

## THE CRYSTAL STRUCTURE OF $\text{Mn}(\text{NO})_3\text{P}(\text{C}_6\text{H}_5)_3$ : THE FIRST X-RAY ANALYSIS OF A MONONUCLEAR METAL TRINITROSYL COMPLEX\*

ROBERT D. WILSON\*\* and ROBERT BAU\*\*\*

*Department of Chemistry, University of Southern California, University Park, Los Angeles, CA 90007 (U.S.A.)*

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### Summary

The structure of  $\text{Mn}(\text{NO})_3\text{PPh}_3$  has been analyzed by single-crystal X-ray diffraction. It shows a tetrahedral geometry with essentially linear nitrosyl groups, and an eclipsed configuration around the Mn–P bond. Average distances and angles are: Mn–N 1.686(7) Å, Mn–P 2.315(2) Å, N–O 1.165(10) Å, P–C 1.815(4) Å, Mn–N–O 177.2(7)°, P–Mn–N 103.6(2)°, N–Mn–N 114.7(4)°. Final *R* factor 7.3% for 2064 non-zero reflections. The structure of the five-coordinate nitrito complex  $\text{Mn}(\text{NO})_2(\text{ONO})(\text{PEt}_3)_2$  is also mentioned briefly.

### Introduction

The nitrosyl group is an impressively flexible ligand in its mode of bonding to transition metals [1,2]. It exhibits, besides doubly- and triply-bridging capabilities, the intriguing ability to bind terminally with a range of M–N–O angles of ~120 to ~180°. The two extreme values of this angle can be viewed in simple valence bonding terms as coordination of an  $\text{NO}^-$  ligand (isoelectronic to  $\text{O}_2$ ; NO acting as a net 1-electron donor) or as  $\text{NO}^+$  (isoelectronic to CO; NO acting as a net 3-electron donor). And, although the poorer  $\sigma$ -donating and much better  $\pi$ -accepting characteristics of the linear 3-electron donor compared to the bent 1-electron donor significantly reduces the disparity in the effective electron density donated, there is evidence that a transformation between these extreme bonding configurations can be considered a stereochemically controlled internal redox reaction [1].

Since nitrosylmetals display such a rich and varied chemistry, it is useful to

\* Dedicated to Professor Helmut Behrens on the occasion of his 65th birthday at May 30th 1980.

\*\* Present address: Kodak Research Laboratories, Lake Ave., Rochester, N.Y. 14612.

\*\*\* Author to whom correspondence should be sent.

have a collection of structural data from which theoretical models of bonding can be developed. Yet, while numerous structural analyses have been made on mono- and di-nitrosyl complexes, to our knowledge no crystallographic studies of mononuclear tri-nitrosyl complexes have been carried out. It is thus of interest to examine the structure of the long-known species  $\text{Mn}(\text{NO})_3\text{CO}$ , a molecule of some historical note since it is a member of the pseudo-nickel carbonyl series  $\text{Ni}(\text{CO})_4$ ,  $\text{Co}(\text{CO})_3\text{NO}$ ,  $\text{Fe}(\text{CO})_2(\text{NO})_2$ ,  $\text{Mn}(\text{CO})(\text{NO})_3$ ,  $\text{Cr}(\text{NO})_4$ . The geometries of the members of this group are generally assumed to be approximately tetrahedral, with linear ligands\*. However, it was recently suggested that  $\text{Mn}(\text{NO})_3(\text{CO})$  might have distinctly bent M—NO linkages and thus be different from the other members of the series [1]. In order to explore this question, the X-ray diffraction analysis of the triphenylphosphine derivative was performed. The far lower volatility and the less disorder-prone  $\text{PPh}_3$  moiety made the substituted compound a much better choice for X-ray study than the parent carbonyl. And the similarities between the IR spectra of  $\text{Mn}(\text{NO})_3\text{CO}$  and  $\text{Mn}(\text{NO})_3\text{PPh}_3$  in the nitrosyl stretching region hopefully permits the same conclusions to be drawn regarding the  $\text{Mn}(\text{NO})_3$  portions of both molecules.

## Experimental

Compounds of the type  $\text{Mn}(\text{NO})_3\text{PR}_3$  were originally prepared by Hieber and Tengler [5] from  $\text{Mn}(\text{CO})_4(\text{PR}_3)\text{I}$ , but we followed a more convenient photolytic route described recently by Herberhold and Razavi [6], using " $\text{Mn}(\text{NO})_3 \cdot \text{THF}$ " as an intermediate. A similar procedure for the photolytic preparation of  $\text{Mn}(\text{NO})_3(\text{CO})$  has also been reported by Satija and Swanson [7].

*Preparation of " $\text{Mn}(\text{NO})_3 \cdot \text{THF}$ " in tetrahydrofuran.*  $\text{Mn}_2(\text{CO})_{10}$  (0.30 g, 0.77 mol) is dissolved in 100 ml dry tetrahydrofuran (distilled over  $\text{LiAlH}_4/\text{N}_2$ ), and the solution is cooled in a dry ice/acetone bath. The flask is fitted with a gas delivery tube and is purged with  $\text{N}_2$  for about 30 minutes. This stream is then replaced by  $\text{NO}$ , which was purified by passage through a column of Linde 13A molecular sieves at  $-76^\circ\text{C}$ . After some minutes to allow for  $\text{NO}$  saturation of the solution, photolysis (with a medium-pressure 400-watt Hanovia mercury vapor lamp) is started and is continued for about 5 h with intermittent replenishment of the dry ice. A solution IR spectrum, taken after about 30 minutes of  $\text{N}_2$  bubbling, reveals the two strong bands of the " $\text{Mn}(\text{NO})_3 \cdot \text{THF}$ " species [6] at 1778 and 1666  $\text{cm}^{-1}$ , and nothing in the carbonyl region. This solution,

\* The electron diffraction patterns [3a,b] of  $\text{Ni}(\text{CO})_4$ ,  $\text{Co}(\text{CO})_3(\text{NO})$  and  $\text{Fe}(\text{CO})_2(\text{NO})_2$  were interpreted, in terms of a tetrahedral molecular model with no bending in the ligands, to yield the following bonding distances in Å

	M—C	C—O	M—N	N—O
Fe	1.84	1.15	1.77	1.12
Co	1.83	1.14	1.76	1.10
Ni	1.82	1.15		

In addition to this rather dated work, there has been reported a more recent electron diffraction investigation of the remaining members of the pseudo-nickel carbonyl series, [i.e.,  $\text{Mn}(\text{CO})_3(\text{NO})$  and  $\text{Cr}(\text{NO})_4$ ], which suggest the same overall molecular structure [4a,b]. Finally, a more accurate electron diffraction analysis of  $\text{Ni}(\text{CO})_4$  has recently been published [4c].

which is approximately 15 mmolar since the reaction proceeds cleanly in high yield, can be stored for at least 2 months under  $N_2$  at  $-10^\circ C$ .

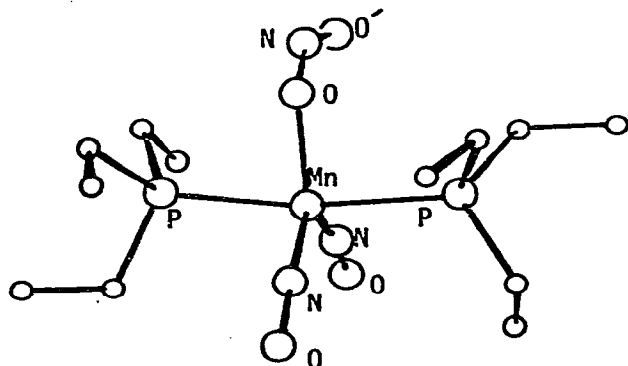
**Preparation of  $Mn(NO)_3PPh_3$ .** An excess of  $PPh_3$  was added to a portion of the above solution. After 3 h of stirring at room temperature, the mixture had changed from the almost opaque olive green of " $Mn(NO)_3 \cdot THF$ " to a clear, lighter-green solution. Evaporation of the solvent under vacuum, redissolution of the residue in dry degassed pentane, and subsequent slow cooling to about  $-10^\circ C$  yielded two crystalline materials. They were shown by IR to be  $Mn(NO)_3PPh_3$  (dark green crystals) and excess  $PPh_3$  (white crystals). Crystals of  $Mn(NO)_3PPh_3$  lose their shiny luster after several months but otherwise appear essentially air stable. The IR spectrum of this compound, taken in a KBr pellet, displays two peaks in the nitrosyl stretching region, 1780(m) and 1670(s, broad)  $cm^{-1}$ , in fair agreement with published data [6].

We also isolated, as an impurity in the preparation of the analogous  $Mn(NO)_3PEt_3$ , the five coordinate nitrito complex  $Mn(NO)_2(ONO)(PEt_3)_2$ , whose X-ray structure shows the presence of a unidentate, O-bonded  $NO_2$  ligand\*.

### Crystallographic details

An irregularly-shaped specimen exhibiting shiny facets was wedged inside a 0.3 mm diameter thin-walled glass capillary and sealed. Precession photos showed Laue symmetry  $\bar{1}$ , consistent with either of the triclinic space groups  $P1$  or  $P\bar{1}$ . The refined unit cell parameters, obtained from the setting angles of 14 pairs of Friedel-related reflections, are given in Table 1 along with other crystal data. Data were collected on a Nonius CAD-3 diffractometer with  $Mo-K_\alpha$  radiation up to a  $2\theta$  limit of  $45^\circ$ . One unique hemisphere of data (3116 mea-

\* The structure of  $Mn(NO)_2(ONO)(PEt_3)_2$  [8a] consists of a trigonal bipyramidal arrangement of ligands around Mn, with the two phosphine ligands in axial positions. As mentioned in the text, the nitrito ligand is unidentate and oxygen-bonded. Average distances and angles: Mn-P 2.33 Å, Mn-N(NO) 1.67 Å, Mn-O( $NO_2$ ) 2.08 Å, N-O(NO) 1.17 Å, N-O( $NO_2$ ) 1.19 Å, Mn-N-O(NO)  $165^\circ$ , Mn-O-N( $NO_2$ )  $123^\circ$ , O-N-O( $NO_2$ )  $118^\circ$ , P-Mn-P  $167^\circ$ . Crystal data for  $Mn(NO)_2(ONO)(PEt_3)_2$ : space group  $P2_1$  (monoclinic),  $a$  8.745(9) Å,  $b$  15.157(16) Å,  $c$  7.584(13) Å,  $\beta$   $92.69(6)^\circ$ ,  $Z$  = 2;  $\rho$ (obs)  $1.30 g cm^{-3}$ ,  $\rho$ (calc)  $1.32 g cm^{-3}$ .  $R$  factor 9.8% for 1488 observed reflections [ $I > 3\sigma(I)$ ]. This structure is very similar to that of  $Mn(NO)_2[P(OMe)_2Ph]_2Cl$  [8b].



The formation of nitrito complexes in reactions between NO and a transition metal compound is not unprecedented [9].

TABLE 1  
CRYSTAL DATA FOR  $\text{Mn}(\text{NO})_3\text{P}(\text{C}_6\text{H}_5)_3$

Space group $P\bar{1}$ (triclinic)	Mol. wt. 407.3 g/mole
$a$ 10.411(5) Å	$\rho(\text{calc})$ 1.456 g/cm <sup>3</sup>
$b$ 11.070(7) Å	$\rho(\text{obs})$ 1.46 g/cm <sup>3</sup>
$c$ 10.189(6) Å	$\mu$ 8.56 cm <sup>-1</sup> (for Mo- $K_\alpha$ X-rays)
$\alpha$ 77.88(3) <sup>o</sup>	Mount axis (100)
$\beta$ 115.52(3) <sup>o</sup>	
$\gamma$ 118.67(2) <sup>o</sup>	
$V$ 929.78 Å <sup>3</sup>	
$Z = 2$	

sured reflections) yielded 2064 observed intensities [with  $I > 3\sigma(I)$ ] after processing. In view of the small value of the linear absorption coefficient ( $\mu$  8.56 cm<sup>-1</sup>), and the fact that the intensity of an axial reflection did not vary appreciably with the spindle angle  $\phi$ , no absorption correction was deemed necessary.

The structure was solved in the centric space group  $P\bar{1}$  (suggested by the observed density, which indicated the presence of two molecules per unit cell) by standard heavy atom methods. The Mn and P atomic positions were derived from an examination of a Patterson map. Subsequent difference Fourier maps disclosed all the remaining non-hydrogen coordinates. Several cycles of least-squares refinement were then performed in which the Mn, P and O atoms were assigned anisotropic temperature factors. For reasons of economy, the phenyl rings were treated as rigid groups. The  $R$  factor converged to a final value of 7.3% in the last few cycles of refinement.

## Discussion

The geometry of  $\text{Mn}(\text{NO})_3\text{PPh}_3$  is depicted in Fig. 1–3, and various distances and angles listed in Tables 2–4. A table of the observed and calculated structure factors is available as supplementary material\*. The molecule possesses non-crystallographic  $C_3$  symmetry, but the salient feature is the appearance of essentially linear nitrosyls (average M–N–O 177.2(7)<sup>o</sup>) and bond lengths appropriate for that mode of coordination (average M–N 1.686(7) Å)\*\*.

The three independent oxygen atoms were allowed to vary anisotropically during the least-squares refinement in order to see if they might be disordered. The anisotropic thermal ellipsoids for the oxygens are elongated in a direction perpendicular to their respective NO bonds, but not grossly so\*\*\*. This type  $\text{Fe}(\text{NO})_2(\text{CO})\text{PPh}_3$  [12],  $\text{Co}(\text{CO})_2(\text{NO})\text{L}$  (L =  $\text{PPh}_3$  [15],  $\text{AsPh}_3$  [16], and  $\text{SbPh}_3$ -[17]), even though one might expect the staggered configuration to be sterically

\* A listing of the table of structure factors has been deposited as NAPS Document. Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017.

\*\* Reflecting the substantially increased retrodonative bonding, the metal–nitrogen lengths for linear arrangements are in the range 1.57–1.78 Å in a host of 5 coordinate species, while those for the bent examples lie between 1.98 and 1.86 Å (see p. 83 of ref. 2). A more valid comparison can be obtained by examining the M–N lengths in a single compound containing both forms of binding:  $[\text{Ru}(\text{NO})_2(\text{PPh}_3)_2\text{Cl}]^+$ ; 1.859(16) vs. 1.738(16) Å [10].

\*\*\* The root mean square amplitudes of motion (in Å) of the oxygen atoms along the principal axes of the ellipsoids are: O(1), 0.252, 0.312, 0.423; O(2), 0.245, 0.280, 0.334; O(3), 0.231, 0.300, 0.494.

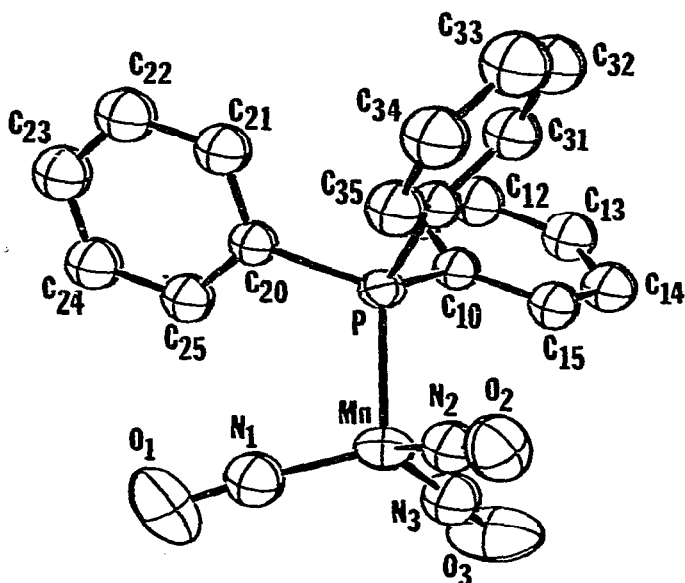


Fig. 1. A molecular plot of  $\text{Mn}(\text{NO})_3\text{PPh}_3$ , showing the numbering scheme used.

of elongation is commonly seen in carbonyl and nitrosyl complexes, and can be attributed to the fact that the direction of greatest vibrational motion (corresponding to the  $\text{M}-\text{N}-\text{O}$  bend) is perpendicular to the  $\text{M}-\text{N}$  axis. Furthermore, in a difference Fourier map calculated without the oxygen atoms, no double maxima were observed at the oxygen positions. We can thus conclude that the nitrosyl groups are truly linear and not a disordered superposition of bent ligands.

Although inconsistent with the suggestion of bent  $\text{M}-\text{N}-\text{O}$  bonds [1], the X-ray results generally agree with the proposed model of Beck and co-workers [11]. They assumed linear  $\text{NO}$ 's with  $C_{3v}$  geometry and obtained  $\text{N}-\text{Mn}-\text{N}$

(Continued on p. 130)

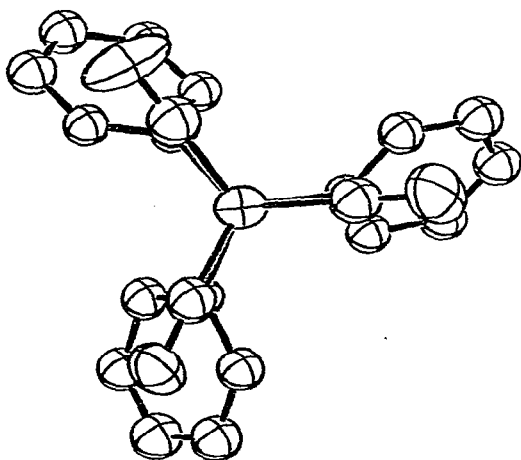


Fig. 2. An alternative view of  $\text{Mn}(\text{NO})_3\text{PPh}_3$ , showing the eclipsing of groups around the  $\text{Mn}-\text{P}$  axis.

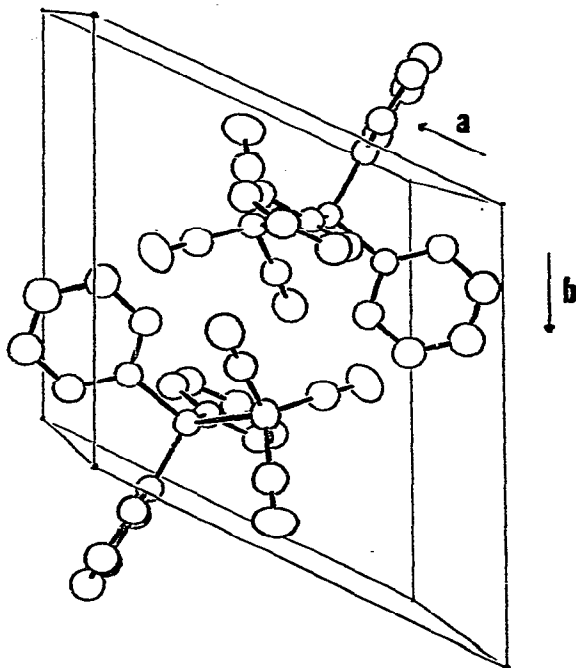
Fig. 3. A unit cell plot of  $\text{Mn}(\text{NO})_3\text{PPh}_3$ .

TABLE 2

FINAL ATOMIC PARAMETERS FOR  $\text{Mn}(\text{NO})_3\text{P}(\text{C}_6\text{H}_5)_3$ .(a) Atomic positions (fractional coordinates) <sup>a</sup>

Atom	x	y	z
Mn	-0.03597(11)	0.28838(10)	0.22426(11)
P	-0.21389(18)	0.18108(16)	0.33836(16)
N(1)	0.1345(8)	0.3915(6)	0.3516(7)
N(2)	-0.1210(7)	0.3746(6)	0.0872(6)
N(3)	-0.0335(7)	0.1541(7)	0.1720(7)
O(1)	0.2577(7)	0.4640(6)	0.4361(8)
O(2)	-0.1766(6)	0.4367(6)	-0.0083(6)
O(3)	-0.0294(9)	0.0671(6)	0.1316(10)
C(10)	-0.3112(5)	-0.0053(3)	0.3266(4)
C(11)	-0.3305(5)	-0.0886(4)	0.4465(3)
C(12)	-0.4123(6)	-0.2313(4)	0.4316(4)
C(13)	-0.4748(6)	-0.2908(3)	0.2967(5)
C(14)	-0.4556(5)	-0.2075(4)	0.1768(4)
C(15)	-0.3738(6)	-0.0648(4)	0.1918(3)
C(20)	-0.1289(4)	0.2181(5)	0.5310(3)
C(21)	-0.2092(4)	0.2428(5)	0.5941(4)
C(22)	-0.1442(5)	0.2651(5)	0.7434(4)
C(23)	0.0011(5)	0.2628(6)	0.8296(3)
C(24)	0.0813(4)	0.2380(6)	0.7665(4)
C(25)	0.0164(5)	0.2157(4)	0.6172(4)
C(30)	-0.3749(4)	0.2304(4)	0.2623(5)
C(31)	-0.5336(5)	0.1347(3)	0.2242(5)
C(32)	-0.6516(4)	0.1795(4)	0.1694(6)
C(33)	-0.6109(5)	0.3199(5)	0.1529(6)
C(34)	-0.4522(5)	0.4155(3)	0.1910(6)
C(35)	-0.3342(4)	0.3708(4)	0.2457(5)

(b) Group parameters for the phenyl rings <sup>b</sup>

Group	Ring 1 <sup>c</sup>	Ring 2 <sup>c</sup>	Ring 3 <sup>c</sup>
$x_0$	-0.3930(3)	-0.0639(3)	-0.4929(4)
$y_0$	-0.1481(3)	0.2404(3)	0.2751(3)
$z_0$	0.3117(3)	0.6803(3)	0.2076(3)
$\phi$	-0.585(3)	0.944(3)	-0.791(2)
$\theta$	-2.721(2)	-2.906(2)	2.939(3)
$\rho$	1.442(3)	-1.951(3)	0.096(3)

(c) Anisotropic temperature factors <sup>d</sup>

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Mn	156(2)	118(1)	153(2)	56(1)	88(1)	17(1)
P	119(3)	98(2)	98(2)	50(2)	45(2)	4(1)
O(1)	207(11)	174(8)	287(12)	33(8)	36(9)	8(8)
O(2)	218(10)	175(8)	159(7)	79(7)	52(7)	26(6)
O(3)	414(16)	152(8)	531(18)	110(9)	325(14)	-7(9)

## (d) Isotropic temperature factors

Atom	B(Å <sup>2</sup> )	Atom	B(Å <sup>2</sup> )
N(1)	5.4(1)	C(22)	5.8(2)
N(2)	4.7(1)	C(23)	5.6(1)
N(3)	5.7(1)	C(24)	5.4(1)
C(10)	3.6(1)	C(25)	4.6(1)
C(11)	4.6(1)	C(30)	3.8(1)
C(12)	5.5(1)	C(31)	5.0(1)
C(13)	5.6(2)	C(32)	6.1(2)
C(14)	5.5(2)	C(33)	6.8(2)
C(15)	4.5(1)	C(34)	5.9(2)
C(20)	3.7(1)	C(35)	4.9(1)
C(21)	4.9(1)		

<sup>a</sup> Carbon atom positions, although given here individually, were never refined independently and are calculated along with their errors from the rigid group parameters and errors. <sup>b</sup> The coordinates  $x_0$ ,  $y_0$  and  $z_0$  are the fractional coordinates of the center of the group; the angles  $\phi$ ,  $\theta$ , and  $\rho$  (in radians) are the three rotational angles defined by Doedens [19]. <sup>c</sup> The phenyl rings were treated as rigid groups with ideal  $D_{6h}$  symmetry and the following molecular parameters were used: C—C—C 120° and C—C 1.394 Å. <sup>d</sup> The form of the anisotropic thermal ellipsoid is:  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}kl + 2\beta_{23}kl)]$ .

TABLE 3  
SELECTED BOND DISTANCES (Å) IN  $\text{Mn}(\text{NO})_3\text{P}(\text{C}_6\text{H}_5)_3$

Mn—P	2.315(2)
Mn—N(1)	1.682(7)
Mn—N(2)	1.682(7)
Mn—N(3)	1.695(8)
N(1)—O(1)	1.175(10)
N(2)—O(2)	1.171(9)
N(3)—O(3)	1.149(12)
P—C(10)	1.815(5)
P—C(20)	1.816(3)
P—C(30)	1.813(5)

TABLE 4  
SELECTED BOND ANGLES (°) IN  $\text{Mn}(\text{NO})_3\text{P}(\text{C}_6\text{H}_5)_3$

<i>(A) Bond angles</i>			
P—Mn—N(1)	105.0(2)	N(1)—Mn—N(2)	113.6(4)
P—Mn—N(2)	102.8(2)	N(1)—Mn—N(3)	115.5(4)
P—Mn—N(3)	102.9(2)	N(2)—Mn—N(3)	114.9(3)
Mn—N(1)—O(1)	176.5(7)	Mn—P—C(10)	114.1(2)
Mn—N(2)—O(2)	178.3(6)	Mn—P—C(20)	114.7(2)
Mn—N(3)—O(3)	176.8(7)	Mn—P—C(30)	112.9(2)
<i>(B) Torsion angles<sup>a</sup></i>			
Mn—P—C(10)—C(15)	44.2	N(1)—Mn—P—C(20)	5.3
Mn—P—C(20)—C(25)	48.4	N(2)—Mn—P—C(30)	5.1
Mn—P—C(30)—C(35)	46.8	N(3)—Mn—P—C(10)	5.4

<sup>a</sup> The torsion angle ABCD is equivalent to the dihedral angle between plane ABC and plane BCD.

angles of  $109^\circ$  for  $\text{Mn}(\text{NO})_3\text{CO}$  and  $111^\circ$  for  $\text{Mn}(\text{NO})_3\text{PPh}_3$  by analyzing the intensity ratios of the  $\nu(\text{NO})$  infrared absorption bands. The corresponding angles from our results average to  $114.7(4)^\circ$ . Notice that this means the nitrosyls are bent away from the idealized tetrahedral positions toward the bulky phosphine, a seemingly sterically unfavorable condition. This distortion of the nitrosyls in the "wrong direction" has been reported previously for a few di-nitrosyl complexes [12,13].

In general, the triphenylphosphine ligand yielded the expected structural values. The phenyl rings are arranged in a helical way and are roughly perpendicular to each other. The "3-blade propeller" is nearly rigorously symmetric, with the phenyl rings tilted  $44.2^\circ$ ,  $48.4^\circ$ , and  $46.8^\circ$  from the three-fold axis\*. These values are not effectively different from those obtained by Brock and Ibers in their conformational analysis of the idealized, isolated  $\text{PPh}_3$  molecule [14].

Overall, the molecular geometry is in excellent agreement with the isoelectronic, isostructural and trigonally disordered compounds  $\text{Co}(\text{CO})_2(\text{NO})\text{PPh}_3$  [15] and  $\text{Fe}(\text{CO})(\text{NO})_2\text{PPh}_3$  [16]. Some trends observed in the three compounds are:

	X—M—X	M—X	M—P
M = Mn, X = N	$114.7(4)^\circ$	1.686(7) Å	2.315(2) Å
M = Fe, X = (2/3)N + (1/3)C	$114.4(4)^\circ$	1.709(7) Å	2.260(3) Å
M = Co, X = (1/3)N + (2/3)C	$113.4(3)^\circ$	1.740(6) Å	2.224(3) Å

The first two trends mainly represent a carbonyl dilution effect in the weighted average values, but the third series represents "real" M—P distances and presumably reflect the normal contraction of the covalent radii in the order  $\text{Mn} > \text{Fe} > \text{Co}$ .

A noteworthy result in the structure of  $\text{Mn}(\text{NO})_3\text{PPh}_3$  was the nearly eclipsed configuration of the phenyl and NO groups: the average N—Mn—P—C dihedral angle is only  $5.3^\circ$ . The same eclipsing is found for the isostructural compounds

\* The tilt angles are defined as the Mn—P—C—C(*ortho*) dihedral angles.



more favorable. Curiously enough, the 17-electron paramagnetic species  $\text{Fe}(\text{NO})_2(\text{PPh}_3)\text{Cl}$  does exhibit a staggered conformation [18].

The main conclusion derived from this study is that the NO ligands in  $\text{Mn}(\text{NO})_3\text{PPh}_3$  are linear, which strongly suggests that the nitrosyl groups in  $\text{Mn}(\text{NO})_3\text{CO}$  are also linear. In arriving at their prediction of bent NO groups in  $\text{Mn}(\text{NO})_3\text{CO}$ , Enemark and Feltham drew attention to a particular molecular orbital (labelled  $1a_1$  in Fig. 28 of ref. 1), which contains contributions from the  $\pi^*$  orbitals of NO as well as the  $d_{z^2}$  orbital of the metal atom. It was argued that if this orbital is primarily  $\pi^*(\text{NO})$  in character, it would be bonding with respect to the three NO ligands and hence would be stabilized by the bending of the M—N—O angles. The authors, however, also point out that, should the  $1a_1$  orbital be primarily  $d_{z^2}$  in character, essentially linear MNO groups would result. The latter statement seems to be more appropriate in view of the present results.

### Note added in proof

In a private communication to us, Prof. Enemark has made two important points: (a) The opening up of the N—Mn—N angles is unusual on steric grounds but consistent with a pair of electrons in  $d_{z^2}$  which would have a density along the  $C_3$  axis between the nitrosyl ligands. (b) The eclipsed geometry is also consistent with the Enemark/Feltham MO scheme (Figure 28a in reference 1), since the relatively high-lying HOMO  $1e'$  [ $xy$ ,  $x^2 - y^2$ ,  $\pi^*(\text{NO})$ ] localizes electron density in non-bonding orbitals of trigonal symmetry in the  $xy$  plane. The eclipsed geometry should minimize the non-bonded repulsions between the electrons in  $1e'$  and the electrons in the P—C and Mn—N bonds.

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