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The Structure of Nitrosyltricarbonyltriphenylphosphinemanganese, $Mn(NO)(CO)_3(P(C_6H_5)_3)$

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The crystal and molecular structure of nitrosyltricarbonyltriphenylphosphinemanganese, $Mn(NO)(CO)_3(P(C_6H_5)_3)$, has been determined from three-dimensional X-ray diffraction data collected by counter methods. The compound crystallizes in space group C_i^1-$P\bar{1}$ of the triclinic system. There are two molecules in a cell of dimensions $a = 9.812$ (11), $b = 10.803$ (12), $c = 14.936$ (17) Å; $\alpha = 117.75$ (2), $\beta = 109.12$ (3), and $\gamma = 112.73$ (2)°. The observed and calculated densities are 1.41 g cm^{-3}. Least-squares refinement of the structure has led to a final value of the conventional R factor of 0.056 for the 1297 observed reflections with $F^2 \geq 3\sigma(F^2)$. The structure consists of well-separated monomeric units. Each molecule has the Mn atom at the center of a trigonal bipyramid with the $P(C_6H_5)_3$ group in an axial position. It has not been possible to distinguish the nitrosyl group from the carbonyl groups from the X-ray data. However, the presence of three carbonyl infrared stretching frequencies implies that the nitrosyl group occupies an equatorial coordination site. It is thus assumed that a carbonyl group is *trans* to $P(C_6H_5)_3$ and that the nitrosyl group and two carbonyl groups are disordered among the three equatorial coordination positions. The Mn–P distance is 2.305 (4) Å, the axial Mn–C distance is 1.83 (1) Å, and the equatorial Mn–C (or Mn–N) distances are 1.76 (1), 1.78 (1), and 1.80 (1) Å.

Introduction

Five-coordinate transition metal compounds—a chemical curiosity only a few years ago—are now fairly commonplace in inorganic chemistry. However, as structural details of these compounds have become available, it has become increasingly apparent that the energy differences between various five-coordinate geometries are quite small. Consequently, definitive structural information on closely related compounds is needed in order to evaluate the significant factors governing the stereochemistry of five-coordinate compounds. The series of compounds $Mn(NO)(CO)_4$, $Mn(NO)(CO)_3(P(C_6H_5)_3)$, and $Mn(NO)(CO)_2(P(C_6H_5)_3)_2$ is a potentially useful one for studying the structural chemistry of five-coordinate complexes. This series permits one to observe the changes in molecular geometry as the ligands are varied systematically while the metal remains in the same formal oxidation state. The structure of $Mn(NO)(CO)_2(P(C_6H_5)_3)_2$ has been described,[1] and this paper is concerned with the structure of $Mn(NO)(CO)_3(P(C_6H_5)_3)$.

The dipole moment[2] of $Mn(NO)(CO)_3(P(C_6H_5)_3)$ is interpreted as evidence for a trigonal-bipyramidal structure with $P(C_6H_5)_3$ and CO in the apical positions. The presence of three CO stretching frequencies in the infrared spectrum[3] makes unlikely a structure with a threefold axis (*e.g.*, a trigonal bipyramid with NO and $P(C_6H_5)_3$ *trans* to one another). The presence of three CO bands does not, however, rule out alternative trigonal-bipyramidal or tetragonal-pyramidal structures which have *trans* NO and CO groups. Moreover, such alternative structures are also consistent with the observed[3] first-order reaction kinetics for the replacement of CO by $P(C_6H_5)_3$ in $Mn(NO)(CO)_3(P(C_6H_5)_3)$. This structural ambiguity further encouraged us to continue our research on the structures of the $Mn(NO)(CO)_{4-x}(P(C_6H_5)_3)_x$ (where $x = 0, 1, 2$) compounds in the solid state.

Collection and Reduction of Data

A sample of $Mn(NO)(CO)_3(P(C_6H_5)_3)$, prepared as previously described,[4] was kindly supplied by Professor F. Basolo and Dr. H. Wawersik. Single crystals were grown by allowing *n*-pentane to diffuse slowly into a solution of $Mn(NO)(CO)_3(P(C_6H_5)_3)$ in toluene. (Solutions of the compound react rapidly with oxygen. Dry, oxygen-free solvents were used, and the entire recrystallization was carried out under a nitrogen atmosphere.) The crystals are thin, orange, rectangular plates with {001} being the major faces.

For data collection, a crystal of dimensions 0.07 × 0.19 × 0.23 mm was selected and was sealed in a thin-walled glass capillary to prevent oxidative decomposition. Preliminary precession photographs (Cu Kα) suggested that the crystal was triclinic. Neither a Delaunay reduction nor a series of precession photographs taken at 10° intervals around the spindle axis revealed any additional symmetry elements. The unit cell parameters for the reduced triclinic cell at 25 ± 1° are $a = 9.812$ (11), $b = 10.803$ (12), $c = 14.936$ (17) Å; $\alpha = 117.75$ (2), $\beta = 109.12$ (3), and $\gamma = 112.73$ (2)° (λ 0.70930 Å). These parameters were determined by a least-squares refinement of the setting angles of 20 reflections which has been accurately centered on a Picker four-circle automatic diffractometer as previously described.[5] The crystal density of 1.41 ± 0.02 g cm^{-3} observed by flotation in heptane–Freon 113 agrees with the value of 1.41 g cm^{-3} calculated for two molecules per unit cell. Two space groups, C_1^1-P1 or C_i^1-$P\bar{1}$, are possible; $P\bar{1}$ was assumed because it is more common and because P1 would require two molecules in the asymmetric unit. The assumption of $P\bar{1}$

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(1) J. H. Enemark and J. A. Ibers, *Inorg. Chem.*, **6**, 1575 (1967).
(2) W. Hieber and H. Tengler, *Z. Anorg. Allgem. Chem.*, **318**, 136 (1962).
(3) H. Wawersik and F. Basolo, *J. Am. Chem. Soc.*, **89**, 4626 (1967).
(4) R. F. Lambert and J. D. Johnston, *Chem. Ind.* (London), 1267 (1960).
(5) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

was confirmed by the successful solution and refinement of the structure.

Intensities were recorded with a Picker four-circle automatic diffractometer by a procedure similar to that already described.[5] Mo Kα radiation was used and the takeoff angle was 1.0°. At this angle the intensity of the diffracted beam was ~75% of the maximum intensity. (The mosaicity of the crystal was checked by doing ω scans on several reflections using a takeoff angle of 0.5°; the peak widths at half-height were always less than 0.1°.) The diffracted beam was filtered through 3.0-mil Zr foil, and the intensities were gathered by the θ–2θ scan technique using a symmetric scan range of 1.2° in 2θ and a scan rate of 0.5°/min. Stationary-counter, stationary-crystal background counts of 10 sec were taken at each end of the scan range and were typically 10–40 counts. The scintillation counter was 31 cm from the crystal and had an aperture of 4×4 mm, and the pulse height analyzer was set to admit about 90% of the Mo Kα peak. Whenever the counting rate exceeded ~7000 counts/sec, Cu foils with attenuation factors of 2.3 were inserted in the diffracted beam.

A unique set of reflections having $2\theta \leqslant 39°$ was generated and arranged into an efficient order to minimize slewing time. After ~600 intensities had been recorded, it was noted that the crystal had moved slightly since the peaks were no longer centered on the recorder chart tracings. However, the entire reflection was still being recorded within the 1.2° scan range. After 960 data had been collected, a mechanical failure of the diffractometer necessitated the removal of the crystal. When the crystal was returned to the diffractometer, the orientation process was repeated, and new angular settings were generated for the remaining reflections in the region $2\theta \leqslant 39°$. This simultaneously corrected for the slight movement of the crystal which had occurred and nullified any nonreproducibility in returning the goniometer head to the diffractometer. The data from the two orientations were later assigned separate scale factors in the least-squares refinement of the structure. It was apparent from the recorder chart tracings that there were few, if any, useful data beyond $2\theta = 39°$.

The raw intensities were reduced to F^2 and $\sigma(F^2)$, with p taken as 0.04.[5] Of the 1755 independent observations, 458 had $F^2 < 3\sigma(F^2)$. The maximum raw intensity was about 3×10^5 counts for reflection $(20\bar{2})$. Four intense reflections in diverse regions of reciprocal space were monitored at least once a day during the entire data collection; none of the four showed any systematic variation in intensity. Although separate scale factors were assigned to the data gathered before and after the reorientation of the crystal, the constancy of the four standard reflections indicated that the data were essentially on the same scale.

Absorption is not a major problem in this crystal ($\mu_{\text{Mo K}\alpha} = 7.8$ cm^{-1}, where μ is the linear absorption coefficient). However, because of the crystal morphology, there is a significant difference between the minimum and maximum path lengths through the crystal. Therefore, an absorption correction was made;[6] the correction factors ranged from 1.05 to 1.15. Secondary extinction is not a problem in this crystal (see Table I), and no extinction correction was made.

Solution of the Structure

The positions of the Mn and P atoms were readily obtained from a three-dimensional Patterson function. A structure factor calculation phased by these two atoms followed by a difference electron density map clearly revealed all remaining nonhydrogen atoms. Full-matrix least-squares refinement of the structure was begun using those 1297 reflections with $F^2 \geqslant 3\sigma(F^2)$. Refinement was based on F, with the weights w taken as $4F^2/\sigma^2(F^2)$. The atomic scattering factors used for Mn, P, O, N and C were those tabulated by Ibers,[7] while those for H were taken from Stewart, *et al.*[8] The effects of anomalous dispersion were included in F_c;[9] Cromer's[10] values of f' and f'' for Mn and P were used. Phenyl rings were treated as rigid groups[11] (C–C = 1.397 Å, D_{6h} symmetry) with each ring assigned a single variable temperature factor. All nongroup atoms were allowed to vibrate isotropically. No attempt was made to distinguish the N atom, and four carbonyl groups were assumed. The initial structure factor calculation with all nonhydrogen atoms included gave

$$R_1 = \frac{\Sigma\big||F_o| - |F_c|\big|}{\Sigma|F_o|} = 0.31$$

and

$$R_2 = \left[\frac{\Sigma w(F_o - F_c)^2}{\Sigma w F_o^2}\right]^{1/2} = 0.39$$

Three cycles of isotropic refinement reduced these to $R_1 = 0.087$ and $R_2 = 0.110$. At this point H atoms were included as fixed contributions (C–H = 1.084 Å), the Mn and P atoms were refined anisotropically, and group C atoms were given individual temperature factors. Two additional cycles of least-squares refinement gave $R_1 = 0.063$ and $R_2 = 0.079$. Finally, all nongroup atoms were allowed to vibrate anisotropically (128 variable parameters) and two more cycles of least-squares refinement were carried out to give $R_1 = 0.056$ and $R_2 = 0.070$.

A plot of the thermal ellipsoids of the atoms after anisotropic refinement showed no significant differences in the shapes or sizes of the four "carbonyl" groups. Consequently, it was not possible to distinguish N from C solely by crystallographic criteria. This is in contrast to $Mn(NO)(CO)_2(P(C_6H_5)_3)_2$,[1] where N was dis-

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[6] The general absorption program GONO was used for this calculation. Other computer programs used included local versions of Zalkin's FORDAP Fourier summation program, Busing and Levy's ORFFE bond distance and angle program, and Johnson's ORTEP plotting program.

[7] J. A. Ibers, "International Tables for X-ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

[8] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

[9] J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, **17**, 781 (1964).

[10] D. T. Cromer, *ibid.*, **18**, 17 (1965).

[11] S. J. La Placa and J. A. Ibers, *ibid.*, **18**, 511 (1965); R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

TABLE I

VALUES OF $10|F_o|$ AND $10|F_c|$ (IN ELECTRONS) FOR $Mn(NO)(CO)_3(P(C_6H_5)_3)$

K	L	FO	FC
*****	H =	0	*****
0	1	108	104
0	2	579	580
0	3	577	587
0	4	211	219
0	5	487	469
0	6	381	414
0	7	396	395
0	8	71	70
0	9	67	73
1	-10	60	52
1	-9	171	157
1	-8	61	70
1	-7	158	165
1	-6	19	12
1	-5	135	142
1	-4	286	287
1	-3	408	395
1	-2	884	897
1	-1	62	57
1	0	485	462
1	1	57	54
1	2	472	471
1	3	80	101
1	4	451	448
1	5	511	545
1	6	205	208
1	7	211	203
1	8	108	102
2	-11	108	127
2	-10	152	138
2	-9	248	249
2	-8	83	76
2	-7	28	42
2	-6	38	36
2	-5	285	284
2	-4	117	108
2	-3	454	429
2	-2	917	902
2	-1	281	255
2	0	319	300
2	1	23	15
2	2	82	74
2	3	394	381
2	4	294	302
2	5	314	330
2	6	121	154
2	7	64	76
3	-12	16	32
3	-11	156	159
3	-10	39	29
3	-9	68	75
3	-8	182	180
3	-7	182	176
3	-6	289	282
3	-5	312	332
3	-4	640	643
3	-3	278	287
3	-2	859	871
3	-1	56	66
3	0	478	494
3	1	83	90
3	2	327	334
3	3	142	137
3	4	26	21
3	5	41	47
3	6	0	36
4	-12	53	63
4	-11	58	49
4	-10	61	70
4	-9	139	142
4	-8	105	120
4	-7	402	405
4	-6	696	684
4	-5	110	113
4	-4	112	93
4	-3	0	15
4	-2	256	270
4	-1	140	137
4	0	258	263
4	1	172	173
4	2	77	94
4	3	50	36
4	4	81	76
5	-13	63	73
5	-12	124	141
5	-11	205	199
5	-10	186	179
5	-9	342	356
5	-8	309	320
5	-7	99	113
5	-6	163	173
5	-5	205	218
5	-4	385	401
5	-3	109	104
5	-2	318	331
5	-1	302	318
5	0	235	247
5	1	115	111
5	2	48	63
5	3	100	112
6	-13	55	44
6	-12	47	51
6	-11	177	171
6	-10	111	126
6	-9	75	75
6	-8	192	185
6	-7	94	86
6	-6	234	264
6	-5	85	96
6	-4	173	176
6	-3	120	113
6	-2	167	167
6	-1	141	129
6	0	79	54
6	1	62	73
7	-13	71	90
7	-12	54	73
7	-11	0	13
7	-10	149	157
7	-9	58	63
7	-8	38	26
7	-7	37	34
7	-6	306	317
7	-5	0	17
7	-4	220	233
7	-3	105	102
7	-2	26	10
7	-1	77	94
8	-12	51	11
8	-11	72	75
8	-10	14	21
8	-9	151	152
8	-8	219	224
8	-7	86	85
8	-6	59	43
8	-5	29	30
8	-4	0	18
8	-3	0	39
9	-11	68	93
9	-10	112	82
9	-9	75	82
9	-8	129	102
9	-7	68	74
9	-6	0	45
*****	H =	1	*****
-9	4	29	41
-9	5	156	153
-9	6	88	73
-9	7	0	30
-9	8	215	211
-9	9	159	147
-9	10	9	14
-9	11	65	56
-8	2	107	88
-8	3	56	43
-8	4	23	4
-8	5	55	71
-8	6	85	56
-8	7	158	159
-8	8	61	33
-8	9	181	183
-8	10	43	24
-8	11	58	59
-8	12	16	3
-7	-1	106	108
-7	0	178	181
-7	1	27	11
-7	2	83	82
-7	3	49	25
-7	4	250	223
-7	5	239	272
-7	6	348	355
-7	7	71	75
-7	8	91	95
-7	9	6	23
-7	10	32	62
-7	11	30	34
-7	12	43	0
-6	-2	125	102
-6	-1	31	25
-6	0	32	22
-6	1	106	109
-6	2	154	148
-6	3	0	19
-6	4	422	426
-6	5	302	268
-6	6	190	197
-6	7	20	26
-6	8	106	86
-6	9	208	189
-6	10	20	18
-6	11	181	186
-6	12	83	70
-5	-4	92	93
-5	-3	46	46
-5	-2	41	34
-5	-1	202	212
-5	0	114	126
-5	1	221	234
-5	2	276	266
-5	3	483	513
-5	4	275	260
-5	5	59	76
-5	6	142	112
-5	7	112	115
-5	8	86	75
-5	9	479	475
-5	10	20	8
-5	11	177	165
-5	12	31	15
-4	-6	84	65
-4	-5	82	59
-4	-4	0	17
-4	-3	96	106
-4	-2	274	267
-4	-1	21	5
-4	0	245	247
-4	1	93	88
-4	2	355	386
-4	3	322	348
-4	4	516	515
-4	5	59	42
-4	6	176	173
-4	7	373	353
-4	8	35	47
-4	9	195	199
-4	10	40	7
-4	11	0	31
-3	-7	79	95
-3	-6	196	196
-3	-5	72	60
-3	-4	250	247
-3	-3	53	42
-3	-2	428	438
-3	-1	198	187
-3	0	436	424
-3	1	291	301
-3	2	293	293
-3	3	47	44
-3	4	88	94
-3	5	204	218
-3	6	72	79
-3	7	91	103
-3	8	54	48
-3	9	32	16
-3	10	22	10
-3	11	25	28
-2	-8	109	118
-2	-7	0	18
-2	-6	201	215
-2	-5	131	145
-2	-4	330	343
-2	-3	90	84
-2	-2	564	553
-2	-1	852	850
-2	0	418	386
-2	1	284	291
-2	2	603	614
-2	3	848	863
-2	4	144	153
-2	5	542	517
-2	6	30	49
-2	7	130	131
-2	8	0	15
-2	9	200	193
-2	10	67	49
-1	-9	61	47
-1	-8	97	119
-1	-7	254	243
-1	-6	172	162
-1	-5	108	100
-1	-4	452	467
-1	-3	456	466
-1	-2	380	364
-1	-1	69	54
-1	0	665	635
-1	1	551	542
-1	2	103	77
-1	3	720	736
-1	4	158	148
-1	5	173	177
-1	6	30	8
-1	7	279	297
-1	8	97	107
-1	9	206	200
0	-10	139	131
0	-9	45	57
0	-8	126	132
0	-7	196	195
0	-6	245	254
0	-5	53	49
0	-4	574	555
0	-3	619	576
0	-2	550	552
0	-1	424	389
0	0	849	828
0	1	1002	956
0	2	125	115
0	3	610	625
0	4	23	13
0	5	201	199
0	6	122	110
0	7	261	252
0	8	187	171
1	-11	88	82
1	-10	183	173
1	-9	211	214
1	-8	33	21
1	-7	0	9
1	-6	105	90
1	-5	76	95
1	-4	106	90
1	-3	74	67
1	-2	510	495
1	-1	119	125
1	0	0	4
1	1	530	516
1	2	185	170
1	3	65	62
1	4	0	5
1	5	253	254
1	6	158	187
1	7	196	198
2	-12	29	55
2	-11	109	121
2	-10	236	247
2	-9	30	25
2	-8	95	99
2	-7	140	128
2	-6	0	7
2	-5	329	307
2	-4	706	684
2	-3	516	514
2	-2	594	566
2	-1	87	74
2	0	44	41
2	1	82	80
2	2	36	37
2	3	155	167
2	4	41	4
2	5	196	191
2	6	48	44
3	-12	200	195
3	-11	101	95
3	-10	119	127
3	-9	18	11
3	-8	105	99
3	-7	98	123
3	-6	759	761
3	-5	689	664
3	-4	167	162
3	-3	0	12
3	-2	126	129
3	-1	18	37
3	0	318	337
3	1	425	447
3	2	59	47
3	3	124	107
3	4	86	86
3	5	62	83
4	-13	68	68
4	-12	0	22
4	-11	43	31
4	-10	59	67
4	-9	223	209
4	-8	307	295
4	-7	90	105
4	-6	533	510
4	-5	38	67
4	-4	132	120
4	-3	41	42
4	-2	177	162
4	-1	341	350
4	0	138	140
4	1	198	189
4	2	50	39
4	3	31	35
5	-13	27	53
5	-12	131	134
5	-11	200	215
5	-10	149	137
5	-9	50	64
5	-8	169	184
5	-7	198	199
5	-6	78	70
5	-5	103	101
5	-4	0	14
5	-3	156	172
5	-2	0	8
5	-1	332	355
5	0	0	16
5	1	129	139
5	2	27	19
6	-13	88	106
6	-12	52	30
6	-11	166	181
6	-10	307	310
6	-9	131	128
6	-8	43	60
6	-7	11	17
6	-6	153	174
6	-5	80	87
6	-4	84	73
6	-3	245	248
6	-2	43	21
6	-1	84	69
6	0	75	49
7	-13	107	132
7	-12	112	126
7	-11	65	41
7	-10	56	50
7	-9	27	49
7	-8	177	173
7	-7	71	71
7	-6	306	312
7	-5	79	73
7	-4	96	87
7	-3	40	47
7	-2	120	122
8	-12	37	18
8	-11	38	26
8	-10	94	106
8	-9	50	60
8	-8	118	120
8	-7	31	21
8	-6	46	44
8	-5	67	62
*****	H =	2	*****
-10	8	147	155
-9	3	65	37
-9	4	0	22
-9	5	126	132
-9	6	127	115
-9	7	215	213
-9	8	76	86
-9	9	150	131
-9	10	26	20
-9	11	62	50
-8	0	174	174
-8	1	35	57
-8	2	170	172
-8	3	32	6
-8	4	27	54
-8	5	249	277
-8	6	189	234
-8	7	226	185
-8	8	17	26
-8	9	116	86
-8	10	31	29
-8	11	81	97
-7	-2	200	200
-7	-1	22	22
-7	0	203	208
-7	1	76	74
-7	2	113	119
-7	3	148	150
-7	4	249	245
-7	5	328	326
-7	6	34	26
-7	7	50	72
-7	8	45	55
-7	9	76	60
-7	10	49	42
-7	11	71	94
-6	-3	69	69
-6	-2	116	100
-6	-1	66	72
-6	0	31	23
-6	1	45	27
-6	2	195	199
-6	3	488	522
-6	4	203	235
-6	5	257	236
-6	6	34	7
-6	7	40	51
-6	8	0	25
-6	9	301	308
-6	10	171	155
-6	11	76	85
-5	-5	37	51
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-2	-3	564	541
-2	-2	25	14
-2	-1	17	9
-2	0	182	185
-2	1	142	147
-2	2	492	483
-2	3	50	43
-2	4	25	15
-2	5	16	11
-1	-11	117	120
-1	-10	132	130
-1	-9	169	165
-1	-8	14	37
-1	-7	238	236
-1	-6	145	145
-1	-5	178	166
-1	-4	69	64
-1	-3	62	69
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-1	3	38	61
-1	4	0	13
0	-12	66	52
0	-11	60	74
0	-10	93	93
0	-9	114	138
0	-8	15	2
0	-7	220	239
0	-6	252	238
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0	-4	24	33
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0	-2	307	310
0	-1	50	40
0	0	381	351
0	1	81	75
0	2	35	11
0	3	106	114
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1	-12	142	133
1	-11	190	182
1	-10	33	12
1	-9	201	216
1	-8	134	139
1	-7	73	79
1	-6	84	83
1	-5	296	290
1	-4	126	137
1	-3	177	201
1	-2	299	319
1	-1	50	10
1	0	92	101
1	1	0	12
1	2	48	80
2	-13	169	173
2	-12	76	65
2	-11	247	242
2	-10	49	51
2	-9	165	176
2	-8	0	11
2	-7	137	127
2	-6	109	130
2	-5	170	167
2	-4	308	318
2	-3	83	82
2	-2	43	37
2	-1	13	12
2	0	63	43
3	-13	199	195
3	-12	27	50
3	-11	155	152
3	-10	70	74
3	-9	128	126
3	-8	83	82
3	-7	326	306
3	-6	255	261
3	-5	37	70
3	-4	153	171
3	-3	0	18
3	-2	133	141
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4	-12	0	9
4	-11	54	64
4	-10	0	6
4	-9	152	155
4	-8	125	134
4	-7	100	94
4	-6	131	143
4	-5	35	46
4	-4	58	68
5	-12	51	54
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5	-10	106	98
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5	-8	89	88
5	-7	93	96
5	-6	62	39
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-9	6	98	98
-8	-2	108	110
-8	-1	103	115
-8	0	106	105
-8	1	0	7
-8	2	0	33
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-8	5	63	50
-8	6	159	146
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-7	-4	50	37
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-7	-2	80	73
-7	-1	108	109
-7	0	58	62
-7	1	83	82
-7	2	228	235
-7	3	41	32
-7	4	281	286
-7	5	133	134
-7	6	156	149
-7	7	55	56
-6	-6	26	22
-6	-5	129	126
-6	-4	55	59
-6	-3	179	175
-6	-2	129	121
-6	-1	156	152
-6	0	247	248
-6	1	241	239
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-6	4	148	153
-6	5	4	11
-6	6	119	123
-5	-7	136	137
-5	-6	0	28
-5	-5	184	177
-5	-4	168	180
-5	-3	26	32
-5	-2	88	84
-5	-1	118	118
-5	0	149	160
-5	1	34	15
-5	2	165	180
-5	3	73	71
-5	4	44	45
-5	5	12	27
-5	6	79	80
-4	-8	0	28
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-4	-6	27	25
-4	-5	125	136
-4	-4	69	91
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-4	-2	151	158
-4	-1	97	110
-4	0	152	168
-4	1	96	98
-4	2	0	8
-4	3	104	85
-4	4	209	210
-4	5	33	28
-3	-9	138	114
-3	-8	30	31
-3	-7	65	67
-3	-6	29	38
-3	-5	261	274
-3	-4	316	322
-3	-3	112	106
-3	-2	135	153
-3	-1	131	118
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-2	-10	0	13
-2	-9	47	50
-2	-8	10	19
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-2	-2	125	135
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-2	2	174	174
-2	3	107	88
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-1	-10	63	71
-1	-9	205	198
-1	-8	56	65
-1	-7	180	190
-1	-6	104	103
-1	-5	80	71
-1	-4	0	11
-1	-3	133	98
-1	-2	64	74
-1	-1	50	61
-1	0	265	259
-1	1	27	42
-1	2	17	18
0	-12	77	84
0	-11	137	131
0	-10	59	55
0	-9	180	170
0	-8	159	174
0	-7	34	23
0	-6	27	61
0	-5	208	199
0	-4	0	42
0	-3	86	56
0	-2	219	216
0	-1	127	130
0	0	37	4
0	1	70	32
1	-12	40	34
1	-11	190	185
1	-10	173	167
1	-9	222	229
1	-8	35	51
1	-7	94	101
1	-6	101	81
1	-5	249	254
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1	-2	127	132
1	-1	63	38
1	0	33	66
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2	-12	0	8
2	-11	172	165
2	-10	86	76
2	-9	68	62
2	-8	43	54
2	-7	118	113
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2	-5	17	17
2	-4	172	162
2	-3	0	12
2	-2	27	30
3	-12	76	68
3	-11	0	25
3	-10	24	21
3	-9	60	52
3	-8	21	32
3	-7	35	11
3	-6	185	181
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4	-11	124	138
4	-10	0	5
4	-9	45	52
4	-8	79	93
4	-7	91	85
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-8	3	0	17
-8	4	165	161
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-7	-3	121	112
-7	-2	159	164
-7	-1	35	7
-7	0	51	1
-7	1	11	13
-7	2	149	146
-7	3	155	158
-7	4	182	170
-7	5	100	93
-6	-6	163	159
-6	-5	93	97
-6	-4	199	200
-6	-3	115	125
-6	-2	46	41
-6	-1	55	45
-6	0	217	208
-6	1	49	46
-6	2	214	199
-6	3	167	162
-6	4	103	105
-5	-7	125	123
-5	-6	199	177
-5	-5	169	166
-5	-4	57	41
-5	-3	28	22
-5	-2	254	244
-5	-1	0	7
-5	0	247	244
-5	1	103	103
-5	2	54	38
-5	3	128	118
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-4	-7	80	64
-4	-6	227	227
-4	-5	0	13
-4	-4	146	126
-4	-3	23	3
-4	-2	289	284
-4	-1	192	189
-4	0	134	147
-4	1	24	30
-4	2	0	7
-4	3	60	60
-3	-9	102	108
-3	-8	152	146
-3	-7	0	8
-3	-6	249	262
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-2	-10	31	34
-2	-9	53	44
-2	-8	99	90
-2	-7	154	152
-2	-6	279	260
-2	-5	142	136
-2	-4	257	270
-2	-3	49	85
-2	-2	0	32
-2	-1	119	94
-2	0	124	102
-2	1	51	66
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-1	-10	25	14
-1	-9	79	61
-1	-8	301	292
-1	-7	95	76
-1	-6	189	193
-1	-5	111	114
-1	-4	0	6
-1	-3	61	50
-1	-2	67	81
-1	-1	157	149
-1	0	93	104
0	-11	99	109
0	-10	135	132
0	-9	196	200
0	-8	145	151
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0	-6	0	31
0	-5	29	45
0	-4	185	180
0	-3	131	125
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0	-1	0	29
1	-12	21	22
1	-11	74	74
1	-10	182	182
1	-9	42	46
1	-8	93	96
1	-7	73	84
1	-6	100	99
1	-5	0	15
1	-4	174	187
1	-3	29	41
2	-11	169	173
2	-10	26	22
2	-9	18	24
2	-8	60	50
2	-7	29	29
2	-6	130	126
2	-5	43	43
3	-10	82	67
3	-9	30	17
3	-8	117	110
*****	H =	8	*****
-8	0	120	117
-8	1	130	129
-7	-3	45	66
-7	-2	106	97
-7	-1	13	34
-7	0	0	39
-7	1	123	109
-7	2	46	60
-6	-5	88	79
-6	-4	193	187
-6	-3	98	87
-6	-2	7	10
-6	-1	30	47
-6	0	71	77
-6	1	205	196
-6	2	0	42
-5	-7	69	53
-5	-6	251	267
-5	-5	46	40
-5	-4	39	29
-5	-3	46	29
-5	-2	69	69
-5	-1	235	233
-5	0	0	4
-5	1	167	154
-5	2	39	41
-4	-8	92	84
-4	-7	81	71
-4	-6	54	49
-4	-5	207	188
-4	-4	32	7
-4	-3	98	85
-4	-2	39	16
-4	-1	240	222
-4	0	0	11
-4	1	81	85
-3	-9	11	27
-3	-8	59	76
-3	-7	39	25
-3	-6	187	197
-3	-5	88	98
-3	-4	117	115
-3	-3	204	195
-3	-2	18	2
-3	-1	38	28
-3	0	0	12
-2	-9	0	5
-2	-8	259	248
-2	-7	132	115
-2	-6	260	279
-2	-5	93	105
-2	-4	44	58
-2	-3	0	6
-2	-2	12	23
-2	-1	33	52
-1	-10	14	25
-1	-9	56	48
-1	-8	158	156
-1	-7	140	131
-1	-6	120	115
-1	-5	108	107
-1	-4	49	47
-1	-3	43	28
0	-10	143	125
0	-9	19	7
0	-8	109	112
0	-7	110	106
0	-6	58	42
0	-5	48	44
0	-4	61	55
1	-9	81	63
1	-8	2	20
1	-7	30	3
*****	H =	9	*****
-5	-5	66	86
-5	-4	146	135
-5	-3	18	39
-5	-2	49	25
-4	-6	56	39
-4	-5	0	20
-4	-4	73	50
-4	-3	126	135
-3	-7	0	25
-3	-6	163	157
-3	-5	171	164
-3	-4	76	58
-2	-7	50	42
-2	-6	96	94

tinguished from C with reasonable certainty by the shapes of the thermal ellipsoids of the atoms. (Distinction of N from C by this method has also been possible in $Ir(Cl)(CO)(NO)(P(C_6H_5)_3)_2$.[12]) The position of the nitrosyl group can be inferred, however, by interpreting the infrared carbonyl stretching frequencies on the basis of the molecular geometry found here. As can be seen in Figures 1 and 2, the molecule is a trigonal bipyramid. Although no symmetry is imposed by the space group, the molecule would nearly have C_3 symmetry if the nitrosyl group were *trans* to the P atom. The infrared spectrum in xylene solution[3] shows three carbonyl bands and one nitrosyl band, and the spectrum of the solid (Nujol mull) before and after recrystallization shows the same set of carbonyl and nitrosyl bands. The presence of the maximum possible number of carbonyl stretching frequencies suggests that the molecule does not possess a threefold axis. Consequently, it is unlikely that the nitrosyl group is in an axial position. Thus, it was assumed that a carbonyl group occupies the axial position *trans* to the P atom. There were no significant differences in the root-mean-square amplitudes of vibration of the three equatorial atoms. Therefore, a disordered model having $^1/_3$N and $^2/_3$C at each of the equatorial sites was assumed and two additional cycles of least-squares refinement were carried out. There was no change in the R factor from that for the model having four carbonyl groups, and refinement was considered complete. The two scale factors differed by only 0.5%.

There is, of course, the possibility that the true space group is P1 and that the resultant two independent molecules are ordered. Yet on the basis of the present refinement it follows that these two molecules would be very nearly related by a pseudo center of symmetry. This would lead to singularity problems in refinement in P1 that would preclude a proper test of the space group. On the basis of the values of R_1 and R_2, the reasonableness of the thermal ellipsoids, and our past experience with similar data sets on similar compounds, we feel that the present refinement in P$\bar{1}$ in a satisfactory one.

The average standard deviation for an observation of unit weight for the 1297 reflections used in the refinement is 2.25. However, an analysis of this quantity as a function of the magnitude of F_o and also as a function of $\lambda^{-1} \sin \theta$ revealed a range of only 1.90–2.65. Thus, the relative weights are essentially correct, while the absolute weights are about twice as large as they should be.

A final structure factor calculation on all 1755 reflections gave $R_1 = 0.079$. Six reflections had $F_o^2 < \sigma(F_o^2)$ and $F_c^2 > 2\sigma(F_o^2)$. Examination of the recorder chart tracings showed that three of these reflections were in error because of the slight movement of the crystal. The three reflections are marked by asterisks in Table I.

In a final difference electron density map from which the contributions of all atoms had been subtracted and which was calculated from all 1755 reflections, the maximum residual was 0.6 e Å^{-3} with an estimated uncertainty[13] of 0.09 e Å^{-3}. On the same scale a C atom had a height of ~5 e Å^{-3}. The maximum residuals were associated with the phenyl groups, and they may reflect slight departures of the groups from D_{6h} symmetry and/or the inadequacy of describing the thermal motion of the phenyl C atoms by an isotropic model.

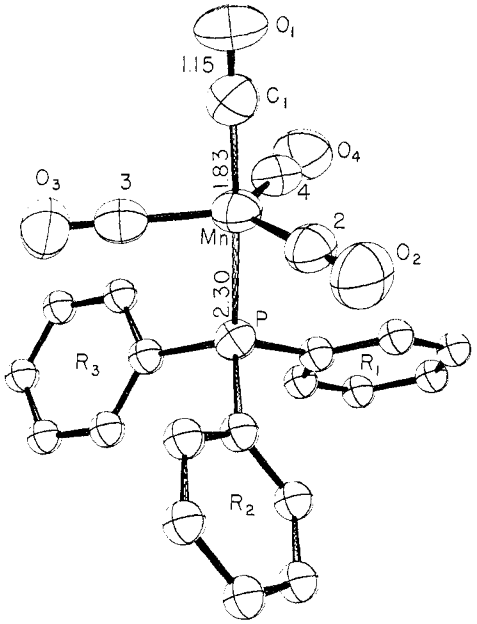

Figure 1.—Perspective view of the $Mn(NO)(CO)_3(P(C_6H_5)_3)$ molecule. The atoms labeled 2, 3, and 4 are $^1/_3$N and $^2/_3$C. The sizes and shapes of the nongroup atoms are determined by their final anisotropic thermal parameters. For clarity, phenyl C atoms have been arbitrarily given isotropic temperature factors of 3.0 Å^2.

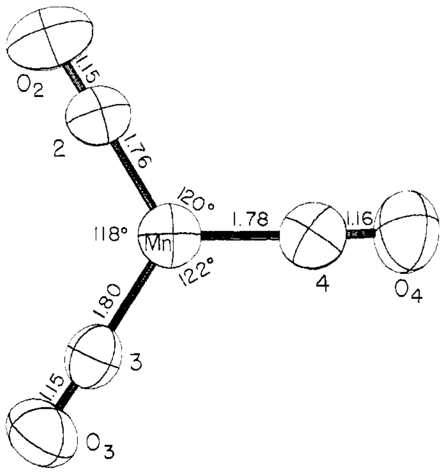

Figure 2.—View of the $Mn(NO)(CO)_2$ plane.

Values of $10|F_o|$ and $10|F_c|$ (in electrons) for all 1755 reflections appear in Table I. The 458 reflections not used in the refinement all have $10|F_o| < 70$. On the same scale $10F_{000} = 4280$. The final structural parameters are given in Table II, and derived fractional coordinates of the group atoms are shown in Table III.

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[12] D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **7**, 2345 (1968).

[13] D. W. J. Cruickshank, *Acta Cryst.*, **2**, 65 (1949).

TABLE II

FINAL ATOMIC AND GROUP PARAMETERS

Atom[a]	x	y	z	$10^3\beta_{11}$	$10^3\beta_{22}$	$10^3\beta_{33}$	$10^3\beta_{12}$	$10^3\beta_{13}$	$10^2\beta_{23}$
Mn	0.3832 (2)	0.3506 (2)	0.6507 (1)	25.8 (4)	20.3 (4)	10.7 (2)	16.2 (3)	10.9 (2)	9.0 (2)
P	0.4242 (3)	0.6047 (3)	0.7901 (2)	17.9 (6)	18.0 (5)	8.6 (3)	12.5 (5)	8.1 (4)	8.4 (3)
C_1	0.349 (1)	0.151 (1)	0.5343 (10)	35 (3)	27 (3)	12 (1)	20 (3)	14 (2)	13 (2)
2[b]	0.484 (1)	0.355 (1)	0.7744 (8)	28 (2)	23 (2)	11 (1)	18 (2)	12 (1)	11 (1)
3	0.539 (1)	0.483 (1)	0.6363 (7)	22 (2)	21 (2)	9 (1)	14 (2)	8 (1)	8 (1)
4	0.136 (1)	0.231 (1)	0.5510 (9)	28 (3)	22 (2)	10 (1)	16 (2)	10 (2)	8 (1)
O_1	0.327 (1)	0.025 (1)	0.4619 (7)	57 (3)	30 (2)	19 (1)	32 (2)	24 (2)	13 (1)
O_2	0.555 (1)	0.360 (1)	0.8558 (7)	50 (3)	38 (2)	16 (1)	31 (2)	18 (1)	20 (1)
O_3	0.642 (1)	0.568 (1)	0.6291 (6)	31 (2)	34 (2)	16 (1)	18 (2)	16 (1)	16 (1)
O_4	−0.025 (1)	0.149 (1)	0.4875 (7)	25 (2)	32 (2)	13 (1)	14 (2)	8 (1)	11 (1)

Group[c]	x_0	y_0	z_0	δ	ϵ	η	B_1	B_2	B_3	B_4	B_5	B_6
R_1	0.0965 (5)	0.5186 (5)	0.8182 (3)	−3.097 (4)	−3.060 (4)	0.777 (4)	4.0 (2)	5.0 (2)	6.8 (2)	6.8 (2)	6.3 (2)	5.1 (2)
R_2	0.8030 (5)	0.8915 (5)	1.0815 (4)	−1.938 (7)	2.140 (3)	1.771 (7)	3.6 (2)	5.1 (2)	6.4 (2)	5.8 (2)	6.3 (2)	5.4 (2)
R_3	0.4528 (5)	0.8407 (5)	0.7122 (4)	1.845 (4)	2.466 (4)	−0.514 (4)	3.8 (2)	4.6 (2)	5.7 (2)	6.3 (2)	7.2 (3)	6.2 (2)

[a] x, y, and z are in fractional triclinic coordinates. Thermal parameters are in the form: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The standard deviation of the least significant figure is given in parentheses. [b] Atoms 2, 3, and 4 are $^2/_3$C and $^1/_3$N. [c] x_c, y_c, and z_c are the fractional coordinates of the group centers. The angles δ, ϵ, and η (in radians) which bring about alignment (except for translation) of an internal-coordinate system within the ring with a fixed external-coordinate system are those previously described.[11] B_i is the isotropic thermal parameter in Å^2 of atom i in a given ring. The rings are numbered so that C_1 is attached to P; C_4 is *para* to C_1.

TABLE III

DERIVED PARAMETERS FOR GROUP CARBON ATOMS[a]

	x	y	z
		R_1	
C_1	0.2375 (7)	0.5558 (8)	0.8043 (5)
C_2	0.1595 (8)	0.6391 (7)	0.8006 (5)
C_3	0.0186 (9)	0.6020 (9)	0.8144 (6)
C_4	−0.0444 (7)	0.4814 (9)	0.8320 (6)
C_5	0.0336 (8)	0.3982 (7)	0.8358 (6)
C_6	0.1745 (8)	0.4353 (7)	0.8220 (5)
		R_2	
C_1	0.6371 (7)	0.7663 (14)	0.9550 (4)
C_2	0.6343 (7)	0.8466 (12)	1.0588 (6)
C_3	0.8003 (9)	0.9718 (7)	1.1852 (4)
C_4	0.9690 (7)	1.0168 (14)	1.2079 (4)
C_5	0.9717 (7)	0.9364 (12)	1.1041 (6)
C_6	0.8058 (8)	0.8112 (7)	0.9777 (5)
		R_3	
C_1	0.4410 (11)	0.7403 (7)	0.7478 (5)
C_2	0.5750 (8)	0.9311 (7)	0.8417 (4)
C_3	0.5868 (9)	1.0315 (5)	0.8062 (5)
C_4	0.4645 (12)	0.9412 (8)	0.6768 (6)
C_5	0.3305 (9)	0.7504 (9)	0.5828 (4)
C_6	0.3188 (8)	0.6500 (6)	0.6183 (5)

[a] The estimated standard deviations are derived from those of the group parameters and are meant to be used in error analyses on inter-ring distance. Intra-ring C–C = 1.397 Å.

TABLE IV

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)[a]

Atom	Min	Intermed	Max
Mn	0.208 (2)	0.256 (2)	0.262 (2)
P	0.199 (4)	0.216 (4)	0.223 (4)
C_1	0.24 (1)	0.27 (1)	0.30 (1)
2	0.22 (1)	0.24 (1)	0.27 (1)
3	0.22 (1)	0.23 (1)	0.27 (1)
4	0.22 (1)	0.27 (1)	0.28 (1)
O_1	0.21 (1)	0.36 (1)	0.39 (1)
O_2	0.24 (1)	0.30 (1)	0.36 (1)
O_3	0.24 (1)	0.30 (1)	0.34 (1)
O_4	0.24 (1)	0.32 (1)	0.34 (1)

[a] Figures 1 and 2 provide an indication of the directions of these principal axes of vibration.

TABLE V

INTERATOMIC DISTANCES

Atoms	Dist, Å	Atoms	Dist, Å
Mn–P	2.305 (4)	P–2	2.902 (10)
Mn–C_1	1.833 (11)	P–3	2.879 (9)
Mn–2	1.756 (10)	P–4	2.864 (10)
Mn–3	1.798 (10)	C_1–O_1	1.146 (10)
Mn–4	1.782 (11)	2–O_2	1.149 (9)
Mn–O_1	2.979 (8)	3–O_3	1.154 (9)
Mn–O_2	2.905 (8)	4–O_2	1.161 (9)
Mn–O_3	2.951 (8)	C_1–2	2.598 (14)
Mn–O_4	2.942 (9)	C_1–3	2.558 (14)
P–R_1C_1[a]	1.814 (8)	C_1–4	2.587 (14)
P–R_2C_1	1.813 (9)	2–3	3.044 (14)
P–R_3C_1	1.821 (10)	2–4	3.068 (14)
P–C_1	4.136 (12)	3–4	3.128 (14)

[a] R_iC_1 means C_1 on group R_i.

Description and Discussion

The numbering scheme and perspective view of the molecule are shown in Figure 1. The size and shape of the atoms are determined by the vibrational ellipsoids associated with their final thermal parameters and by the perspective view. Phenyl C atoms have been made artificially small for clarity. Root-mean-square (rms) amplitudes of vibration appear in Table IV, and their directions can be deduced from Figures 1 and 2. Interatomic distances and angles computed from the final atomic parameters of Table II are given in Tables V and VI, respectively. The estimated standard deviations of the distances and angles were derived from the inverse least-squares matrix from the final refinement. Selected distances and angles are also indicated in Figures 1 and 2.

From Figures 1 and 2 it is readily apparent that the coordination symmetry about the Mn atom is trigonal bipyramidal. Triphenylphosphine occupies one of the axial positions, and a carbonyl group is assumed to be *trans* to it. This is the structure previously predicted[2] on the basis of dipole moment measurements. The Mn

TABLE VI

BOND ANGLES

Atoms	Angle, deg	Atoms	Angle, deg
P–Mn–C_1	176.9 (3)	Mn–C_1–O_1	179.0 (9)
2–Mn–3	117.8 (4)	Mn–2–O_2	178.3 (8)
2–Mn–4	120.3 (4)	Mn–3–O_3	177.9 (8)
3–Mn–4	121.8 (4)	Mn–4–O_4	177.5 (8)
C_1–Mn–2	92.7 (4)	R_1C_1–P_1–R_2C_1	104.0 (3)
C_1–Mn–3	89.5 (4)	R_1C_1–P–R_3C_1	104.6 (5)
C_1–Mn–4	91.4 (4)	R_2C_1–P–R_3C_1	104.3 (4)
P–Mn–2	90.2 (3)		
P–Mn–3	88.2 (3)		
P–Mn–4	88.0 (3)		

atom is 0.04 Å out of the weighted least-squares plane through the equatorial nitrosyl and carbonyl groups in the direction of the axial carbonyl group. The equation of the plane in triclinic coordinates is $-5.65x + 7.43y + 4.64z - 3.51 = 0$, and all six atoms are within 0.01 Å of the plane. No symmetry is imposed on the molecule by the space group, and although the apparent symmetry of the disordered molecules is nearly C_3, the effective coordination symmetry of an individual molecule can be no higher than *m* if the nitrosyl group is in the equatorial plane.

As mentioned above, the nitrosyl groups and two carbonyl groups are disordered in the equatorial plane of the trigonal bipyramid. The average equatorial Mn–C (or Mn–N) distance of 1.78 (1) Å is similar to the metal–carbon distance of 1.79 Å in $Fe(CO)_5$.[14] The axial Mn–C distance of 1.83 (1) Å is slightly longer than the equatorial distances. The difference is only $\sim 3\sigma$ and may not be significant. On the other hand, electron diffraction studies on $Fe(CO)_2(NO)_2$ and $Co(NO)(CO)_3$[15] have shown metal–nitrogen distances 0.07 Å shorter than metal–carbon distances, and the Mn–N distance in $Mn(NO)(CO)_2(P(C_6H_5)_3)_2$[1] appears to be 0.04 Å shorter than the average Mn–C distance. The fact that the average equatorial Mn–C distance found here is shorter than the axial Mn–C distance is further justification for assigning the nitrosyl group to the equatorial plane. Of course, the difference in axial and equatorial bond lengths may also be due to a *trans* effect of the $P(C_6H_5)_3$ group. In $Co(SiCl_3)(CO)_4$,[16] the axial Co–C bond is 0.03 Å longer than the equatorial Co–C bond. These slight axial–equatorial differences observed for the five-coordinate compounds are just the reverse of the differences found for several six-coordinate carbonyl derivatives of Mn, where the axial Mn–C distances are *shorter* than the equatorial Mn–C distances. In $Mn_2Fe(CO)_{14}$[17] the average axial and equatorial Mn–C distances are 1.805 (10) and 1.855 (10) Å, respectively, and similar differences have also been found in $Mn_2(CO)_{10}$[18] and $HMn(CO)_5$.[19] The mean axial–equatorial nonbonded C···C interaction of 2.58 Å in $Mn(NO)(CO)_3(P(C_6H_5)_3)$ is identical with those observed in $Mn_2(CO)_{10}$.[18] The C–O distances of 1.15 Å are similar to those typically found in carbonyl derivatives of the transition metals, and N–O distances ranging from 1.10 to 1.26 Å are known.[20] All of the Mn–C–O (or Mn–N–O) groups in this molecule are linear. The Mn–P distance is 2.305 Å, to be compared with the average Mn–P distance of 2.278 Å in $Mn(NO)(CO)_2(P(C_6H_5)_3)_2$.[1]

There are no unusual intermolecular contacts between the molecules. No O···O contact is less than 3.0 Å; the shortest interactions with O atoms are with H atoms 2.5 Å away. The shortest Mn···Mn distance is 7.11 Å.

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