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STRUCTURAL STUDY OF $Mn_2(CO)_8[P(NMe_2)_3]_2$

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Summary

An X-ray crystal structure determination for the bimetallic complex $Mn_2(CO)_8[P(NMe_2)_3]_2$ reveals that the $P(NMe_2)_3$ ligands are *trans* to the Mn–Mn bond and the Mn–Mn bond distance is relatively long, 2.946(1) Å.

Introduction

There has been considerable interest in the chemistry and structures of aminophosphanes in recent years; however, a number of problems remain unsolved regarding coordination properties of these ligands. For example, Cowley and coworkers [1] have outlined an intriguing controversy surrounding the structure of $(Me_2N)_3P$, and they have shown the utility of studying molecular structure perturbations of tris-aminophosphanes on metal carbonyl fragments. They have reported that $[(Me_2N)_3PFe(CO)_4]$ and $[(Me_2N)_3P]_2Fe(CO)_3$ adopt trigonal bipyramidal geometries at the central iron atoms with the phosphanes occupying axial sites. The local phosphorus and nitrogen atom geometric picture, on the other hand, has proven to be more complex [1].

The molecular structures of $Mn_2(CO)_8L_2$ complexes and the influence of the donor character of L on the Mn–Mn bond distance have also attracted interest [2]. Unfortunately, systematic synthetic studies have not been accomplished, and very few accurate single crystal X-ray analyses of appropriate complexes have been reported. The Mn–Mn bond distance in $Mn_2(CO)_{10}$ has been accurately determined to be 2.9038(6) Å [3] and the Mn–Mn distances in the bisphosphane complexes $Mn_2(CO)_8(PEt_3)_2$ [2], 2.903(1) Å, and $Mn_2(CO)_8(PMePh_2)_2$ [4] 2.90 Å are essentially identical. The Mn–Mn bond distance in one corresponding arsenic complex, $Mn_2(CO)_8(AsMePh_2)_2$, is 2.94 Å [4].

King and Korenowski [5] have reported a synthesis for $Mn_2(CO)_8[P(NMe_2)_3]_2$; however, the molecular structure for this complex has never been reported. Since $P(NMe_2)_3$ would be expected to be a better π acceptor and poorer σ donor than PEt_3 [6], it was of interest to determine the molecular structure of $Mn_2(CO)_8[P(NMe_2)_3]_2$ and hence the influence of these electronic factors on the Mn–Mn separation.

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Experimental

$Mn_2(CO)_{10}$ was purchased from Strem Chemicals and $P(NMe_2)_3$ was prepared by literature methods [7]. Solvents were dried with appropriate drying agents, distilled and stored under nitrogen. Infrared spectra were recorded on a Nicolet 6000 FT-IR, and NMR spectra were recorded on Varian FT-80A and GE-360 spectrometers. NMR references were 85% H_3PO_4 (^{31}P) and Me_4Si (^1H, ^{13}C), and downfield shifts are indicated by $+\delta$ values.

Preparation of $Mn_2(CO)_8[P(NMe_2)_3]_2$

The complex was prepared in a manner similar to that described by King and Korenowski [5]. A combination of 5 g (12.8 mmol) $Mn_2(CO)_{10}$ and 6 g (37.5 mmol) $P(NMe_2)_3$ in 50 ml decane and 50 ml toluene was refluxed with stirring for 24 h. The resulting red-yellow solution was evaporated to dryness, and the residue extracted with 200 ml acetone. The filtrate was cooled to −78°C overnight and yellow crystals (4.0 g, 52% yield) were collected by filtration. A second crop (~ 1.1 g) was collected by partial evaporation of the solvent followed by cooling. M.p. 198–200°C; IR (cyclohexane): 1979w, 1952vs and 1942w, sh cm^{-1}; ^{31}P NMR δ 178.7, ^1H: δ 2.5, (d, $J(PH)$ 10 Hz), ^{13}C {^1H}: δ 38.6.

Collection of X-ray diffraction data

A suitable yellow crystal of dimensions 0.18 × 0.24 × 0.47 mm was sealed in a glass capillary under nitrogen and the crystal was centered on a Syntex P3/F

TABLE 1

EXPERIMENTAL DATA FOR THE X-RAY DIFFRACTION STUDY OF $Mn_2(CO)_8[P(NMe_2)_3]_2$

(A) Crystallographic parameters (14°C)

Crystal system: Monoclinic
a 20.067(5) Å
b 7.379(1) Å
c 29.160(7) Å
β 135.62(1)°
V 3020.1(11) Å^3
$Z = 4$

Space group: $P2/c$
$F(000)$ 1368
Formula $Mn_2P_2O_8N_6C_{20}H_{36}$
Mol. wt. 660.45
D (calc) 1.45 g cm^{-3}
μ (Mo-K_α) 10.4 cm^{-1}

(B) Measurement of intensity data

Diffractometer: Syntex P3/F
Radiation: Mo-K_α (λ 0.71069 Å)
Monochromator: highly oriented graphite crystal
Reflections collected: $-h, +k, \pm l$
2θ range: 1–60°
Scan type: $\theta - 2\theta$
Scan speed: 5–30°/min
Scan range: from $[2\theta(K_{\alpha 1}) - 1.1]°$ to $[2\theta(K_{\alpha}) + 1.25]°$
Backgrd counting time/total scan time: 0.5
Std. reflections: 2 measured every 94 reflections. No significant changes in intensity
Reflections collected: 9402 total yielding 8620 unique reflections
Reflections observed: 4892 $F > 5\sigma(F)$
$R(F) = \Sigma || F_o - F_c || \Sigma | F_o | = 0.0489$
$R_w(F) = [\Sigma w(| F_o | - | F_c |)^2 / \Sigma w | F_o |^2]^{1/2} = 0.513$
$GOF = [\Sigma w(| F_o | - | F_c |^2/(m - n)]^{1/2} = 0.975$
$W = (\sigma(F)^2 + | g | F_o^2)$, $g = 0.00232$

automated diffractometer. Determinations of the crystal class, orientation matrix and accurate unit cell parameters were performed in a standard manner [8]. The data were collected at 14°C by the θ–2θ technique using Mo-K_α radiation, a scintillation counter and pulse height analyzer. Details of the data collection are summarized in Table 1. Inspection of a short data set indicated the space group $P2/c$. The data were corrected for Lorentz and polarization effects and a small empirical absorption correction based on a series of ψ scans was applied. Redun-

TABLE 2

POSITIONAL PARAMETERS AND THEIR EDS'S FOR $Mn_2(CO)_8[P(NMe_2)_3]_2$

Atom	x/a	y/b	z/c	U (Å^2) [a]
Mn(1)	0.10157(3)	0.47121(8)	0.31265(2)	0.0302(3)
P(1)	0.25945(6)	0.46928(13)	0.40674(4)	0.0314(5)
N(1)	0.3334(2)	0.5402(5)	0.4007(1)	0.0405(21)
C(1)	0.3369(3)	0.4245(8)	0.3611(1)	0.0609(34)
C(2)	0.3295(3)	0.7331(7)	0.3866(2)	0.0577(33)
N(2)	0.2945(2)	0.6133(5)	0.4655(2)	0.0421(21)
C(3)	0.2405(3)	0.6252(7)	0.4812(2)	0.0579(36)
C(4)	0.3962(3)	0.6480(7)	0.5243(2)	0.0624(31)
N(3)	0.3073(2)	0.2612(4)	0.4390(2)	0.0422(21)
C(5)	0.2573(4)	0.1297(7)	0.4418(2)	0.0557(36)
C(6)	0.4101(3)	0.2341(7)	0.4914(2)	0.0647(34)
C(7)	0.1124(3)	0.5751(6)	0.2614(2)	0.0409(24)
O(1)	0.1175(2)	0.6400(5)	0.2279(2)	0.0637(25)
C(8)	0.0849(3)	0.7012(6)	0.3276(2)	0.0428(26)
O(2)	0.0736(3)	0.8433(4)	0.3361(2)	0.0697(30)
C(9)	0.0584(3)	0.3731(6)	0.3450(2)	0.0410(25)
O(3)	0.0317(2)	0.3167(5)	0.3659(2)	0.0677(26)
C(10)	0.1109(3)	0.2459(6)	0.2898(2)	0.0416(26)
O(4)	0.1194(3)	0.1112(5)	0.2761(2)	0.0676(31)
Mn(2)	0.39747(4)	0.85153(7)	0.21077(2)	0.0310(3)
P(2)	0.23891(6)	0.85143(13)	0.14797(4)	0.0327(6)
N(4)	0.1666(2)	0.9187(5)	0.0693(2)	0.0456(21)
C(11)	0.1696(3)	1.1126(7)	0.0581(2)	0.0653(37)
C(12)	0.1621(4)	0.8018(9)	0.0264(2)	0.0720(36)
N(5)	0.2024(2)	0.9981(5)	0.1709(2)	0.0431(24)
C(13)	0.2546(3)	1.0109(6)	0.2390(2)	0.0540(37)
C(14)	0.1006(4)	1.0349(8)	0.1286(3)	0.0653(41)
N(6)	0.1903(2)	0.6455(4)	0.1336(2)	0.0460(23)
C(15)	0.2402(3)	0.5094(6)	0.1855(2)	0.0552(36)
C(16)	0.0874(3)	0.6181(7)	0.0855(3)	0.0712(38)
C(17)	0.3874(3)	0.9517(6)	0.1487(2)	0.0433(25)
O(5)	0.3825(2)	1.0125(5)	0.1100(2)	0.0692(26)
C(18)	0.4145(3)	1.0813(6)	0.2420(2)	0.0460(28)
O(6)	0.4257(3)	1.2244(4)	0.2618(2)	0.0695(32)
C(19)	0.4380(3)	0.7537(5)	0.2849(2)	0.0405(26)
O(7)	0.4620(2)	0.6948(5)	0.3312(2)	0.0653(25)
C(20)	0.3890(3)	0.6269(6)	0.1793(2)	0.0406(27)
O(8)	0.3816(3)	0.4918(4)	0.1574(2)	0.0654(31)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U tensor. B.T.M. Willis and A.W. Pryor, Thermal Vibrations in Crystallography, Cambridge University Press, Cambridge, 1975, pp. 101–102.

dant and equivalent reflection data were averaged and converted to unscaled $|F_0|$ values.

Solution and refinement of the structure

All calculations were performed on the Syntex R3/XTL structure solution system. Scattering factors for neutral atoms were resident in the program and both real ($\Delta f'$) and imaginary ($\Delta f''$) components of the anomalous dispersion were included. The function minimized during the least-squares refinement process was $\Sigma w(|F_o| - |F_c|)^2$ where $w^{-1} = (\sigma(F)^2 + |g|F_c^2)$, $g = 0.00232$.

TABLE 3

ANISOTROPIC THERMAL PARAMETERS FOR $Mn_2(CO)_8[P(NMe_2)_3]_2$ [a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn(1)	0.0237(2)	0.0362(3)	0.0261(2)	0.0014(2)	0.0162(2)	−0.0014(2)
P(1)	0.0259(4)	0.0370(5)	0.0267(4)	0.0017(4)	0.0172(4)	0.0000(4)
N(1)	0.0288(15)	0.0549(20)	0.0350(15)	0.008(15)	0.0218(14)	−0.0037(15)
C(1)	0.0446(23)	0.1013(40)	0.0496(24)	−0.0022(26)	0.0381(22)	0.0048(25)
C(2)	0.0443(23)	0.0670(31)	0.0541(25)	0.0133(23)	0.0325(22)	−0.0079(22)
N(2)	0.0369(16)	0.0491(20)	0.0297(15)	−0.0095(14)	0.0202(14)	−0.0049(15)
C(3)	0.0622(28)	0.0713(33)	0.0483(23)	−0.0146(23)	0.0422(23)	−0.0069(25)
C(4)	0.0455(24)	0.0737(34)	0.0374(21)	−0.0129(23)	0.0192(19)	−0.0079(24)
N(3)	0.0332(16)	0.0427(19)	0.0374(16)	0.0065(15)	0.0207(14)	0.0049(14)
C(5)	0.0582(27)	0.0436(25)	0.0602(27)	0.0133(22)	0.0405(24)	0.0054(21)
C(6)	0.0400(23)	0.0572(30)	0.0608(28)	0.0117(24)	0.0237(22)	0.0101(22)
C(7)	0.0287(17)	0.0502(24)	0.0366(18)	0.0063(17)	0.0209(16)	0.0004(16)
O(1)	0.0522(18)	0.0910(26)	0.0538(17)	0.0168(17)	0.0399(16)	−0.0034(17)
C(8)	0.0327(18)	0.0406(23)	0.0414(20)	−0.0011(17)	0.0218(17)	−0.0036(17)
O(2)	0.0631(22)	0.0440(19)	0.0803(24)	−0.0086(17)	0.0438(20)	0.0009(16)
C(9)	0.0331(18)	0.0515(25)	0.0345(18)	0.0012(17)	0.0228(16)	0.0017(17)
O(3)	0.0541(19)	0.0993(28)	0.0560(18)	0.0147(19)	0.0416(17)	0.0074(18)
C(10)	0.0366(19)	0.0502(25)	0.0332(18)	−0.0033(18)	0.0234(17)	−0.0034(18)
O(4)	0.0787(24)	0.0523(21)	0.0698(22)	−0.0121(17)	0.0524(21)	0.0036(18)
Mn(2)	0.0263(2)	0.0348(3)	0.0285(2)	0.0024(2)	0.0184(2)	0.0019(2)
P(2)	0.0280(4)	0.0350(5)	0.0310(4)	−0.0010(4)	0.0197(4)	0.0023(4)
N(4)	0.0331(16)	0.0609(22)	0.0332(15)	0.0080(16)	0.0204(14)	0.0121(16)
C(11)	0.0511(26)	0.0777(35)	0.0597(27)	0.0336(26)	0.0370(24)	0.0266(25)
C(12)	0.0583(28)	0.1118(45)	0.0369(22)	−0.0058(27)	0.0309(22)	0.0133(30)
N(5)	0.0387(17)	0.0466(20)	0.0466(18)	−0.0051(15)	0.0314(16)	0.0048(15)
C(13)	0.0649(28)	0.0599(29)	0.0550(25)	−0.0099(21)	0.0489(25)	−0.0019(22)
C(14)	0.0474(26)	0.0773(35)	0.0778(33)	−0.0084(30)	0.0470(27)	0.0078(25)
N(6)	0.0329(16)	0.0380(18)	0.0504(19)	−0.0050(15)	0.0241(15)	−0.0031(14)
C(15)	0.0527(25)	0.0403(24)	0.0689(29)	0.0009(21)	0.0422(24)	−0.0060(19)
C(16)	0.0379(24)	0.0545(30)	0.0760(34)	−0.0128(25)	0.0253(24)	−0.0117(21)
C(17)	0.0324(18)	0.0516(25)	0.0373(19)	0.0082(18)	0.0220(16)	0.0056(17)
O(5)	0.0607(20)	0.0987(28)	0.0500(17)	0.0240(18)	0.0402(17)	0.0054(19)
C(18)	0.0361(20)	0.0455(23)	0.0481(22)	0.0045(19)	0.0272(19)	0.0016(17)
O(6)	0.0691(22)	0.0404(18)	0.0898(25)	−0.0146(18)	0.0537(21)	−0.0030(16)
C(19)	0.0354(19)	0.0442(23)	0.0397(20)	−0.0017(17)	0.0261(17)	−0.0050(17)
O(7)	0.0595(19)	0.0872(25)	0.0452(17)	0.0153(17)	0.0361(16)	−0.0026(18)
C(20)	0.0392(20)	0.0443(24)	0.0418(20)	0.0013(18)	0.0302(18)	0.0026(17)
O(8)	0.0763(23)	0.0489(20)	0.0784(23)	−0.0129(17)	0.0578(21)	0.0012(16)

[a] The anisotropic temperature factor exponent takes the form: $-2(\pi)(\pi)[U_{11}(ha^\star)(ha^\star) + U_{22}(kb^\star)(kb^\star) + U_{33}(lc^\star)(lc^\star) + 2(U_{23}(kb^\star)(kb^\star)(lc^\star) + U_{13}(ha^\star)(lc^\star) + U_{12}(ha^\star)(kb^\star))]$

The structure was solved using direct methods option SOLV Isotropic refinement on all non-hydrogen atoms converged to R 9.2%. Subsequent anisotropic refinement on the non-hydrogen atoms converged at R 6.3%. A difference map showed reasonable positions for most of the hydrogen atoms. These atoms were included and allowed to vary in position with their U_{iso} held at 1.2 times the last U_{equiv} of the parent atom. The agreement factor converged to R 4.87% with 451 parameters. All hydrogen atom positions appeared to be stable; however, two internal H–C–H angles on C(15) and C(11) were 81(6)°. Consequently, the hydrogen atoms on these methyl carbon atoms were held fixed in idealized positions. A final series of refinements on 433 parameters with 4892 unique reflections with $F > 5\sigma(F)$ resulted in R_F 4.89% and R_{wF} 5.13% with $GOF = 0.975$. A final difference map showed the top seven peaks (0.48–0.35 eÅ^{-3}) to be within 0.91 Å of the Mn or P atoms.

Description of the structure

There are two independent half dimer units of $Mn(CO)_4P(NMe_2)_3$ in the structure. One unit, Mn(1) to O(4) is related to its other half by a two-fold axis at 0, y, 1/4 and the other unit Mn(2) to O(8) is related to its other half by a two-fold axis at 1/2, y, 1/4. The crystal contains discrete dimer units, and there are no unusually short intermolecular contacts. The geometry of both dimers is the same within experimental error. The overall molecular geometry and atom labelling scheme for one dimer unit is shown in Fig. 1. Interatomic distances and angles are summarized in Tables 4 and 5.

The molecular structure shows that the $Mn(CO)_4P(NMe_2)_3$ units are dimerized through a Mn–Mn bond. The terminal carbonyl groups form an approximate square planar arrangement about each Mn atom with the Mn atoms displaced toward the phosphane ligand. Calculations of best planes through Mn(1), C(7), C(8), C(9) and C(10) and Mn(2), C(17), C(18), C(19) and C(20) show deviations from the

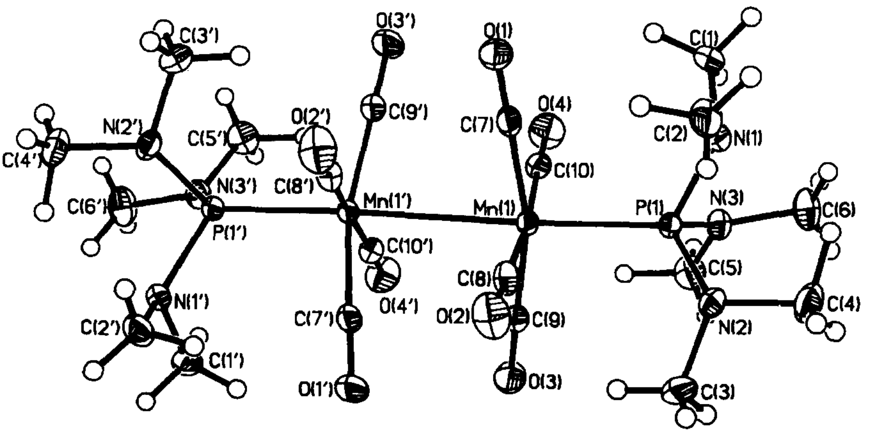

Fig. 1. Molecular geometry and labelling scheme for $Mn_2(CO)_8[P(NMe_2)_3]_2$ (25% probability ellipsoids).

TABLE 4. BOND DISTANCES (Å) AND THEIR ESD'S FOR $Mn_2(CO)_8[P(NMe_2)_3]_2$

Mn(1)–P(1)	2.267(1)	Mn(1)–C(7)	1.826(6)
Mn(1)–C(8)	1.842(5)	Mn(1)–C(9)	1.826(7)
Mn(1)–C(10)	1.850(5)	Mn(1)–Mn(1′)	2.946(1)
P(1)–N(1)	1.697(5)	P(1)–N(2)	1.685(4)
P(1)–N(3)	1.695(3)	N(1)–C(1)	1.478(9)
N(1)–C(2)	1.468(6)	N(2)–C(3)	1.447(10)
N(2)–C(4)	1.473(5)	N(3)–C(5)	1.439(9)
N(3)–C(6)	1.458(5)	C(7)–O(1)	1.157(8)
C(8)–O(2)	1.137(6)	C(9)–O(3)	1.139(9)
C(10)–O(4)	1.128(7)	Mn(2)–P(2)	2.269(1)
Mn(2)–C(17)	1.827(6)	Mn(2)–C(18)	1.838(5)
Mn(2)–C(19)	1.829(5)	Mn(2)–C(20)	1.843(5)
Mn(2)–Mn(2′)	2.951(1)	P(2)–N(4)	1.691(4)
P(2)–N(5)	1.690(5)	P(2)–N(6)	1.689(4)
N(4)–C(11)	1.478(7)	N(4)–C(12)	1.469(9)
N(5)–C(13)	1.441(7)	N(5)–C(14)	1.472(7)
N(6)–C(15)	1.460(6)	N(6)–C(16)	1.461(6)
C(17)–O(5)	1.151(8)	C(18)–O(6)	1.146(6)
C(19)–O(7)	1.146(7)	C(20)–O(8)	1.135(6)

TABLE 5. BOND ANGLES (°) AND THEIR ESD'S FOR $Mn_2(CO)_8[P(NMe_2)_3]_2$

P(1)–Mn(1)–C(7)	96.5(1)	P(1)–Mn(1)–C(8)	93.0(1)
C(7)–Mn(1)–C(8)	87.4(3)	P(1)–Mn(1)–C(9)	98.1(1)
C(7)–Mn(1)–C(9)	165.4(1)	C(8)–Mn(1)–C(9)	90.6(3)
P(1)–Mn(1)–C(10)	91.0(1)	C(7)–Mn(1)–C(10)	88.9(2)
C(8)–Mn(1)–C(10)	174.8(2)	C(9)–Mn(1)–C(10)	92.2(3)
P(1)–Mn(1)–Mn(1′)	177.6(1)	C(7)–Mn(1)–Mn(1′)	81.6(1)
C(8)–Mn(1)–Mn(1′)	88.2(1)	C(9)–Mn(1)–Mn(1′)	83.9(1)
C(10)–Mn(1)–Mn(1′)	87.7(1)	Mn(1)–P(1)–N(1)	116.2(1)
Mn(1)–P(1)–N(2)	115.7(1)	N(1)–P(1)–N(2)	98.7(2)
Mn(1)–P(1)–N(3)	115.1(1)	N(1)–P(1)–N(3)	98.4(2)
N(2)–P(1)–N(3)	110.3(2)	P(1)–N(1)–C(1)	115.9(3)
P(1)–N(1)–C(2)	117.0(4)	C(1)–N(1)–C(2)	111.3(5)
P(1)–N(2)–C(3)	119.8(3)	P(1)–N(2)–C(4)	121.1(4)
C(3)–N(2)–C(4)	110.5(4)	P(1)–N(3)–C(5)	120.1(4)
P(1)–N(3)–C(6)	121.5(3)	C(5)–N(3)–C(6)	111.7(4)
Mn(1)–C(7)–O(1)	178.8(3)	Mn(1)–C(8)–O(2)	179.2(2)
Mn(1)–C(9)–O(3)	178.0(4)	Mn(1)–C(10)–O(4)	177.3(6)
P(2)–Mn(2)–C(17)	95.9(1)	P(2)–Mn(2)–C(18)	93.2(2)
C(17)–Mn(2)–C(18)	88.2(3)	P(2)–Mn(2)–C(19)	97.8(2)
C(17)–Mn(2)–C(19)	166.3(2)	C(18)–Mn(2)–C(19)	90.5(2)
P(2)–Mn(2)–C(20)	91.2(1)	C(17)–Mn(2)–C(20)	88.0(2)
C(18)–Mn(2)–C(20)	174.4(3)	C(19)–Mn(2)–C(20)	92.2(2)
P(2)–Mn(2)–Mn(2′)	178.5(1)	C(17)–Mn(2)–Mn(2′)	82.7(1)
C(18)–Mn(2)–Mn(2′)	87.4(2)	C(19)–Mn(2)–Mn(2′)	83.6(2)
C(20)–Mn(2)–Mn(2′)	88.1(1)	Mn(2)–P(2)–N(4)	116.3(2)
Mn(2)–P(2)–N(5)	115.8(1)	N(4)–P(2)–N(5)	98.9(2)
Mn(2)–P(2)–N(6)	115.4(1)	N(4)–P(2)–N(6)	98.3(2)
N(5)–P(2)–N(6)	109.7(3)	P(2)–N(4)–C(11)	116.9(3)
P(2)–N(4)–C(12)	117.0(3)	C(11)–N(4)–C(12)	111.6(5)
P(2)–N(5)–C(13)	119.6(3)	P(2)–N(5)–C(14)	121.4(4)
C(13)–N(5)–C(14)	110.5(6)	P(2)–N(6)–C(15)	121.0(2)
P(2)–N(6)–C(16)	122.2(3)	C(15)–N(6)–C(16)	110.6(5)
Mn(2)–C(17)–O(5)	178.6(5)	Mn(2)–C(18)–O(6)	179.5(5)
Mn(2)–C(19)–O(7)	178.5(5)	Mn(2)–C(20)–O(8)	177.1(4)

planes as follows: Mn(1) 0.118, C(7) −0.115, C(8) 0.056, C(9) −0.111, C(10) 0.052; Mn (2) 0.116, C(17) −0.103, C(18) 0.044, C(19) −0.100, C(20) 0.043 Å. These displacements also show that two carbonyls in each half of the molecule are displaced toward the Mn–Mn bond. This distortion is evidenced further by the *trans*-OC–Mn–CO bond angles involving C(7) and C(9) and C(17) and C(19): C(7)–Mn(1)–C(9) 165.4(1), C(8)–Mn(1)–C(10) 174.8(2), C(17)–Mn(2)–C(19) 166.3(2) and C(18)–Mn(2)–C(20) 174.4(3)°. Furthermore, the carbonyl groups in the two planes are staggered with respect to each other, and the $P(NMe_2)_3$ ligands are *trans* to the Mn–Mn bond.

Discussion

The complex $Mn_2(CO)_8[P(NMe_2)_3]_2$ was prepared in a manner similar to that described by King and Korenowski [5]. NMR spectra were not previously reported and they are presented here. The $^{31}P\{^1H\}$ spectrum shows a singlet at δ 178.7 which is displaced downfield of the uncoordinated ligand, δ 122 [9,10]. Inspection of collected shift data for metal-phosphane complexes indicates that the magnitude and direction of the coordination shift (Δ) [11–13] are not unexpected [11–16]. Unfortunately, there are few ^{31}P shift data for $P(NR_2)_3$ complexes available for specific comparison. McFarlane and coworkers [14,15] have reported small downfield shifts, $\delta(^{31}P)$, for $Mo(CO)_5[P(NMe_2)_3]$ and $W(CO)_5[P(NMe_2)_3]$ of 145.3 and 125.9, respectively. The $^{13}C\{^1H\}$ spectrum shows a single slightly broadened resonance δ 38.6, which does not show resolved coupling. The resonance for the free ligand appears as a doublet, δ 38.9, J(PC) 19 Hz [10]. The ^1H NMR spectrum for the complex shows a doublet at δ 2.53, J(HP) 9 Hz which compares with data for the free ligand, δ 2.50, J(HP) 10 Hz [10], and for $W(CO)_5[P(NMe_2)_3]$, δ 2.66, J(HP) 10.6 Hz [14].

It is appropriate to compare the molecular structure of the complex with the structures of $Mn_2(CO)_8(PEt_3)_2$ and $Mn_2(CO)_8(PPh_2Me)_2$ which also display dimeric structures with staggered $Mn(CO)_4$ planes and phosphane ligand coordination *trans* to the Mn–Mn bond. Despite these similarities, the average Mn–Mn bond distance in $Mn_2(CO)_8[P(NMe_2)_3]_2$, 2.948(1) Å, is significantly longer than the distances in $Mn_2(CO)_{10}$, 2.9038(6) Å [3], $Mn_2(CO)_8(PEt_3)_2$ 2.903(1) Å [2] and $Mn_2(CO)_8(PPh_2Me)_2$ 2.90 Å [4]. The average Mn–CO and C–O bond distances in $Mn_2(CO)_8$ $[P(NMe_2)_3]_2$ are 1.835 and 1.142 Å, respectively. These are essentially identical to the average distances in $Mn_2(CO)_8(PEt_3)_2$, 1.834 and 1.140 Å. The average Mn–P bond distance in $Mn_2(CO)_8[P(NMe_2)_3]_2$, 2.268(1) Å is noticeably longer than the Mn–P distance in $Mn_2(CO)_8(PEt_3)_2$, 2.253(2) Å. The bond distance variations in the core of the $Mn_2(CO)_8[P(NMe_2)_3]_2$ molecule suggest that the $P(NMe_2)_3$ ligands are indeed imposing a different balance of σ donor/π acceptor effects than are provided by the strongly π accepting axial CO ligands in $Mn_2(CO)_{10}$ or the strongly σ donating axial PEt_3 and PPh_2Me ligands in their respective $Mn_2(CO)_8L_2$ complexes.

The structural features involving the $P(NMe_2)_3$ ligands in $Mn_2(CO)_8[P(NMe_2)_3]_2$ are also interesting especially in comparison with the structure of $Fe(CO)_4$-$[P(NMe_2)_3]$ [1]. In the latter compound, two of the nitrogen atom environments are nearly planar (sums of the bond angles at N: $\Sigma N = 358.4$ and $359.1°$) while the third nitrogen atom is distorted slightly toward a tetrahedral geometry ($\Sigma N =$

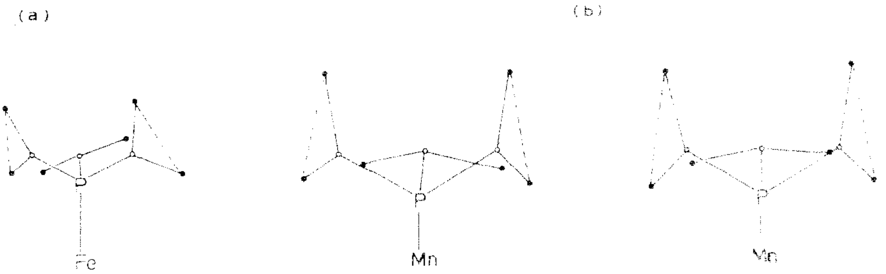

Fig. 2. Atomic projections on the nitrogen atom planes in (a) $Fe(CO)_4[P(NMe_2)_3]$ and (b) $Mn_2(CO)_8[P(NMe_2)_3]_2$: ● = carbon atom; ○ = nitrogen atoms.

353.0°). Furthermore, the NC_2 planes associated with the more nearly planar nitrogen atoms are "twisted" in the same sense out of alignment with the respective FePN planes (Fig. 2a) while the more tetrahedral nitrogen is more strongly twisted away from its corresponding FePN plane. In $Mn_2(CO)_8[P(NMe_2)_3]_2$ all three nitrogen atoms on each phosphorus atom are distorted away from trigonal planar although, once again, one nitrogen geometry is more strongly affected: ΣN(1) 344.2, ΣN(2) 351.4, ΣN(3) 353.3, ΣN(4) 345.5, ΣN(5) 351.5, ΣN (6) 353.8°. In addition, the NC_2 planes containing the more nearly planar nitrogen atoms N(2), N(3), N(5) and N(6) are twisted in an opposite sense or towards each other with respect to the MnPN planes (Fig. 2b).

The average P–N bond length in $Mn_2(CO)_8[P(NMe_2)_3]_2$, 1.691 Å (range 1.685(4) to 1.699(5) Å), is essentially the same as the P–N distance in the free ligand, 1.70 Å, [17], but significantly longer than the average distance in $Fe(CO)_4[P(NMe_2)_3]$, 1.664 Å. The PN bond lengthening in the Mn compound is consistent with the observed greater tetrahedral distortion of the nitrogen atoms and presumed reduced P–N π bonding [1,18]. The Mn–P–N bond angles (range 116.3(2) to 115.1(1)°, avg. 115.8°) are comparable to the Fe–P–N bond angles (range 116.6 to 113.2°, avg. 114.6°), but the variation in N–P–N bond angles in the Mn compound is greater than in the Fe compound: $Mn_2(CO)_8[P(NMe_2)_3]_2$ range 110.3 to 98.3°, avg. 102.4°; $Fe(CO)_4[P(NMe_2)_3]$ range 100.2 to 105.9°, avg. 103.9°. The primary contributions to the greater range in the Mn compound are the large angles N(2)–P(1)–N(3) and N(5)–P(2)–N(6) involving the more tetrahedral nitrogen atoms.

At this time simple, qualitative bonding models do not provide a complete rationalization for all of the interesting structural variations outlined above, and extensive speculation seems unwarranted. Additional syntheses and structural investigations of new metal aminophosphane complexes will be required to clearly sort out factors responsible for Mn–Mn bond distance and PN_3 structural variations.

Additional material

Tables of observed and calculated structure factors, hydrogen atom positional parameters and hydrogen atom thermal factors are available upon request from R.T.P.

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