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The Molecular Structure of Nitrosyldicarbonylbis(triphenylphosphine)manganese, $Mn(NO)(CO)_2(P(C_6H_5)_3)_2$

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The crystal and molecular structure of nitrosyldicarbonylbis(triphenylphosphine)manganese, $Mn(NO)(CO)_2(P(C_6H_5)_3)_2$, has been determined from three-dimensional X-ray data collected by counter methods. The material crystallizes in space group D_{2h}^{15}-Pbca of the orthorhombic system with eight molecules in a cell of dimensions $a = 18.15$, $b = 17.07$, and $c = 21.86$ A. The observed and calculated densities are 1.31 g/cm^3. Least-squares refinement of the structure has led to a final value of the conventional R factor of 0.073 for the 1337 reflections having $F^2 > \sigma(F^2)$. The nitrosyl group has been distinguished from the carbonyl groups with reasonable certainty on the basis of differences in root-mean-square amplitudes of vibration of the various atoms. The crystal structure consists of the packing of well-separated monomeric molecular units. In the molecular structure, the Mn atom is at the center of a trigonal bipyramid and is coplanar with the NO and CO groups; the two $P(C_6H_5)_3$ groups are at the apices of the trigonal bipyramid and hence are *trans* to one another. The Mn–P distances are 2.278 and 2.279 ($\pm$0.005) A; the Mn–N distance is 1.73 $\pm$ 0.01 A, and the Mn–C distances are 1.75 and 1.78 ($\pm$0.02) A.

Introduction

In recent years five-coordinate transition metal complexes have been the object of considerable interest.[1,2] As part of a continuing investigation of five-coordinate complexes being conducted in these laboratories, we have undertaken the determination of the structures of the series of compounds $Mn(NO)(CO)_4$, $Mn(NO)(CO)_3(P(C_6H_5)_3)$ and $Mn(NO)(CO)_2(P(C_6H_5)_3)_2$. These compounds are of particular interest because one may study the changes in molecular geometry of a series of presumably five-coordinate transition metal complexes, where the metal is in the same formal oxidation state, as the ligands are varied systematically. Also through a comparison of the Mn–NO and Mn–CO distances in these compounds one should obtain information of use in theoretical discussions of the relative amounts of multiple bonding involved in bonds between these ligands and transition metals.

No X-ray structural information is available on any of these complexes. However, the isoelectronic compound $Fe(CO)_5$ is a trigonal bipyramid.[3] By analogy to $Fe(CO)_5$ and on the basis of analysis of the CO infrared stretching frequencies, a trigonal-bipyramidal geometry with an apical NO has been proposed[4] for $Mn(NO)(CO)_4$. From infrared spectroscopy and dipole moment measurements, $Mn(NO)(CO)_3(P(C_6H_5)_3)$ and $Mn(NO)(CO)_2(P(C_6H_5)_3)_2$ were predicted[5] to have trigonal-bipyramidal structures with apical triphenylphosphine groups and with NO in an equatorial position. Recently kinetic studies have been conducted[6] on the replacement of CO from $Mn(NO)(CO)_4$ by R_3P ligands. These experiments indicate that the reaction for the addition of a second molecule of triphenylphosphine

$$Mn(NO)(CO)_3(P(C_6H_5)_3) + P(C_6H_5)_3 \xrightarrow[p\text{-xylene}]{120^\circ} Mn(NO)(CO)_2(P(C_6H_5)_3)_2 + CO$$

is a first-order reaction—the rate depending only upon the concentration of $Mn(NO)(CO)_3(P(C_6H_5)_3)$. Presumably the mechanism involves loss of CO as the rate-determining step, followed by rapid addition of a second molecule of triphenylphosine. Usually NO is thought to be a better π-bonding ligand than CO. If so, such first-order kinetics would then seem to be conveniently explained by loss of CO from a $Mn(NO)(CO)_3(P(C_6H_5)_3)$ molecule having CO and NO *trans* to one another. However, neither a trigonal bipyramid with *trans* NO and CO nor a tetragonal pyramid with *trans* CO and NO is the structure predicted for $Mn(NO)(CO)_3(P(C_6H_5)_3)$ from infrared spectroscopy. However, because of the low energy barrier for interconversion among various five-coordinate structures and because the reaction is run at a relatively high temperature, it is possible that the configuration of the reacting species is not the same as the ground-state configuration of the molecule and that the molecule has rearranged to some other five-coordinate geometry before losing CO. Thus there may be no basis for comparison of the kinetic and infrared data. On the other hand, structural assignments based upon the number of CO bands observed in the infrared region have often been wrong. The current kinetic work on this series of compounds and the uncertainty inherent in spectroscopic assignments of structures further encouraged us to pursue the structures of the $Mn(NO)(CO)_{4-x}(P(C_6H_5)_3)_x$ compounds in the solid state. We report here on the structure of the most stable member of the series, $Mn(NO)(CO)_2(P(C_6H_5)_3)_2$.

Collection and Reduction of Data

Excellent orange crystals of $Mn(NO)(CO)_2(P(C_6H_5)_3)_2$, prepared as previously described,[5] were kindly supplied by Professor F. Basolo and Dr. H. Wawersik. Preliminary Weissenberg and precession photographs (Mo Kα) showed systematic absences:

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[1] E. L. Muetterties and R. A. Shunn, *Quart. Rev.* (London), **20**, 245 (1966).

[2] J. A. Ibers, *Ann. Rev. Phys. Chem.*, **16**, 375 (1965).

[3] J. Donohue and A. Caron, *Acta Cryst.*, **17**, 663 (1964), and references therein.

[4] P. M. Treichel, E. Pitcher, R. B. King, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 2593 (1961).

[5] W. Hieber and H. Tengler, *Z. Anorg. Allgem. Chem.*, **318**, 136 (1962).

[6] H. Wawersik and F. Basolo, private communication.

$0kl$ when $k \neq 2n$, $h0l$ when $l \neq 2n$, and $hk0$ when $h \neq 2n$. These absences are consistent with the space group D_{2h}^{15}-Pbca. The unit cell parameters at 22° are a = 18.147 ± 0.008, b = 17.071 ± 0.008, and c = 21.860 ± 0.011 A (λ (Mo $K\alpha_1$) 0.70926 A). These parameters were determined by a least-squares refinement of the setting angles of 16 reflections which had been accurately centered on a Picker automatic diffractometer, as previously described.[7] The crystal density of 1.31 g cm^{-3}, calculated for eight moleculeses in the cell, is in excellent agreement with the experimental density of 1.31 g cm^{-3} determined by flotation.

For data collection, a crystal having approximate dimensions 0.07 × 0.07 × 0.15 mm was mounted on a thin glass fiber along its long axis (c). Before data collection began, however, the crystal was deliberately "misset" to a completely general orientation in relation to the diffractometer coordination system so that the possibility of multiple reflections[8] would be minimized.

Because Mn is near the absorption edge for Cu $K\alpha$ radiation, its mass absorption coefficient is not accurately known; therefore, Mo $K\alpha$ radiation was used ($\mu_{Cu} \sim 45.5$, $\mu_{Mo} = 5.47$ cm^{-1}, where μ is the linear linear absorption coefficient). The large unit cell raised the possibility of overlapping reflections. To minimize overlap, a small crystal of low mosaicity was selected. However, it was desirable to calculate whether any reflections would overlap for a given 2θ scan range on a four-circle diffractometer.

Overlap was treated by separating it into vertical and equatorial components. Vertical overlap will occur when the χ values for two reflections having the same ϕ and 2θ settings are not sufficiently different and intensity from both reflections enters the counter. If δ_v is taken as the vertical angular spread of the diffracted beam, then two reflections with $|\Delta\chi| \geqslant \delta_v/\sin\theta$ should not overlap.

Similarly, two reflections having the same settings of χ and ϕ but different 2θ values should not overlap if $|2\theta_1 - 2\theta_2| \geqslant \delta_{eq} + s$, where δ_{eq} is the equatorial angular spread of the diffracted beam and s is the 2θ scan range (assuming a symmetric scan). For small missettings of ϕ, on the other hand, the intensity of a reflection can be regained by missetting 2θ in the opposite direction. A composite equatorial overlap expression can be written as $\Delta_{eq} \sim |2(\phi_1 - \phi_2)\cos\chi + (2\theta_1 - 2\theta_2)|$. If $\Delta_{eq} \geqslant \delta_{eq} + s$, as mentioned above, the reflections should not overlap. (Counter motion has been neglected in this approximation.) This limit can probably be relaxed slightly if the recorder charts are examined visually because equatorial overlap would probably be revealed as uneven backgrounds or abnormal peak contours. Pure vertical overlap, on the other hand, would be difficult to detect on the recorder chart because both peaks would be centered on the same 2θ value. For this structure, values of $\delta_v = 0.6°$ and $\Delta_{eq} = 1.5°$ were determined from several test scans. A calculation using these parameters resulted in only seven pairs of reflections being rejected for possible overlap out of the 9679 intensities gathered. No indication of overlap for other pairs of reflections was found upon inspecting the recorder chart tracings.

Intensities were collected on a Picker four-circle automatic diffractometer and processed similarly to the previously described procedure.[7] The diffracted beam was filtered through a 3.0-mil Zr foil, and the intensities were collected by the θ–2θ scan technique at a take-off angle of 1.0°. A symmetric scan range of 1° in 2θ was used and the scan rate was 1°/min. No attenuators were used because no reflection exceeded 7000 counts/sec during the scan. Stationary-counter, stationary-crystal background counts of 10 sec were taken at each end of the scan range and were typically 10–20 counts. The scintillation counter was 21 cm from the crystal and had an aperture 4 × 4 mm.

Initially a unique data set having $2\theta < 40°$ was gathered and reduced to F^2 and $\sigma(F^2)$ with $p = 0.04$.[7] An additional three forms were then generated and collected for those reflections having $F^2 > \sigma(F^2)$. Finally a unique outer sphere of data ($40° < 2\theta < 45°$) was collected and three additional forms were generated and collected for those reflections having $F^2 > 2\sigma(F^2)$. A total of 9679 intensities were recorded for the four non-Friedel equivalent forms (hkl, $\bar{h}kl$, $h\bar{k}l$, $hk\bar{l}$). The intensities of three standard reflections, monitored at least twice daily during the 20 days required to collect the data, remained essentially constant throughout the run.

The data were merged to yield 4438 independent observations of which 1337 had $F^2 > \sigma(F^2)$. In subsequent discussions reflections having $F^2 > \sigma(F^2)$ are termed "above background," while those having $F^2 < \sigma(F^2)$ are termed "below background." Estimated standard deviations of the intensities were adjusted[9] for the number of forms observed for a given reflection. No corrections were made for absorption because a test calculation indicated that the absorption correction factor (A^*) only varied from 1.04 to 1.06. This variation in A^* is less than the estimated uncertainty of the intensities themselves. Of those 1951 reflections observed more than once, 1249 had $\sigma_{av} > \sigma_{range}$ and 702 had $\sigma_{av} \leqslant \sigma_{range}$;[7] 614 reflections observed as being above background for the form hkl ended up being below background when combined with the other three forms of data. From the averaging of the equivalent forms, a weighted R factor of 0.086 was predicted for a refinement on F^2.

Solution of the Structure

The structure was solved from the unique data set (while the intensities of equivalent reflections were being gathered) by direct methods using Sayre's equation[10] in the form of a modified version of Long's[11] computer program. Normalized structure factors were com-

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[7] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

[8] W. H. Zachariasen, *Acta Cryst.*, **18**, 705 (1965).

[9] W. T. Robinson and J. A. Ibers, *Inorg. Chem.*, **6**, 1208 (1967).

[10] D. Sayre, *Acta Cryst.*, **5**, 60 (1952).

[11] R. E. Long, Ph.D. Thesis, part III, UCLA, 1965.

puted from the equation $E_{hkl}^2 = F_{hkl}^2[\epsilon \sum_{j=1}^{N} f_j^2(hkl)]^{-1}$ where $\epsilon = 2$ for $0kl$, $h0l$, and $hk0$ reflections, and $\epsilon = 1$ for all other reflections. The statistical distribution of E values is given in Table I.

TABLE I

DISTRIBUTION OF NORMALIZED STRUCTURE FACTORS

	Theoret	Obsd		Theoret	Obsd
$\langle E^2 \rangle$	1.000	1.000	$\lvert E\rvert > 3$	0.3%	0.2%
$\lvert E^2 - 1\rvert$	0.968	1.037	$\lvert E\rvert > 2$	5.0%	4.9%
$\langle \lvert E\rvert \rangle$	0.798	0.727	$\lvert E\rvert > 1$	32.0%	32.8%

Three linearly independent reflections were selected to fix the origin of the unit cell,[12] and four additional reflections were assumed to initiate phasing. These reflections were selected within the program on the basis of their large values of $|E_{\bar{h}}|\sum_{\bar{h}}|E_{\bar{h}'}||E_{\bar{h}+\bar{h}'}|$. Of the 16 possible solutions, the largest value of the consistency index[11] was

$$C = \frac{\langle |E_{\bar{h}}\sum_{\bar{h}'}E_{\bar{h}'}E_{\bar{h}+\bar{h}'}| \rangle}{\langle |E_{\bar{h}}||E_{\bar{h}'}|\sum_{\bar{h}'}|E_{\bar{h}+\bar{h}'}| \rangle} = 0.89$$

(where the average is taken over all values of $\bar{h}$). This solution also required the smallest number of reiterations to reach self-consistency. An E map based upon the 203 signs from this solution clearly revealed the Mn and P atoms and one CO group. Two cycles of least-squares refinement[13] on these atoms followed by a difference electron density map revealed all of the remaining nonhydrogen atoms.

Least-squares refinement based on F was then begun, with the weights w taken as $4F^2/\sigma^2(F^2)$. The atomic scattering factors used for Mn, P, C, N, and O were those tabulated by Ibers,[14] while those for H were taken from Stewart, *et al.*[15] The effects of anomalous dispersion were included in F_c;[16] Cromer's[17] values of f' and f'' for Mn and P were used. Phenyl rings were treated as rigid groups[18] (C–C = 1.397 A, 6/mmm 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 three carbonyl groups were assumed. After two cycles of least squares, the temperature factor on one ring was quite large (13 A^2), suggesting that the ring center was misplaced. A second difference electron density map gave a somewhat better position approximately 0.2 A away.[19] Two additional cycles of least-squares refinement—the latter with individual isotropic thermal parameters for group carbon atoms—gave $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.087$ and $R_2 = (\Sigma w(F_o - F_c)^2/\Sigma wF_o^2)^{1/2} = 0.071$. Hydrogen atoms were then included as fixed contributions to F_c (C–H = 1.084 A,[20] with each H atom assigned the temperature factor of the C atom to which it was bonded); and one cycle of least-squares refinement allowing the Mn atom to vibrate anisotropically and all other atoms isotropically then gave $R_1 = 0.076$ and $R_2 = 0.061$. Next, all nongroup atoms were allowed to vibrate anisotropically (154 parameters). Two cycles of refinement resulted in convergence with $R_1 = 0.072$ and $R_2 = 0.058$. An R factor ratio test[21] indicated that this improvement was significant at the 0.5% level.

A plot of the thermal ellipsoids of the atoms after anisotropic refinement showed that one of the "carbonyl" C atoms was a thin disk of very different shape from the other two C atoms (Figure 1). The root-mean-square (rms) amplitudes of vibration of the atoms (Table II) indicated that this difference was not an artifact of the perspective view. The minimum rms amplitude for the different carbonyl C atom was only about one-third as large as the minimum rms amplitudes for the other two carbonyl C atoms. However, the standard deviation of the minimum rms amplitude for the unusual atom was large (0.10 A), and this amplitude was thereby only one standard deviation smaller than the corresponding amplitudes for the other two atoms. The rms amplitudes of vibration along the intermediate and along the long axes of the thermal ellipsoids for the three atoms were more nearly equal. Moreover, the "Mn–C" bond length for the unusual atom was 0.07 A (3σ) less than the shorter of the other two Mn–C bonds. Therefore, this unique "carbonyl" group was taken to be the nitrosyl group. Two additional cycles of anisotropic refinement with the N scattering factor assigned to the presumed N atom gave $R_1 = 0.073$ and $R_2 = 0.057$ for the 1337 reflections having $F^2 > \sigma(F^2)$. This change in the weighted R factor is significant[21] at the 1% level. A plot of the thermal ellipsoids after the above refinement (Figure 1) now showed a more reasonably shaped N atom. The N atom was now larger, as would be expected from the additional scattering power. Also, this model resulted in similar ratios among the minimum, intermediate, and maximum rms amplitudes for each of the three atoms, and the standard deviations of the amplitudes were similar for all three atoms. The root-mean-square amplitudes of vibration obtained by these two models are given in Table II and the relevant distances appear in Figure 1. However, the major axes of the thermal ellipsoids of N and C are not oriented perpendicularly to the Mn–N or Mn–C bonds in either model as

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[12] M. M. Woolfson, "Direct Methods in Crystallography," Oxford University Press, London, 1961.

[13] In addition to various local programs for the CDC 3400, other programs used were local modifications of Zalkin's FORDAP Fourier program, the Busing–Levy ORFFE error function program, Johnson's ORTEP plotting program, and Long's[11] REL direct methods program.

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

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

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

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

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

[19] Group refinement of the orientation angles of phenyl rings will converge rapidly even when angles are off by 30–40°. However, the fractional coordinates of the center of mass of the ring must be determined more accurately. Errors of 0.2 A may result in nonconvergence or very slow convergence of the group.

[20] A. Langseth and B. P. Stoicheff, *Can. J. Phys.*, **34**, 350 (1956).

[21] W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

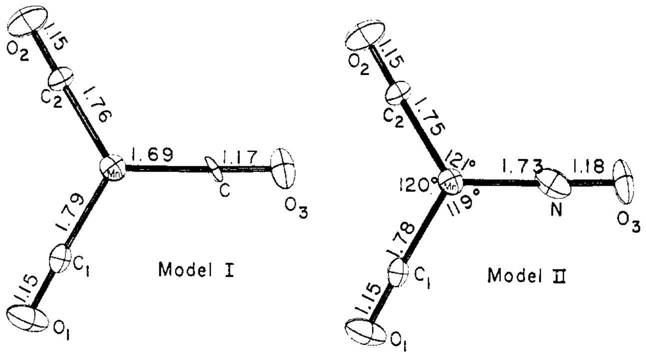

Figure 1.—View of the $Mn(NO)(CO)_2$ plane after refinement as $Mn(CO)_3$ (model I) and refinement as $Mn(NO)(CO)_2$ (model II). The C–Mn–C angles for model I are the same as the corresponding C–Mn–C and C–Mn–N angles in model II.

Table II

Root-Mean-Square Amplitudes of Vibration (A)[a]

	Minimum		Intermediate		Maximum	
Atom	I[b]	II[c]	I[b]	II[c]	I[b]	II[c]
Mn	0.190 (5)[d]	0.192 (5)	0.222 (5)	0.216 (5)	0.237 (5)	0.235 (4)
P_1	0.193 (8)	0.192 (8)	0.209 (8)	0.207 (8)	0.228 (7)	0.227 (7)
P_2	0.194 (8)	0.191 (8)	0.205 (8)	0.206 (8)	0.218 (8)	0.217 (8)
C_1	0.14 (4)	0.14 (4)	0.20 (3)	0.19 (3)	0.25 (3)	0.25 (3)
C_2	0.14 (4)	0.13 (4)	0.20 (3)	0.20 (4)	0.24 (3)	0.24 (3)
"N"	0.05 (10)	0.17 (2)	0.17 (3)	0.24 (2)	0.25 (3)	0.33 (2)
O_1	0.20 (2)	0.20 (2)	0.27 (2)	0.27 (2)	0.39 (2)	0.39 (2)
O_2	0.22 (2)	0.21 (2)	0.27 (2)	0.27 (2)	0.37 (2)	0.37 (2)
O_3	0.19 (2)	0.15 (3)	0.25 (2)	0.28 (2)	0.36 (2)	0.40 (1)

[a] Figures 1 and 2 provide an indication of the directions of these principal axes of vibration. [b] From refinement of the model assuming three CO groups. [c] From refinement of the final model containing one NO group and two CO groups. [d] Standard deviations of the last significant figures are given in parentheses here and in subsequent tables.

might be expected from chemical intuition and as is observed for the O atoms. More disturbing is the lengthening of the Mn–N bond by 0.04 A (~3σ) to 1.73 A, so that the presumed Mn–N distance is now only 0.02 A (1σ) less than the shorter of the Mn–C distances. It appears, therefore, that in this structure, with the data at hand, N cannot be unambiguously distinguished from C, and a disordered structure cannot be completely eliminated. However, model II (one NO and two CO groups) is preferred over model I (three CO groups) on the basis of the shapes of the thermal ellipsoids of the atoms and the "Mn–C" bond distances resulting from refinement of the two models. This model is also preferred from an R factor ratio test. However, an R factor ratio test assumes only random errors in the data, and such may not be the case here, as the final weighted R factor is higher than predicted (see below).

The average standard deviation for an observation of unit weight for the 1337 reflections used in the refinement is 1.43 (theory 1.0) and

$$R_2' = \left(\frac{\Sigma w|F_o^2 - F^2|^2}{\Sigma w F_o^4}\right)^{1/2} = 0.114$$

(for the refinement based on F). This compares with 0.086 predicted from merging the equivalent forms of data. Since the refinement did not proceed as far as predicted, it was thought that the data set might have been affected by secondary extinction. Several low-angle reflections were examined for possible extinction, and an extinction correction[22] was determined for several low-order reflections of high raw count which had $|F_o| < |F_c|$. A structure factor calculation including the correction improved these reflections but made the agreement for several other large F values much worse and R_2 increased slightly to 0.058. A cycle of least-squares refinement which included a variable extinction parameter did not improve the agreement; in fact, the converged value of the extinction parameter was so small as to have a negligible effect on the data. Consequently, it was concluded that extinction was not an important effect in this crystal.

A final structure factor calculation on all 4438 reflections gave $R_1 = 0.323$ and $R_2 = 0.070$. If reflections with $F_o = 0$ were omitted, then $R_1 = 0.189$ and $R_2 = 0.070$. No reflection with $F_o < \sigma(F)$ had $F_c > 1.5\sigma(F)$.

The large value of R_1 for all of the data is undoubtedly due to the large number of very weak reflections present in the data. The number of reflections with $F^2 > \sigma(F^2)$ would certainly have been greater if a larger crystal had been used. However, a larger crystal would have increased the problem of overlapping reflections because of the greater width of the peak profiles and would also have necessitated an absorption correction. Even so, it would probably have been preferable to have used a larger crystal for data collection.

The values of $10|F_o|$ and $10|F_c|$ (in electrons) are given in Table III. In a final difference electron density map from which all atoms have been subtracted, the highest peak is a random noise peak of 0.40 e A^{-3}. The clean difference map is further justification for the refinement of the phenyl rings as rigid groups with isotropic carbon atoms. Of the 203 E values used to solve the structure, 202 had the same sign as the final values of F_c; the one incorrect sign was found to be a reflection whose intensity was mispunched by the diffractometer and actually had $|E| << 1.7$. The final atomic and group parameters appear in Table IV, and Table V shows the derived fractional coordinates of the group carbon atoms.

Description and Discussion

The numbering scheme and a perspective view of the molecule are shown in Figure 2. The size and shape of the atoms are determined by the vibrational ellipsoids associated with the final anisotropic thermal parameters and the perspective view. Phenyl C atoms have been made artificially small for clarity. Root-mean-square amplitudes of vibration appear in Table II and their directions can be deduced from Figure 2. Interatomic distances and angles computed from the final atomic parameters of Table IV are shown in Tables VI and VII, respectively. Estimated standard deviations for 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 Figure 2, it is readily apparent that the co-

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[22] W. H. Zachariasen, *Acta Cryst.*, **16**, 1139 (1963).

TABLE III

VALUES OF $10|F_o|$ AND $10|F_c|$ (IN ELECTRONS) FOR $Mn(NO)(CO)_2(P(C_6H_5)_3)_2$

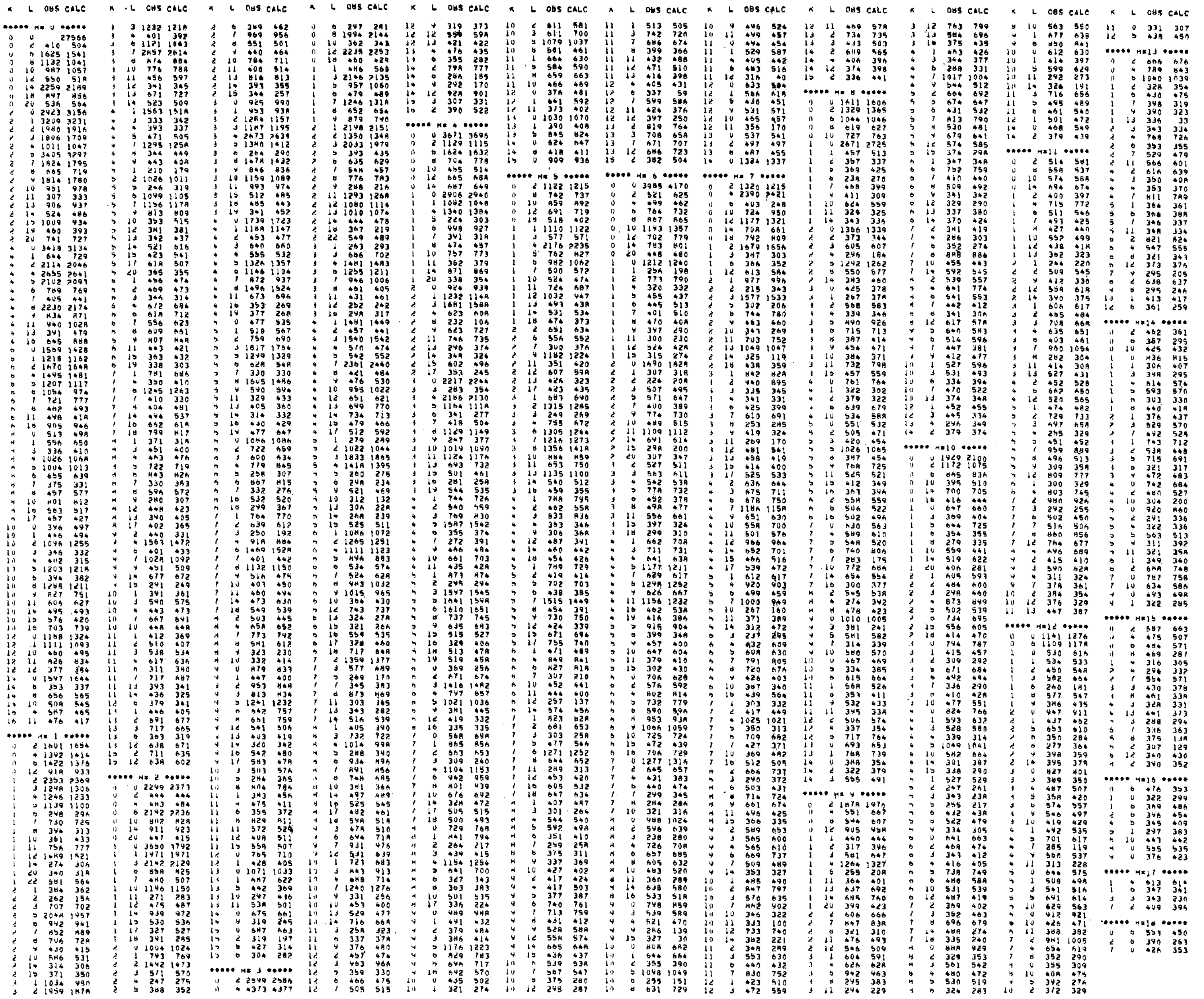

TABLE IV

FINAL ATOMIC AND GROUP PARAMETERS

Atom[a]	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Mn	0.4104 (1)	0.3176 (1)	0.6471 (1)	32 (1)	29 (1)	18 (1)	−3 (1)	0 (1)	−3 (1)
P_1	0.4385 (2)	0.2554 (2)	0.5579 (2)	29 (2)	28 (2)	17 (1)	−3 (2)	−1 (1)	−1 (2)
P_2	0.3919 (2)	0.3978 (2)	0.7289 (2)	28 (2)	26 (2)	17 (1)	1 (2)	−1 (1)	−2 (1)
C_1	0.4938 (9)	0.3711 (8)	0.6362 (8)	36 (8)	17 (7)	14 (5)	6 (7)	1 (6)	−2 (5)
C_2	0.3282 (10)	0.3510 (9)	0.6141 (7)	24 (9)	19 (8)	19 (5)	9 (6)	−2 (5)	−6 (5)
N	0.4127 (7)	0.2332 (6)	0.6907 (5)	38 (5)	58 (6)	20 (3)	−13 (6)	13 (4)	−8 (4)
O_1	0.5482 (7)	0.4052 (7)	0.6307 (6)	32 (6)	51 (7)	55 (6)	−15 (5)	9 (5)	−13 (5)
O_2	0.2734 (7)	0.3735 (7)	0.5947 (6)	39 (7)	74 (8)	32 (4)	22 (6)	−5 (4)	−8 (4)
O_3	0.4120 (7)	0.1756 (6)	0.7205 (5)	92 (7)	32 (6)	25 (4)	−14 (6)	−1 (5)	15 (4)

Group[b]	x_c	y_c	z_c	δ	ϵ	η	B_1	B_2	B_3	B_4	B_5	B_6
R_1	0.6090 (4)	0.2038 (4)	0.5465 (3)	2.935 (14)	−2.169 (6)	3.257 (13)	3.5 (4)	6.0 (4)	5.6 (5)	5.6 (4)	6.3 (5)	4.3 (4)
R_2	0.4014 (3)	0.3577 (4)	0.4368 (4)	−0.177 (8)	−2.577 (9)	−1.899 (7)	3.9 (4)	5.4 (4)	7.2 (5)	7.4 (5)	7.7 (5)	6.1 (5)
R_3	0.3570 (3)	0.0906 (4)	0.5317 (3)	1.183 (9)	−2.525 (6)	−2.938 (7)	3.2 (4)	4.2 (4)	4.2 (4)	4.3 (4)	5.0 (4)	3.9 (4)
R_4	0.2606 (4)	0.3502 (3)	0.8210 (3)	−0.768 (9)	−2.281 (8)	1.976 (9)	2.8 (4)	5.9 (4)	6.6 (5)	4.9 (4)	5.8 (5)	5.2 (4)
R_5	0.5322 (4)	0.4123 (4)	0.8187 (3)	−3.122 (8)	−3.084 (8)	2.471 (6)	3.9 (4)	6.2 (5)	7.8 (6)	6.5 (4)	7.0 (5)	5.3 (4)
R_6	0.3479 (4)	0.5762 (4)	0.6939 (3)	−1.480 (8)	2.600 (6)	−2.864 (7)	3.7 (4)	4.6 (4)	5.7 (4)	5.0 (4)	5.6 (4)	4.8 (4)

[a] x, y, and z are in fractional 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 deviations of the least significant figures are given in parentheses. [b] 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.[18] B_i is the isotropic thermal parameter in A^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 V

DERIVED PARAMETERS FOR GROUP CARBON ATOMS[a]

	x	*y*	*z*		*x*	*y*	
		R_1				R_4	
C_1	0.5356 (6)	0.2281 (14)	0.5507 (5)	C_1	0.3197 (6)	0.3687 (9)	0.7827 (5)
C_2	0.5800 (8)	0.2550 (8)	0.5029 (4)	C_2	0.2600 (6)	0.3262 (6)	0.7599 (4)
C_3	0.6533 (5)	0.2307 (9)	0.4988 (4)	C_3	0.2008 (6)	0.3077 (8)	0.7982 (6)
C_4	0.6823 (6)	0.1795 (14)	0.5424 (6)	C_4	0.2015 (6)	0.3316 (10)	0.8593 (5)
C_5	0.6380 (8)	0.1526 (8)	0.5901 (4)	C_5	0.2612 (6)	0.3741 (6)	0.8820 (3)
C_6	0.5646 (5)	0.1769 (9)	0.5943 (4)	C_6	0.3204 (6)	0.3927 (7)	0.8438 (5)
		R_2				R_5	
C_1	0.4190 (7)	0.3122 (7)	0.4879 (5)	C_1	0.4719 (5)	0.4081 (7)	0.7791 (4)
C_2	0.4003 (7)	0.2760 (4)	0.4328 (6)	C_2	0.5007 (7)	0.4809 (5)	0.7957 (5)
C_3	0.3827 (5)	0.3215 (8)	0.3816 (4)	C_3	0.5610 (7)	0.4851 (5)	0.8354 (6)
C_4	0.3838 (8)	0.4031 (7)	0.3857 (5)	C_4	0.5924 (5)	0.4165 (8)	0.8583 (4)
C_5	0.4025 (8)	0.4393 (4)	0.4408 (7)	C_5	0.5636 (7)	0.3437 (6)	0.8417 (5)
C_6	0.4201 (5)	0.3938 (7)	0.4919 (5)	C_6	0.5034 (7)	0.3395 (5)	0.8021 (5)
		R_3				R_6	
C_1	0.3938 (7)	0.1612 (6)	0.5422 (5)	C_1	0.3655 (7)	0.4989 (5)	0.7089 (4)
C_2	0.4257 (4)	0.1041 (7)	0.5050 (4)	C_2	0.2998 (6)	0.5320 (6)	0.7299 (4)
C_3	0.3889 (6)	0.0335 (5)	0.4944 (4)	C_3	0.2823 (5)	0.6093 (7)	0.7148 (4)
C_4	0.3202 (7)	0.0200 (6)	0.5212 (5)	C_4	0.3303 (8)	0.6535 (5)	0.6788 (5)
C_5	0.2883 (4)	0.0772 (7)	0.5584 (4)	C_5	0.3960 (6)	0.6204 (6)	0.6579 (4)
C_6	0.3251 (6)	0.1478 (5)	0.5689 (4)	C_6	0.4136 (5)	0.5430 (7)	0.6729 (4)

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

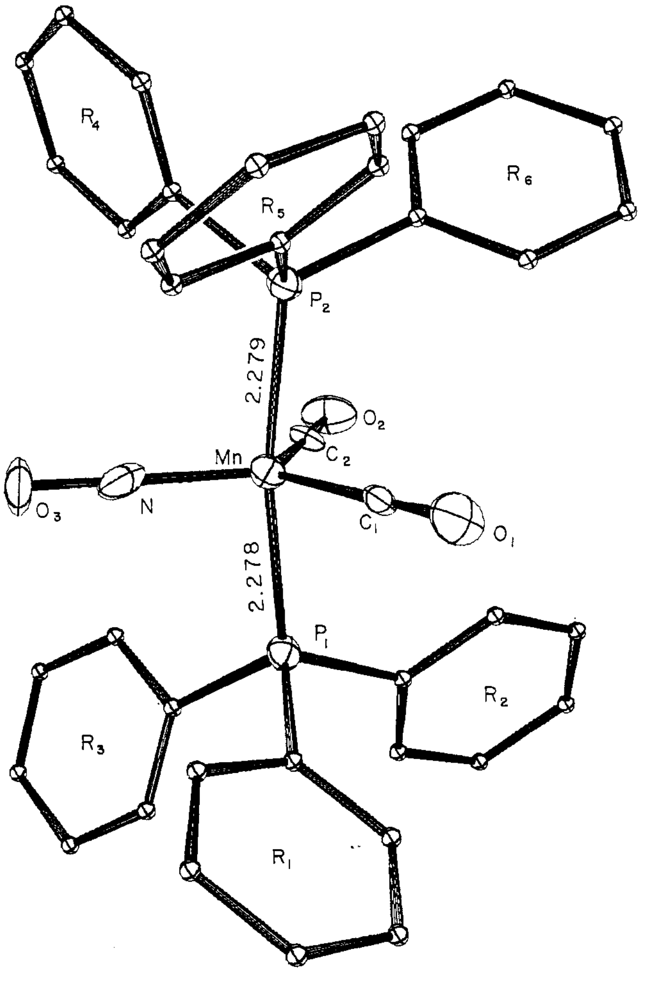

Figure 2.—Perspective view of the $Mn(NO)(CO)_2(P(C_6H_5)_3)_2$ molecule. Phenyl C atoms have been made artificially small for clarity. The size and shape of the other atoms are determined by their final anisotropic thermal parameters.

TABLE VI

INTERATOMIC DISTANCES (A)

Atoms	Distance	Atoms	Distance
Mn–P_1	2.278 (5)	C_1–O_1	1.15 (2)
Mn–P_2	2.279 (5)	C_2–O_2	1.15 (2)
Mn–N	1.73 (1)	N–O_3	1.18 (1)
Mn–C_1	1.78 (2)	P_1–C_1	2.80 (2)
Mn–C_2	1.75 (2)	P_1–C_2	2.86 (2)
Mn–O_1	2.94 (1)	P_1–N	2.96 (1)
Mn–O_2	2.90 (1)	P_2–C_1	2.78 (2)
Mn–O_3	2.91 (1)	P_2–C_2	2.88 (2)
P_1–R_1C_1[a]	1.83 (1)	P_2–N	2.96 (1)
P_1–R_2C_1	1.85 (1)	P_1–P_2	4.540 (6)
P_1–R_3C_1	1.83 (1)	C_1–N	3.02 (2)
P_2–R_4C_1	1.83 (1)	C_2–N	3.03 (2)
P_2–R_5C_1	1.83 (1)	C_1–C_2	3.06 (2)
P_2–R_6C_1	1.84 (1)	O_1–O_2	5.08 (2)
		O_1–O_3	5.03 (2)
		O_2–O_3	5.03 (2)

[a] R_iC_1 means C_1 on group R_i.

TABLE VII

BOND ANGLES (DEG)

Atoms	Angle	Atoms	Angle
P_1–Mn–P_2	170.2 (2)	P_1–Mn–C_1	86.2 (5)
C_1–Mn–C_2	120.0 (7)	P_1–Mn–C_2	89.4 (5)
C_1–Mn–N	118.7 (7)	P_1–Mn–N	94.5 (4)
C_2–Mn–N	121.3 (7)	P_2–Mn–C_1	85.5 (5)
Mn–C_1–O_1	178.2 (18)	P_2–Mn–C_2	90.1 (5)
Mn–C_2–O_2	177.4 (17)	P_2–Mn–N	94.1 (4)
Mn–N–O_3	178.0 (13)		
R_1C_1–P_1–R_2C_1	104.3 (6)	R_4C_1–P_2–R_5C_1	102.1 (5)
R_1C_1–P_1–R_3C_1	100.8 (8)	R_4C_1–P_2–R_6C_1	102.7 (6)
R_2C_1–P_1–R_3C_1	102.7 (5)	R_5C_1–P_2–R_6C_1	105.0 (6)

ordination symmetry about the Mn atom is nearly trigonal bipyramidal with *trans* triphenylphosphine groups. There is a very good plane passing through the Mn atom and the NO and CO groups. The equation of the weighted least-squares plane through these atoms is $3.44x - 9.12y - 18.01z - 13.14 = 0$, and the maximum deviation of any atom from this plane is 0.03 A for O_2. Although no symmetry is required of the molecule by the space group, the effective coordination symmetry is m, with the mirror plane passing through the Mn atom and the NO and CO groups, and perpendicular to a vector between the two P atoms. Even if the phenyl rings are included, the symmetry is still very nearly m because the rings on the two P atoms are essentially in an eclipsed conformation. The phenyl rings are staggered with respect to the NO and CO groups. However, the effective coordination symmetry is not mm2, the highest symmetry possible for an MXY_2Z_2 complex. The two triphenylphosphine groups are bent away from the NO group but preferentially toward C_1, so that the P–Mn–P angle is 170.2°. This distortion preserves the equatorial mirror plane but destroys the twofold axis along the Mn–N bond. Thus, the average P–Mn–C_1 angle is 85.8°, the average P–Mn–C_2 angle is 89.8° and the average P–Mn–N angle is 94.3°, all ±0.5°.

The average Mn–P bond distance of 2.278 A compares well with 2.28 A found in $Mn_2H(CO)_8(P(C_6H_5)_2)$.[23]

The average Mn–C distance of 1.77 A is slightly shorter than the average Mn–C distances of 1.823 and 1.836 A in the six-coordinate compounds $Mn_2(CO)_{10}$[24] and $HMn(CO)_5$,[25] but similar to the average Fe–C distance of 1.79 A in $Fe(CO)_5$.[3] An Mn–N distance of 1.73 A is on the long end of the range observed for first-row transition metals. Values from 1.57 to 1.73 A have been reported[26] for Fe–NO bonds. The N–O distances of coordinated NO range from 1.10 to 1.26 A.[26] The N–O distance of 1.18 A reported here compares favorably with the average N–O distance of 1.19 A found for the six chemically similar NO groups in Roussin's black salt.[26] The C–O distances of 1.15 A are similar to values typically found for carbonyl derivatives of transition metals. Triphenylphosphine distances and angles are similar to those observed in a large number of complexes.

It is interesting to note that there is little difference between the final Mn–N and Mn–C distances. The Mn–N distance of 1.73 A is 0.04 A (2σ) shorter than the average Mn–C distance of 1.77 A. Only two other structures have been done[27] of compounds containing both NO and CO as ligands, namely, $Fe(CO)_2(NO)_2$ and $Co(NO)(CO)_3$. Both of these electron diffraction results indicated an M–N distance 0.07 A (3σ) shorter than the M–C distance. These differences between M–N and M–C distances are similar to the difference in the double- (or triple-) bond radii of N and C of ~0.05 A given by Pauling.[28] Of course, these bond distance arguments should be interpreted with caution because of the uncertainty in the assignment of the NO group and the possibility of molecular disorder. One definite conclusion that can be made independent of the assignment of the NO group is that the Mn–N–O group is linear in this compound. Such appears to be the rule in most transition metal–nitrosyl complexes.

The molecular packing of the complex is primarily controlled by the bulky triphenylphosphine groups, and van der Waals contacts between H atoms are the shortest intermolecular distances. The volume per triphenylphosphine group is 423 A^3. This compares with 418 A^3 in $Os(CO)_3(P(C_6H_5)_3)_2$, which has a similar structure,[29] 404 A^3 in square-pyramidal $ReNCl_2(P(C_6H_5)_3)_2$,[30] and 364 A^3 in triphenylphosphine itself.[31] The distortion of the P–Mn–P angle to 170° may be due to packing considerations. A similar distortion has also been observed[32] in the six-coordinate compound $((C_6H_5)_3P)Mn(CO)_4(Sn(C_6H_5)_3)$, where the P–Mn–Sn angle is 176° and has been attributed to packing considerations. Interligand repulsions may also be partially responsible for the observed P–Mn–P angle. The P–N and P–C nonbonded interactions (Table VI) are at least 0.4 A less than the sum of the van der Waals radii of the atoms.[28] However, interligand repulsions alone would be expected to produce a symmetric distortion (preserving mm2 symmetry) with the triphenylphosphines probably distorting toward the smaller nitrogen atom.

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(23) R. J. Doedens, W. T. Robinson, and J. A. Ibers, *J. Am. Chem. Soc.*, in press.

(24) L. F. Dahl and R. E. Rundle, *Acta Cryst.*, **16**, 419 (1963).

(25) S. J. La Placa, W. C. Hamilton, and J. A. Ibers, *Inorg. Chem.*, **3**, 1491 (1964).

(26) G. Johansson and W. N. Lipscomb, *Acta Cryst.*, **11**, 594 (1958).

(27) L. O. Brockway and J. S. Anderson, *Trans. Faraday Soc.*, **33**, 1233 (1937).

(28) L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 228, 260.

(29) J. Pieper and J. A. Ibers, to be published.

(30) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967).

(31) J. J. Daly, *J. Chem. Soc.*, 3799 (1964).

(32) R. F. Bryan, *ibid.*, 172 (1967).