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Metal–Phosphole and –Phospholyl Complexes. Crystal and Molecular Structures of (1-*tert*-Butyl-3,4-dimethylphosphole)heptacarbonyldimanganese and (3,4-Dimethylphospholyl)undecacarbonyltrimanganese

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The crystal and molecular structures of (1-*tert*-butyl-3,4-dimethylphosphole)heptacarbonyldimanganese (I) and (3,4-dimethylphospholyl)undecacarbonyltrimanganese (II) were determined from diffractometer data. I crystallizes as orange parallelepipeds in space group *Cc*, $Z = 4$, with the cell parameters $a = 17.312$ (3) Å, $b = 8.156$ (2) Å, $c = 17.261$ (3) Å, and $\beta = 124.28$ (2)°. II crystallizes in the space group $P2_{1/n}$, $Z = 4$, with the cell parameters $a = 8.556$ (2) Å, $b = 18.503$ (3) Å, $c = 13.292$ (2) Å, and $\beta = 92.67$ (1)°. The structures were refined by least-squares methods to $R_1 = 0.038$ and $R_2 = 0.039$ for I and $R_1 = 0.055$ and $R_2 = 0.049$ for II. I is a binuclear and II a trinuclear species. The Mn–Mn distances are equal to 2.919 (1) Å in I, 3.053 (1) and 2.917 (1) Å in II. In both I and II the symmetry of the metal–ring fragments is near *Cs* as pointed out by a NMR study. The phosphorus atom lies out of the plane of the four carbon atoms of the diene moiety (mean value 0.223 Å). The C–C bond lengths in the diene moiety are statistically equivalent. The Mn–C(diene) distances also are statistically equivalent.

Introduction

A quantum chemical study of the phospholyl anion $[\overline{\mathrm{CHCHPCHCH}}]^-$ has shown that this heterocyclic ring exhibits most probably a large electron delocalization.[2] In order to synthesize π-(phospholyl)Mn(CO)$_3$, isoelectronic with the known thiophenetricarbonylchromium,[3] one of us has investigated the reaction of $Mn_2(CO)_{10}$ with phospholes (L). He obtained a mixture of σ complexes, $L_xMn_2(CO)_{10-x}$ (x = 1 or 2), and σ and π complexes, $LMn_2(CO)_7$. With L = 1-phenyl-3,4-dimethylphosphole, he also obtained product II, which was erroneously formulated as $Mn_3(CO)_{12}P(C_6H_8)$ mainly on the basis of its mass spectrum.[4a] In the present stage of our research, it seems that, upon heating, this product gives minute amounts of $Mn_3(CO)_{12}P(C_6H_8)$ beside $Mn(CO)_3$-$P(C_6H_8)$ which is the main decomposition product.[4b] Thus, the very weak peak of *m/e* 612 in the mass spectrum of II would be due to its thermal decomposition in the mass spectrometer. We present here the molecular structures of one compound of the type $LMn_2(CO)_7$, with L = 1-*tert*-butyl-3,4-dimethylphosphole (I), and of (3,4-dimethylphospholyl)undecacarbonyltrimanganese (II).

Experimental Section

Crystals of each compound were obtained from concentrated methanol solutions at −30 °C. Preliminary precession photographs indicated the crystal symmetry for both compounds to be monoclinic. Systematic absences for I of *hkl*, $h + k = 2n + 1$, and *h0l*, $l = 2n + 1$, were consistent with the space groups *Cc* or *C*2/*c*. Systematic absences for II of 0*k*0, $k = 2n + 1$, and *h0l*, $h + l = 2n + 1$, identified the space group as $P2_1/n$, a nonstandard setting of $P2_1/c$. Precise lattice constants were obtained by least-squares refinement of the diffraction geometry based on the angular settings of 22 reflections for I and 21 reflections for II. Experimental densities were determined by flotation in aqueous potassium iodide solution for I and in aqueous zinc iodide solution for II. Relevant crystal data are given in Table I with some other details of the experiment.

Table I. Summary of Crystal Data and Intensity Collection

Compd	$Mn_2(C_{17}H_{17}O_7P)$ (I)	$Mn_3(C_{17}H_8O_{11}P)$ (II)
Formula wt	474.17	584.03
a, Å	17.312 (3)	8.556 (2)
b, Å	8.156 (2)	18.503 (3)
c, Å	17.261 (3)	13.292 (2)
β, deg	124.28 (2)	92.67 (1)
V, Å^3	2013.8	2102.0
Z	4	4
Density (calcd), g/cm^3	1.564	1.845
Density (obsd), g/cm^3	1.56 (1)	1.83 (1)
Space group	*Cc*	$P2_1/n^a$
Approximate crystal dimensions, mm	0.12 × 0.10 × 0.08	0.10 × 0.08 × 0.08
Radiation	Mo Kα	Mo Kα
μ, cm^{-1}	14.27	19.93
Data collection method	θ–2θ scan (3°/min along θ)	θ–2θ scan (2°/min along θ)
Scan width	0.84 + 0.69 tan θ	0.84 + 0.69 tan θ
Background counts at both ends of the scan, s	10	10
θ limits, deg	2–30	2–30
Measd reflections	3216	6589
Obsd reflections ($F_o^2 > 3\sigma(F_o^2)$)	1914	1850
Temperature during data collection, °C	20 ± 2	20 ± 2

[a] The cell dimensions in space group $P2_1/c$ (obtained from those of $P2_1/n$ by the transformation $a' = -a$, $b' = -b$, $c' = a + c$) are a' = 8.556, b' = 18.503, c' = 15.469 Å, and β' = 120.87°.

Crystals of I and II were mounted in thin-walled glass capillary tubes. Data were collected on a Philips PW1100 automatic four-circle diffractometer equipped with a graphite monochromator and a molybdenum tube. Data with θ < 30° were recorded within a unique quadrant. Three standard reflections were measured after intervals of 120 min. No significant change in their intensities occurred during data collection. The intensity data for the two compounds were reduced to relative squared amplitudes $|F_o|^2$ by application of standard Lorentz and polarization factors. No correction for absorption was made to either data set. Standard deviations were calculated as previously described,[5] using a *p* value of 0.04.

The structure of I was solved by the heavy-atom method while that of II was solved by direct methods. Both structures were refined by full-matrix least-squares techniques, the quantity minimized being $\sum w(|F_o| - |F_c|)^2$, where the weights *w* were taken as $1/\sigma^2(F_o)$. Scattering factors for all nonhydrogen atoms were those of Doyle and Turner[6] and for hydrogen atoms were those of Stewart et al.[7] The effects of anomalous dispersion were included for manganese, phosphorus, and oxygen, using values of $\Delta f'$ and $\Delta f''$ given by Cromer and Liberman.[8]

The Patterson map of I contained no large peaks on the plane $v = 0$ (a Harker plane for space group *C*2/*c*) and contained only one large peak in a general position, thus suggesting space group *Cc*. The two manganese atoms were located and the *x* and *z* coordinates of one were arbitrarily set at 0.75. A subsequent structure factor calculation, using the contributions from the two manganese atoms only, gave an $R_1 = (\sum||F_o| - |F_c||/\sum|F_o|)$ of 0.32. A Fourier synthesis revealed the positions of all 27 nonhydrogen atoms. The structure was refined, using isotropic temperature factors. A difference Fourier map showed maxima in the range of 0.6 ± 0.2 e Å^{-3} at positions close to those calculated for the 17 hydrogen atoms. The nonhydrogen atoms were assigned anisotropic temperature factors, and refinement was continued, including the contributions of the hydrogen atoms in the structure factor calculations but not refining their parameters. Isotropic temperature factors of 1.1 times that of the bonded carbon

Table II. Atomic Positional and Thermal Parameters for $Mn_2(C_{17}H_{17}O_7P)$[a,b]

Atom	x	y	z	U_{11}[c]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn(1)	0.75	0.4124 (1)	0.75	0.0380 (5)	0.0335 (5)	0.0309 (4)	0.0007 (4)	0.0208 (4)	−0.0026 (4)
Mn(2)	0.8409 (1)	0.2199 (1)	0.6803 (1)	0.0324 (4)	0.0348 (5)	0.0297 (4)	0.0091 (4)	0.0151 (4)	0.0031 (4)
P	0.7140 (1)	0.4431 (1)	0.6034 (1)	0.0271 (7)	0.0310 (8)	0.0272 (7)	0.0036 (6)	0.0140 (6)	−0.0018 (6)
O(1)	0.6390 (4)	0.6625 (7)	0.7678 (4)	0.089 (4)	0.065 (3)	0.084 (4)	0.012 (3)	0.065 (3)	−0.005 (3)
O(2)	0.5909 (4)	0.1815 (7)	0.6777 (5)	0.066 (3)	0.070 (4)	0.114 (5)	−0.020 (3)	0.055 (4)	−0.011 (3)
O(3)	0.8990 (4)	0.6622 (6)	0.8160 (4)	0.065 (3)	0.050 (3)	0.070 (3)	−0.024 (2)	0.032 (3)	−0.022 (2)
O(4)	0.8484 (4)	0.2718 (7)	0.9407 (4)	0.103 (4)	0.064 (3)	0.047 (3)	0.003 (3)	0.039 (3)	0.010 (2)
O(5)	0.7880 (4)	0.9796 (6)	0.7702 (4)	0.093 (4)	0.045 (3)	0.072 (3)	0.005 (2)	0.054 (3)	0.013 (2)
O(6)	0.9471 (4)	0.9480 (8)	0.6731 (4)	0.095 (4)	0.079 (4)	0.087 (4)	0.048 (4)	0.053 (4)	0.007 (3)
O(7)	0.9859 (4)	0.3403 (7)	0.8490 (4)	0.051 (3)	0.084 (4)	0.052 (3)	0.001 (3)	−0.002 (2)	−0.002 (3)
C(1)	0.6816 (5)	0.5632 (9)	0.7606 (4)	0.058 (4)	0.052 (4)	0.045 (3)	0.002 (3)	0.038 (3)	−0.003 (3)
C(2)	0.6527 (5)	0.2681 (9)	0.7042 (5)	0.049 (4)	0.048 (4)	0.061 (4)	−0.004 (3)	0.037 (3)	−0.004 (3)
C(3)	0.8421 (4)	0.5662 (8)	0.7897 (4)	0.048 (3)	0.041 (3)	0.039 (3)	−0.002 (3)	0.023 (3)	−0.005 (3)
C(4)	0.8102 (5)	0.3254 (8)	0.8673 (5)	0.052 (4)	0.044 (4)	0.041 (4)	−0.001 (3)	0.026 (3)	0.001 (3)
C(5)	0.8065 (4)	0.0804 (9)	0.7371 (4)	0.045 (3)	0.049 (4)	0.035 (3)	0.000 (3)	0.019 (2)	−0.005 (3)
C(6)	0.9060 (5)	0.0542 (9)	0.6748 (5)	0.045 (3)	0.057 (4)	0.041 (3)	0.018 (3)	0.021 (3)	0.009 (3)
C(7)	0.9469 (3)	0.2933 (8)	0.7853 (5)	0.041 (3)	0.046 (4)	0.043 (3)	0.011 (3)	0.012 (3)	0.007 (3)
C(8)	0.8212 (4)	0.4570 (7)	0.6125 (4)	0.026 (3)	0.039 (3)	0.039 (3)	0.001 (2)	0.019 (2)	0.002 (2)
C(9)	0.8334 (4)	0.3351 (8)	0.5646 (4)	0.041 (3)	0.052 (4)	0.036 (3)	0.012 (3)	0.025 (2)	0.006 (3)
C(10)	0.7617 (4)	0.2139 (8)	0.5280 (4)	0.051 (3)	0.039 (3)	0.030 (3)	0.018 (3)	0.020 (2)	0.003 (2)
C(11)	0.7995 (4)	0.2444 (7)	0.5540 (4)	0.039 (3)	0.035 (3)	0.025 (2)	0.003 (2)	0.013 (2)	−0.001 (2)
C(12)	0.9090 (6)	0.3381 (1)	0.5469 (6)	0.073 (5)	0.089 (6)	0.065 (5)	0.028 (4)	0.056 (4)	0.021 (4)
C(13)	0.7502 (6)	0.0753 (1)	0.4664 (5)	0.086 (5)	0.062 (5)	0.038 (3)	0.031 (4)	0.034 (4)	0.002 (3)
C(14)	0.6229 (4)	0.5860 (7)	0.5154 (4)	0.041 (3)	0.042 (3)	0.034 (3)	0.015 (3)	0.019 (2)	0.004 (2)
C(15)	0.6427 (5)	0.7565 (8)	0.5578 (5)	0.065 (4)	0.036 (4)	0.054 (4)	0.010 (3)	0.028 (3)	0.004 (3)
C(16)	0.5303 (4)	0.5228 (9)	0.4930 (5)	0.040 (3)	0.056 (4)	0.058 (4)	0.018 (3)	0.026 (3)	0.006 (3)
C(17)	0.6238 (5)	0.5866 (9)	0.4277 (4)	0.056 (4)	0.055 (4)	0.042 (3)	0.019 (3)	0.027 (3)	0.011 (3)

[a] Atoms are labeled as indicated in Figure 1. [b] Figures in parentheses here and in subsequent tables are estimated standard deviations. [c] The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(\Sigma_i\Sigma_j a_i^* a_j^* h_i h_j U_{ij})]$.

Table III. Atomic Positional and Thermal Parameters for $Mn_3(C_{17}H_8O_{11}P)$[a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn(1)	−0.2102 (1)	0.2963 (1)	0.3883 (1)	0.0221 (7)	0.0374 (8)	0.0266 (8)	0.0025 (7)	0.0027 (5)	−0.0024 (7)
Mn(2)	−0.1051 (1)	0.1409 (1)	0.3542 (1)	0.0316 (8)	0.0270 (8)	0.0292 (8)	−0.0046 (6)	0.0062 (6)	−0.0000 (6)
Mn(3)	0.0758 (1)	0.3729 (1)	0.3422 (1)	0.0270 (7)	0.0238 (8)	0.0303 (8)	0.0009 (6)	0.0019 (6)	−0.0005 (6)
P	0.0334 (2)	0.2564 (1)	0.3318 (1)	0.024 (1)	0.024 (1)	0.026 (1)	0.001 (1)	0.002 (1)	0.000 (1)
O(1)	−0.3002 (8)	0.4478 (3)	0.4143 (5)	0.056 (4)	0.045 (4)	0.073 (5)	0.017 (3)	0.004 (4)	−0.010 (4)
O(2)	−0.1164 (8)	0.2901 (3)	0.6061 (5)	0.073 (5)	0.068 (5)	0.042 (4)	0.005 (4)	−0.006 (3)	−0.005 (4)
O(3)	−0.3288 (7)	0.3046 (3)	0.1753 (4)	0.051 (4)	0.067 (5)	0.038 (4)	0.002 (3)	−0.010 (3)	0.003 (3)
O(4)	−0.5160 (7)	0.2480 (4)	0.4519 (5)	0.034 (4)	0.095 (6)	0.080 (5)	−0.006 (4)	0.023 (4)	0.017 (5)
O(5)	−0.2075 (9)	0.1291 (4)	0.5616 (5)	0.095 (6)	0.076 (5)	0.044 (4)	−0.008 (4)	0.028 (4)	0.017 (4)
O(6)	−0.132 (1)	−0.0159 (3)	0.3475 (6)	0.114 (7)	0.031 (4)	0.119 (7)	−0.022 (4)	0.049 (5)	−0.003 (4)
O(7)	−0.4271 (8)	0.1384 (4)	0.2655 (5)	0.040 (4)	0.086 (6)	0.062 (5)	−0.017 (4)	−0.012 (3)	0.001 (4)
O(8)	0.3978 (7)	0.3819 (3)	0.2802 (4)	0.033 (3)	0.069 (5)	0.057 (4)	−0.006 (3)	0.012 (3)	0.007 (3)
O(9)	0.2186 (7)	0.3523 (4)	0.5477 (5)	0.056 (4)	0.072 (5)	0.043 (4)	0.016 (4)	−0.009 (3)	0.000 (4)
O(10)	0.0195 (8)	0.5264 (3)	0.3889 (5)	0.092 (6)	0.031 (4)	0.077 (5)	0.015 (4)	0.022 (4)	−0.003 (4)
O(11)	−0.0382 (8)	0.3986 (4)	0.1309 (5)	0.054 (5)	0.128 (7)	0.050 (5)	0.001 (5)	−0.000 (4)	0.025 (5)
C(1)	−0.256 (1)	0.3900 (5)	0.4024 (6)	0.035 (5)	0.055 (7)	0.029 (5)	−0.011 (5)	0.001 (4)	0.004 (5)
C(2)	−0.146 (1)	0.2918 (5)	0.5207 (7)	0.029 (5)	0.044 (6)	0.045 (6)	0.014 (5)	0.004 (4)	0.000 (5)
C(3)	−0.2818 (9)	0.3010 (4)	0.2563 (6)	0.029 (5)	0.034 (5)	0.029 (5)	0.000 (4)	−0.006 (4)	0.006 (4)
C(4)	−0.397 (1)	0.2656 (5)	0.4244 (6)	0.031 (5)	0.062 (7)	0.036 (5)	0.000 (5)	0.004 (4)	−0.003 (5)
C(5)	−0.168 (1)	0.1353 (5)	0.4814 (7)	0.041 (5)	0.048 (6)	0.042 (6)	−0.006 (5)	0.005 (4)	0.012 (5)
C(6)	−0.119 (1)	0.0441 (5)	0.3495 (8)	0.057 (7)	0.042 (6)	0.061 (7)	−0.017 (5)	0.028 (5)	−0.010 (5)
C(7)	−0.304 (1)	0.1436 (5)	0.2980 (6)	0.053 (6)	0.037 (5)	0.035 (5)	−0.015 (5)	0.009 (5)	−0.002 (5)
C(8)	0.272 (1)	0.3790 (4)	0.3018 (6)	0.038 (5)	0.029 (5)	0.034 (5)	−0.015 (4)	0.002 (4)	0.007 (4)
C(9)	0.159 (1)	0.3603 (4)	0.4708 (6)	0.040 (5)	0.025 (5)	0.041 (5)	0.000 (4)	0.009 (4)	0.005 (4)
C(10)	0.038 (1)	0.4669 (5)	0.3715 (7)	0.038 (5)	0.032 (5)	0.048 (6)	0.008 (4)	0.013 (4)	0.003 (4)
C(11)	0.002 (1)	0.3880 (5)	0.2119 (7)	0.031 (5)	0.056 (7)	0.053 (6)	0.001 (5)	0.010 (5)	0.006 (5)
C(12)	0.0021 (9)	0.1976 (4)	0.2276 (6)	0.034 (5)	0.028 (5)	0.033 (5)	−0.015 (4)	0.004 (4)	−0.010 (4)
C(13)	0.0766 (9)	0.1294 (4)	0.2453 (6)	0.028 (4)	0.026 (5)	0.032 (5)	−0.006 (4)	0.005 (3)	−0.002 (4)
C(14)	0.146 (1)	0.1235 (4)	0.3468 (6)	0.034 (5)	0.021 (5)	0.041 (5)	−0.003 (4)	0.007 (4)	−0.000 (4)
C(15)	0.1191 (9)	0.1850 (4)	0.4042 (7)	0.015 (4)	0.031 (5)	0.052 (6)	−0.001 (4)	0.007 (4)	0.009 (5)
C(16)	0.087 (1)	0.0741 (5)	0.1646 (7)	0.068 (7)	0.030 (5)	0.043 (6)	0.005 (5)	0.018 (5)	−0.003 (4)
C(17)	0.243 (1)	0.0596 (5)	0.3821 (8)	0.052 (7)	0.035 (6)	0.077 (8)	0.005 (5)	−0.004 (6)	0.011 (6)

[a] Atoms are labeled as indicated in Figure 2 and the parameters are presented as in Table II.

atom were used for hydrogen atoms. After three cycles of refinement, all parameters were shifting by less than 0.1 esd. The final R_1 was 0.040 and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ was 0.041. At this point the enantiomeric structure was refined under identical conditions to R_1 and R_2 values of 0.038 and 0.039, respectively. Accordingly, this second model was used in the subsequent calculations. The standard deviation of an observation of unit weight was 1.14. A difference Fourier map revealed no peak of electron density greater than 0.15 (9) e Å^{-3}. The final structure revealed no center of symmetry or twofold axis in the molecule, thus confirming the space group *Cc*.

To solve the structure of II, the structure factors were first put on an absolute scale by calculating the statistical distribution of the *E* values for all the reflections. This resulted in 230 reflections with *E* values greater than 2.0. The most consistent set of signs for these reflections was calculated using the program MULTAN.[9] The calculated phases were used to compute an *E* map, which revealed the three

Table IV. Interatomic Bond Distances (Å) and Angles (deg) for $Mn_2(C_{17}H_{17}O_7P)$

Distances			
Mn(1)–Mn(2)	2.920 (1)	P–C(14)	1.858 (5)
Mn(1)–P	2.253 (1)	C(1)–O(1)	1.148 (11)
Mn(1)–C(1)	1.786 (8)	C(2)–O(2)	1.141 (10)
Mn(1)–C(2)	1.830 (7)	C(3)–O(3)	1.133 (8)
Mn(1)–C(3)	1.832 (6)	C(4)–O(4)	1.136 (8)
Mn(1)–C(4)	1.820 (6)	C(5)–O(5)	1.145 (10)
Mn(2)–P	2.573 (1)	C(6)–O(6)	1.132 (11)
Mn(2)–C(5)	1.808 (8)	C(7)–O(7)	1.127 (7)
Mn(2)–C(6)	1.796 (8)	C(8)–C(9)	1.384 (10)
Mn(2)–C(7)	1.806 (5)	C(9)–C(10)	1.425 (9)
Mn(2)–C(8)	2.186 (6)	C(10)–C(11)	1.404 (12)
Mn(2)–C(9)	2.144 (7)	C(9)–C(12)	1.503 (14)
Mn(2)–C(10)	2.175 (5)	C(10)–C(13)	1.487 (10)
Mn(2)–C(11)	2.184 (4)	C(14)–C(15)	1.518 (8)
P–C(8)	1.775 (7)	C(14)–C(16)	1.511 (10)
P–C(11)	1.781 (6)	C(14)–C(17)	1.524 (11)

Angles			
Mn(2)–Mn(1)–P	58.0 (1)	C(8)–P–C(11)	87.7 (4)
Mn(2)–Mn(1)–C(1)	162.7 (3)	C(8)–P–C(14)	113.3 (4)
Mn(2)–Mn(1)–C(2)	93.2 (3)	C(11)–P–C(14)	110.7 (4)
Mn(2)–Mn(1)–C(3)	88.0 (2)	Mn(1)–C(1)–O(1)	178.6 (4)
Mn(2)–Mn(1)–C(4)	98.3 (3)	Mn(1)–C(2)–O(2)	177.2 (4)
P–Mn(1)–C(1)	105.0 (3)	Mn(1)–C(3)–O(3)	178.3 (4)
P–Mn(1)–C(2)	88.9 (3)	Mn(1)–C(4)–O(4)	179.5 (4)
P–Mn(1)–C(3)	88.6 (2)	Mn(2)–C(5)–O(5)	173.0 (4)
P–Mn(1)–C(4)	156.3 (3)	Mn(2)–C(6)–O(6)	178.3 (5)
C(1)–Mn(1)–C(2)	89.1 (4)	Mn(2)–C(7)–O(7)	177.8 (4)
C(1)–Mn(1)–C(3)	88.8 (4)	P–C(8)–C(9)	113.9 (4)
C(1)–Mn(1)–C(4)	98.7 (5)	C(8)–C(9)–C(10)	112.1 (6)
C(2)–Mn(1)–C(3)	176.2 (6)	C(8)–C(9)–C(12)	123.6 (6)
C(2)–Mn(1)–C(4)	92.3 (5)	C(12)–C(9)–C(10)	124.2 (7)
C(3)–Mn(1)–C(4)	91.1 (4)	C(9)–C(10)–C(11)	111.6 (6)
Mn(1)–Mn(2)–C(5)	72.3 (2)	C(9)–C(10)–C(13)	125.2 (7)
Mn(1)–Mn(2)–C(6)	157.9 (3)	C(13)–C(10)–C(11)	123.1 (6)
Mn(1)–Mn(2)–C(7)	83.5 (2)	C(10)–C(11)–P	112.8 (4)
C(5)–Mn(2)–C(6)	88.0 (4)	P–C(14)–C(15)	108.9 (4)
C(5)–Mn(2)–C(7)	97.1 (4)	P–C(14)–C(16)	106.5 (4)
C(6)–Mn(2)–C(7)	89.4 (4)	P–C(14)–C(17)	109.6 (4)
Mn(1)–P–C(8)	107.1 (2)	C(15)–C(14)–C(16)	110.8 (6)
Mn(1)–P–C(11)	108.1 (2)	C(15)–C(14)–C(17)	110.5 (6)
Mn(1)–P–C(14)	123.9 (2)	C(16)–C(14)–C(17)	110.5 (6)

manganese atoms as the three largest peaks in the map. The positions of these were used to calculate phases for the set of structure factors with $F_o^2 > 3\sigma(F_o^2)$, thus giving an R_1 of 0.39. A Fourier synthesis based on this set revealed the positions of the other nonhydrogen atoms. Subsequent refinement followed the same lines as for I. The final R_1 was 0.055 and R_2 0.049. All parameters at the end of refinement were shifting by less than 0.1 esd. The standard deviation of an observation of unit weight was 1.19. A difference Fourier map revealed no peak larger than 0.56 (10) e Å^{-3}. Tables of observed and calculated structure factors (x10) are available.[10]

Description and Discussion

The listings of atomic coordinates and thermal parameters for those atoms refined anisotropically are given in Tables II and III. The bond distances and bond angles for I and II are given in Tables IV and V, respectively. Some pertinent molecular planes are described in Table VI. The crystal structures of both I and II consist of discrete $Mn_2(CO)_7$(*t*-BuP(C_6H_8)) and $Mn_3(CO)_{11}P(C_6H_8)$ molecules, respectively, with no unusually short intermolecular contacts. Views of the complex molecules are presented in Figures 1 and 2.

In I there is a manganese–manganese bond; the Mn(1)–Mn(2) distance of 2.920 (1) Å compares well with the value of 2.923 (7) Å found in $Mn_2(CO)_{10}$[11] and is similar to the values found in the $[Mn_3(CO)_{14}]^-$ anion (2.906 (5) and 2.883 (4) Å).[12] Each manganese atom has the optimal 18-valence electron configuration. The equatorial carbonyl groups are staggered. The axial carbonyl groups are not parallel to the Mn(1)–Mn(2) bond, the angles C(1)–Mn(1)–Mn(2) and C(6)–Mn(2)–Mn(1) being 162.7 (3) and 157.9 (3)°, respectively. The group CO(6) bends away from the phosphole

Table V. Interatomic Bond Distances (Å) and Angles (deg) for $Mn_3(C_{17}H_8O_{11}P)$

Distances			
Mn(1)–Mn(2)	3.053 (1)	Mn(3)–C(11)	1.839 (10)
Mn(1)–Mn(3)	2.917 (1)	C(1)–O(1)	1.149 (12)
Mn(1)–P	2.366 (2)	C(2)–O(2)	1.151 (12)
Mn(1)–C(1)	1.787 (10)	C(3)–O(3)	1.134 (11)
Mn(1)–C(2)	1.822 (9)	C(4)–O(4)	1.144 (11)
Mn(1)–C(3)	1.833 (9)	C(5)–O(5)	1.138 (12)
Mn(1)–C(4)	1.785 (9)	C(6)–O(6)	1.115 (12)
Mn(2)–C(5)	1.803 (10)	C(7)–O(7)	1.125 (11)
Mn(2)–C(6)	1.797 (10)	C(8)–O(8)	1.128 (11)
Mn(2)–C(7)	1.826 (9)	C(9)–O(9)	1.130 (11)
Mn(2)–P	2.468 (2)	C(10)–O(10)	1.137 (11)
Mn(2)–C(12)	2.217 (8)	C(11)–O(11)	1.130 (12)
Mn(2)–C(13)	2.183 (8)	P–C(12)	1.772 (8)
Mn(2)–C(14)	2.180 (8)	C(12)–C(13)	1.429 (12)
Mn(2)–C(15)	2.161 (8)	C(13)–C(14)	1.453 (12)
Mn(3)–P	2.189 (2)	C(13)–C(16)	1.488 (12)
Mn(3)–C(8)	1.789 (9)	C(14)–C(15)	1.396 (12)
Mn(3)–C(9)	1.836 (9)	C(14)–C(17)	1.504 (13)
Mn(3)–C(10)	1.815 (9)	C(15)–P	1.774 (8)

Angles			
Mn(2)–Mn(1)–Mn(3)	99.8 (1)	P–Mn(3)–C(10)	158.0 (3)
Mn(2)–Mn(1)–P	52.3 (1)	P–Mn(3)–C(11)	92.4 (3)
Mn(2)–Mn(1)–C(1)	174.6 (3)	C(8)–Mn(3)–C(9)	87.5 (4)
Mn(2)–Mn(1)–C(2)	91.3 (2)	C(8)–Mn(3)–C(10)	100.5 (4)
Mn(2)–Mn(1)–C(3)	89.5 (2)	C(8)–Mn(3)–C(11)	89.8 (4)
Mn(2)–Mn(1)–C(4)	90.8 (2)	C(9)–Mn(3)–C(10)	89.3 (4)
Mn(3)–Mn(1)–P	47.6 (1)	C(9)–Mn(3)–C(11)	177.0 (5)
Mn(3)–Mn(1)–C(1)	74.9 (2)	C(10)–Mn(3)–C(11)	90.0 (4)
Mn(3)–Mn(1)–C(2)	90.4 (2)	Mn(1)–P–Mn(2)	78.3 (1)
Mn(3)–Mn(1)–C(3)	91.3 (2)	Mn(1)–P–Mn(3)	79.6 (1)
Mn(3)–Mn(1)–C(4)	169.2 (3)	Mn(1)–P–C(12)	109.7 (3)
P–Mn(1)–C(1)	122.4 (3)	Mn(1)–P–C(15)	114.1 (3)
P–Mn(1)–C(2)	93.5 (2)	Mn(2)–P–Mn(3)	157.5 (1)
P–Mn(1)–C(3)	88.4 (2)	Mn(2)–P–C(12)	60.4 (2)
P–Mn(1)–C(4)	143.1 (3)	Mn(2)–P–C(15)	58.6 (2)
C(1)–Mn(1)–C(2)	90.1 (4)	Mn(3)–P–C(12)	132.3 (3)
C(1)–Mn(1)–C(3)	89.4 (4)	Mn(3)–P–C(15)	129.5 (3)
C(1)–Mn(1)–C(4)	94.5 (4)	C(12)–P–C(15)	90.6 (4)
C(2)–Mn(1)–C(3)	178.1 (5)	P–C(12)–C(13)	111.3 (7)
C(2)–Mn(1)–C(4)	87.7 (4)	C(12)–C(13)–C(14)	112.3 (7)
C(3)–Mn(1)–C(4)	90.5 (4)	C(12)–C(13)–C(16)	122.0 (8)
Mn(1)–Mn(2)–P	49.4 (1)	C(14)–C(13)–C(16)	125.6 (8)
Mn(1)–Mn(2)–C(5)	79.1 (2)	C(13)–C(14)–C(15)	112.1 (7)
Mn(1)–Mn(2)–C(6)	157.6 (3)	C(13)–C(14)–C(17)	123.0 (8)
Mn(1)–Mn(2)–C(7)	76.1 (2)	C(15)–C(14)–C(17)	124.9 (8)
P–Mn(2)–C(5)	109.2 (3)	C(14)–C(15)–P	112.7 (5)
P–Mn(2)–C(6)	153.0 (3)	Mn(1)–C(1)–O(1)	172.7 (6)
P–Mn(2)–C(7)	111.7 (3)	Mn(1)–C(2)–O(2)	174.9 (6)
C(5)–Mn(2)–C(6)	87.3 (5)	Mn(1)–C(3)–O(3)	178.6 (6)
C(5)–Mn(2)–C(7)	94.1 (4)	Mn(1)–C(4)–O(4)	176.5 (6)
C(6)–Mn(2)–C(7)	87.4 (5)	Mn(2)–C(5)–O(5)	177.4 (6)
Mn(1)–Mn(3)–P	52.9 (1)	Mn(2)–C(6)–O(6)	178.2 (7)
Mn(1)–Mn(3)–C(8)	154.3 (2)	Mn(2)–C(7)–O(7)	173.4 (6)
Mn(1)–Mn(3)–C(9)	92.1 (2)	Mn(3)–C(8)–O(8)	177.2 (6)
Mn(1)–Mn(3)–C(10)	105.2 (2)	Mn(3)–C(9)–O(9)	176.3 (6)
Mn(1)–Mn(3)–C(11)	90.9 (2)	Mn(3)–C(10)–O(10)	177.8 (6)
P–Mn(3)–C(8)	101.5 (3)	Mn(3)–C(11)–O(11)	177.1 (6)
P–Mn(3)–C(9)	89.4 (2)		

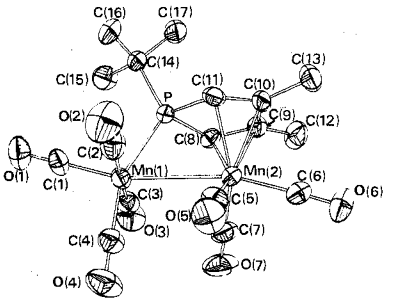


Figure 1. Molecular structure and numbering of the atoms in $Mn_2(C_{17}H_{17}O_7P)$. Ellipsoids are scaled to include 50% probability. H atoms are omitted.

Table VI. Selected Weighted Least-Squares Planes in I and II[a]

Atom	Dist, Å	Atom	Dist, Å
$Mn_2(C_{17}H_{17}O_7P)$ (I)			
Plane 1: C(8), C(9), C(10), C(11) ($\chi^2 = 17$)			
$-0.1205X + 0.5215Y - 0.8447Z - 2.2710 = 0$			
C(8)	+0.008 (6)	C(12)	+0.034 (9)
C(9)	−0.016 (7)	C(13)	+0.121 (8)
C(10)	+0.017 (6)	P	−0.271 (2)
C(11)	−0.008 (6)		
Plane 2: Mn(1), Mn(2), P ($\chi^2 = 0.0$)			
$-0.6335X - 0.7013Y - 0.3267Z - 5.7280 = 0$			
Mn(1)	0.000 (13)	C(9)	0.750 (8)
Mn(2)	0.000 (1)	C(10)	−0.675 (8)
P	0.000 (2)	C(11)	−1.220 (7)
C(8)	1.242 (7)	C(14)	−0.050 (7)
$Mn_3(C_{17}H_8O_{11}P)$ (II)			
Plane 3: C(12), C(13), C(14), C(15) ($\chi^2 = 3.7$)			
$0.8718X + 0.3891Y - 0.2977Z - 0.4103 = 0$			
C(12)	0.006 (9)	P	0.194 (2)
C(13)	−0.009 (8)	C(16)	0.036 (10)
C(14)	0.010 (9)	C(17)	0.112 (10)
C(15)	−0.006 (8)		
Plane 4: Mn(1), Mn(2), Mn(3) ($\chi^2 = 0.0$)			
$-0.2736X + 0.0636Y - 0.9597Z + 4.0411 = 0$			
Mn(1)	0.000 (1)	O(6)	−0.039 (9)
Mn(2)	0.000 (1)	O(8)	0.037 (7)
Mn(3)	0.000 (1)	C(1)	0.039 (9)
P	0.093 (2)	C(6)	−0.023 (11)
O(1)	0.061 (7)	C(8)	0.055 (9)
Plane 5: Mn(1), Mn(2), Mn(3), P ($\chi^2 = 1330$)			
$-0.2840X + 0.0672Y - 0.9565Z + 3.9898 = 0$			
Mn(1)	0.007 (1)	Mn(3)	−0.016 (1)
Mn(2)	−0.015 (1)	P	0.072 (2)
Angles between the Planes: 1–2, 89.3°; 3–4, 85.9			

[a] Their equations are in the form $AX + BY + CZ - D = 0$, where X, Y, and Z refer to the axial system $\vec{a}, \vec{a} \times \vec{c}^*, \vec{c}^*$.

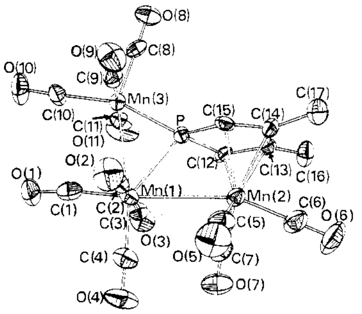
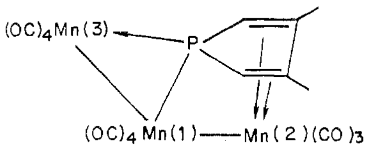


Figure 2. Perspective view of the $Mn_3(C_{17}H_8O_{11}P)$ molecule showing the numbering scheme. The vibrational ellipsoids are drawn at the 50% probability level. H atoms are omitted.

ligand due to nonbonding interactions with C(9) and C(10) of the phosphole. This in turn causes a bending of the groups CO(5) and CO(7) away from CO(6) toward Mn(1). The bending of CO(1) toward the phosphorus and the "opening-out" of angles Mn(2)–Mn(1)–C(x) (x = 2, 4) all reduce the degree of intramolecular crowding between the carbonyl groups.

In II the three manganese atoms form a bent trinuclear system, with bond lengths of 3.053 (1) Å for Mn(1)–Mn(2) and 2.917 (1) Å for Mn(1)–Mn(3). The angle Mn(2)–Mn(1)–Mn(3) is 99.8 (1)°. The phosphorus atom forms a strong bond with Mn(3), the distance Mn(3)–P being 2.189 (2) Å, and a weaker bond with Mn(1) (2.366 (2) Å). The distance Mn(2)–P of 2.468 (2) Å indicates some interaction between these two atoms also. It is noteworthy that the analogous distance in I (2.573 (1) Å) is 0.11 Å longer and thus indicates only a very weak interaction, if any, in this complex. The increase of the Mn(2)–P interaction and the weakening of the Mn(1)–Mn(2) bond when passing from I to II can be correlated with the great tendency of II to yield the π-aromatic $Mn(CO)_3P(C_6H_8)$ complex.[4] The diene system of the phosphole ligand forms π bonds with Mn(2). Thus II can be represented schematically as



In this model, Mn(2) and Mn(3) are formally six-coordinate while Mn(1) is seven-coordinate. Such a scheme allows each metal to attain a noble gas configuration. Writing II in this way allows it to be considered as derived from the hypothetic cation $(OC)_5Mn{-}Mn^+(CO)_4{-}Mn(CO)_5$ or from the hypothetical anion $(OC)_5Mn{-}Mn^-(CO)_4{-}Mn(CO)_5$. The latter is isoelectronic with $(OC)_5Mn{-}Fe(CO)_4{-}Mn(CO)_5$.[13] The phosphorus atom lies 0.093 (2) Å out of the plane of the three manganese atoms. The angle between this plane and that through the four diene carbon atoms is 85.9°.

The geometry of the phosphole, particularly the C–P–C angles and the P–C bond lengths, changes little on coordination of the ligand. This is not too surprising as the ring is quite strained (as is shown by comparison of the intracyclic C–P–C angles with the remaining C–P–C angles in both 1-benzylphosphole and I;[14] compare also with the values calculated for free *tert*-butylphosphole[2]). In fact, in general, even acyclic phosphines change little on coordination.[15] Moreover, the similarity between analogous H–H and H–P coupling constants in the NMR spectra of free 1-methylphosphole[16] and of the coordinated phosphole in heptacarbonyl-1-phenyl-3-methylphospholedimanganese(*Mn–Mn*)[4a] indicates only slight differences between the geometry of the rings in these two phospholes.

In both I and II, the phosphorus atom lies out of the least-squares plane of the four carbon atoms of the diene moiety (−0.262 (2) Å in I and 0.194 (2) Å in II), and on the opposite side to the manganese atoms Mn(1) and Mn(2). A similar nonplanarity of the heterocycle is seen in free 1-benzylphosphole,[14] in which the phosphorus atom lies 0.208 Å from the least-squares plane of the four carbon atoms. The three carbon–carbon bond lengths of the diene system in both I and II are statistically equivalent. The manganese–carbon(diene) distances also are statistically equivalent in each complex.

It has been suggested[14] that the apparent shortening of the P–C(diene) bonds from 1.84 Å (expected from the sum of covalent radii) to 1.783 (5) Å as observed for 1-benzylphosphole is consistent with a certain degree of delocalization of the phosphorus lone pair into the ring. However, the remarkable agreement between this observed value and the values observed in I and II, where the lone pair is no longer available for delocalization into the ring, indicates that another process can be responsible for the shortening—for example, a 2pπ–3dπ conjugation including the empty 3d orbitals of the phosphorus atom. Such a process would be facilitated by a donation of electron density from the manganese atom to the diene system. In any case, whatever the cause, the contraction of the P–C bonds cannot be taken as proof of delocalization of the electron pair of the phosphorus atom.

Registry No. I, 56991-97-0; II, 63989-28-6.

Supplementary Material Available: Listing of structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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On the Mechanism of Ion Exchange in Zirconium Phosphates. 20. Refinement of the Crystal Structure of α-Zirconium Phosphate

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The preparation of high-quality zirconium phosphate, $Zr(HPO_4)_2 \cdot H_2O$, crystals permitted refinement of the previously determined structure to the state where positional parameters of the exchangeable hydrogen atoms could be determined. A new unit cell, in space group $P2_1/n$ rather than the standard $P2_1/c$, was chosen because of its smaller β angle. The new cell dimensions are $a = 9.060$ (2) Å, $b = 5.297$ (1) Å, $c = 15.414$ (3) Å, $\beta = 101.71$ (2)° and Z = 4. Intensity data were collected by the θ–2θ scan procedure using an automated four-circle diffractometer (Enraf-Nonius CAD-4). Refinement of the data (2005 independent reflections with $I \geq 3\sigma(I)$ of 3178 measured) by the full-matrix least-squares procedure with anisotropic temperature factors for all nonhydrogen atoms resulted in a final R value of 0.027. The average Zr–O bond distance is 2.064 (5) Å. Each P–OH group forms a hydrogen bond with the water molecule (O–O distances 2.807 (3) and 2.769 (3) Å). The water molecule in turn acts as donor in forming one hydrogen bond with a P–O–H oxygen. The other water hydrogen is not involved in hydrogen bonding. There are no hydrogen bonds between layers so that only van der Waals forces must hold the layers together.

Introduction

Zirconium bis(monohydrogen orthophosphate) monohydrate, $Zr(HPO_4)_2 \cdot H_2O$, hereafter referred to as α-ZrP, is a crystalline ion exchanger with many interesting properties.[1] This compound has a layered structure in which the metal atoms lie nearly in a plane and are bridged by phosphate groups.[2] Three oxygens of each phosphate are bonded to three different zirconium atoms arranged at the apices of a near equilateral triangle. The fourth points away from the layer and bonds to a hydrogen atom. Adjacent layers are staggered in a pseudo-hexagonal fashion so as to form six-sided cavities between the layers. A water molecule sits in the center of each cavity.

Exchange occurs by replacement of the orthophosphate hydrogen by cations which then occupy positions between the layers.[3] It is not known whether the hydrogen atoms are present as covalent P–O–H or as hydronium ion. Infrared data are not conclusive on this point.[1] Formulation of a mechanism for the exchange precess would be greatly aided by a knowledge of the type and disposition of the hydrogen atoms. This information was not forthcoming from the previous crystal structure determination. Crystals of α-ZrP tend to be disordered with streaked or broadened reflections the rule. Film methods were used to obtain intensity data and refinement could only be carried to partial completion ($R = 0.084$).[2] Errors (esd's) in the bond distances were 0.02–0.03 Å. Thus, many of the finer features of the structure, as well as the hydrogen atom positions and hydrogen bonding scheme, could not be ascertained with certainty. We have now been able to grow much better crystals which permitted a significant improvement in refinement of the structure. When this work was near completion, it came to our attention that a neutron diffraction study had been carried out on α-ZrP powders to determine the hydrogen atom positions.[4] The results of that study will be discussed along with our findings.

Table I. Comparison of Present with Previously Determined Crystal Data

Unit cell constants	Present study	Previous study	
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a, A	9.060 (2)	9.076 (3)	
b, A	5.297 (1)	5.298 (6)	
c, A	15.414 (3)	16.22 (2)	15.41
β, deg	101.71 (2)	111.5 (1)	101.7
V, A^3	724.3 (5)	725.7	
d_{calcd}, g cm^{-3}	2.762	2.76	
d_{obsd}, g cm^{-3}		2.72	
Z	4	4	

Experimental Section

Crystals were grown by a variation of that described by Alberti and Torracca.[5] Zirconium phophate was dissolved in concentrated HF and the solution, contained in a 12-mm i.d. quartz tube, kept at 60–65 °C in an oil bath. In 17–48 h crystals formed on the walls of the tube. The contents were then poured into a boric acid solution. The fluoroborate precipitate which formed was separated from the zirconium phosphate crystals by extensive washing followed by decantation.

A pentagonal-shaped platelet 0.34 × 0.25 × 0.076 mm was mounted in a random orientation on a CAD-4 four-circle counter diffractometer (Enraf-Nonius). Accurate unit cell dimensions were determined from 25 reflections at high and moderate 2θ angles. A graphite crystal incident-beam monochrometer was used with Mo Kα radiation (λ(Mo Kα_1) 0.709 30 Å)). The data were collected at a takeoff angle of 5.6° using the θ–2θ scan technique. The results are collected in Table I

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