Applied Organometallic Chemistry (1990) 4 503–506
0268-2605/90/050503-04$05.00

Orthomanganated arenes in synthesis VII. Transition-metal mediated formation of a P–P bond; the X-ray crystal structure of $Mn_2(\mu\text{-}\eta^1, \eta^1\text{-}Ph_2PPPh_2)(\mu\text{-}Cl)_2(CO)_6$*

Leslie J Arnold, Lyndsay Main and Brian K. Nicholson
School of Science, University of Waikato, Private Bag, Hamilton, New Zealand

Received 7 September 1989 Accepted 22 December 1989

The reaction of PPh_2Cl with orthomanganated acetophenone, $2'\text{-}CH_3C(O)C_6H_4Mn(CO)_4$, gives $Mn_2(\mu\text{-}\eta^1,\eta^1\text{-}Ph_2PPPh_2)(\mu\text{-}Cl)_2(CO)_6$. An X-ray structure determination [triclinic, space group $P\bar{1}$, $a=10.908(4)$ Å, $b=11.756(3)$ Å, $c=12.186(3)$ Å, $\alpha=96.20(2)°$, $\beta=99.51(2)°$, $\gamma=96.52(2)°$] shows two $Mn(CO)_3$ groups held together by two bridging Cl ligands, and further bridged by a $Ph_2P—PPh_2$ group prepared *in situ*.

Keywords: Orthomanganated, diphosphine, chloro-bridged, manganese, crystal and molecular structure

INTRODUCTION

We are currently exploring the use of orthomanganated arenes in synthesis.[1-3] A general synthesis of 2-acetylarylmercury chlorides has been developed[2] based on coupling reactions between the appropriate orthomanganated arene and mercury(II) chloride and we are examining the reactivity of other covalent Main-Group halides in similar reactions.

In this paper we show that reaction of orthomanganated acetophenone (1) with PPh_2Cl does not lead to formation of a P–C bond; instead unprecedented P–P formation is found.

Experimental

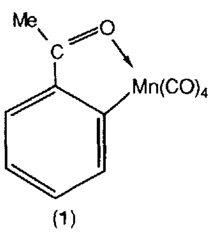
Reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Orthomanganated acetophenone was prepared as described previously.[4] Infrared spectra were recorded on a Digilab FTS60 spectrometer, electron-impact mass spectra on a Varian CH7, and FABS mass spectra on a VG ZAB SE instrument.

Preparation of *fac*-$(2'\text{-}MeC(O)C_6H_4)Mn(CO)_3(PPh_2Cl)$

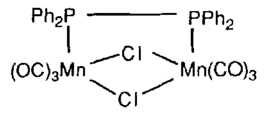
A solution of $2'\text{-}MeC(O)C_6H_4Mn(CO)_4$ (0.461 g, 1.61 mmol) and PPh_2Cl (0.307 g, 1.39 mmol) in petroleum spirits (40–60 °C fraction, 42 ml) was refluxed for 48 h. The solution was concentrated and cooled to give orange crystals identified spectroscopically as *fac*-$(2'\text{-}MeC(O)C_6H_4)Mn(CO)_3(PPh_2Cl)$ [ν(CO) 2016s, 1949s, 1910s cm^{-1}; FABS mass spectrum M^+ peak at 478, and other prominent peaks corresponding to $(M-CO)^+$, $(M-Cl)^+$, $(M-3CO)^+$, $(M-3CO-Cl)^+$].

Preparation of $Mn_2(\mu\text{-}\eta^1,\eta^1\text{-}Ph_2PPPh_2)(\mu\text{-}Cl)_2(CO)_6$ (2)

Further reflux of a solution of *fac*-$(2'\text{-}MeC(O)C_6H_4)Mn(CO)_3PPh_2Cl)$, prepared as above, for 6 days led to an orange solution. Removal of solvent and recrystallization of the residue from CH_2Cl_2/petroleum spirit, gave $Mn_2(\mu\text{-}\eta^1,\eta^1\text{-}Ph_2PPPh_2)(\mu\text{-}Cl)_2(CO)_6$, (0.136 g, 17 %). ν(CO) (hexane) 2058 s, 2042 m, 1996 s, 1969 m, 1934 m cm^{-1}. An electron-impact mass spectrum gave peaks at m/z 676, 592, 564, 535, 480 (base peak) which are assignable to $Mn_2(\mu\text{-}PPh_2)_2(CO)_7$ and breakdown fragments. The compound was characterized by X-ray crystallography.



(1)



(2)

---

* Supplementary material is deposited with the Cambridge Crystallographic Data Centre, UK.

X-ray Crystal Structure of $Mn_2(\mu\text{-}\eta^1, \eta^1\text{-}Ph_2PPPh_2)(\mu\text{-}Cl)_2(CO)_6$ (2)

An orange crystal of dimensions 0.26 mm × 0.16 mm × 0.08 mm was obtained from CH_2Cl_2/hexane. The space group was defined by precession photography and intensity data were collected on a Nicolet P3 diffractometer using monochromated Mo-Kα X-rays.

Crystal Data: $C_{30}H_{20}Cl_2Mn_2O_6P_2$, M 719.22, triclinic, space group $P\bar{1}$, $a = 10.908(4)$ Å, $b = 11.756(3)$ Å, $c = 12.186(3)$ Å, $\alpha = 96.20(2)°$, $\beta = 99.51(2)°$, $\gamma = 96.56(2)°$, $U = 1518.2(8)$ Å^3, $D_c = 1.57$ g cm^{-3}, $Z = 2$, $F(000) = 720$, μ(Mo-Kα) = 9.7 cm^{-1}, $T = -110$ °C.

A total of 3908 unique reflections were collected in the range $4° < 2\theta < 45°$. After correction for Lorentz, polarization and absorption (based on ϕ-scans) effects, 1502 data had $I > 3\sigma(I)$ and were used in all calculations. The structure was solved by direct methods (SHELXS-86)[5] and routinely developed. In the final cycles of least-squares refinement the manganese, phosphorus and chlorine atoms were assigned anisotropic temperature factors, while other atoms were modelled isotropically. Phenyl rings were included as rigid hexagons with hydrogen atoms in calculated positions. Refinement converged at $R = 0.0808$, $R_w = 0.0820$, where $w = [\sigma^2(F) + 0.00306F^2]^{-1}$. The largest final shift was $0.02\,\sigma$ and the largest feature in a final difference map was 0.9 e Å^{-3} near one of the chlorine atoms. Calculations were performed using SHELX-76.[5] Final positional parameters are given in Table 1, whilst selected bond lengths and angles are compared in Table 2 with those of the bromine and iodine analogues.

RESULTS AND DISCUSSION

The initial reaction between 2′-MeC(O)C_6H_4Mn$(CO)_4$ (**1**) and PPh_2Cl involves CO replacement to give *fac*-(2′-MeC(O)C_6H_4)Mn$(CO)_3$(PPh_2Cl) in essentially quantitative yield. This assignment is based on a FABS mass spectrum, and on the similarity of the ν(CO) pattern (2023 s, 1954 s, 1915 s cm^{-1}) to that of well-characterized species such as *fac*-2′-(MeC(O)C_6H_4)Mn$(CO)_3$(PPh_3) (2005 s, 1925 s, 1891 s cm^{-1})[6]; the shift of *ca* 20 cm^{-1} to higher frequencies is as expected when PPh_2Cl replaces PPh_3. Thermal reactions between cyclometallated ketones and phosphines are known to give direct substitution of a CO ligand rather than displacement of the coordinated oxygen atom.[6,7]

Prolonged reflux of this first-formed species gives an orange solution from which $Mn_2(\mu\text{-}\eta^1, \eta^1\text{-}Ph_2PPPh_2)(\mu\text{-}Cl)_2(CO)_6$ (**2**) was isolated as a

Table 1 Positional parameters for $Mn_2(\mu\text{-}\eta^1, \eta^1\text{-}Ph_2PPPh_2)Cl_2(CO)_6$

Atom	X	Y	Z	Atom	X	Y	Z
Mn(1)	0.2336(4)	0.1916(3)	0.9167(3)	Mn(2)	0.2384(4)	0.4465(3)	0.7874(3)
Cl(1)	0.3486(6)	0.3811(5)	0.9528(4)	Cl(2)	0.0959(5)	0.2720(5)	0.7755(4)
P(1)	0.3639(6)	0.1656(5)	0.7803(4)	P(2)	0.3506(6)	0.3270(5)	0.6850(5)
C(11)	0.327(2)	0.135(2)	1.025(2)	O(11)	0.388(2)	0.094(1)	1.100(1)
C(12)	0.144(2)	0.054(2)	0.878(2)	O(12)	0.091(2)	−0.040(1)	0.856(1)
C(13)	0.140(3)	0.230(2)	1.020(2)	O(13)	0.076(2)	0.255(1)	1.086(1)
C(21)	0.355(2)	0.569(2)	0.801(2)	O(21)	0.426(1)	0.654(1)	0.807(1)
C(22)	0.151(2)	0.501(2)	0.672(2)	O(22)	0.097(2)	0.549(1)	0.603(1)
C(23)	0.143(3)	0.522(2)	0.878(2)	O(23)	0.085(2)	0.564(1)	0.936(1)
C(101)	0.534(1)	0.166(1)	0.821(1)	C(102)	0.606(1)	0.143(1)	0.738(1)
C(103)	0.736(1)	0.148(1)	0.768(1)	C(104)	0.794(1)	0.175(1)	0.881(1)
C(105)	0.722(1)	0.197(1)	0.963(1)	C(106)	0.592(1)	0.193(1)	0.933(1)
C(111)	0.309(1)	0.033(1)	0.680(1)	C(112)	0.378(1)	−0.060(1)	0.684(1)
C(113)	0.332(1)	−0.163(1)	0.613(1)	C(114)	0.219(1)	−0.173(1)	0.538(1)
C(115)	0.150(1)	−0.079(1)	0.535(1)	C(116)	0.195(1)	0.024(1)	0.606(1)
C(201)	0.516(1)	0.389(1)	0.683(1)	C(202)	0.597(1)	0.425(1)	0.785(1)
C(203)	0.719(1)	0.474(1)	0.786(1)	C(204)	0.761(1)	0.488(1)	0.686(1)
C(205)	0.680(1)	0.452(1)	0.584(1)	C(206)	0.557(1)	0.402(1)	0.582(1)
C(211)	0.284(1)	0.264(1)	0.5402(8)	C(212)	0.355(1)	0.197(1)	0.4813(8)
C(213)	0.305(1)	0.143(1)	0.3729(8)	C(214)	0.184(1)	0.156(1)	0.3235(8)
C(215)	0.112(1)	0.223(1)	0.3824(8)	C(216)	0.162(1)	0.277(1)	0.4908(8)

Table 2 A comparison of bond parameters for $Mn_2(\mu\text{-}\eta^1,\eta^1\text{-}Ph_2PPPh_2)(\mu\text{-}X)_2(CO)_6$

	X = Cl	X = Br[b]	X = I[b]
Mn · · · Mn (Å)	3.533	3.661	3.863
Mn—X[a] (Å)	2.411(6)	2.533(2)	2.718(2)
Mn—P[a] (Å)	2.366(7)	2.355(4)	2.362(3)
P—P (Å)	2.335(3)	2.322(4)	2.333(4)
Mn–P–P[a] (degrees)	104.4(3)	106.4(2)	108.7(2)
Mn–X–Mn[a] (degrees)	94.2(2)	92.5(1)	90.5(1)
X–Mn–X[a] (degrees)	84.6(2)	85.4(1)	84.8(1)
Dihedral angle[c] (degrees)	15.1	21.0	31.5

[a] Average values given. [b] Taken from Ref. 8. [c] The angle between the planes defined by the equatorial ligands about each manganese atom.

major product. An electron-impact mass spectrum of **2** was misleading in that the only peaks observed corresponded to $Mn_2(\mu\text{-}PPh_2)_2(CO)_{7 or 8}$ and breakdown fragments therefrom, but the infrared spectrum was inconsistent with these species so full characterization was by X-ray crystallography. The structure is illustrated in the Figure, and consists of two $Mn(CO)_3$ fragments joined by two bridging chloride ligands, with a Ph_2P—PPh_2 group further linking the two metal atoms together. The bromine and iodine analogues of **2** have been prepared previously by direct reaction of preformed Ph_2P—PPh_2 with the appropriate $XMn(CO)_5$ species,[8] but the synthesis reported here is novel in that the diphosphine ligand is assembled in the reaction system. Calderazzo *et al.*[8] have also shown that the bromine and iodine analogues of **2** rearrange thermally to give $Mn_2(\mu\text{-}PPh_2)_2(CO)_8$, and this explains the anomolous mass spectrum of **2**; clearly decomposition at the probe temperatures gives $Mn_2(\mu\text{-}PPh_2)_2(CO)_8$ which then dominates the spectrum.

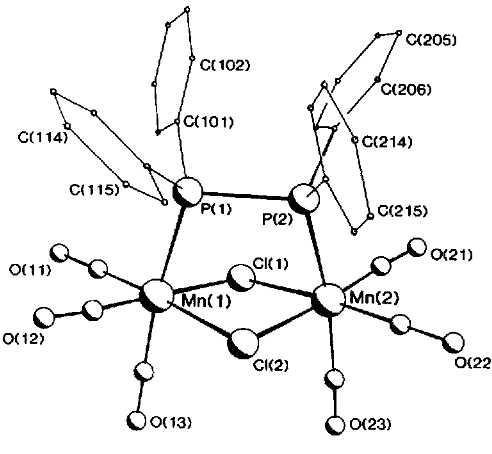


Figure 1 A general view of $Mn_2(\mu\text{-}\eta^1,\eta^1\text{-}Ph_2PPPh_2)(\mu\text{-}Cl)_2(CO)_6$ (**2**).

The mechanism of formation is as yet unclear. The first-formed species is *fac*-(2′-MeC(O)C_6H_4)$Mn(CO)_3(PPh_2Cl)$ and this subsequently rearranges to **2**. The fate of the organic fragment is not known but it is probably lost as acetophenone by abstraction of a hydrogen atom from the solvent. A migration of the chlorine from phosphorus manganese followed by dimerization of two '$ClMn(PPh_2)(CO)_3$' fragments would give the final product. Another route would involve the oxidative addition of a P–Cl bond of a coordinated ligand to a second manganese centre. This seems less likely because it would form species with μ-PPh_2 groups and, as mentioned above, compounds of type **2** have been shown[8] to be intermediates on the way to $Mn_2(\mu\text{-}PPh_2)_2(CO)_8$ complexes; it therefore seems unlikely that two (μ-PPh_2) groups would revert to a Ph_2P—PPh_2 ligand. We note that oxidative addition of the P–Cl bond of PPh_2Cl to a molybdenum centre, with subsequent P–C bond formation, has been observed recently.[9] We are examining the reactions of orthomanganated acetophenone with other Group 14 and 15 halides to gain more definite information concerning reaction pathways.

The structural parameters for **2** are given in Table 2. The bromine and iodine analogues of **2** have been discussed in detail[8] so it is sufficient here to note that **2** adopts essentially the same conformation, with expected changes to accommodate the smaller halogen. These include a shorter Mn · · · Mn distance, and more acute Mn–P–P and Mn–X–Mn angles as X goes from I to Br to Cl. The 'fold angle' between the two tetragonal planes also decreases so that the Ph_2PPPh_2 ligand maintains a constant geometry in all three complexes.

Acknowledgments We thank the New Zealand Universities Grants Committee for financial support, Dr Ward T Robinson, University of Canterbury, New Zealand, for collection of X-ray intensity data, and Professor M I Bruce, University of Adelaide, Australia, for FABS mass spectra.

REFERENCES

1. For Part VI, see Robinson, N P, Main, L and Nicholson, B K *J. Organomet. Chem.*, 1989, 364: C37
2. Cooney, J M, Gommans, L H P, Main, L and Nicholson, B K *J. Organomet. Chem.*, 1987, 336: 293
3. Gommans, L H P, Main, L and Nicholson, B K *J. Chem. Soc., Chem. Commun.*, 1987, 761
4. Cooney, J M, Gommans, L H P, Main L and Nicholson, B K *J. Organomet. Chem.*, 1988, 349: 197; McKinney, R J, Firestein, G and Kaesz, H D *Inorg. Chem.*, 1975, 14: 2057
5. Sheldrick, G M, *SHELXS-86, a Program for Solving Crystal Structures*, University of Gottingen, 1986; *idem*, *SHELX-76, a Program for Determination of X-ray Structures*, University of Cambridge, 1976
6. Gommans, L H P D.Phil. Thesis, University of Waikato, 1986
7. Deshong, P, Slough, G A, Sidler, D R, Rybczynski, P J, Von Philipsborn, W, Kunz, R W, Bursten, B E and Clayton, T W *Organometallics*, 1989, 8: 1381
8. Calderazzo, F, Poli, R, Vitali, D, Korp, J, Bernal, I, Pelizzi, G, Atwood, J and Hunter, W *Gazz. Chim. Ital.*, 1983, 113: 761
9. Conole, G, Hill, K A, McPartlin, M, Mays, M J and Morris, M J *J. Chem. Soc., Chem. Comun.*, 1989, 688