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Reaction of $[Mn(CH_3\text{-}\eta^5\text{-}C_5H_4)(CO)_2PPh_3]$ with iodine. Crystal structure of diiodobis(triphenylphosphineoxide)manganese(II)

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Abstract

Treatment of the complex $Mn(CH_3\text{-}\eta^5\text{-}C_5H_4)(CO)_2PPh_3$ with a one molar proportion of iodine yields $MnI_2(OPPh_3)_2$ as the only isolable product. An X-ray crystal structure determination shows that the complex has a distorted tetrahedral geometry. The Mn^{II}–I bond lengths are 2.6687(5) and 2.6614(8) Å and the I–Mn–I bond angle is 113.67(2)°, while the Mn^{II}–O bond lengths are 2.008(3) and 2.005(4) Å and the O–Mn–O bond angle is 104.9(2)°.

Introduction

The compound $MnI_2(OPPh_3)_2$ was prepared for the first time by Goodgame and Cotton [1] by direct reaction between manganous iodide and phosphine oxide. An early claim by Naldini [2] to have made $MnI_2(PPh_3)_2$ was questioned by McAuliffe et al. [3], who obtained $MnI_2(OPPh_3)_2$ by the same procedure, involving treatment of manganese(II) iodide with triphenylphosphine in THF. They suggested that the source of P=O was probably water in the incompletely dehydrated MnI_2 salt, since all the reactions were carried out under an inert atmosphere. Phosphines are well known to be oxidized to phosphine oxides in air, a process catalysed by, for example, $M(PPh_3)_4$ (M = Pd, Pt) [4] and cobalt(II) chloride [5]. We obtained the title compound unexpectedly from the reaction of $Mn(CH_3\text{-}\eta^5\text{-}C_5H_4)(CO)_2PPh_3$ with iodine. (This reaction was examined in the hope that iodine would add oxidatively to the manganese with release of carbon monoxide to yield a compound similar to the recently described $[Mn(CH_3\text{-}\eta^5\text{-}C_5H_4)I(PEt_3)]_2$[6].) An X-ray diffraction study was undertaken in order to confirm the identity of the complex isolated and to provide details of its molecular structure.

Results and discussion

Chemical studies

Treatment of the compound $Mn(CH_3\text{-}\eta^5\text{-}C_5H_4)(CO)_2PPh_3$ with iodine in a 1/1 ratio gave $MnI_2(OPPh_3)_2$ as the only isolable product, eq. 1. The solvent was

$$Mn(CH_3\text{-}\eta^5\text{-}C_5H_4)(CO)_2PPh_3 + I_2 \xrightarrow[CH_2Cl_2]{1/1} MnI_2(OPPh_3)_2 \quad (1)$$

dichloromethane, and we observed that the colour change during the reaction depended on the degree of dryness of the solvent; when the dichloromethane had been stored after distillation the reaction mixture became yellow, and yellow crystals of $MnI_2(OPPh_3)_2$ were isolated in ca. 30% yield. When the solvent was freshly distilled, the mixture was initially green and became an intense blue during ca. 2 h. Attempts to isolate and characterize the blue species were unsuccessful. The blue solution turned yellow on addition of traces of water, and the $MnI_2(OPPh_3)_2$ could subsequently be recovered as the only product.

Although we do not know the mechanism of the reaction, it seems likely that the intense blue colour that appears when the solvent used is freshly distilled and free from water arises from the presence of a manganese(III) species. McAuliffe et al. [7] reported that the deeply coloured intermediates observed during the reaction of $MnCl_3$ with PPh_3 were manganese(III) phosphine oxide complexes, although the only compound they could isolate was $MnCl_2(OPPh_3)_2$.

In view of our experiments it seems likely that the iodine oxidatively added to manganese to change the oxidation state of the metal from I to III and displace the methylcyclopentadienyl ligand. The intense blue colour formed in the absence of traces of water could be due to manganese(III). We have no evidence for oxidation of phosphine at this step, and since there is no source of oxygen, the manganese(III) could be stabilized by iodide and triphenylphosphine ligands.

McAuliffe et al. described the crystal structure of *trans*-triiodobis(trimethylphosphine)manganese(III) [8], a compound which is also highly coloured. In the presence of water the Mn^{III} is immediately reduced to Mn^{II}, the triphenylphosphine is oxidized to the oxide, and $MnI_2(OPPh_3)_2$ is formed.

Crystallography

The molecular structure of the complex $[MnI_2(OPPh_3)_2]$ is shown in Fig. 1. The manganese atom is coordinated to four ligands in a distorted tetrahedral environment made up of the two iodide and two phosphine oxide ligands. The angle between the planes defined by O(1)MnO(2) and I(1)MnI(2) is 86.9 °.

The metal atom in $[MnI_2(PEt_3)_2]$ [9] is in a similar environment. All other known monomeric species [10] containing manganese coordinated to halogen and phosphine oxide ligands are either penta- [8,11] or hexa-coordinate [12,13,15]. There are two other species with the metal in a distorted tetrahedral environment, one of them is polymeric with octahedral alternating with tetrahedral manganese units [14], and the other is composed of centrosymetric dimers with iodo bridges between tetrahedrally coordinated manganese centers [6].

The Mn^{II}–I bond lengths in the title complex, 2.6687(5) and 2.6624(8) Å are comparable to those in the two complexes mentioned above in which Mn^{II} is tetrahedrally coordinated to iodide, namely $[MnI_2(PEt_3)_2]$ [9], where Mn–I are

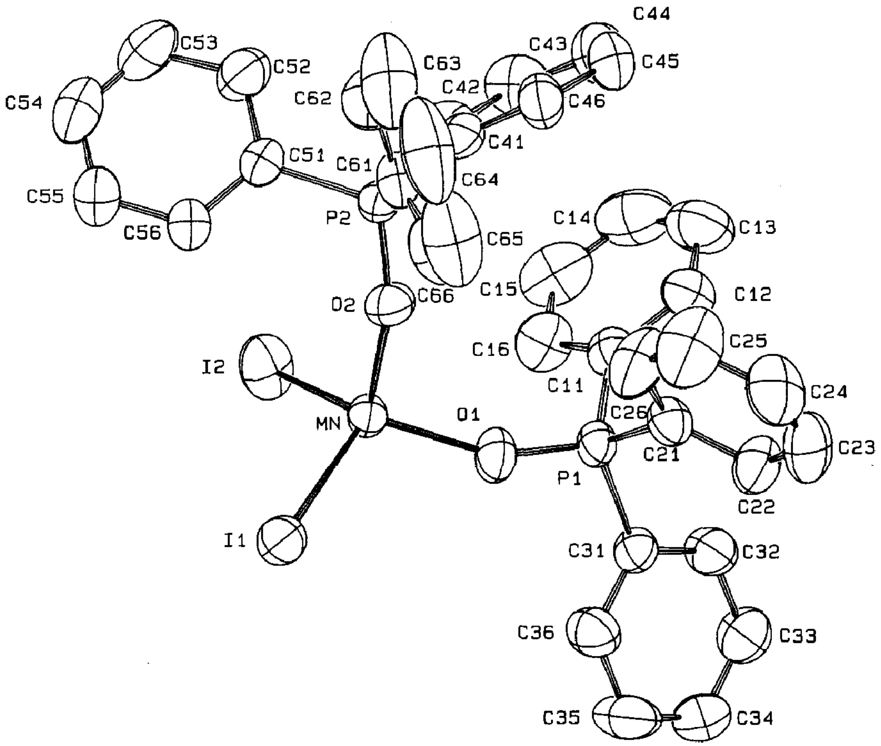

Fig. 1. Molecular structure of $MnI_2(OPPh_3)_2$ with 50% probability thermal ellipsoids showing the atom labeling scheme.

2.662(2) and 2.670(2) Å and the tetrahedral units in $[MnI_2(PMe_2Ph)]$ where Mn–I are 2.698(4) and 2.720(4) Å. These bond lengths are, as expected, shorter than the corresponding lengths in the octahedral units in $[MnI_2(PMe_2Ph)]$ [14], where the Mn–I bond lengths are 2.973(4) and 3.004(4) Å, and in $[MnI(OPPh_3)_4]^+$ [11] where the bond length Mn–I is 2.811(8) Å.

Although in the dimeric complex $[(MeCp)MnI(PEt_3)]_2$ [6] the manganese is in a pseudo tetrahedral coordination, the Mn–I bonds are longer, averaging 2.865(3) Å, comparable to the corresponding value in the octahedral complexes. This difference may arise from the closing up of the angle at I–Mn–I, 93.5(2)°, required by the bridging positions of the iodide ligands, whereas in the title complex, and other monomeric Mn complexes this angle, 113.67(2)°, is closer to the tetrahedral value. The Mn–O bonds, 2.009(3) and 2.005(4) Å, in the title complex are shorter than the corresponding values in the two other cited species in which Mn^{II} is also coordinated to $OPPh_3$ ligands but with a higher coordination. In $[Mn(OPPh_3)_4(SO_2)_2]^{2+}$ [15] these distances are 2.084(3) and 2.147(3) Å, with the hexacoordination completed by two OSO ligands, while in $[MnI(OPPh_3)_4]^+$ [11], where the metal atom is in a square pyramidal configuration with C_{4v} crystallographic symmetry, the Mn–O distance is 2.12(2) Å.

With only two $OPPh_3$ ligands present, and a coordination number of four, a shorter Mn–O distance in the title complex is not surprising, since both electronic and steric effects will tend to a decrease of that bond length. Steric effects are also important in this complex, in which there is a slightly smaller O–Mn–O angle, 104.9(2)°, compared with that, 115.1(2)°, in the complex in which there are phosphine rather than phosphine oxide ligands [9].

The phosphine oxide ligands have similar geometries to those in $[MnI(OPPh_3)_4]^+$ [11] and $[Mn(OPPh_3)_4(SO_2)_2]^{2+}$ [15].

Experimental

All experiments were performed under nitrogen or by standard vacuum line and Schlenk tube techniques. Solvents were dried by standard methods and distilled under nitrogen before use. $Mn(CH_3\text{-}\eta^5\text{-}C_5H_4)(CO)_2PPh_3$ used as starting material was prepared as previously described [16]. Other chemicals were reagent grade.

Reaction of $Mn(CH_3\text{-}\eta^5\text{-}C_5H_4)(CO)_2PPh_3$ (1) with I_2

Method A. To a stirred bright yellow solution of **1** (1.14 g, 2.52 mmol) in dichloromethane (30 cm^3) was slowly added a solution of iodine (0.7 g, 2.75 mmol) in dichloromethane, which had been stored overnight after distillation. The mixture was stirred at room temperature and gas evolution was observed. The initial colour of the reaction mixture was a superposition of the colours of the reagents, but after a few minutes the solution became yellow brownish, and stayed like that for 24 h. The solution was then concentrated under reduced pressure, and petroleum ether 60–80 °C was added to yield yellow crystals of $MnI_2(OPPh_3)_2$, which were filtered off, washed, and dried under vacuum. Yield ca. 30%.

Method B. The reaction was performed as described above, but in freshly distilled dichloromethane. The initial colour of the reaction mixture was again a superposition of the colours of the reagents, but after a few minutes the solution became green, and after ca. 2 h was an intense bright blue. Attempts to isolate the blue species failed. Addition of incompletely dried petroleum ether (b.p. 60–80 °C) caused the solution to become yellow, and yellow crystals of $MnI_2(OPPh_3)_2$ were isolated in ca. 30% yield.

Crystal structure of $[MnI_2(OPPh_3)_2]$

Crystal data. $C_{36}H_{30}O_2P_2I_2Mn$, $M = 865.33$, triclinic, $P1$, a 10.125(2), b 10.481(3), c 10.724(2) Å, α 114.76(2), β 116.41(2), γ 90.10(2)°, V 900.5 Å^3, D_c 1.45 g cm^{-3}, $Z = 1$.

Data collection. Graphite monochromatized Mo-K_α radiation, λ 0.71069 Å, μ(Mo-K_α) 20.51 cm^{-1}. The intensities of 4136 reflections were measured in the range $1.5 < \theta < 28.0°$ by the ω–2θ scan mode, with scan widths of $0.80 + 0.35 \tan \theta$, on a CAD4 diffractometer and 3775 reflections with $F > 3\sigma(F)$ were used in the subsequent structure determination and refinement. The data were corrected for absorption empirically by use of the Enraf Nonius CAD4 software (minimum and maximum transmission factors of 0.7853 and 0.9998 respectively).

Structure determination. A Patterson map revealed the iodide and the manganese atoms. The remaining non-hydrogen atoms were found from difference Fourier synthesis. Refinement was by full matrix least-squares, using SHELX [17]. In the final stages all non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the phenyl rings C11–C16, C31–C36, C51–C56, were located in the ΔF map and included in the refinement with individual isotropic thermal parameters, while all the other hydrogen atoms were placed at calculated and idealized positions.

In the final cycles of refinement the UPALS program [18] was used. The weighting scheme $w = [(2.0\sigma)^2 + (0.02F)^2]^{1/2}$ was applied, and the final agreement factors were $R(F) = 0.0255$ and $R_w(F^2) = 0.0332$ and $S = 1.239$ for 505 refined parameters. The maximum parameter shift/e.s.d. ratio in the final refinement cycle was 0.08516, and the highest positive and negative peak heights in the final difference

Table 1

Fractional atomic coordinates (Å × 10^3) and equivalent isotropic thermal parameters for $MnI_2(OPPh_3)_2$

Atom	x	y	z	B or B_{eq} [a]
I1	0(0)	1000(0)	0(0)	500(1)
I2	325(0)	884(0)	362(0)	677(2)
Mn	277(0)	955(0)	136(0)	342(3)
P1	598(0)	1197(0)	269(0)	360(4)
P2	321(0)	647(0)	−109(0)	330(4)
O1	444(0)	1122(0)	223(0)	490(16)
O2	292(1)	794(0)	−40(1)	436(16)
C11	606(1)	1180(1)	99(1)	419(21)
C12	673(1)	1297(1)	99(1)	559(28)
C13	669(1)	1276(1)	−39(1)	795(42)
C14	601(1)	1149(1)	−172(1)	738(41)
C15	537(2)	1035(1)	−170(1)	922(50)
C16	538(1)	1050(1)	−38(1)	745(41)
C21	747(1)	1128(1)	372(1)	423(19)
C22	872(1)	1112(1)	350(1)	569(29)
C23	989(1)	1068(1)	441(1)	744(43)
C24	980(1)	1036(1)	548(1)	762(39)
C25	855(1)	1050(1)	568(1)	741(37)
C26	738(1)	1096(1)	481(1)	610(29)
C31	633(1)	1386(1)	397(1)	383(18)
C32	779(1)	1473(1)	501(1)	495(25)
C33	800(1)	1619(1)	588(1)	598(28)
C34	679(1)	1681(1)	577(1)	569(31)
C35	535(1)	1596(1)	475(1)	599(34)
C36	511(1)	1448(1)	385(1)	524(26)
C41	231(1)	522(1)	−80(1)	385(18)
C42	95(1)	538(1)	−84(1)	570(29)
C43	14(1)	439(1)	−75(1)	754(41)
C44	72(1)	330(1)	−53(1)	730(35)
C45	207(1)	314(1)	−43(1)	726(39)
C46	290(1)	409(1)	−60(1)	587(29)
C51	519(1)	654(1)	−23(1)	405(19)
C52	601(1)	679(1)	132(1)	511(26)
C53	755(1)	700(1)	206(1)	629(30)
C54	832(1)	703(1)	129(1)	723(36)
C55	754(1)	680(1)	−23(1)	685(35)
C56	596(1)	652(1)	−102(1)	570(28)
C61	244(1)	580(1)	−316(1)	452(19)
C62	199(1)	675(1)	−377(1)	706(34)
C63	133(1)	624(2)	−539(1)	1141(67)
C64	118(1)	486(2)	−633(1)	1256(66)
C65	165(1)	387(2)	−575(1)	1063(56)
C66	219(1)	439(1)	−418(1)	636(38)

[a] B_{eq} for non-hydrogens multiplied by 100.

Table 2

Selected bonds lengths (Å) and bond angles (°) for [Mn(I)$_2$(OPPh$_3$)$_2$]

I(1)–Mn	2.6687(5)	I(2)–Mn	2.6614(8)
O(1)–Mn	2.008(3)	O(2)–Mn	2.005(4)
P(1)–O(1)	1.506(3)	P(2)–O(2)	1.501(3)
C(11)–P(1)	1.792(5)	C(21)–P(1)	1.792(4)
C(31)–P(1)	1.793(4)	C(41)–P(2)	1.792(3)
C(51)–P(2)	1.778(4)	C(61)–P(2)	1.781(5)
I(1)–Mn–I(2)	113.67(2)	I(1)–Mn–O(1)	113.63(9)
I(1)–Mn–O(2)	105.01(9)	I(2)–Mn–O(1)	109.0(1)
I(2)–Mn–O(2)	110.2(1)	O(1)–Mn–O(2)	104.9(2)
Mn–O(1)–P(1)	157.3(1)	Mn–O(2)–P(2)	149.9(1)
O(1)–P(1)–C(11)	111.0(2)	O(1)–P(1)–C(21)	112.2(2)
O(1)–P(1)–C(31)	109.5(2)	C(11)–P(1)–C(21)	108.6(3)
C(11)–P(1)–C(31)	107.8(3)	C(21)–P(1)–C(31)	107.6(2)
O(2)–P(2)–C(41)	111.4(2)	O(2)–P(2)–C(51)	110.7(2)
O(2)–P(2)–C(61)	109.1(3)	C(41)–P(2)–C(51)	109.5(2)
C(41)–P(2)–C(61)	107.5(2)	C(51)–P(2)–C(61)	108.7(3)

Fourier synthesis were respectively 0.696 and −0.320 e/Å^3. Atomic positional and thermal parameters are given in the Table 1, and selected molecular dimensions in Table 2. The drawing was made by use of ORTEP [19]. Atomic scattering values were taken from ref. 20. Lists of hydrogen atom positions, a complete table of bond lengths and angles, and lists of observed and calculated structure factors are available from the authors.

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