

contacts in $\text{RuCl}_2(\text{P}(\text{C}_6\text{H}_5)_2(o\text{-C}_6\text{H}_4\text{OCH}_3))_2\text{CH}_2\text{Cl}_2$ (20 pages). Ordering information is given on any current masthead page.

References and Notes

- Addresses for correspondence: J.C.J., Department of Inorganic Chemistry, The University of Bristol, BS8 1TS, England; T.B.R., School of Chemical Sciences, University of Illinois, Urbana-Champaign, Urbana, Ill. 61801.
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Contribution from the Department of Chemistry, University of Natal, Durban 4001, Republic of South Africa, and the National Chemical Research Laboratory, CSIR, Pretoria 0001, Republic of South Africa

Structures of Five-Coordinate Dinitrosyls of Manganese.

3. Dinitrosyltris(dimethyl phenylphosphonite)manganese(I) Tetrafluoroborate,



MICHAEL LAING,* ROLF H. REIMANN, and ERIC SINGLETON

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The crystal structure of dinitrosyltris(dimethyl phenylphosphonite)manganese(I) tetrafluoroborate, $[\text{Mn}(\text{NO})_2\{\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5\}_3]\text{BF}_4$, has been determined by X-ray diffraction. The compound crystallizes from ether/ CH_2Cl_2 in the monoclinic space group $P2_1/c$, with $a = 14.585(5) \text{ \AA}$, $b = 13.085(5) \text{ \AA}$, $c = 18.610(10) \text{ \AA}$, $\beta = 110.45(5)^\circ$, $V = 3327 \text{ \AA}^3$, $\rho_{\text{obsd}} = 1.41 \text{ g cm}^{-3}$, and $Z = 4$. The structure was solved by conventional Patterson and Fourier methods and refined by block-diagonal least squares to $R = 0.064$ for 2999 reflections with $I > 2.0\sigma(I)$. The coordination about the manganese is trigonal bipyramidal with the two NO groups equatorial. The two axial phosphonite ligands bend toward the equatorial phosphonite ligand. The NO groups are ordered and are bent in toward each other. The atoms of the $\{\text{Mn}(\text{NO})_2\text{P}_{\text{eq}}\}$ group are coplanar. Bond lengths and angles of interest are as follows: $\text{Mn}-\text{P}_{\text{ax}} = 2.303, 2.312(5) \text{ \AA}$; $\text{Mn}-\text{P}_{\text{eq}} = 2.356(5) \text{ \AA}$; $\text{Mn}-\text{N} = 1.649, 1.649(10) \text{ \AA}$; $\text{N}-\text{O} = 1.18, 1.19(1) \text{ \AA}$; $\text{Mn}-\text{N}-\text{O} = 168, 170(1)^\circ$; $\text{P}_{\text{ax}}-\text{Mn}-\text{P}_{\text{ax}} = 175.5(5)^\circ$; $\text{P}_{\text{ax}}-\text{Mn}-\text{P}_{\text{eq}} = 87.7, 89.8(5)^\circ$; $\text{N}-\text{Mn}-\text{N} = 116.5(5)^\circ$; $\text{O}-\text{Mn}-\text{O} = 107.4(5)^\circ$, $\text{N}-\text{Mn}-\text{P}_{\text{eq}} = 114.0, 129.4(5)^\circ$. Short nonbonded separations are as follows: $\text{P}_{\text{ax}}\cdots\text{N} = 2.82, 2.82, 2.85, 2.92 \text{ \AA}$; $\text{P}_{\text{ax}}\cdots\text{P}_{\text{eq}} = 3.23, 3.29 \text{ \AA}$.

Introduction

Although neutral nitrosyl complexes of the 3d transition metals are well-known,¹ relatively few cationic species have

been prepared.² The compound $[\text{Mn}(\text{NO})_2\{\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5\}_3]\text{BF}_4$ was readily made³ from $[\text{Mn}(\text{NO})_2\{\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5\}_2\text{Cl}]$, a compound of known crystal structure.⁴ Although the manganese atom has the same formal electron count in these two complexes, the frequencies of the nitrosyl stretching

* To whom correspondence should be addressed at the University of Natal.

Table I. Fractional Atomic Coordinates

atom	x	y	z	atom	x	y	z
Mn	0.18725 (8)	0.19077 (9)	0.23274 (6)	C(220)	0.1335 (7)	0.4719 (7)	0.2498 (5)
P(1)	0.32279 (15)	0.09184 (16)	0.29616 (11)	C(310)	0.4122 (6)	0.3727 (6)	0.2567 (5)
P(2)	0.06021 (15)	0.30042 (16)	0.17219 (12)	C(320)	0.2650 (7)	0.4043 (7)	0.0563 (5)
P(3)	0.27558 (15)	0.25695 (16)	0.15867 (11)	C(11)	0.4360 (5)	0.1519 (5)	0.3556 (4)
N(1)	0.1186 (5)	0.0911 (5)	0.1939 (4)	C(12)	0.5214 (5)	0.1436 (6)	0.3366 (4)
N(2)	0.1851 (5)	0.2294 (5)	0.3165 (4)	C(13)	0.6087 (6)	0.1903 (6)	0.3858 (5)
O(1)	0.0641 (4)	0.0211 (5)	0.1746 (4)	C(14)	0.6077 (6)	0.2422 (6)	0.4517 (5)
O(2)	0.1724 (5)	0.2419 (6)	0.3755 (3)	C(15)	0.5225 (6)	0.2502 (6)	0.4699 (4)
O(11)	0.3645 (3)	0.0155 (4)	0.2488 (3)	C(16)	0.4347 (6)	0.2047 (6)	0.4212 (4)
O(12)	0.2878 (4)	0.0246 (4)	0.3530 (3)	C(21)	-0.0043 (6)	0.2879 (6)	0.0705 (4)
O(21)	-0.0193 (4)	0.2745 (4)	0.2107 (3)	C(22)	0.0045 (7)	0.3611 (7)	0.0188 (5)
O(22)	0.0759 (4)	0.4207 (4)	0.1787 (3)	C(23)	-0.0434 (8)	0.3422 (8)	-0.0617 (5)
O(31)	0.3872 (4)	0.2873 (4)	0.2010 (3)	C(24)	-0.0992 (8)	0.2553 (8)	-0.0861 (6)
O(32)	0.2248 (4)	0.3560 (4)	0.1109 (3)	C(25)	-0.1076 (8)	0.1840 (8)	-0.0339 (6)
B	0.6683 (9)	0.1617 (8)	0.1896 (6)	C(26)	-0.0609 (7)	0.1984 (7)	0.0460 (5)
F(1)	0.7164 (6)	0.1626 (6)	0.1401 (4)	C(31)	0.2861 (6)	0.1670 (6)	0.0882 (4)
F(2)	0.6160 (6)	0.0767 (5)	0.1760 (5)	C(32)	0.3788 (7)	0.1299 (7)	0.0920 (5)
F(3)	0.6038 (5)	0.2424 (5)	0.1770 (4)	C(33)	0.3811 (9)	0.0555 (7)	0.0376 (6)
F(4)	0.7309 (6)	0.1670 (7)	0.2595 (3)	C(34)	0.2944 (9)	0.0236 (7)	-0.0173 (6)
C(110)	0.3028 (6)	-0.0603 (6)	0.1962 (5)	C(35)	0.2009 (9)	0.0587 (7)	-0.0215 (5)
C(120)	0.3544 (6)	-0.0497 (6)	0.4070 (5)	C(36)	0.1972 (7)	0.1336 (6)	0.0337 (4)
C(210)	-0.1130 (6)	0.3319 (8)	0.1888 (6)				

modes were 1760 and 1712 cm^{-1} in the cationic species compared to 1723 and 1674 cm^{-1} in the neutral molecule.³ This increase in stretching frequency on going from a neutral to a cationic species could be ascribed⁵ solely to the introduction of the positive charge, but what was not clear was whether this presumed strengthening of the NO bond had caused the Mn-N-O bond angle to become closer to linearity. The availability of good crystals of the BF_4^- salt thus presented an ideal opportunity not only to study the effect on the bonding between the Mn atom and the NO group on going from neutral molecule to isoelectronic cation but also to determine what differences (if any) there are between the lengths of the axial and equatorial Mn-P bonds.

Experimental Section

The compound was prepared as described previously,³ and suitable crystals were obtained from dichloromethane/diethyl ether. Preliminary Weissenberg and precession photographs showed that the crystals were monoclinic, space group $P2_1/c$.

The crystal data are as follows: $\text{C}_{24}\text{H}_{33}\text{MnN}_2\text{O}_8\text{P}_3\text{BF}_4$, mol wt 711.7, monoclinic space group $P2_1/c$, $a = 14.585$ (5) Å, $b = 13.085$ (5) Å, $c = 18.610$ (10) Å, $\beta = 110.45$ (5)°, $V = 3327$ Å³, $\rho_{\text{obsd}} = 1.41$ g cm^{-3} , $Z = 4$, $\mu(\text{Mo K}\alpha) = 6.35$ cm^{-1} .

Accurate unit cell dimensions were determined from least-squares refinement of the 2θ , χ , and ϕ angles of 25 reflections measured on a Philips PW 1100 four-circle diffractometer (CSIR, Pretoria) with graphite-monochromated Mo K α radiation ($\lambda = 0.7107$ Å). Intensity data were collected at ambient temperature for θ between 3 and 22° from a crystal of dimensions $0.4 \times 0.4 \times 0.4$ mm. Three reflections were used as intensity standards and remeasured after every 60 reflections; no decomposition of the crystal was detectable. The diffractometer was operated in the standard mode; the ω - 2θ scan technique was used; the scan width was 1.2°, each peak was scanned over 30 s, and the background was counted for 30 s. Of the 4295 reflections measured (including space group extinctions), 2999 were classed as observed: $I > 2.0\sigma(I)$. Lorentz-polarization corrections were applied; corrections for absorption were considered unnecessary as μ was small.

The coordinates of the Mn atom were readily obtained from a three-dimensional Patterson map, and the remaining atoms were located in the subsequent Fourier maps. The structure was refined by block-diagonal least squares, first isotropically and then anisotropically. Weighting was proportional to $1/\sigma(F)$; scattering factors were taken from ref 6; that of manganese was corrected for the real part of anomalous dispersion; the hydrogen atoms were not included. At convergence, the conventional $R = 0.064$ for 2999 observed data. The only residual electron density in the final difference Fourier map was in the vicinity of the F atoms, showing that the BF_4^- was slightly disordered. No attempt was made to correct for this disordering. The values of F_c for the unobserved data were satisfactorily small.

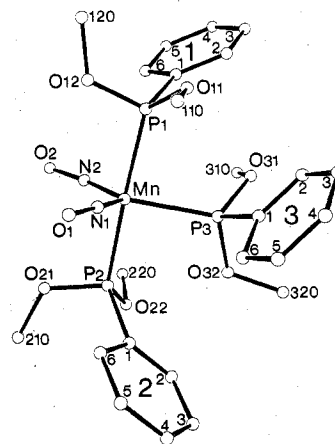


Figure 1. Projection of the cation showing the numbering system. C atoms are identified by number only; viz., atom 2 in phenyl ring 3 is C(32). The coplanarity of atoms Mn, P(3), P(2), P(1), O(12), O(21), C(120), and C(210) is evident.

All calculations were done with the local set of programs⁷ on a Burroughs 5100 computer. A list of observed and calculated structure factors is available.⁸

The fractional atomic coordinates are given in Table I, and the anisotropic thermal parameters are in Table II; estimated standard deviations in the last significant figure are given in parentheses.

Results and Discussion

As expected, the coordination about the manganese atom is trigonal bipyramidal (see Figure 1) with the nitrosyl groups equatorial.

The Mn-P bonds to the two axial phosphonite ligands are similar to, but slightly longer than, the analogous bonds found⁹ in the neutral chloro compound, mean value 2.307 (5) Å vs. 2.294 (5) Å. The bond to the unique equatorial group is considerably longer, 2.356 Å, implying not only that this Mn-P bond has a character different from that of the other two Mn-P bonds but also that this equatorial bond is weaker than the axial bonds. This equatorial Mn-P bond is almost identical in length with the equatorial Mn-Cl bond found in the chloro analogue; the mean bond length is 2.354 (5) Å.

The geometry of the $\{\text{Mn}(\text{NO})_2\}$ group is closely similar to that found in the chloro molecule,⁹ the main difference being an increase in the N-Mn-N angle and an increased linearity of the Mn-N-O moiety. Once again the NO groups are bent in toward each other (see Tables III and IV). Neither the

Table II. Anisotropic Thermal Parameters^a

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mn	467 (7)	480 (8)	237 (4)	-13 (13)	212 (9)	23 (10)
P(1)	479 (13)	451 (14)	263 (8)	-15 (23)	163 (17)	3 (18)
P(2)	478 (13)	526 (16)	311 (8)	18 (25)	141 (17)	30 (19)
P(3)	548 (14)	457 (15)	275 (8)	-67 (24)	321 (17)	16 (18)
N(1)	63 (5)	50 (5)	46 (3)	-14 (8)	26 (6)	9 (6)
N(2)	69 (5)	87 (6)	32 (3)	30 (9)	29 (6)	9 (6)
O(1)	81 (5)	70 (5)	86 (4)	-53 (8)	21 (7)	1 (7)
O(2)	136 (6)	167 (8)	34 (3)	74 (11)	69 (7)	-6 (7)
O(11)	54 (4)	57 (4)	33 (2)	4 (6)	19 (4)	-26 (5)
O(12)	61 (4)	64 (4)	34 (2)	-3 (6)	32 (5)	23 (5)
O(21)	61 (4)	87 (5)	48 (2)	3 (7)	48 (5)	8 (6)
O(22)	68 (4)	45 (4)	45 (2)	6 (6)	26 (5)	0 (5)
O(31)	51 (3)	71 (4)	46 (2)	-10 (6)	41 (5)	-2 (5)
O(32)	75 (4)	58 (4)	40 (2)	14 (7)	37 (5)	26 (5)
B	99 (10)	79 (9)	52 (5)	16 (15)	53 (12)	4 (11)
F(1)	206 (8)	189 (8)	86 (4)	-114 (12)	181 (9)	-82 (9)
F(2)	168 (7)	80 (5)	204 (7)	-45 (10)	155 (11)	39 (10)
F(3)	141 (6)	92 (5)	117 (4)	47 (9)	55 (8)	18 (8)
F(4)	174 (7)	361 (13)	43 (3)	239 (16)	-26 (7)	-69 (10)
C(110)	81 (7)	57 (7)	43 (4)	-32 (11)	17 (8)	-53 (8)
C(120)	83 (7)	67 (7)	43 (4)	37 (11)	8 (8)	63 (8)
C(210)	36 (6)	153 (11)	79 (6)	67 (13)	44 (9)	17 (13)
C(220)	92 (7)	84 (8)	36 (4)	-17 (12)	-4 (8)	-54 (9)
C(310)	85 (7)	57 (7)	57 (4)	-56 (11)	21 (9)	-41 (9)
C(320)	126 (9)	85 (8)	54 (4)	-10 (14)	95 (10)	61 (10)
C(11)	55 (5)	44 (5)	26 (3)	-8 (9)	12 (6)	-3 (6)
C(12)	45 (5)	50 (6)	43 (4)	11 (9)	19 (7)	8 (7)
C(13)	59 (6)	62 (6)	43 (4)	-7 (10)	10 (7)	5 (8)
C(14)	70 (6)	66 (6)	40 (4)	-1 (11)	-1 (8)	9 (8)
C(15)	76 (7)	71 (7)	38 (4)	13 (11)	10 (8)	0 (9)
C(16)	78 (6)	60 (6)	25 (3)	-1 (10)	7 (7)	-11 (7)
C(21)	62 (6)	56 (6)	32 (3)	12 (10)	-4 (7)	-2 (7)
C(22)	98 (7)	81 (7)	40 (4)	34 (12)	18 (9)	37 (9)
C(23)	128 (10)	122 (10)	39 (4)	21 (16)	-14 (10)	33 (10)
C(24)	135 (10)	118 (10)	49 (5)	-32 (17)	-24 (11)	6 (11)
C(25)	143 (11)	116 (10)	47 (5)	-50 (17)	-43 (11)	-2 (11)
C(26)	89 (7)	82 (8)	51 (4)	-33 (13)	-36 (9)	-15 (10)
C(31)	109 (7)	48 (6)	33 (3)	-6 (10)	79 (8)	3 (7)
C(32)	136 (9)	66 (7)	66 (5)	7 (13)	149 (11)	-8 (10)
C(33)	182 (12)	91 (9)	85 (6)	15 (17)	191 (15)	6 (12)
C(34)	226 (13)	75 (8)	55 (5)	-22 (17)	140 (14)	-1 (10)
C(35)	209 (12)	69 (8)	36 (4)	-51 (16)	61 (11)	3 (9)
C(36)	132 (9)	64 (7)	26 (3)	-56 (13)	23 (9)	0 (8)

^a Values are $\times 10^5$ for Mn and P atoms and $\times 10^4$ for N, O, C, B, and F atoms. The form of the anisotropic thermal ellipsoids is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table III. Bond Lengths (Å)

Mn-P(1)	2.312 (5)	P(1)-C(11)	1.81 (1)
Mn-P(2)	2.303 (5)	P(2)-C(21)	1.80 (1)
Mn-P(3)	2.356 (5)	P(3)-C(31)	1.81 (1)
Mn-N(1)	1.649 (10)	O(11)-C(110)	1.46 (2)
Mn-N(2)	1.649 (10)	O(12)-C(120)	1.49 (2)
N(1)-O(1)	1.18 (1)	O(21)-C(210)	1.49 (2)
N(2)-O(2)	1.19 (1)	O(22)-C(220)	1.46 (2)
P(1)-O(11)	1.59 (1)	O(31)-C(310)	1.48 (2)
P(1)-O(12)	1.59 (1)	O(32)-C(320)	1.48 (2)
P(2)-O(21)	1.60 (1)	B-F	1.30-1.38
P(2)-O(22)	1.59 (1)	mean	1.34
P(3)-O(31)	1.59 (1)	C-C	1.38-1.44
P(3)-O(32)	1.60 (1)	mean	1.41

Table IV. Bond Angles (deg)

P(1)-Mn-P(2)	175.5 (5)	Mn-P(3)-O(31)	118 (1)
N(1)-Mn-N(2)	116.5 (5)	Mn-P(3)-O(32)	112 (1)
O(1)-Mn-O(2)	107.4 (5)	Mn-P(3)-C(31)	113 (1)
P(3)-Mn-P(1)	87.7 (5)	P(1)-O(11)-C(110)	122 (1)
P(3)-Mn-P(2)	89.8 (5)	P(1)-O(12)-C(120)	122 (1)
P(3)-Mn-N(1)	114.0 (5)	P(2)-O(21)-C(210)	121 (1)
P(3)-Mn-N(2)	129.4 (5)	P(2)-O(22)-C(220)	123 (1)
P(1)-Mn-N(1)	93.5 (5)	P(3)-O(31)-C(310)	120 (1)
P(1)-Mn-N(2)	89.1 (5)	P(3)-O(32)-C(320)	121 (1)
P(2)-Mn-N(1)	91.0 (5)	O(11)-P(1)-O(12)	107 (1)
P(2)-Mn-N(2)	89.7 (5)	O(11)-P(1)-C(11)	100 (1)
Mn-N(1)-O(1)	170 (1)	O(12)-P(1)-C(11)	106 (1)
Mn-N(2)-O(2)	168 (1)	O(21)-P(2)-O(22)	107 (1)
Mn-P(1)-O(11)	120 (1)	O(21)-P(2)-C(21)	105 (1)
Mn-P(1)-O(12)	104 (1)	O(22)-P(2)-C(21)	100 (1)
Mn-P(1)-C(11)	120 (1)	O(31)-P(3)-O(32)	106 (1)
Mn-P(2)-O(21)	104 (1)	O(31)-P(3)-C(31)	101 (1)
Mn-P(2)-O(22)	121 (1)	O(32)-P(3)-C(31)	105 (1)
Mn-P(2)-C(21)	120 (1)		

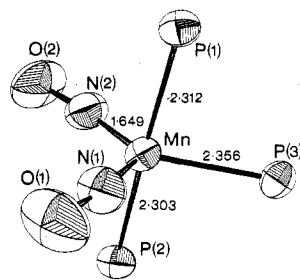


Figure 2. $[\text{Mn}(\text{NO})_2\text{P}_3]$ unit oriented to show the relative size and orientation of the thermal ellipsoids.

Mn-N nor the N-O bond lengths are significantly different from the values found in the chloro compound.⁹

The atoms in the equatorial plane, $\{\text{Mn}(\text{NO})_2\text{P}_{\text{eq}}\}$, are coplanar within 0.01 Å (see Figure 2). The two N-Mn-P angles differ by over 15°, a distortion very much like that observed in molecule "2" of the triclinic form of the chloride.^{9b} This angular asymmetry is associated with two short sepa-

Table V. Intramolecular Nonbonded Contacts (Å)

N(1)···N(2)	2.81	P(3)···P(2)	3.29
O(1)···O(2)	4.55	N(1)···P(3)	3.38
N(1)···P(1)	2.92	N(2)···P(3)	3.63
N(1)···P(2)	2.85	N(1)···O(12)	3.24
N(2)···P(1)	2.82	N(1)···O(21)	3.22
N(2)···P(2)	2.82	N(2)···O(12)	3.03
P(3)···P(1)	3.23	N(2)···O(21)	3.00

Table VI. Least-Squares Planes^a

(i) {Mn(NO) ₂ P _{eq} } Group						
A		B		C		D
-0.638		0.616		-0.461		-1.114
Deviations						
Mn	P(3)	N(1)	O(1)	N(2)	O(2)	P(1) P(2)
0.00	0.00	-0.01	0.01	0.01	0.00	-2.31 2.30
(ii) {Mn(P) ₃ } Group						
A		B		C		D
-0.168		-0.719		-0.674		-4.786
Deviations						
Mn	P(1)	P(2)	P(3)	O(12)	O(21)	O(32)
0.05	-0.03	-0.03	0.00	0.09	0.00	-0.30
C(120)	C(210)	C(320)				
0.05	-0.08	-0.27				

^a The equation of the plane is of the form $Ax + By + Cz + D = 0$ where A, B, C are direction cosines, x, y, z are orthogonalized coordinates, and D is in Å.

Table VII. Torsion Angles (deg)

P(3)-Mn-P(1)-O(12)	-176
P(3)-Mn-P(2)-O(21)	180
O(12)-P(1)-P(2)-O(21)	3
C(11)-P(1)-P(2)-C(21)	128
Mn-P(3)-O(32)-C(320)	-175
P(1)-P(2)-O(21)-C(210)	176
P(2)-P(1)-O(12)-C(120)	-177
P(2)-Mn-P(3)-O(32)	9
P(1)-Mn-P(3)-O(32)	-167

rations between the nitrogen atom with the *large* N-Mn-P_{eq} angle and an oxygen atom of one OCH₃ group on each of the axial phosphonite ligands: N(2)···O(12) = 3.03 Å, N(2)···O(21) = 3.00 Å (see Table V). Precisely the same effect was found^{9b} in molecule "2" of [Mn(NO)₂{P(OCH₃)₂C₆H₅}₂Cl].

A comparison of Figure 1 (above) with Figure 1a in ref 9b shows that the relative conformation of the pairs of axial phosphonite ligands is almost identical. (In fact, the cation has effective symmetry 2 if the C₆H₅ and two OCH₃ groups of the equatorial phosphonite ligand are ignored.) As before, the OCH₃ group which is bent away from the equatorial plane has a small Mn-P-O angle (104, 104°) while the OCH₃ group which is folded toward the equatorial plane has a far larger Mn-P-O angle (120, 121°) (see Tables IV and VII). The difference here is larger than that found in the neutral chloro molecule⁹ because the large bulk of the equatorial {P(OC₆H₅)₂C₆H₅} ligand causes greater internal compression strains. This effect is also seen in the bond angle P(1)-Mn-P(2), 175.5°, compared with 166.9 and 163.9° found previously. Nevertheless, the two axial phosphonite ligands are bent toward the equatorial phosphonite ligand.

Angles O(11)-P(1)-C(11) and O(22)-P(2)-C(21) are likewise small, 100°, because these OCH₃ groups are bent away from the phenyl rings. This result is also found in the equatorial phosphonite ligand; C(310) is turned away from phenyl 3, and angle C(31)-P(3)-O(31) is 101°. However, the Mn-P-X angles are now all larger than 110° because of the large nonbonded repulsions between this ligand and the two axial phosphonite ligands (see Table V). A comparison of the N···P_{ax} and P_{eq}···P_{ax} distances with the analogous N···P and Cl···P distances found in the chloride⁹ shows this effect

Table VIII. Thermal Ellipsoids: Amplitudes of Vibration (Å)

	min	intermed	max
Mn	0.19	0.20	0.21
P(1)	0.19	0.20	0.23
P(2)	0.19	0.20	0.23
P(3)	0.20	0.21	0.24
N(1)	0.20	0.24	0.28
N(2)	0.21	0.24	0.29
O(1)	0.21	0.30	0.40
O(2)	0.21	0.32	0.41

Table IX. Intermolecular Nonbonded Contacts (Å)

atom in position 1	to atom in position ^a	dist
O(31)	F(3)	1 3.39
C(33)	F(2)	1 3.50
C(13)	F(4)	1 3.42
C(32)	F(2)	1 3.33
C(32)	F(3)	1 3.44
C(34)	F(1)	2 (100) 3.31
C(24)	F(4)	3 (101) 3.23
C(120)	F(3)	4 (110) 3.30
C(210)	F(1)	1 (100) 3.22
C(310)	F(2)	4 (100) 3.04
C(220)	F(4)	4 (100) 3.27
O(2)	C(35)	3 3.18
O(1)	C(210)	4 (010) 3.44
C(14)	C(120)	2 (101) 3.53
C(15)	C(120)	2 (101) 3.54

^a Equivalent positions are as follows: 1, x, y, z ; 2, $-x, -y, -z$; 3, $x, 1/2 - y, 1/2 + z$; 4, $-x, 1/2 + y, 1/2 - z$. Numbers in parentheses indicate translations parallel to the cell edges.

quite clearly: the N···P_{ax} distances in the cation are smaller, while the P_{ax}···P_{eq} distances are larger (see Table V in ref 9a and Table VI in ref 9b).

It is quite clear that the axial phosphonite ligands bend away from the two nitrosyl groups simply to relieve excessive P···N compression strain. The same effect is well-known in metal carbonyls.¹⁰

Martin and Taylor¹¹ observed that there was a general correlation between O-M-O angles and N-M-N angles in four-coordinate dinitrosyl complexes. What is remarkable (and may well be purely fortuitous) is that the O-M-N and N-M-N angles found⁹ in these trigonal-bipyramidal dinitrosyl compounds also seem to fit this correlation.

A closer examination of the complexes listed in ref 11 shows that there may be yet another (and different) correlation. If one restricts attention to only those 3d metal complexes with phosphorus or sulfur as the donor atom in the ligand, a relationship between the N-M-N angle and the M-N-O angle becomes evident (see Table X and Figure 3).

Such a correlation between N-M-N and M-N-O angles has been discussed by Kaduk and Ibers¹⁵ and is also consistent with the molecular orbital schemes proposed by Enemark and Feltham.¹⁷ In the terminology of Martin and Taylor,¹¹ it appears that 3d metal dinitrosyls will have the "attracto" conformation when the N-M-N angle is less than 125°, the "repulso" conformation when the N-M-N angle is greater than 130°, and linear MNO groups for N-M-N angles between 125 and 130°. What is more, this appears to be true for both four- and five-coordinate complexes as well as neutral molecules and monovalent cations. This is quite certainly an electronic and not a steric effect.

Inspection of Table X shows that there is no general relationship between the values of the NO stretching frequencies and any of the angular parameters. The frequencies of the stretching modes are too complicated a function of the atomic number of the metal atom, the electronic character of the ligand, and the coordination geometry of the metal atom. A correlation between $\nu(\text{NO})$ and M-N-O angle has been

Table X. Structural Parameters of Some 3d Metal-Dinitrosyl Complexes

identity no.	compd	N-M-N, deg	M-N-O, ^a deg	O-M-O, deg	NO str freq, cm ⁻¹	ref
1	[Mn(NO) ₂ {P(OMe) ₂ Ph} ₂ Cl] (mono)	111.5	166, 163	99.0		9a
2	[Mn(NO) ₂ {P(OMe) ₂ Ph} ₂ Cl] ("2")	113.5	167, 165	101.9	1723, 1674	9b
3	[Mn(NO) ₂ {P(OMe) ₂ Ph} ₂ Cl] ("M")	112.1	166, 165	99.8		9b
4	[Co(NO) ₂ SacSac]	115.5	168.9	106.6	1820, 1750	11
5	[Mn(NO) ₂ {P(OMe) ₂ Ph} ₃] ⁺	116.5	168, 170	107.4	1760, 1712	this work
6	[Fe(NO) ₂ (SEt) ₂]	117.4	167.5	106.6	1773, 1748	12
7	[Fe(NO) ₂ (PPh ₃) ₂]	123.8	178.1	122.4	1714, 1674	13
8	[Fe(NO) ₂ (f ₆ fos)]	125.4	176.9, 177.8	123.8	1746, 1702	14
9	[Co(NO) ₂ diphos] ⁺	131.7	187.7, 183.4	135.9	1860, 1790	15
10	[Co(NO) ₂ (PPh ₃) ₂] ⁺	132.4	189.1, 188.8	134.6	1836, 1784	11
11	[Co(NO) ₂ (PPh ₃) ₂] ⁺	136.7	189			16

^a Angles greater than 180° are for NO groups which bend away from each other, i.e., the "repulso" conformation,¹¹ and are obtained by subtracting the value reported for the M-N-O angle from 360°.

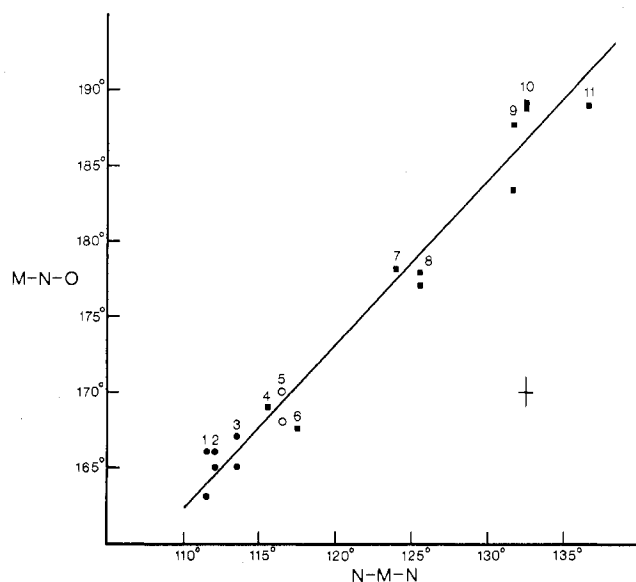


Figure 3. Relationship between the N-M-N and the M-N-O angles for dinitrosyl complexes of 3d metals. The identity numbers on the graph correspond to those given in Table X: ●, compound [Mn(NO)₂{P(OCH₃)₂C₆H₅}₂Cl]; ○, cation [Mn(NO)₂{P(OCH₃)₂C₆H₅}₃]⁺; ■, tetrahedral complexes. The magnitude of the mean probable error in these data is indicated by the cross, i.e., ±0.5° for N-M-N and ±1.0° for M-N-O.

observed for a limited series of compounds.^{15,18}

The large difference between the two N-Mn-P_{eq} angles implies that the force constant for oscillation of the Mn-P bond in the equatorial plane must be very small. The effect has been found in two other trigonal-bipyramidal nitrosyl complexes: molecule "2" of [Mn(NO)₂{P(OCH₃)₂C₆H₅}₂Cl]^{9b} and [CoCl₂(NO){PCH₃(C₆H₅)₂}₂].¹⁹ These three compounds obey the 18-electron (effective atomic number) rule. It seems reasonable, therefore, to predict that any trigonal-bipyramidal complex of a 3d metal which has the general formula [ML₂X₂Y] and which obeys the 18-electron rule can suffer a large angular distortion in the equatorial plane. Examples of compounds that fall into this category are [Fe(PR₃)₂(PR'₃)₂CO], [Fe(PR₃)₂PR'₃(CO)₂], [Fe(PR₃)₂(CO)₂NO]⁺, [Mn(PR₃)₂(CO)₂NO], [Cr(PR₃)₂PR'₃(NO)₂], and [Fe(PR₃)₂(NO)₂Cl]⁺, where R and R' can be any of C₆H₅, CH₃, OCH₃, OC₆H₅, Cl, F, etc. The only compound, representative of this group, whose crystal structure has been determined, is [Mn{P(C₆H₅)₃}₂(CO)₂NO].²⁰ Unfortunately the NO group is not well ordered, and in addition, only about one-third of the recorded reflections (1337 out of 4438) had intensities

observable above background in this room-temperature study. It is conceivable that reduction of the temperature to about -100 °C would lead not only to an increase in the fraction of observable data but also to an ordering of the NO group and the possible observation of the distortion which is predicted above.

Conclusion

On going from a neutral dinitrosyl complex to a cationic species, the Mn-N-O group becomes more linear and the N-Mn-N angle opens. It is evident that there is a correlation between N-M-N and M-N-O angles in four- and five-coordinate dinitrosyls of 3d metals.

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Registry No. [Mn(NO)₂{P(OCH₃)₂C₆H₅}₃]BF₄, 67379-23-1.

Supplementary Material Available: A listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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