\sigma(I)$), 0.0243 (all data), $wR_2 0.0530$, $GoF 1.062$, final $\Delta e +0.32$. Refined coordinates are in Table 4, and selected bond parameters are in the caption to Fig. 3.

3. Results and discussion

3.1. Cyclomanganation of $\text{Ph}_3\text{P=NPh}$

Cyclometallation of $\text{Ph}_3\text{P=NPh}$ proceeded smoothly in refluxing heptane, according to Eq. (1):



The new complex **5a** does not survive chromatography on silica but it could be readily purified by crystallisation, giving reasonably air-stable yellow crystals. As far as we are aware, this is the first example of a orthometallated iminophosphorane, giving a novel metal-cyclic ring. The closest analogue appears to be a cyclic zirconium phosphazene [18] involving a non-aromatic ligand.

Surprisingly, compound **5a** is thermochromic in solution. When heptane or toluene solutions are heated to 100°C the normal golden-yellow colour of cyclomanganated compounds is replaced abruptly by an intense purple colour. This is reproducible on carefully purified samples, and the colour change can be cycled through several times by simply heating and cooling over the range 90–100°C. No colour change is found in the solid state, samples remaining yellow up to the decomposition temperature of about 140°C. This behaviour is unprecedented in manganese chemistry. Thermochromicity in other systems is often associated with major changes in geometry but this does not seem likely for this example as the crystal structures discussed below show nothing unusual. Possibly there is a thermally-accessible electronically excited state giving rise to the colour change, but no confirmation of this could be obtained.

The corresponding rhenium analogue **5b** could be made readily though higher temperatures were needed for the cyclometallation reaction. This compound was the expected pale-yellow and showed no signs of thermochromism.

The infrared spectra of compounds **5** in the carbonyl region gave the expected pattern for a *cis*-LL'M(CO)₄ group. The positions of the peaks for the manganese example **5a** correspond most closely to the Se compound in the series of orthomanganated $\text{Ph}_3\text{P=X}$ (X=O, S, Se), rather than the X=O example which might have been expected on electronegativity grounds [10]. The Raman spectrum of **5a** in the solid state gave doubled peaks corresponding to those in the IR spectrum. The explanation for this lies in the polymorphism of the compound (see below), with the two different crystal forms giving slightly shifted bands.

There is some inconsistency in the literature concerning the P=N stretching frequency in $\text{Ph}_3\text{P=NPh}$, having been assigned to both the 1160–1180 and the 1325

1385 cm^{-1} regions [19]. Only IR spectra appear to have been used previously. We find that in both the IR and Raman spectra of $\text{Ph}_3\text{P}=\text{NPh}$ there is a strong peak at 1346 cm^{-1} and a weaker peak at 1171 cm^{-1} . In the orthomanganated complex the 1346 cm^{-1} peak has disappeared, to be replaced by one at 1257 cm^{-1} , so these are assigned to the $\text{P}=\text{N}$ stretches in the free and complexed ligand respectively. The decrease of 89 cm^{-1} on coordination parallels the changes in the $\text{P}=\text{X}$ frequencies of $\text{Ph}_3\text{P}=\text{X}$ on cyclomanganation [10].

The ^{31}P resonance of free $\text{Ph}_3\text{P}=\text{NPh}$ is at δ 3.5, and this moves to δ 44.3 and 50.6 in the manganated and rheniated derivatives respectively. Usually incorporation of phosphorus into a five-membered chelate ring causes a shift in the ^{31}P resonance of 21–33 ppm [20], so the shifts observed here are unusually large and are significantly more than the corresponding changes for $\text{Ph}_3\text{P}=\text{X}$ ($\text{X}=\text{O}$, S, Se) [10].

X-ray crystallography was used to fully characterise the new metalcyclic ring in **5a**. Batches of crystals from heptane consistently gave two types of crystals. Both crystal structures were determined and were shown to be polymorphs. The well-shaped parallelepipeds were assigned to the space group Cc , while the irregularly shaped ones were $C2/c$ with two independent molecules in the asymmetric unit. Therefore the individual bond parameters were determined for three independent molecules in all. However differences between the molecules is confined to conformational changes involving the free phenyl groups, so the following discussion is based on average values.

A molecule of orthomanganated $\text{Ph}_3\text{P}=\text{NPh}$ is illustrated in Fig. 1, and Table 5 compares selected bond parameters for the crystallographically independent

Table 5

Selected bond parameters for the three crystallographically independent molecules of orthomanganated $\text{Ph}_3\text{P}=\text{NPh}$, and for the free ligand

Parameter	$C2/c$ form	$C2/c$ form	Cc form	Free ligand [20]
	(molecule 1)	(molecule 2)		
<i>Bond lengths</i> (Å)				
Mn–N(1)	2.110(3)	2.101(3)	2.105(4)	–
Mn–C(46)	2.069(4)	2.080(5)	2.068(5)	–
P=N	1.603(3)	1.597(4)	1.594(4)	1.602(3)
P–C(41)	1.781(4)	1.784(4)	1.793(6)	1.808(3)
N–C(11)	1.438(5)	1.435(5)	1.426(6)	1.330(5)
Mn–C(1)	1.826(5)	1.860(5)	1.857(8)	–
Mn–C(2)	1.834(5)	1.832(5)	1.825(7)	–
Mn–C(3)	1.775(5)	1.794(5)	1.786(6)	–
Mn–C(4)	1.852(5)	1.843(5)	1.849(7)	–
<i>Bond angles</i> (°)				
Mn–N–P	117.2(2)	118.5(2)	117.9(2)	–
N–P–C(41)	103.5(2)	103.5(2)	103.2(3)	115.3(2)
C(1)–Mn–C(4)	166.1(2)	170.9(2)	171.6(3)	–
N–Mn–C(46)	84.0(2)	83.2(2)	83.4(2)	–
P–N–C(11)	120.5(3)	121.1(2)	119.8(3)	130.4(3)

molecules with the equivalent ones for the free ligand [21]. The molecule consists of a $\text{Mn}(\text{CO})_4$ fragment coordinated to the ligand via the expected Mn–N and Mn–C bonds, with a bite angle at the Mn of 83.5°. This generates a five-membered metalcycle containing four different atom types, and incorporates a $\text{P}=\text{N}$ bond. The metalcyclic ring is essentially planar in all three independent molecules to within 0.08 Å. The phenyl ring attached to the Mn is almost coplanar with the metalcycle, with a maximum dihedral angle of 4.3° for one of the molecules in the $C2/c$ form. The *N*-phenyl ring is twisted away from coplanarity with the metalcyclic ring by 89, 83 and 76° for the three cases, in contrast to the free ligand where the corresponding angle is 11°. This presumably arises from steric interactions with the CO ligands on Mn, and results in a lengthening of the $\text{N}-\text{C}_{\text{phenyl}}$ distance from 1.330(5) Å in the parent [21] to an average value of 1.433 Å in the complexes as π -delocalisation with the $\text{P}=\text{N}$ group is prevented. At the same time the $\text{P}-\text{N}-\text{C}$ angle decreases from 130 to 120°. Surprisingly the $\text{P}=\text{N}$ bond length has not altered observably between the free and complexed ligand, despite the drop in bond order suggested by the change in the IR stretching frequency. In the structures of orthomanganated $\text{Ph}_3\text{P}=\text{X}$ ($\text{X}=\text{S}$, Se) there were significant changes [10]. In **5a** the expected lengthening of the $\text{P}=\text{N}$ bond on coordination is presumably compensated for by the twisting of the phenyl group out of plane; it is the $\text{N}-\text{C}$ bond rather than the $\text{P}=\text{N}$ bond that changes.

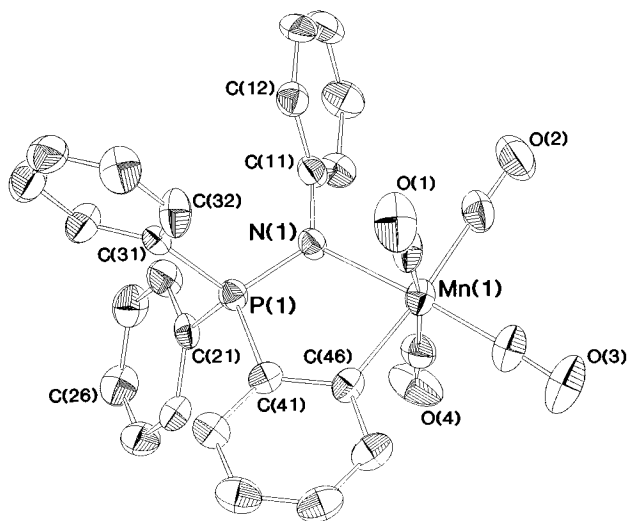
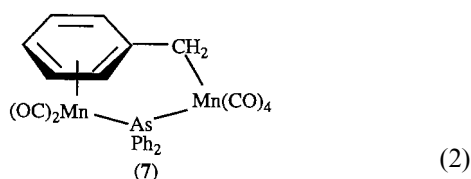
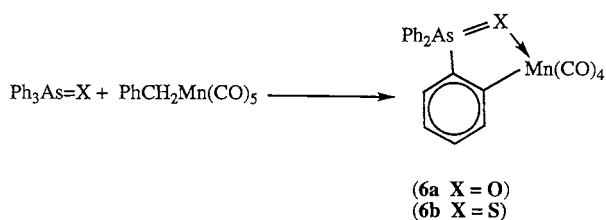


Fig. 1. The structure of one of the independent molecules of orthomanganated $\text{Ph}_3\text{P}=\text{NPh}$, **5a**. The other molecules differ mainly in the conformation of the free phenyl rings. The numbering scheme is such that C(41), C(141), C(241), for example, refer to the same atom in the Cc form, and molecules 1 and 2 of the $C2/c$ form, respectively.

The Mn–N distance of 2.105 Å is marginally longer than in an orthomanganated organic imine (2.070 Å) [22] or arylhydrazone (2.053 Å) [23]. The Mn–CO bond *trans* to the N atom is significantly shorter than that *trans* to the metallated C atom, which in turn is shorter than the two Mn–CO bonds *trans* to each other, following the established pattern [1].

3.2. Cyclomanganation of $\text{Ph}_3\text{As}=\text{O}$ and $\text{Ph}_3\text{As}=\text{S}$

Reaction of $\text{Ph}_3\text{As}=\text{X}$ with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ in refluxing heptane (the usual conditions for cyclomanganation) gave extensive decomposition and formed only low yields of the expected products. However, under milder conditions (refluxing hexane) the orthomanganated species **6** were formed in moderate yields Eq. 2.



The new complexes were identified readily by IR, NMR and ESMS spectra, which matched those of the corresponding phosphorus analogues [10].

The low yield of the oxide derivative was similar to that for the equivalent $\text{Ph}_3\text{P}=\text{O}$ system, and can be attributed to combining the hard O-donor with the soft acceptor Mn(I), and possibly to the need for an acute angle at O when the metallocyclic ring is formed (see below).

For the sulfide the low yield can be attributed to decomposition of the arsenic sulfide, since appreciable quantities of *cis*- $\text{PhCH}_2\text{Mn}(\text{CO})_4(\text{AsPPh}_3)$ were also formed. $\text{Ph}_3\text{As}=\text{S}$ is known to be relatively unstable (the corresponding selenide cannot be isolated) and in situ formation of Ph_3As provides an alternative ligand for attack at the manganese atom. In this respect the reaction is similar to that of $\text{Ph}_3\text{P}=\text{Se}$, where by-products incorporating Ph_3P and Se separately were found [10].

These are the first examples of cyclometallation reactions involving arsenic chalcogenides so a structure determination of the oxide was carried out. The molecule is illustrated in Fig. 2, and shows the expected planar $\overline{\text{MnOAsC}_2}$ metallocyclic ring, with a C–Mn–O chelating angle of 87°, close to the ideal for octahedral manganese. The As=O distance has increased by 0.04 Å

on coordination, while the Mn–O and Mn–C_{aryl} bond lengths are similar to those in other orthomanganated O-donors. The only other parameter worth commenting on is the As–O–Mn angle of 114.8°. In $\eta^1\text{-R}_3\text{As}=\text{O}$ complexes the As–O–M angles average 135° [24], so this presumably is the naturally preferred arrangement. However formation of the metallocyclic ring of **6a** requires the more acute angle at the O atom and this presumably introduces some strain. The parallel situation was discussed in more detail for the analogous phosphorus compounds, where similar observations hold [10].

3.3. Attempted cyclometallation of Ph_3As

As mentioned in the introduction Kaez's group successfully characterised orthomanganated PPh_3 , compound **2**, with a four-membered ring [7]. We attempted the parallel reaction of $\text{PhCH}_2\text{Mn}(\text{CO})_5$ with AsPh_3 . This proved to be a complicated system, giving rise to many products in low yields, none of which appeared to correspond to the arsenic analogue of **2**. Presumably the larger size of As compared to P discourages the formation of a small ring. The only species identified were $\text{PhCH}_2\text{Mn}(\text{CO})_4(\text{AsPh}_3)$ (the expected first-formed compound), cyclomanganated $\text{Ph}_3\text{As}=\text{O}$ (arising from in situ oxidation of Ph_3As) and a red complex which was shown by an X-ray structure determination to be a dimanganese complex **7** with a bridging AsPh_2 ligand and a bridging, η^1 , η^6 -benzyl group. The structure is shown in Fig. 3.

The coordination around Mn(1) is equivalent to that in a molecule such as *cis*- $\text{PhCH}_2\text{Mn}(\text{CO})_4(\text{AsPh}_3)$, while that around Mn(2) is related to (η^6 -

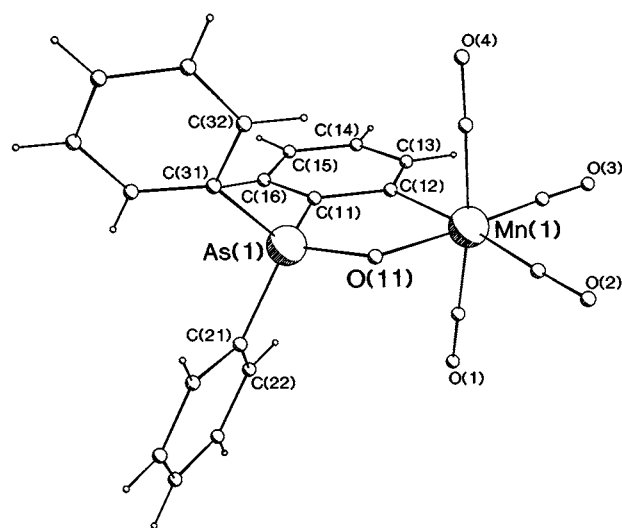


Fig. 2. The structure of orthomanganated $\text{Ph}_3\text{As}=\text{O}$, **6a**. Selected bond lengths (Å): As(1)–O(11) 1.684(2), Mn(1)–O(11) 2.084(2), Mn(1)–C(12) 2.080(3), As(1)–C(11) 1.884(3), Mn(1)–C(1) 1.842(3), Mn(1)–C(2) 1.839(3), Mn(1)–C(3) 1.774(3), Mn(1)–C(4) 1.851(3); bond angles: O(11)–Mn(1)–C(12) 87.34(9)°, As(1)–O(11)–Mn(1) 114.8(1)°, C(11)–As(1)–O(11) 104.3(1)°.

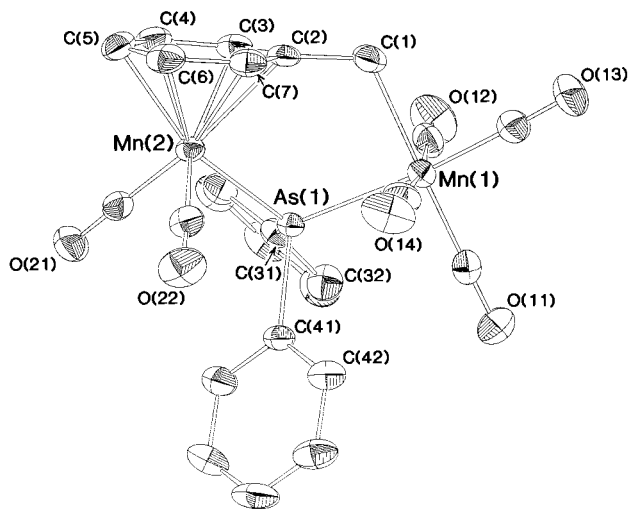


Fig. 3. The molecular structure of $(\mu\text{-}\eta^1, \eta^6\text{-C}_6\text{H}_5\text{CH}_2)(\mu\text{-AsPh}_2)\text{Mn}_2(\text{CO})_6$, **7**. Selected bond lengths (Å): Mn(1)–As(1) 2.465(1), Mn(2)–As(1) 2.400(1), Mn(1)–C(1) 2.189(2), As(1)–C(31) 1.970(2), As(1)–C(41) 1.964(2), Mn(1)–CO(av.) 1.826(2), Mn(2)–CO(av.) 1.790(2); bond angles: Mn(1)–As(1)–Mn(2) 112.00(1)°, C(31)–As(1)–C(41) 97.27(7)°, Mn(1)–C(1)–C(2) 117.4(1)°.

$\text{C}_6\text{H}_6\text{Mn}(\text{CO})_2(\text{SPh})$, for example [25]. Electron counting suggests that the bridging AsPh_2 ligand is acting as a two-electron donor to Mn(1) and a one-electron donor to Mn(2); this is not obvious from the As–Mn bond lengths (As(1)–Mn(1) 2.465 Å, As(1)–Mn(2) 2.400 Å) but any effects will be masked by the electronic differences at the two Mn centres. This is indicated by the average Mn–CO distances of 1.826 and 1.790 Å for Mn(1) and Mn(2), respectively. The Mn–C(1)–C(2) angle of 117° and the Mn(1)–As(1)–Mn(2) angle of 112° shows the molecule fits together with little strain, though the C–As–C angle of 97.27° is noticeably acute. Although this doubly bridged arrangement appears to be unique the individual parts have parallels in the literature. Ph_2P is a common bridging ligand in manganese chemistry so Ph_2As is acting in the same way, and there are examples of benzyl acting as an η^6 -ligand to $\text{Cr}(\text{CO})_3$, and binding η^1 to another metal [26]. A more complicated example of a η^1, η^6 -benzyl ligand on a Ru_8 cluster is also established [27].

How compound **7** forms in the reaction mixture is obscure, though clearly As–C bond cleavage is involved and presumably takes place more readily than corresponding cleavage of P–C bonds.

Pyrolysis of pre-formed $\text{cis-PhCH}_2\text{Mn}(\text{CO})_4(\text{AsPh}_3)$ was attempted in the hope of a more specific reaction, but again many compounds formed in small yields so the system was not further investigated.

4. Conclusions

Several substrates have formed cyclometallated rings for the first time. $\text{Ph}_3\text{P}=\text{NPh}$ is a good substrate for

cyclomanganation reactions and presumably will form corresponding species with other metallating agents, such as Pd(II). The product **5** is stable showing that the P=N bond can be accommodated readily in a metal-cyclic ring.

The triphenylarsine oxide and sulfide do form cyclomanganated complexes analogous to those of triphenyl phosphine, but the yields are rather low. However once formed they show appreciable stability.

Cyclometallation of Ph_3As with manganese is less favourable than for Ph_3P , presumably because of the larger size of As and because the weaker As–C bond allows alternative reaction paths.

5. Supplementary material

Crystallographic data for structural analysis has been deposited with the Cambridge Crystallographic Data Centre, for compounds **5a**, **6a** and **7**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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