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Note

Complexes of functional phosphines [1]. Manganese(II) complexes containing β-keto- and 2-pyridylphosphine ligands. The molecular structure of $MnI_2(Ph_2Ppy)_2$

Pierre Braunstein[1]*, David G Kelly[1], Antonio Tiripicchio[2], Franco Ugozzoli[2]

[1] *Laboratoire de chimie de coordination, associé au CNRS (URA 416),*
Université Louis-Pasteur, 4, rue Blaise-Pascal, 67070 Strasbourg Cedex, France
[2] *Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica,*
Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR,
Viale delle Scienze 78, I-43100 Parma, Italy

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Summary – The complexes MnI_2L_2 (**1**, L = Ph_2Ppy; **2**, L = $Ph_2PCH_2C(O)Ph$) have been synthesized. The solid state structure of **1** has been determined by single crystal X-ray analysis. The structure exhibits grossly distorted tetrahedral coordination of iodide and pyridine moieties with additional unusual long-range Mn···P interactions (Mn···P = 3.143(5) and 3.080(5) Å). Infrared characterization of **2** indicates coordination of the ketone function, although not as a classical P,O chelate. However, **2** does not react with $AuI(SEt_2)$ or $Mo(CO)_4$(norbornadiene) to form heterometallic complexes, thus suggesting that true pendant phosphines are not present in **2** and that the mode of ligand coordination is similar to that in **1**.

manganese complex / functional phosphine / hybrid ligand

Introduction

Numerous derivatives of phosphine ligands incorporating potentially coordinating group 15 or 16 centers have been reported. Examples of such 'functionalized phosphines', where the additional donor coordinates instead of the phosphine, are extremely rare [2]. In general, coordination is primarily by the phosphorus center, with the contribution from the additional donor ranging from significant (giving a bidentate ligand) to negligible (giving a monodentate phosphine).

The coordination chemistry of both $Ph_2PCH_2C(O)Ph$ and 2-(diphenylphosphino)pyridine (Ph_2Ppy) has been extensively examined [1, 3, 4]. The ketone group in the former exhibits little propensity for coordination to first row metals such as cobalt(II) or nickel(II), although P,O chelation can be initiated by replacing coordinated halides by non-coordinating anions [5, 6]. Deprotonation by base invariably produces chelation of the phosphinoenolate anion, $[Ph_2PCH\underline{\cdots}C(\underline{\cdots}O)Ph]^-$, *eg*, with nickel, cobalt and rhenium [6-8]. The ligand Ph_2Ppy can act as a monodentate phosphine, but is more often bonded as a P,N bridge [4g].

The conditions necessary to stimulate coordination of functionalized phosphines solely *via* the secondary donor center have been illustrated in the literature [2]. Thus, for example, α-phosphino-enolates act as η^1-*O*-bound ligands towards 'hard' zirconium(IV) and coordination of the pendant phosphine occurs only on exposure to a low valent metal species, such as $Cr(CO)_5(THF)$. The present work examines the behavior of Ph_2Ppy and $Ph_2PCH_2C(O)Ph$ towards another 'hard' metal, manganese(II).

Results and discussion

The ligands Ph_2Ppy (L^1) and $Ph_2PCH_2C(O)Ph$ (L^2) both react with MnI_2 in a 2:1 ratio to afford MnI_2L_2 complexes **1** and **2**, respectively. Conventional characterization provided little information regarding **1**, thus crystals of the complex were prepared for X-ray diffraction. The latter indicates an usual geometry at the manganese(II) center, as well as a notable form of Ph_2Ppy coordination (fig 1).

Crystal Structure of $MnI_2(Ph_2Ppy)_2$ 1

The structure of complex **1** is shown in figure 1 together with the atomic numbering scheme; bond distances and angles are given in table I. The tetrahedral coordination around manganese is strongly distorted and involves two iodine atoms [Mn-I = 2.736(3) and 2.741(3) Å]

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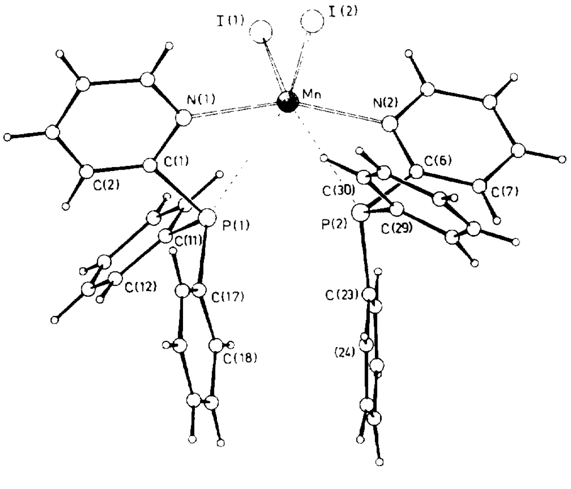

Fig 1. Perspective view of the molecular structure of the complex $MnI_2(Ph_2Ppy)_2$ **1**.

and two N atoms from the pyridine functions [Mn-N = 2.269(13) and 2.244(13) Å]. If the I(1)-Mn-I(2) angle, 109.6(1)°, is perfectly tetrahedral, the N(1)-Mn-N(2) one, 159.4(4)°, is so large to be closer to the linearity than to the expected tetrahedral value; the values of the other angles at manganese are in the range 94.2(4)-97.5(3)°. This strong distortion is due to the presence of two long Mn···P interactions [Mn···P(1) = 3.143(5) and Mn···P(2) = 3.080(5) Å]. By also taking into account these long interactions the coordination around manganese could be described as strongly distorted octahedral with the two N atoms occupying two apical positions.

Table I. Selected bond distances (Å) and angles (°) of complex $MnI_2(Ph_2PPy)_2$ **1**.

Mn-I(1)	2.736(3)	Mn-I(2)	2.741(3)
Mn-N(1)	2.269(13)	Mn-N(2)	2.244(13)
P(1)-C(1)	1.849(15)	P(1)-C(11)	1.824(14)
P(1)-C(17)	1.832(12)	P(2)-C(6)	1.802(16)
P(2)-C(23)	1.839(14)	P(2)-C(29)	1.814(16)
N(1)-C(1)	1.387(19)	N(1)-C(5)	1.332(17)
N(2)-C(6)	1.356(20)	N(2)-C(10)	1.365(18)
I(1)-Mn-I(2)	109.6(1)	I(2)-Mn-N(2)	96.7(4)
I(2)-Mn-N(1)	95.4(3)	I(1)-Mn-N(2)	97.5(3)
I(1)-Mn-N(1)	94.2(4)	N(1)-Mn-N(2)	159.4(4)
C(11)-P(1)-C(17)	103.6(6)	C(1)-P(1)-C(17)	100.9(6)
C(1)-P(1)-C(11)	102.6(7)	C(23)-P(2)-C(29)	106.6(7)
C(6)-P(2)-C(29)	104.0(8)	C(6)-P(2)-C(23)	101.8(7)
Mn-N(1)-C(5)	125.5(10)	Mn-N(1)-C(1)	119.1(8)
C(1)-N(1)-C(5)	114.7(13)	Mn-N(2)-C(10)	125.4(10)
Mn-N(2)-C(6)	116.0(9)	C(6)-N(2)-C(10)	118.3(14)
P(1)-C(1)-N(1)	109.3(10)	N(1)-C(1)-C(2)	122.3(13)
P(1)-C(1)-C(2)	128.3(12)	P(2)-C(6)-N(2)	113.3(11)
N(2)-C(6)-C(7)	121.1(14)	P(2)-C(6)-C(7)	125.6(13)

Comparisons with previously reported structures illustrate the novelty of such coordination, thus:

(i) The predominant nitrogen coordination of the Ph_2Ppy ligand contrasts with that found in the structure of $Ni(CO)_2(Ph_2Ppy)_2$ in which the same ligand acts as a monodentate phosphine [9].

(ii) The Mn-P distances in manganese(II)-phosphine complexes are normally longer than those found, for example, in the corresponding nickel(II) complexes (values for Ni-P bonds are 2.341(3)-2.423(3) Å in $NiI_2(PPh_3)_2$) [10]. In fact in the structure of $MnI_2(PPh_3)_2$ values of 2.74(1) and 2.75(2) Å have been found [11], and in the structure of $MnI_2(PEt_3)_2$ the reported values are 2.53(4) and 2.544(4) Å [12]. These results show that the Mn-P bond distances are strongly influenced by the nature of the phosphines and the remarkable differences in the Mn-P distances in very similar complexes could be due to the reduced basicity of PPh_3 compared with PEt_3 and the greater bulk of the PPh_3 ligand. It is noteworthy that in **1** the mean Mn-P distance is 0.37 Å longer than in the complex with PPh_3.

Clearly the structure of **1** suggests that coordination of the functional phosphine occurs primarily *via* the 'hard' nitrogen center and that the manganese(II)-phosphorus interaction is extremely poor. However, the latter is not simply forced upon the complex by effects such as crystal packing, since it requires very significant distortion of the N-Mn-N bond angle. Moreover, the Mn-P interaction appears to be more favored than the halide bridging; the latter being employed by many $MnX_2(PR_3)$-type complexes (X = Br, I; PR_3 = tertiary phosphine) and by $CoCl_2(Py)_2$ to increase the metal coordination number [13-15].

The $Ph_2PCH_2C(O)Ph$ (L^2) ligand consistently produces an $MnI_2(L^2)_2$ complex; higher and lower stoichiometries of L^2 lead to the isolation of **2** in correspondingly lower yields. In the absence of crystallographic evidence, an unequivocal structural assignment is impossible. However, a shift in the ligand ν(C=O) infrared band from 1 670 cm^{-1} to 1 628 cm^{-1} is indicative of coordination of the ketone function. Moreover, this band is significantly different from those observed in chelated examples of L^2 [5, 6], suggesting either the absence of phosphine coordination, structure I, or a similar long-range Mn-P interaction to that observed in **1**, structure II (fig 2).

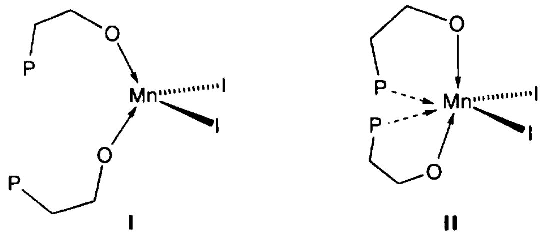

Fig 2. Proposed modes of $Ph_2PCH_2C(O)Ph$ coordination in **2**.

The hypothesis that **2** exists as structure I was tested by reaction of the complex with one/two equivalents of $Mo(CO)_4(nbd)$ (nbd = norbornadiene) and $AuI(SEt_2)$, respectively; a pendant phosphine should readily coordinate to both metals displacing nbd/Et_2S to afford heterometallic products. Whilst reactions occur and nbd/Et_2S are liberated, MnI_2 is concurrently precipitated giving $AuI(L^2)$ and $Mo(CO)_4(L^2)_2$ as final products. Such reactivity is more easily rationalized on the basis of structure II, where a weak manganese–phosphorus interaction is necessary to maintain ligand coordination to the metal center. When such bonding is lost, due to the more favored phosphine bonding to the 'softer' metal species, ligand coordination cannot be maintained by the ketone function alone and breakdown of the complex occurs. Thus, it can be suggested that the coordination of both L^1 and L^2 involves primary bonding *via* the pyridine and ketone functions, but a secondary metal-phosphine bonding is also present.

In conclusion, Ph_2Ppy and $Ph_2PCH_2C(O)Ph$ bonding to manganese(II) differs radically from that observed with other metals, with coordination occurring here primarily *via* the nitrogen/oxygen functional group. Such a behavior can be related to the 'hard' nature of manganese(II), which will favor the 'hard' N/O donors over the 'softer' phosphine ligands.

Experimental section

Syntheses were performed under nitrogen using standard Schlenk techniques, although products are air stable and could be stored without the exclusion of air. Solvents were dried using conventional techniques and stored under nitrogen. Infrared spectra were recorded on a Bruker IFS66 using KBr discs and Nujol mulls. Magnetic measurements were made using a Johnson Matthey bench-top balance.

Preparation of the complexes

- *$MnI_2(Ph_2Ppy)_2$* **1**

Anhydrous MnI_2 (0.297 g; 0.96 mmol) and Ph_2Ppy (0.480 g; 1.80 mmol) were vigorously stirred in Et_2O (25 mL) for 4 d. The pink suspension of MnI_2 gave an off-white solid **1** which was isolated by filtration and dried *in vacuo* (0.733 g; 91%). μ_{eff} = 5.9 μB. Anal calc for $C_{34}H_{28}I_2MnN_2P_2$ (M = 835.3): C, 48.9; H 3.4; N 3.4. Found: C, 48.3; H 3.2; N 3.2. **1** was recrystallized by slow Et_2O diffusion in a CH_2Cl_2 solution of the complex to yield pale pink crystals suitable for X-ray diffraction (see below).

- *$MnI_2[Ph_2PCH_2C(O)Ph]_2$* **2**

2 was prepared similarly to **1** using anhydrous MnI_2 (0.365 g; 1.18 mmol) and $Ph_2PCH_2C(O)Ph$ (0.718 g; 2.36 mmol). Isolation after 2 d afforded **2** as a pale yellow solid (0.964 g; 89%). mp 176°C, μ_{eff} = 5.9 μB. IR; ν(C=O) 1 628 cm^{-1}, FAB mass spectrum *m/e* 790.0 (25% M – I), 486.0 (50% M – L – I), 305.0 (100% L + 1). Anal calc for $C_{40}H_{34}I_2MnO_2P_2$ (M = 917.4): C, 52.3; H 3.5; I 27.7. Found: C, 52.0; H 3.5; I 27.7. **2** could be recrystallized by slow Et_2O diffusion in a CH_2Cl_2 solution of the complex. Whilst accurate elemental analyses could be obtained for such crystals, none of them proved suitable for X-ray diffraction studies.

Table II. Crystallographic data for complex **1**.

mol formula	$C_{34}H_{28}I_2MnN_2P_2$
mol wt	835.30
cryst system	orthorhombic
space group	$Pna2_1$
radiation (λ, Å)	graphite-monochromated Mo$K\alpha$ (0.71073)
a, Å	13.975(2)
b, Å	11.755(2)
c, Å	20.147(5)
V, Å^3	3 310(1)
Z	4
D_{calcd}, g cm^{-3}	1.676
$F(000)$	1 628
linear abs, cm^{-1}	23.49
$R(F_0)$[a]	0.0335
$R_w(F_0)$[b]	0.0353

[a] $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$.

[b] $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w(F_0)^2]^{1/2}$

X-ray crystal structure determination of $[MnI_2(Ph_2Ppy)_2]$ **1**

The crystallographic data are summarized in table II. Data were collected at room temperature on a Enraf Nonius CAD-4 single-crystal diffractometer using the graphite-monochromated Mo-$K\alpha$ radiation and the $\omega/2\theta$ scan mode.

Table III. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Å^2 $\times$ 10^4) with esd's in parentheses for the non-hydrogen atoms of $MnI_2(Ph_2Ppy)_2$ **1**.

	x/a	y/b	z/c	U_{eq}[a]
I(1)	5 204(1)	1 712(1)	0	758(4)
I(2)	7 432(1)	1 753(1)	−1 596(1)	677(4)
Mn	6 286(2)	391(1)	−829(2)	493(6)
P(1)	6 230(3)	−1 709(3)	136(2)	510(13)
P(2)	6 374(3)	−1 621(3)	−1 806(2)	523(13)
N(1)	7 419(7)	21(9)	−52(7)	480(41)
N(2)	5 160(7)	74(10)	−1 601(7)	492(41)
C(1)	7 255(10)	−832(12)	410(8)	503(55)
C(2)	7 824(12)	−988(13)	940(8)	626(64)
C(3)	8 561(13)	−316(14)	1 052(11)	835(79)
C(4)	8 768(11)	539(14)	606(9)	642(58)
C(5)	8 188(10)	658(11)	68(10)	580(57)
C(6)	5 324(11)	−809(12)	−2 019(9)	486(54)
C(7)	4 721(15)	−1 028(15)	−2 543(12)	984(92)
C(8)	3 916(12)	−317(14)	−2 657(10)	718(67)
C(9)	3 761(11)	565(12)	−2 226(11)	683(66)
C(10)	4 384(10)	750(12)	−1 717(10)	578(58)
C(11)	5 605(9)	−1 995(10)	913(7)	465(46)
C(12)	5 916(12)	−2 785(13)	1 377(8)	588(53)
C(13)	5 375(15)	−2 943(16)	1 943(11)	818(80)
C(14)	4 622(15)	−2 395(18)	2 082(11)	746(63)
C(15)	4 267(12)	−1 581(16)	1 647(11)	818(75)
C(16)	4 798(13)	−1 381(14)	1 035(9)	692(64)
C(17)	6 829(10)	−3 058(9)	−50(8)	479(49)
C(18)	6 294(10)	−4 026(11)	−45(7)	549(50)
C(19)	6 700(14)	−5 081(12)	−188(9)	724(71)
C(20)	7 651(13)	−5 103(13)	−386(9)	702(67)
C(21)	8 156(12)	−4 152(15)	−413(9)	718(68)
C(22)	7 750(11)	−3 133(12)	−249(8)	587(56)
C(23)	5 882(11)	−3 066(11)	−1 730(7)	433(50)
C(24)	6 373(12)	−4 011(11)	−1 923(9)	687(65)
C(25)	6 065(15)	−5 076(13)	−1 822(9)	763(76)
C(26)	5 216(15)	−5 261(15)	−1 544(12)	885(91)
C(27)	4 680(13)	−4 270(17)	−1 325(10)	803(76)
C(28)	5 004(11)	−3 227(14)	−1 421(9)	632(60)
C(29)	7 086(10)	−1 603(11)	−2 559(8)	483(50)
C(30)	7 957(13)	−1 090(17)	−2 520(10)	775(71)
C(31)	8 576(14)	−1 050(19)	−3 035(12)	1 038(101)
C(32)	8 318(16)	−1 504(18)	−3 623(10)	923(82)
C(33)	7 428(21)	−1 977(31)	−3 668(13)	1 653(189)
C(34)	6 839(18)	−2 091(29)	−3 151(14)	1 516(155)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

All reflections with θ in the range 3–24° were measured. No correction for absorption was applied. Only the observed reflections were used in the structure solution and refinement.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares first with isotropic and then with anisotropic thermal parameters in the last cycles for all the non-hydrogen atoms. All hydrogen atoms were placed at their geometrically calculated positions (C-H = 0.96 Å) and refined "riding" on the corresponding carbon atoms. The final cycles of refinement were carried out on the basis of 375 variables; after the last cycles, no parameter shifted by more than 0.35 esd. The largest remaining peak in the final difference map was equivalent to about 0.87 e/Å^3. In the final cycles of refinement a weighting scheme, $w = 1/[\sigma^2(F_o) + gF_o^2]$, was used with $g = 0.010$. The atomic scattering factors, corrected for the real and imaginary parts of anomalous dispersion, were taken from reference 16.

All calculations were carried out on the Gould Powernode 6040 and Encore 91 computers of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs [17]. The final atomic coordinates for the non-hydrogen atoms are given in table III.

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Supplementary material available

Coordinates for the hydrogen atoms (table S-I); anisotropic thermal parameters for the non-hydrogen atoms (table S-II); complete list of bond distances and angles (table S-III); crystallographic data (table S-IV) and calculated and observed structure factors (table S-V) for complex **1** have been deposited with the British Library, Document Supply Centre at Boston Spa, Wetherby, West Yorkshire, UK, as supplementary publication N° SUP 90393 and is available on request from the Document Supply Centre. Ordering information is given on any current masthead page.

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