Photochemical Reaction of $(PhO)_2P(OC_6H_4)Mn(CO)_4$ with Ph_2C_2; Definitive Characterisation of an Insertion Product with a Seven-Membered Metallocyclic Ring

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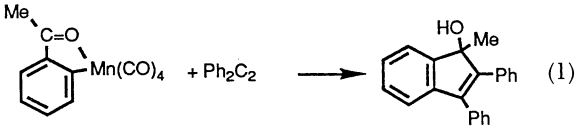
Synopsis. The main isolated product from the photochemical reaction of $(PhO)_2P(OC_6H_4)Mn(CO)_4$ with Ph_2C_2 (previously characterised as a η^2-acetylene adduct) is shown by an X-ray crystal structure analysis to be $(PhO)_2P(OC_6H_4)C(Ph)=C(Ph)Mn(CO)_4$, formed by insertion of the alkyne into the Mn-C bond. [Crystals are tetragonal, space group $I4_1/a$, a=30.813(6) Å, c=12.647(5) Å, V=12007(6) Å^3, Z=16, R=0.0793 for 1589 reflections with $I>3\sigma(I)$].

The reactions of alkynes with organo-transition metal complexes provide many useful syntheses.[1] We[2] and others[3] have recently shown that alkynes react with orthomanganated aryl ketones and related species to form products with fused five-membered rings, e.g. Eq. 1:



(1)

The mechanism of this reaction is not known, but a reasonable sequence of steps can be proposed.[2] The first of these involves displacement of a CO ligand to give a η^2-alkyne complex, which subsequently undergoes an alkyne insertion reaction into the Mn-C bond. No direct evidence for these intermediates could be found in our orthomanganated ketone study, so it was of interest that we noted the report by Onaka et al.,[4] which described the product of the photochemical reaction of Ph_2C_2 with the related orthomanganated triphenyl phosphite $(PhO)_2P(OC_6H_4)Mn(CO)_4$, **1**, as the adduct **2**. However the spectroscopic characterization of **2** did not seem to be completely unambiguous so we have examined the system in more detail and now report that the product of the reaction is, in fact, the novel, seven-membered metallocycle **3**.

Experimental

Photolysis was performed under a nitrogen atmosphere using a Hanovia 125 W medium-pressure mercury lamp. Infrared spectra were recorded on a Digilab FTS-45 FTIR and NMR spectra on a JEOL FX-90Q instrument.

Synthesis of $(PhO)_2P(OC_6H_4)C(Ph)=C(Ph)Mn(CO)_4$ (3). A mixture of **1**[5] (1.10 g, 2.30 mmol) and Ph_2C_2 (0.42 g, 2.30 mmol) was irradiated in benzene (50 ml) for 14 h. The solvent was evaporated and the residue was chromatographed on silica plates, eluting with petroleum ether. The third band was removed from the plate and recrystallized from cyclohexane-petroleum ether to give white crystals of **3**. A CO-region infrared spectrum in hexane solution showed four bands at 2080s, 2011s, 1995vs, 1973m cm^{-1} (c.f. Onaka et al.,[4] 2080vs, 1995vs, 1961s as a Nujol mull). ^{13}C and ^{31}P NMR spectra of **3** were indistinguishable from those published by Onaka et al.[4] The compound was unambiguously identified by an X-ray structure analysis.

X-Ray Crystallography. White needle-shaped crystals were obtained from cyclohexane-petroleum ether. Preliminary precession photography showed $4/m$ Laue symmetry, with systematic absences consistent with space group $I4_1/a$. Accurate cell dimensions and intensity data were recorded on a Nicolet $P3$ automatic diffractometer using monochromated Mo $K\alpha$ X-rays (0.7107 Å).

Crystal data: $C_{36}H_{24}O_7MnP$, M_r=654.5, tetragonal, space group $I4_1/a$, a=30.813(6) Å, c=12.647(5) Å, V=12007(6) Å^3. D_c=1.42 g cm^{-3} for Z=16. $F(000)$=5376, μ(Mo $K\alpha$)=5.6 cm^{-1}, T=−110 °C, crystal size 0.60×0.12×0.12 mm.

A total of 3923 diffraction intensities were collected using Wyckoff scans in the range $4°<2\theta<45°$. These were corrected for Lorentz, polarization, and absorption effects. The 1589 reflections for which $I>3\sigma(I)$ were used in all calculations.

The structure was solved by direct methods and developed and refined routinely. In the final cycles of full-matrix least-squares refinement the Mn and P atoms were treated anisotropically, other non-hydrogen atoms isotropically, and hydrogen atoms were included in their calculated positions with isotropic temperature factors. The four monosubstituted phenyl rings were included as rigid hexagons, but the phenyl group incorporated in the metallocyclic ring was refined without constraints. Refinement converged at R=0.0793, R_w=0.0845, where $w=[\sigma^2(F)+0.00694F^2]^{-1}$. No parameter showed final shifts $>0.1\sigma$, and a final difference map showed no features greater than ±0.6 e Å^{-3}. Positional parameters are given in Table 1 and selected bond lengths and angles are included in the caption to Fig. 1, which shows the geometry of the complex. Calculations used SHELXS-86 and SHELX-76 programs.[6]

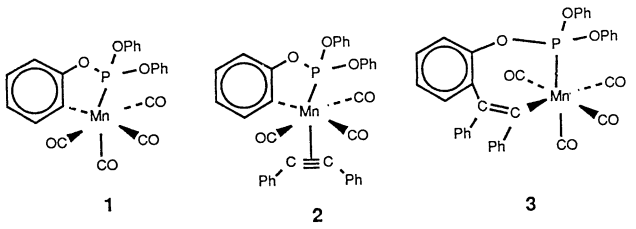
Discussion

The reaction between $(PhO)_2P(OC_6H_4)Mn(CO)_4$ (**1**) and diphenylacetylene in benzene under UV photolysis proceeds exactly as described by Onaka et al.[4] Pure **3** was obtained by chromatography, together with unreacted starting materials. That our product **3** was the same as that previously assigned structure **2** was shown by the IR, ^{13}C and ^{31}P NMR spectra, and by the relationship between the triclinic unit cell found in the earlier study[4] and that described herein.[7] The formulation as **3** was proved by a structure determination.

The geometry of the complex is shown in Fig. 1. It is a tetracarbonylmanganese derivative, with the manganese further bonded to the P atom of the phosphite ligand and to a carbon atom of the inserted acetylene group which forms a bridge to the ortho-carbon of the phenyl group originally attached to the manganese. The insertion of the alkyne has increased the metallo-

Table 1. Final Positional Parameters for $(PhO)_2\overline{POC_6H_4C(Ph)C(Ph)}Mn(CO)_4$

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
Mn(1)	0.8778(1)	0.6907(1)	0.0281(2)	1.6	C(23)	0.7462(3)	0.5745(3)	−0.2830(7)	2.8(4)
P(1)	0.8487(1)	0.6683(1)	−0.1211(4)	1.7	C(24)	0.7705(3)	0.5569(3)	−0.3655(7)	3.0(4)
O(1)	0.8804(3)	0.6642(4)	−0.2227(9)	2.2(2)	C(25)	0.8157(3)	0.5605(3)	−0.3647(7)	2.4(3)
O(2)	0.8322(3)	0.6195(3)	−0.1159(9)	2.1(2)	C(26)	0.8364(3)	0.5818(3)	−0.2815(7)	2.5(4)
O(3)	0.8072(3)	0.6937(3)	−0.1676(9)	1.8(2)	C(31)	0.7930(6)	0.7341(6)	−0.126(1)	2.3(3)
O(6)	0.9099(5)	0.7176(4)	0.239(1)	4.1(3)	C(32)	0.7769(5)	0.7380(5)	−0.028(1)	1.8(3)
O(7)	0.8658(4)	0.7859(4)	−0.0052(9)	2.6(2)	C(33)	0.7597(5)	0.7791(5)	0.002(1)	1.6(3)
O(8)	0.9641(5)	0.6984(4)	−0.071(1)	4.0(3)	C(34)	0.7616(5)	0.8146(6)	−0.068(1)	1.9(3)
O(9)	0.8978(4)	0.5983(4)	0.076(1)	3.5(3)	C(35)	0.7801(6)	0.8093(6)	−0.171(2)	2.4(4)
C(4)	0.7772(5)	0.7020(5)	0.052(1)	1.7(3)	C(36)	0.7939(5)	0.7686(5)	−0.198(1)	2.1(3)
C(5)	0.8130(5)	0.6822(5)	0.081(1)	0.9(3)	C(41)	0.7324(3)	0.6945(4)	0.1024(8)	1.7(3)
C(6)	0.8967(6)	0.7081(6)	0.161(2)	2.6(4)	C(42)	0.7259(3)	0.6997(4)	0.2108(8)	2.9(4)
C(7)	0.8673(5)	0.7482(5)	0.004(1)	2.1(3)	C(43)	0.6851(3)	0.6917(4)	0.2546(8)	3.5(4)
C(8)	0.9306(6)	0.6953(6)	−0.030(2)	2.9(4)	C(44)	0.6509(3)	0.6785(4)	0.1900(8)	3.0(4)
C(9)	0.8907(5)	0.6327(6)	0.061(1)	2.2(4)	C(45)	0.6574(3)	0.6734(4)	0.0816(8)	2.4(4)
C(11)	0.8853(3)	0.6894(3)	−0.3101(7)	1.5(3)	C(46)	0.6981(3)	0.6814(4)	0.0378(8)	2.1(3)
C(12)	0.9256(3)	0.7083(3)	−0.3289(7)	1.8(3)	C(51)	0.8081(4)	0.6460(3)	0.1644(8)	2.1(3)
C(13)	0.9327(3)	0.7317(3)	−0.4217(7)	3.6(4)	C(52)	0.8203(4)	0.6535(3)	0.2690(8)	2.3(3)
C(14)	0.8995(3)	0.7361(3)	−0.4958(7)	3.5(4)	C(53)	0.8165(4)	0.6204(3)	0.3437(8)	3.2(4)
C(15)	0.8591(3)	0.7171(3)	−0.4770(7)	3.3(4)	C(54)	0.8006(4)	0.5798(3)	0.3138(8)	3.6(4)
C(16)	0.8520(3)	0.6938(3)	−0.3841(7)	2.8(4)	C(55)	0.7885(4)	0.5724(3)	0.2091(8)	3.5(4)
C(21)	0.8121(3)	0.5994(3)	−0.1990(7)	2.1(3)	C(56)	0.7922(4)	0.6055(3)	0.1344(8)	2.3(4)
C(22)	0.7669(3)	0.5957(3)	−0.1997(7)	1.2(3)					



cyclic ring from five-membered in **1** (generally accepted as the most favorable size for cyclomanganated rings[8]) to seven-membered in **3**. Seven membered rings have been formed by insertion reactions of alkynes with orthocobaltated azobenzenes but these contain unsaturated bonds further coordinated to the cobalt atom.[9] With cyclopalladated complexes, reactions with Ph_2C_2 gave nine-membered rings by a double insertion process, with no mono-inserted species being detected. Only with alkynes containing electron-withdrawing CF_3 or COOMe groups were seven-membered rings corresponding to that observed for the manganese complex **3** found.[10]

The seven-membered ring of **3** has adopted a boat conformation which can be defined by three planes; (i) O(3)-C(31)-C(32)-C(4) (maximum deviation 0.03 Å), (ii) P-O(3)-C(4)-C(5) (maximum deviation 0.015 Å) and (iii) P-Mn-C(5). The dihedral angle between planes (i) and (ii) is 132°, while that between planes (ii) and (iii) is 135°. There is no indication of strain in the metallocyclic ring, with normal bond lengths and angles, except for the Mn-C(5)-C(4) angle of 130° which is probably deformed as a result of non-bonded interactions between adjacent phenyl groups on C(4) and C(5). The C(4)-C(5) bond at 1.31 (2) Å is a normal double bond, while the Mn-C(5) distance of 2.12 (1) Å is comparable with other Mn-C(sp^2) bonds.[5,11]

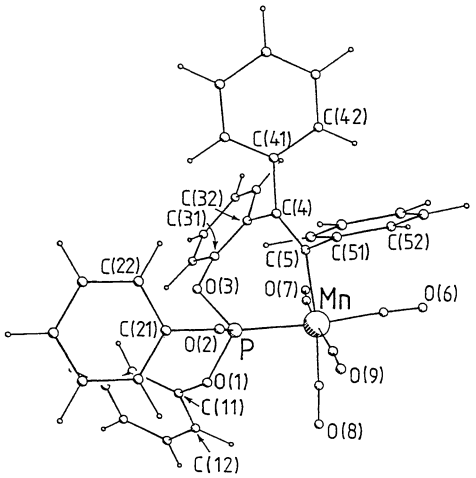


Fig. 1. A view of complex **3** showing the seven-membered ring. Selected bond parameters are: Bond lengths (Å) Mn-P 2.201(5), Mn-C(5) 2.12(1), C(5)-C(4) 1.31(2), C(4)-C(32) 1.50(2), P-O(1) 1.62(1), P-O(2) 1.59(1), P-O(3) 1.61(1), O(3)-C(31) 1.42(2), C(31)-C(32) 1.35(2). Bond angles(°) P-Mn-C(5) 81.8(6), Mn-C(5)-C(4) 130(1), C(5)-C(4)-C(32) 122(1), C(4)-(32)-C(31) 124(1), O(3)-C(31)-C(32) 122(1), Mn-P-O(3) 119.0(5).

With hindsight, the analytical and spectroscopic data reported by Onaka et al. can be equally well assigned to **3**. The four ν(CO) bands found for the complex in solution in the present study, in positions close to those found for other cyclomanganated species with a tetracarbonylmanganese unit,[11] provided the first clue to the reassignment; in the original study[4] only three bands were noted because the middle two bands were not resolved under the solid suspension conditions used. Similarly, the unusually low

^{31}P chemical shift found for **3** arises because of the relaxation of angular strain in the seven-membered ring compared with that in the more normal five-membered species, while the ^{13}C spectrum can not distinguish between structures **2** and **3**.

The full characterizaion of **3** lends support for the first two steps in the mechanism proposed for the reaction of orthomanganated ketones with alkynes.[2] For the ketones subsequent intramolecular addition to the C=O group in the analogue of **3** would lead to the observed products,[2] whereas for **3** the lack of reactive sites in the molecule after insertion allows the isolation of **3** as a stable complex.

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