

- (41) C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, **9**, 2218 (1970).
 (42) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).
 (43) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N.Y., 1968, p 16.
 (44) S. Foner, *Rev. Sci. Instrum.*, **30**, 548 (1959).
 (45) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).
 (46) B. Jezowska-Trzebiatowska and W. Wojciechowski, *Transition Metal Chem.*, **6**, 1 (1970).
 (47) H. Ikeda, I. Kimura, and N. Uryu, *J. Chem. Phys.*, **48**, 4800 (1968).
 (48) J. S. Griffith, *Struct. Bonding (Berlin)*, **10**, 87 (1972).
 (49) J. T. Veal, D. Y. Jeter, J. C. Hempel, R. P. Eckberg, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **12**, 2928 (1973).

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The Phenyldiazo Group as a Bridging Ligand. Crystal Structure and Molecular Configuration of Bis(tetracarbonylphenyldiazomanganese), [PhN=N₂Mn(CO)₄]₂, Including the Location and Refinement of the Hydrogen Atoms

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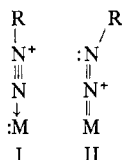
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Bis(tetracarbonylphenyldiazomanganese), [PhN=N₂Mn(CO)₄]₂, crystallizes in the centrosymmetric triclinic space group *P* $\bar{1}$ [*C*₁^h; No. 2] with *a* = 7.236 (1) Å, *b* = 8.889 (2) Å, *c* = 9.468 (2) Å, α = 80.52 (2)°, β = 77.38 (1)°, γ = 71.44 (1)°, and *V* = 560.4 Å³. The observed density is 1.59 (2) g cm⁻³, while ρ (calcd) = 1.613 g cm⁻³ for mol wt 544.2 and *Z* = 1. Single-crystal X-ray diffraction data complete to $2\theta = 50^\circ$ (Mo *K* α radiation) were collected with a Picker FACS-1 diffractometer and the structure was solved using conventional Patterson, Fourier, and least-squares refinement techniques. All atoms, including hydrogens, were located, the final discrepancy indices being *R*_F = 3.43% and *R*_{WF} = 3.61% for the 1974 independent reflections (none rejected). The [PhN=N₂Mn(CO)₄]₂ molecule lies on a crystallographic center of symmetry. The two manganese atoms are separated by 3.235 (1) Å and are bridged by two μ -phenyldiazo ligands. The bridges are not, however, symmetrical; thus Mn-N(1) = 2.031 (2) Å vs. Mn'-N(1) = 2.023 (2) Å and Mn-N(1)-N(2) = 134.5 (1)° as opposed to Mn'-N(1)-N(2) = 119.5 (1)°.

Introduction

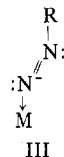
Transition metal complexes having aryldiazo (R-N=N-, R = aryl) ligands in terminal positions have been known for some time.¹⁻⁶ The study of such complexes has been given considerable impetus as a result of (i) the suggestion that these systems may be used as models for the enzymatic reduction of dinitrogen² and (ii) the fact that the aryldiazo system is isoelectronic with nitric oxide in its bonding to transition metal atoms.

As with nitric oxide, the aryldiazo ligand may coordinate to a transition metal in either a linear or a bent manner; within the framework of the valence-bond approach, the aryldiazo ligand can be regarded as behaving as RN₂⁺ (when the M-N-N system is linear) and as RN₂⁻ (when the M-N-N system is bent, with an angle of *ca.* 120°). Each of these cases has, in fact, been observed. Thus, the complexes (PPhMe₂)₃Re(N=NPh)Cl₂,⁷ (HB(pz)₃)Mo(CO)₂(N=NPh),⁸ and (PPh₃)₂Ru(N=N(*p*-tol))Cl₃⁹ each have rather short metal-nitrogen bond lengths (Re-N = 1.80 (1) Å,⁷ Mo-N = 1.825 (4) Å,⁸ and Ru-N = 1.796 (9) Å⁹) and have essentially linear M-N-N structural units (Re-N-N = 172°,⁷ Mo-N-N = 174.21 (12)°,⁸ and Ru-N-N = 171.2 (9)°⁹). Such a stereochemical arrangement is consistent with the aryldiazo ligand being considered as RN₂⁺ and may be represented by forms I and II. Form II would seem to be preferred, for the N-N-R angles are 118° in (PPhMe₂)₃Re(N=NPh)Cl₂,⁷ 121.09 (21)° in (HB(pz)₃)Mo(CO)₂(N=NPh),⁸ and 135.9 (11)° in (PPh₃)₂Ru(N=N(*p*-tol))Cl₃.⁹ [pz = pyrazolyl.]



In contrast to this, a structural study of the [(PhP(CH₂)₃PPH₂)₂Rh(N=NPh)Cl]⁺ ion¹⁰ has revealed "doubly bent" coordination of a phenyldiazo ligand to rhodium

(Rh-N-N = 125 (1)° and N-N-Ph = 119 (1)°) along with a normal rhodium-nitrogen distance of 1.954 (8) Å. This geometric pattern is consistent with the aryldiazo ligand behaving formally as RN₂⁻; the valence-bond description of the aryldiazometal moiety in this system is shown as III.



Recently, Abel and coworkers¹¹ have shown that (trimethylsilyl)phenyldiimine (Me₃SiN=NPh) reacts with bromopentacarbonylmanganese, with loss of Me₃SiBr and CO, yielding [PhN=N₂Mn(CO)₄]₂, a unique complex with bridging phenyldiazo groups. In order to obtain detailed stereochemical information on this newly discovered mode of bonding for an aryldiazo ligand, we have subjected this complex to a full three-dimensional single-crystal X-ray structural analysis. A preliminary account of this work has appeared previously;¹² a full description is reported below.

Collection of the X-Ray Diffraction Data

Transparent yellow crystalline plates of [PhN=N₂Mn(CO)₄]₂ were provided by Professor E. W. Abel of the University of Exeter, Exeter, England. The crystal used during the structural analysis was a thin platelike parallelepiped with six faces, dimensions being (001)→(00 $\bar{1}$) = 0.072 mm, (010)→(0 $\bar{1}$ 0) = 0.550 mm, and (110)→($\bar{1}$ $\bar{1}$ 0) = 0.724 mm. The crystal was mounted along [211]. Preliminary photographs of the reciprocal lattice showed no systematic absences and revealed no symmetry other than *C*_i (1) Friedel symmetry. The crystal was therefore assumed to belong to the triclinic system, possible space groups being the noncentrosymmetric *P*1 [*C*₁^h; No. 1] and the centrosymmetric *P* $\bar{1}$ [*C*₁^h; No. 2].¹³

The crystal was transferred to a Picker FACS-1 diffractometer, was accurately centered, and was aligned precisely along [211]. The intensity of the axial 422 reflection was measured by a θ - 2θ scan at $\chi = 90^\circ$ and at 10° intervals from $\phi = 0^\circ$ to $\phi = 350^\circ$. The observed variation in intensity [(maximum - minimum)/(average) = 18.3%] indicated that an absorption correction would be necessary.

Details of the data collection are given in Table I; a description

Table I. Experimental Data for the X-Ray Diffraction Study of $[\text{PhN}=\text{NMn}(\text{CO})_4]_2$

(A) Crystal Parameters at 23.5° ^{a,b}	
$a = 7.2358$ (13) Å	$\cos \alpha = 0.1647$ (3); $\alpha = 80.52$ (2)°
$b = 8.8893$ (17) Å	$\cos \beta = 0.2185$ (2); $\beta = 77.38$ (1)°
$c = 9.4677$ (18) Å	$\cos \gamma = 0.3183$ (2); $\gamma = 71.44$ (1)° $V = 560.4$ Å ³
Space group $P\bar{1}$	$\rho(\text{calcd}) = 1.613$ g cm ⁻³
$Z = 1$ (dimer)	$\rho(\text{obsd})^c = 1.59$ (2) g cm ⁻³
Mol wt 544.2	

(B) Measurement of Intensity Data

Radiation: Mo $K\alpha$
 Filter(s): Nb foil at counter aperture (~47% transmission of Mo $K\alpha$)
 Attenuators: used if $I > 8500$ counts/sec
 Takeoff angle: 3.0°
 Detector aperture: 4 mm × 4 mm
 Crystal-detector distance: 330 mm
 Crystal orientation: mounted along [211]
 Reflections measured: $+h, \pm k, \pm l$
 Maximum 2θ : 50°
 Scan type: coupled θ (crystal)- 2θ (counter)
 Scan speed: 1.0°/min
 Scan length: $\Delta(2\theta) = (1.2 + 0.692 \tan \theta)^\circ$, starting 0.6° below the Mo $K\alpha_1$ peak
 Background measurement: Stationary crystal, stationary counter; 20 sec each at beginning and end of 2θ scan
 Standard reflections: three remeasured after every 48 reflections; rms deviations (after application of an isotropic linear decay correction) were 1.25% for 21 $\bar{1}$, 1.17% for 213, and 0.59% for 030.
 Reflections collected: 1974 independent measurements, plus 150 $0k\bar{l}$ reflections which were averaged with the $0k\bar{l}$ reflections following correction for absorption

(C) Treatment of Intensity Data

Conversion to $|F_o|$ and $\sigma(|F_o|)$: as in ref 14, using an "ignorance factor" of $p = 0.04^d$
 Absorption coefficient: $\mu = 12.5$ cm⁻¹; maximum and minimum transmission factors were 0.965 and 0.706^e

^a Unit cell parameters are from a least-squares fit to the setting angles of the resolved Mo $K\alpha_1$ peaks (λ 0.70930 Å^b) of 12 reflections with $2\theta = 36$ – 56° . Maximum and root-mean-square deviations were 0.040° and 0.020°, respectively. ^b J. A. Bearden, *Rev. Mod. Phys.*, **39**, 78 (1967). ^c By neutral buoyancy in aqueous BaI₂.

^d Data reduction was performed using the program RDUS, by B. G. DeBoer. ^e Absorption correction was done *via* the program DRAB, by B. G. DeBoer.

of the apparatus and experimental technique is also available.¹⁴

Solution and Refinement of the Structure

All computations were performed on an IBM 370/158 computer at the Computer Center of the University of Illinois at Chicago Circle. Programs used include FORDAP (Fourier synthesis, by A. Zalkin), LSHF (structure factor calculations and least-squares refinement, by B. G. DeBoer), STAN1 (distances and angles with esd's, by B. G. DeBoer), PLOD (least-squares planes, by B. G. DeBoer), and ORTEP (thermal ellipsoid drawings, by C. K. Johnson).

Scattering factors for neutral manganese, oxygen, nitrogen and carbon were taken from the tables of Cromer and Waber;¹⁵ both the real and imaginary components of anomalous dispersion were included specifically in the calculation of structure factors, using the values of Cromer and Liberman.¹⁶ For hydrogen, the scattering curve of Stewart, *et al.*,¹⁷ was used.

Discrepancy indices used below are defined as

$$R_F = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \times 100 (\%)$$

$$R_{wF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right]^{1/2} \times 100 (\%)$$

The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w(F(hkl)) = [\sigma(F(hkl))]^{-2}$.

The analysis was begun using data which had not been corrected

Table II. Positional and Isotropic Thermal Parameters for $[\text{PhN}=\text{NMn}(\text{CO})_4]_2$ ^{a,b}

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
Mn	0.892934 (48)	0.690302 (31)	-0.013943 (31)	3.727
O(1)	0.60494 (30)	0.95360 (18)	0.14900 (18)	6.39
O(2)	0.56178 (31)	0.63640 (23)	-0.12183 (21)	6.60
O(3)	1.20489 (33)	0.76129 (24)	0.10174 (25)	7.51
O(4)	0.94142 (33)	0.93070 (20)	-0.26622 (20)	7.20
N(1)	0.91634 (25)	0.48878 (17)	0.12649 (17)	3.78
N(2)	0.85139 (30)	0.46024 (19)	0.25650 (19)	4.65
C(1)	0.71258 (38)	0.84648 (25)	0.09382 (24)	4.68
C(2)	0.68649 (38)	0.65514 (24)	-0.07968 (24)	4.45
C(3)	1.09160 (40)	0.72948 (25)	0.05710 (26)	4.87
C(4)	0.92112 (38)	0.83902 (25)	-0.17009 (25)	4.97
C(5)	0.72034 (35)	0.58886 (22)	0.33846 (21)	4.17
C(6)	0.79672 (52)	0.65909 (31)	0.42037 (30)	5.72
C(7)	0.66646 (70)	0.77083 (34)	0.51161 (31)	7.07
C(8)	0.46813 (63)	0.80791 (32)	0.51983 (32)	6.86
C(9)	0.39385 (49)	0.73706 (31)	0.43842 (33)	6.23
C(10)	0.51900 (40)	0.62596 (26)	0.34660 (27)	5.13
H(6)	0.9247 (43)	0.6349 (30)	0.4101 (27)	5.1 (6)
H(7)	0.7221 (57)	0.8254 (41)	0.5574 (37)	10.0 (11)
H(8)	0.3727 (48)	0.8817 (37)	0.5874 (33)	7.9 (8)
H(9)	0.2487 (53)	0.7664 (37)	0.4437 (32)	8.2 (8)
H(10)	0.4608 (42)	0.5698 (31)	0.2889 (29)	6.4 (6)

^a Esd's, shown in parentheses, are right-adjusted to the least significant digit of the preceding number. ^b For nonhydrogen atoms the "equivalent isotropic thermal parameters" are given; for their anisotropic thermal parameters, see Table III.

for absorption. The structure was solved by the "heavy-atom" method, the positions of the manganese atoms being located from a three-dimensional Patterson synthesis; the appearance of the Patterson map also suggested strongly that the true space group was the centrosymmetric $P\bar{1}$. (This was confirmed by the subsequent satisfactory solution and refinement of the structure in this space group.) A Fourier synthesis led quickly and unambiguously to the location of all nonhydrogen atoms. Full-matrix least-squares refinement of positional and isotropic thermal parameters of all nonhydrogen atoms, along with the scale factor (69 parameters), led to convergence in three cycles with $R_F = 14.35\%$ and $R_{wF} = 17.26\%$. The inclusion of anisotropic thermal parameters and the refinement of these and the positional parameters for the nonhydrogen atoms (a total of 154 parameters) led to a reduction in the discrepancy indices to $R_F = 5.11\%$ and $R_{wF} = 6.45\%$. A difference-Fourier synthesis now led to the unambiguous location of the five hydrogen atoms of the phenyl group; peak heights ranged from 0.50 to 0.40 e Å⁻³ and these peaks were the five strongest features on the map.

Refinement was continued now using the absorption-corrected data^{18,19} and allowing also the refinement of positional and isotropic thermal parameters of the hydrogen atoms. Three cycles of full-matrix refinement (174 parameters in all) led to final convergence with $R_F = 3.43\%$ and $R_{wF} = 3.61\%$. Maximum shifts during the last cycle of refinement were $\Delta/\sigma = 0.044$ for a positional parameter of a nonhydrogen atom, $\Delta/\sigma = 0.040$ for an anisotropic thermal parameter, $\Delta/\sigma = 0.074$ for a positional parameter of a hydrogen atom, and $\Delta/\sigma = 0.060$ for an (isotropic) thermal parameter of a hydrogen atom.

The final "goodness of fit" defined by $[\sum w(|F_o| - |F_c|)^2 / (m - n)]^{1/2}$ was 1.425, where the number of reflections (m) was 1974 and the number of refined parameters (n) was 174 ($m/n = 11.35$). The function $[\sum w(|F_o| - |F_c|)^2]$ was not markedly dependent either upon $|F_o|$ or upon $(\sin \theta)/\lambda$; the weighting scheme is therefore statistically valid.

The correctness of the refined structure was verified independently by means of a final difference-Fourier synthesis; the highest features were two peaks of height 0.31 e Å⁻³ at (0.105, 0.275, 0.125) and (0.770, 0.525, 0.300).

A listing of observed and calculated structure factor amplitudes may be obtained.²⁰ Final positional parameters are collected in Table II. Anisotropic thermal parameters are shown in Table III, while rms amplitudes of vibration of atoms about the principal axes of their vibration ellipsoids are given in Table IV.

Discussion of the Molecular Structure

Interatomic distances and their estimated standard deviations (esd's) are shown in Table V. Interatomic angles and their

Table III. Anisotropic Thermal Parameters for $[\text{PhN}=\text{NMn}(\text{CO})_4]_2$ ^{a,b}

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn	4.497 (17)	2.504 (13)	3.682 (15)	-0.354 (10)	-0.700 (11)	-0.311 (9)
O(1)	7.94 (11)	3.61 (7)	5.63 (8)	0.64 (7)	-0.13 (8)	-1.05 (6)
O(2)	6.31 (10)	6.86 (10)	7.11 (10)	-1.72 (8)	-2.39 (8)	-0.77 (8)
O(3)	7.05 (12)	6.94 (11)	9.68 (13)	-2.19 (9)	-2.54 (10)	-2.37 (9)
O(4)	9.93 (14)	4.00 (7)	6.06 (9)	-1.25 (8)	-0.42 (9)	1.07 (7)
N(1)	4.26 (8)	2.89 (6)	3.85 (8)	-0.56 (6)	-0.74 (6)	-0.33 (5)
N(2)	5.64 (10)	3.28 (7)	3.98 (8)	-0.31 (7)	-0.25 (7)	-0.23 (6)
C(1)	5.77 (12)	3.32 (9)	4.30 (10)	-0.61 (8)	-0.96 (9)	0.04 (7)
C(2)	5.02 (12)	3.50 (9)	4.10 (10)	-0.34 (8)	-0.73 (9)	-0.30 (7)
C(3)	5.45 (12)	3.40 (9)	5.44 (11)	-0.74 (9)	-0.84 (10)	-0.86 (8)
C(4)	6.01 (13)	3.14 (8)	4.99 (11)	-0.37 (8)	-0.72 (10)	-0.57 (8)
C(5)	5.55 (12)	2.98 (8)	3.33 (8)	-0.59 (8)	-0.62 (8)	-0.05 (6)
C(6)	6.55 (16)	4.54 (11)	5.90 (13)	-0.93 (11)	-2.03 (12)	-0.20 (10)
C(7)	11.77 (27)	4.88 (13)	5.07 (13)	-2.00 (15)	-2.83 (16)	-1.00 (10)
C(8)	9.46 (22)	4.17 (12)	4.10 (13)	-0.65 (13)	0.85 (14)	-0.87 (10)
C(9)	6.07 (15)	4.19 (11)	6.75 (14)	-0.53 (11)	0.67 (12)	-0.27 (10)
C(10)	5.77 (13)	3.78 (10)	5.25 (12)	-0.72 (9)	-0.88 (10)	-0.30 (8)

^a See footnote a to Table II. ^b These anisotropic thermal parameters have units of Å^2 and are analogous to the normal isotropic thermal parameters, entering the expression for the structure factor in the form $\exp[-0.25(B_{11}a^*h^2 + B_{22}b^*k^2 + B_{33}c^*l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$.

Table IV. Root-Mean-Square Amplitudes of Vibration along the Principal Axes of the Atomic Vibration Ellipsoids (Values are in Å)

Atom	$(\bar{U}^2)^{1/2}$		
	Minor axis	Median axis	Major axis
Mn	0.176	0.216	0.253
O(1)	0.192	0.269	0.366
O(2)	0.254	0.291	0.317
O(3)	0.249	0.305	0.364
O(4)	0.205	0.292	0.384
N(1)	0.185	0.222	0.243
N(2)	0.194	0.222	0.297
C(1)	0.205	0.237	0.285
C(2)	0.201	0.228	0.275
C(3)	0.201	0.265	0.273
C(4)	0.191	0.253	0.295
C(5)	0.185	0.211	0.281
C(6)	0.226	0.268	0.306
C(7)	0.219	0.257	0.393
C(8)	0.220	0.250	0.388
C(9)	0.230	0.252	0.349
C(10)	0.217	0.257	0.286

Table V. Interatomic Distances (in Å) with Esd's for $[\text{PhN}=\text{NMn}(\text{CO})_4]_2$ ^{a-c}

Atoms	Dist	Atoms	Dist
(a) Distances Involving Manganese Atom(s)			
Mn···Mn'	3.2349 (8)		
Mn-N(1)	2.0313 (16)	Mn···N(2)	3.0264 (18)
Mn-N(1')	2.0228 (16)	Mn···N(2')	2.8402 (18)
Mn-C(1)	1.8447 (24)	Mn···O(1)	2.9800 (17)
Mn-C(2)	1.8665 (29)	Mn···O(2)	2.9960 (23)
Mn-C(3)	1.8597 (29)	Mn···O(3)	2.9846 (23)
Mn-C(4)	1.8360 (24)	Mn···O(4)	2.9706 (18)
(b) Distances within Carbonyl Groups			
C(1)-O(1)	1.1403 (26)	C(3)-O(3)	1.1265 (30)
C(2)-O(2)	1.1297 (30)	C(4)-O(4)	1.1348 (26)
(c) Distances within PhN=N-Ligand			
N(1)-N(2)	1.2332 (23)	C(7)-C(8)	1.3538 (50)
N(2)-C(5)	1.4454 (25)	C(8)-C(9)	1.3550 (47)
C(5)-C(6)	1.3649 (35)	C(9)-C(10)	1.3859 (34)
C(6)-C(7)	1.3971 (43)	C(10)-C(5)	1.3750 (35)
(d) Carbon-Hydrogen Distances			
C(6)-H(6)	0.868 (28)	C(9)-H(9)	0.990 (34)
C(7)-H(7)	0.925 (38)	C(10)-H(10)	1.024 (28)
C(8)-H(8)	0.986 (33)		

^a The $[\text{PhN}=\text{NMn}(\text{CO})_4]_2$ molecule lies on a center of symmetry at $(1, \frac{1}{2}, 0)$. Atoms in the basic asymmetric unit are labeled normally; those in the "other half" of the molecule are labeled with a prime and are related to the basic unit by the transformation $[x', y', z'] = [2-x, 1-y, -z]$. ^b Esd's were calculated from the full positional correlation matrix using the Fortran IV program STAN1 by B. G. DeBoer. Contributions from errors in the unit cell parameters were included. ^c Bond lengths are not corrected for any possible effects of thermal motion.

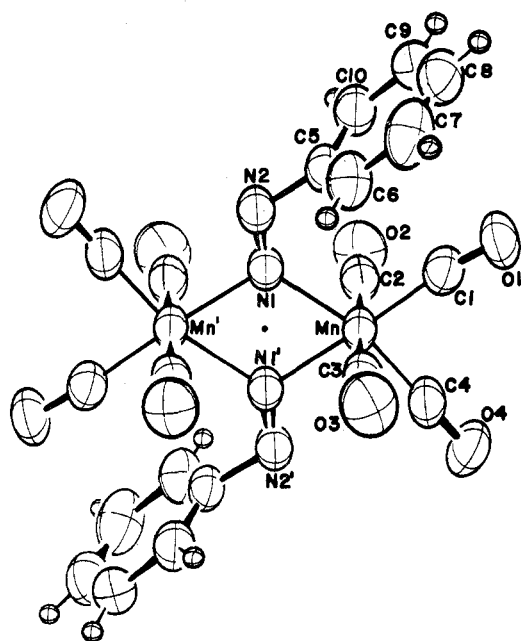
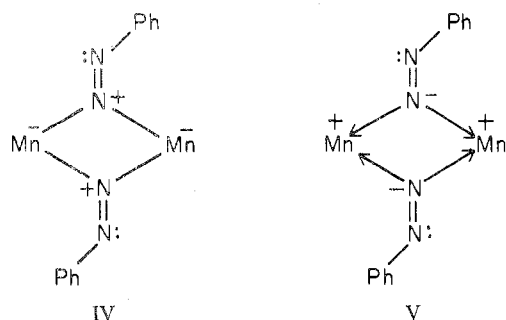


Figure 1. Stereochemistry of the $[\text{PhN}=\text{NMn}(\text{CO})_4]_2$ molecule (ORTEP diagram, 50% probability ellipsoids, with spheres for hydrogen atoms artificially reduced for the sake of clarity). The crystallographic inversion center is shown as a solid circle.

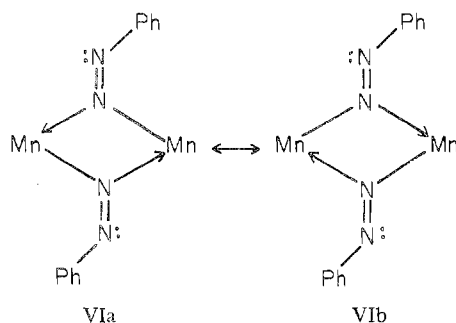
esd's are collected in Table VI. The overall stereochemistry of the $[\text{PhN}=\text{NMn}(\text{CO})_4]_2$ molecule, including the labeling of atoms and the relative orientation of the atomic vibration ellipsoids, is shown in Figure 1.

The $[\text{PhN}=\text{NMn}(\text{CO})_4]_2$ molecule lies on a crystallographic center of symmetry, the two chemically equivalent (and crystallographically related) $\text{Mn}(\text{CO})_4$ groups being linked together by two bridging phenyldiazo ligands.

A consideration of the geometric configuration of the $(\text{PhN}=\text{NMn})_2$ portion of the molecule, taken in conjunction with the valence-bond descriptions for the aryldiazo ligand (see Introduction), reveals that one cannot distinguish (on the basis either of ligand geometry or of electron counting) between the formalisms $\text{PhN}=\text{N}^+$ (see IV) and $\text{PhN}=\text{N}^-$ (see V) when the aryldiazo ligands are in bridging position, since in each case the terminal nitrogen of the aryldiazo ligand is in an

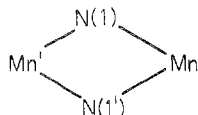


sp^2 -hybridized trigonal geometry. It is, in this case, probably better to regard the phenyldiazo system as a neutral three-electron donor,²¹ *i.e.*, VIa and b.



The manganese atoms may then be regarded as in an oxidation state of zero (d^7 outer electronic configuration) and attain the expected 18-electron "noble gas" configuration by the donation of two electrons from each carbonyl ligand and three electrons from each of the bridging phenyldiazo ligands.

Angles within the strictly planar central



portion of the molecule are $N(1)-Mn-N(1') = N(1')-Mn'-N(1) = 74.13(8)^\circ$ and $Mn-N(1)-Mn' = Mn'-N(1')-Mn = 105.87(8)^\circ$. The obtuse angles at the bridging atoms $N(1)$ and $N(1')$ along with the long $Mn \cdots Mn'$ distance of 3.2349 (8) Å [as opposed, for example, to the bonding $Mn-Mn$ distance of 2.923 Å in $Mn_2(CO)_{10}$ ²²] are consistent with there being no direct bonding interaction between the two manganese atoms. This result is entirely in accord with the predictions for $M(\mu-X)_2M$ systems outlined both by Teo, Hall, Fenske, and Dahl²³ and by Mason and Mingos.²⁴

The present complex is the first in which the presence of bridging aryldiazo ligands has been unambiguously established; we note, however, that Deane and Lalor²⁵ have recently reported the synthesis of some molybdenum and tungsten complexes $\{[(HB(pz)_3)Mo(N=NPh)X]_n (X = Cl, Br, I) \text{ and } [(HB(pz)_3)W(N=NPh)X_2]_2 (X = I), \text{ some (or all) of which may also contain bridging phenyldiazo ligands.}$

An unexpected feature of the present complex is the asymmetry of the phenyldiazo bridges.²⁶⁻²⁸ Thus, $Mn-N(1) = Mn'-N(1') = 2.0313(16)$ Å, while $Mn'-N(1) = Mn-N(1') = 2.0228(16)$ Å. The difference here is small (0.0085 Å) but corresponds to 3.7σ ²⁹ and is thus statistically significant. The asymmetry of the bridges is brought home much more clearly by consideration of the $Mn-N-N$ angles. Thus, $Mn-N(1)-N(2) = 134.51(13)^\circ$ as opposed to $Mn'-N(1)-N(2) = 119.47(13)^\circ$. [Similarly, $Mn'-N(1')-N(2') = 134.51(13)^\circ$ and $Mn-N(1')-N(2') = 119.47(13)^\circ$, by symmetry.] The difference, here, is 15.04 (18) $^\circ$ —corresponding to *ca.* 84σ !

The asymmetry of the phenyldiazo bridges probably results from repulsions between the phenyl group and the ligand

Table VI. Interatomic Angles (in deg) with Esd's for $[PhN=N Mn(CO)_4]_2$

Atoms	Angle	Atoms	Angle
(a) Cis Angles around Manganese			
N(1)-Mn-N(1')	74.13 (8)	N(1')-Mn-C(4)	91.67 (8)
N(1)-Mn-C(1)	103.44 (8)	C(1)-Mn-C(2)	90.00 (10)
N(1)-Mn-C(2)	90.42 (8)	C(1)-Mn-C(3)	87.91 (10)
N(1)-Mn-C(3)	89.49 (9)	C(1)-Mn-C(4)	90.80 (9)
N(1')-Mn-C(2)	88.53 (8)	C(2)-Mn-C(4)	90.86 (11)
N(1')-Mn-C(3)	93.54 (8)	C(3)-Mn-C(4)	89.77 (11)
(b) Trans Angles around Manganese			
N(1)-Mn-C(4)	165.71 (8)	C(2)-Mn-C(3)	177.83 (10)
N(1')-Mn-C(1)	177.15 (8)		
(c) Angles within Carbonyl Groups			
Mn-C(1)-O(1)	173.19 (19)	Mn-C(3)-O(3)	176.16 (21)
Mn-C(2)-O(2)	178.51 (22)	Mn-C(4)-O(4)	178.92 (29)
(d) Angles around Nitrogen Atoms			
Mn-N(1)-Mn'	105.87 (8)	N(1)-N(2)-C(5)	119.62 (16)
Mn-N(1)-N(2)	134.51 (13)		
Mn'-N(1)-N(2)	119.47 (13)		
(e) Angles within Phenyl Ring			
C(10)-C(5)-C(6)	120.71 (24)	C(7)-C(8)-C(9)	120.02 (29)
C(5)-C(6)-C(7)	118.74 (32)	C(8)-C(9)-C(10)	120.67 (32)
C(6)-C(7)-C(8)	120.76 (32)	C(9)-C(10)-C(5)	119.10 (28)
(f) External Angles of Phenyl Ring			
N(2)-C(5)-C(10)	119.62 (21)	H(8)-C(8)-C(7)	122.4 (19)
N(2)-C(5)-C(6)	119.22 (23)	H(8)-C(8)-C(9)	117.5 (19)
H(6)-C(6)-C(5)	118.0 (18)	H(9)-C(9)-C(8)	119.5 (18)
H(6)-C(6)-C(7)	123.2 (18)	H(9)-C(9)-C(10)	119.9 (19)
H(7)-C(7)-C(6)	117.0 (24)	H(10)-C(10)-C(9)	119.9 (16)
H(7)-C(7)-C(8)	122.0 (24)	H(10)-C(10)-C(5)	121.0 (16)

Table VII. Least-Squares Planes, and Deviations Therefrom, for $[PhN=N Mn(CO)_4]_2$ ^{a-c}

Atom	Dev, Å	Atom	Dev, Å
Plane I: $0.83120X + 0.46915Y + 0.29835Z = 8.8653$			
Mn*	0.000	N(2)	0.072
Mn'*	0.000	N(2')	-0.072
N(1)*	0.000	C(1)	-0.048
N(1')*	0.000	C(4)	0.053
		C(5)	0.117
Plane II: $0.09545X - 0.66547Y + 0.74030Z = -2.0932$			
C(5)*	-0.003	N(2)	0.156
C(6)*	0.003	H(6)	-0.027
C(7)*	-0.002	H(7)	-0.101
C(8)*	0.001	H(8)	0.049
C(9)*	-0.000	H(9)	-0.016
C(10)*	0.002	H(10)	0.041
N(1)	-0.843	C(1)	-2.976
Mn	-2.850	O(1)	-3.187

Dehedral Angle I-II = 90.69°

^a All calculations were performed using the Fortran IV program PLOD, by B. G. DeBoer. ^b Atoms identified by an asterisk were assigned unit weights; all others were given zero weight. ^c Equations to planes are given in cartesian coordinates, such that $X = xa \sin \gamma + [z(c \cos \beta - \cos \alpha \cos \gamma) / \sin \gamma]$, $Y = yb + xa \cos \gamma + zc \cos \alpha$, and $Z = zc[(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma) / \sin^2 \gamma]^{1/2}$. This corresponds to defining the mutually orthogonal directions as $(b \times c^*)$, b , and c^* .

C(1)-O(1). Thus, there are some close intramolecular contacts [$C(5) \cdots C(1) = 2.9732(28)$ Å and $C(5) \cdots O(1) = 3.3827(25)$ Å], atoms C(1) and O(1) lie only 2.976 and 3.187 Å below the least-squares plane of the phenyl group (see Table VII), and the angle $N(1)-Mn-C(1)$ has a value of $103.44(8)^\circ$, which is 11.77° (or 107σ !) greater than the value of $91.67(8)^\circ$ found for $N(1')-Mn-C(4)$.

The $N(1)-N(2)$ distance of 1.2332 (23) Å is consistent with its formulation as $N=N$. For the sake of comparison we note that the following $N=N$ distances have been reported: 1.24 (5) Å in $CH_3N=NCH_3$,³⁰ 1.23 Å in *cis*- $PhN=NPh$,³¹ 1.172 (3) and 1.243 (3) Å (two independent molecules in the

asymmetric unit) in crystalline *trans*-PhN=NPh,³² 1.25 (4) Å in FN=NF,³³ and 1.26 (3) Å in [CIN=C(NH₂)N=N]N[C(NH₂)=NCl].³⁴ The unweighted average N=N distance from these five studies is 1.24 Å. Within complexes containing terminal aryldiazo ligands, the observed N=N distances are 1.23 (1) Å in (PPhMe₂)₃Re(N=NPh)Cl₂,⁷ 1.211 (6) Å in (HB(pz)₃)Mo(CO)₂(N=NPh),⁸ 1.144 (10) Å in (PPh₃)₂Ru(N=NC₆H₄Me)Cl₃,⁹ and 1.17 (2) Å in [(PhP((CH₂)₃PPh₂)₂)Rh(N=NPh)Cl]⁺.¹⁰ In the protonated diazo species [(PPh₃)₂Ir(NH=NC₆H₃F)(CO)Cl]⁺, the N=N distance is 1.28 (4) Å.³⁵

In side-bonded azobenzene (and related) complexes, the nitrogen–nitrogen bond length is increased dramatically from the normal N=N distance of ~1.24 Å. Thus, the N–N distance in the mononuclear species (Me₃CCN)₂Ni(PhN=NPh) is 1.385 (5) Å.³⁶ A similar lengthening also occurs in binuclear species, individual N–N distances being 1.366 (8) Å in (MeN=NMe)Fe₂(CO)₆,³⁷ 1.399 (8) Å in (C₁₂H₈N₂)Fe₂(CO)₆,³⁸ and 1.404 (9) Å in (C₅H₈N₂)Fe₂(CO)₆.³⁹

The N(2)–C(5) bond in [PhN=NmMn(CO)₄]₂ is 1.4454 (25) Å in length, in good agreement with the N(sp²)–C(sp²) single-bond distance of 1.432 (7) Å in (HB(pz)₃)Mo(CO)₂(N=NPh)⁸ and close to the accepted C(aromatic)–N single-bond distance of 1.43 ± 0.01 Å;⁴⁰ similarly the angle N(1)–N(2)–C(5) has a value of 119.62 (16)°—very close to the ideal sp² angle of 120° and comparable to the N=N–Ph angle of 121.09 (21)° in (HB(pz)₃)Mo(CO)₂(N=NPh).⁸

Carbon atoms of the phenyl ring have a root-mean-square deviation of only 0.002 Å from their least-squares plane (see plane II of Table VII). Hydrogen atoms are coplanar with the carbocyclic ring within the limits of experimental error, the maximum deviation being –0.101 Å ($\sigma \approx 0.038$ Å) for H(7). Atom N(2) lies +0.156 Å from the plane of the phenyl ring, while N(1) is displaced by –0.843 Å (the opposite sign indicating displacement in an opposite sense). The dihedral angle between the phenyl group and the Mn(μ -N)₂Mn core of the molecule is 90.69°.

Each manganese atom is in a slightly distorted octahedral coordination environment. Thus, the cis angles between ligands [with the exception of N(1)–Mn–C(1) = 103.44 (8)° (which has been discussed above) and N(1)–Mn–N(1') = 74.13 (8)° (which may be regarded as decreased from a normal value of 90° due to Mn···Mn repulsions)] are in the range 87.91 (10)–93.54 (8)°. Angles between mutually trans ligands are N(1)–Mn–C(4) = 165.71 (8)°, N(1')–Mn–C(1) = 177.15 (8)°, and C(2)–Mn–C(3) = 177.83 (10)°.

Manganese–carbonyl distances for carbonyl ligands which are trans to the phenyldiazo ligands [*i.e.*, Mn–C(1) = 1.8447 (24) Å and Mn–C(4) = 1.8360 (24) Å] are slightly, but significantly, shorter than those which are trans to other carbonyl groups [Mn–C(2) = 1.8665 (29) Å and Mn–C(3) = 1.8597 (29) Å]. Such a result is expected and simply reflects the greater π -acceptor characteristics of the carbonyl *vis a vis* the bridging phenyldiazo ligand.

The carbonyl ligands are all close to being collinear with the manganese atom. The greatest distortion is defined by the angle Mn–C(1)–O(1) = 173.19 (19)° [other values ranging from 176.16 (21) to 178.92 (29)°], which presumably results from steric repulsions between C(1)–O(1) and the phenyl group (*vide supra*). Individual carbon–oxygen distances range from 1.1265 (30) to 1.1403 (26) Å. It is interesting to note that the longer C–O bond lengths [C(1)–O(1) = 1.1403 (26) Å and C(4)–O(4) = 1.1346 (26) Å] are associated with the ligands trans to the phenyldiazo ligands, while the shorter C–O distances [C(2)–O(2) = 1.1297 (30) Å and C(3)–O(3) = 1.1265 (30) Å] are associated with carbonyl ligands which are mutually trans. This result, again, is in accord with chemical

expectation but is on the borderline of statistical significance. [The average C–O (trans to N=NPh) distance is 1.1375 ± 0.0040 Å⁴¹ while the average C–O (trans to CO) distance is 1.1281 ± 0.0023 Å;⁴¹ the difference of 0.0094 ± 0.0046 Å²⁹ represents only 2.0 σ .]

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Registry No. [PhN=NmMn(CO)₄]₂, 53140-01-5.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W. Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.50 for microfiche, referring to code number AIC40634T.

References and Notes

- R. B. King and M. B. Bisnette, *J. Amer. Chem. Soc.*, **86**, 5694 (1964).
- G. W. Parshall, *J. Amer. Chem. Soc.*, **87**, 2133 (1965).
- R. B. King and M. B. Bisnette, *Inorg. Chem.*, **5**, 300 (1966).
- M. L. H. Green, J. R. Sanders, and R. N. Whiteley, *Z. Naturforsch. B*, **23**, 106 (1968).
- A. N. Nesmeyanov, U. A. Chapovsky, N. A. Ustyynyuk, and L. G. Makarova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 449 (1968).
- W. E. Carroll and F. J. Lalor, *J. Organometal Chem.*, **54**, C37 (1973).
- V. F. Duckworth, P. G. Douglas, R. Mason, and B. L. Shaw, *Chem. Commun.*, 1083 (1970).
- G. Avitabile, P. Ganis, and M. Nemiroff, *Acta Crystallogr., Sect. B*, **27**, 725 (1971).
- J. V. McArdle, A. J. Schultz, B. J. Corden, and R. Eisenberg, *Inorg. Chem.*, **12**, 1676 (1973).
- A. P. Gaughan, B. L. Haymore, J. A. Ibers, W. H. Myers, T. E. Nappier, and D. W. Meek, *J. Amer. Chem. Soc.*, **95**, 6859 (1973).
- E. W. Abel, C. A. Burton, and R. Rowley, Abstracts of Papers, 6th International Conference on Organometallic Chemistry, University of Massachusetts, Aug 13–17, 1973, paper 141.
- E. W. Abel, C. A. Burton, M. R. Churchill, and K.-K. G. Lin, *J. Chem. Soc., Chem. Commun.*, 269 (1974).
- "International Tables for X-Ray Crystallography," Vol. I, 2nd ed, Kynoch Press, Birmingham, England, 1965, pp 74–75.
- M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **12**, 525 (1973).
- D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
- D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
- R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965); see Table II on p 3178.
- The absorption correction was performed using the Fortran IV program DRAB, by B. G. DeBoer.
- The correctness of the absorption correction was confirmed by processing data from the axial 422 reflection (see text). Following correction for absorption, the ϕ dependence of the intensity of this reflection was reduced from 18.3% to *ca.* 1.5%.
- Supplementary material.
- A well-known chemistry textbook recommends that the linear nitric oxide ligand be considered as a neutral three-electron donor. In discussing the formalism NO⁺ it says: "Its only virtue seems to be that in... certain...cases it leads to an intuitively satisfactory oxidation number for the metal. However, there are many cases where it leads to intuitively unsatisfactory oxidation numbers ..." [See F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience, New York, N.Y., 1972, pp 712–719.] Such a comment may well be equally applicable to aryldiazo complexes. We note also that the linear vs. bent nitrosyl problem has been tackled by the molecular orbital approach: (a) C. G. Pierpont and R. Eisenberg, *J. Amer. Chem. Soc.*, **93**, 4905 (1971); (b) D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **10**, 1035 (1971); (c) D. M. P. Mingos, *ibid.*, **12**, 1209 (1973); (d) J. H. Enemark and R. D. Feltham, *J. Amer. Chem. Soc.*, **96**, 5002 (1974); (e) J. H. Enemark and R. D. Feltham, *ibid.*, **96**, 5004 (1974); (f) R. Hoffmann, M. M. L. Chen, M. Elian, A. R. Rossi, and D. M. P. Mingos, submitted for publication. (We thank Professor Hoffmann for providing a preprint of this article.)
- L. F. Dahl and R. E. Rundle, *Acta Crystallogr.*, **16**, 419 (1963).
- B. K. Teo, M. B. Hall, R. F. Fenske, and L. F. Dahl, *J. Organometal. Chem.*, **70**, 413 (1974).
- R. Mason and D. M. P. Mingos, *J. Organometal. Chem.*, **50**, 53 (1973).
- M. E. Deane and F. J. Lalor, *J. Organometal. Chem.*, **67**, C19 (1974).

- (26) We note here that binuclear species are known both with symmetrical μ -NO ligands (e.g., ref 27) and with highly unsymmetrical μ -NO ligands (e.g., ref 28).
- (27) $(\pi\text{-C}_5\text{H}_5)(\text{NO})\text{Cr}(\mu\text{-NO})(\mu\text{-NH}_2)\text{Cr}(\text{NO})(\pi\text{-C}_5\text{H}_5)$: L. Y. Y. Chan and F. W. B. Einstein, *Acta Crystallogr., Sect. B*, **26**, 1899 (1970).
- (28) $(\pi\text{-C}_5\text{H}_5)(\text{NO}_2)\text{Mn}(\mu\text{-NO})_2\text{Mn}(\text{NO})(\pi\text{-C}_5\text{H}_5)$: J. L. Calderon, F. A. Cotton, B. G. DeBoer, and N. Martinez, *Chem. Commun.*, 1476 (1971).
- (29) Using $\sigma(\text{difference}) = (\sigma_1^2 + \sigma_2^2)^{1/2}$.
- (30) H. Boersch, *Sitzungsber. Akad. Wiss. Wien*, **144**, 1 (1935) [through *Chem. Soc., Spec. Publ.*, No. 11, R7 (1958)]; H. Boersch, *Monatsh. Chem.*, **65**, 311 (1935).
- (31) G. C. Hampson and J. M. Robertson, *J. Chem. Soc.*, 409 (1941).
- (32) C. J. Brown, *Acta Crystallogr.*, **21**, 146 (1966).
- (33) S. H. Bauer, *J. Amer. Chem. Soc.*, **69**, 3104 (1947).
- (34) J. H. Bryden, *Acta Crystallogr.*, **11**, 158 (1958).
- (35) F. W. B. Einstein, A. B. Gilchrist, G. W. Rayner-Canham, and D. Sutton, *J. Amer. Chem. Soc.*, **94**, 645 (1972).
- (36) R. S. Dickson and J. A. Ibers, *J. Amer. Chem. Soc.*, **94**, 2988 (1972); R. S. Dickson, J. A. Ibers, S. Otsuka, and Y. Tatsuno, *ibid.*, **93**, 4636 (1971).
- (37) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **8**, 2709 (1969).
- (38) R. J. Doedens, *Inorg. Chem.*, **9**, 429 (1970).
- (39) R. G. Little and R. J. Doedens, *Inorg. Chem.*, **11**, 1392 (1972).
- (40) *Chem. Soc., Spec. Publ.*, No. 18, S19S (1965).
- (41) The end of the mean of two values is calculated by $\sigma(\text{av}) = (\text{difference})/2^{1/2}$.

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Crystal and Molecular Structure of Tricarbonyl[(methylsulfidomethyl)phenyl-2-C,S]triphenylphosphinemanganese, an Ortho-Metalated Complex of a Sulfur Donor Ligand

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An ortho-metalated structure has been demonstrated for tricarbonyl[(methylsulfidomethyl)phenyl-2-C,S]triphenylphosphinemanganese by a crystal structure analysis. This material crystallizes in space group $P\bar{1}$ of the triclinic system with $a = 11.022$ (7) Å, $b = 13.485$ (9) Å, $c = 9.123$ (6) Å, $\alpha = 94.52$ (1)°, $\beta = 109.90$ (1)°, and $\gamma = 98.14$ (1)°. Calculated ($Z = 2$) and observed densities are 1.43 and 1.42 (1) g/cm³, respectively. The structure analysis was based upon 3385 nonzero intensity data, collected by counter methods and refined by full-matrix least-squares techniques to a final conventional discrepancy factor of 0.057. The complex has a distorted octahedral configuration about Mn, with the organosulfur ligand bound in a chelating fashion via Mn-C and Mn-S bonds. The five-membered chelate ring is nonplanar, with the sulfur atom 0.46 Å out of the plane defined by the Mn and three carbon atoms. The triphenylphosphine ligand occupies an axial position and the methyl group lies on the side of the equatorial plane opposite the phosphine ligand. The structural features of this complex are compared with those of closely related compounds derived from nitrogen donor ligands.

Introduction

Intramolecular ortho-metalation reactions continue to be a subject of much interest among organometallic chemists.¹ This type of reaction was first reported in 1965² and has subsequently been observed in a large number of systems.³ By far the majority of these have involved metal complexes of nitrogen or phosphorus donor ligands. However in recent years ortho-metalation reactions have also been reported for systems involving other donor atoms including As,⁶⁻⁸ Sb,⁶ S,^{5,8-11} and O.¹² In the case of sulfur donor ligands, ortho-metalated complexes have been obtained from aromatic thioketones,^{5,9} benzyl methyl sulfide,¹¹ and *O*-ethyl thiobenzoate.¹⁰ In certain cases, sulfur donor ligands have failed to yield metalated products when subjected to conditions under which metalation readily occurs with the analogous nitrogen donor.^{13,14} The complex $\text{C}_6\text{H}_4\text{CH}_2\text{SCH}_3\text{Mn}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ was obtained by triphenylphosphine substitution of $\text{C}_6\text{H}_4\text{CH}_2\text{SCH}_3\text{Mn}(\text{CO})_4$, the latter compound being a noncrystallizable oil obtained from the reaction of benzyl methyl sulfide with $\text{CH}_3\text{Mn}(\text{CO})_5$. Our crystal structure analysis of the triphenylphosphine derivative was undertaken to document its proposed metalated structure and to compare its structural details with those of closely related complexes derived from the N donor ligands benzylideneaniline¹⁵ and *N,N*-dimethylbenzylamine.¹⁶ A preliminary report of the synthesis and structure of this complex has appeared.¹¹

Experimental Section

Collection and Reduction of Intensity Data. A sample of $\text{C}_6\text{H}_4\text{CH}_2\text{SCH}_3\text{Mn}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ was supplied by Dr. M. I. Bruce of the University of Bristol. Suitable single crystals could be obtained by recrystallization from diethyl ether. Precession photographs showed no evidence of monoclinic or higher symmetry; the assignment of the

crystals to the triclinic crystal system was confirmed by a Delaunay reduction. Statistical analysis of normalized structure factors¹⁷ strongly suggested the centrosymmetric space group $P\bar{1}$ and successful solution and refinement of the structure were achieved on the basis of this group. Lattice parameters were determined from least-squares refinement of the setting angles of 16 reflections which had been accurately centered on a Picker four-circle X-ray diffractometer. The three shortest noncoplanar lattice translations define a cell (23°, $\lambda(\text{Mo K}\alpha)$ 0.70930 Å) with $a = 11.022$ (7) Å, $b = 13.485$ (9) Å, $c = 9.123$ (6) Å, $\alpha = 94.52$ (1)°, $\beta = 109.90$ (1)°, and $\gamma = 98.14$ (1)°. All results reported are referred to this cell, though a different, arbitrarily chosen, cell was employed during data collection. Calculated ($Z = 2$) and observed (floatation in aqueous ZnBr_2) densities are 1.43 and 1.42 (1) g/cm³, respectively.

Intensity data were collected from a yellow tabular crystal of dimensions 0.43 × 0.30 × 0.17 mm mounted in a thin-walled glass capillary. The shortest dimension of the crystal was perpendicular to the well-developed {110} faces; other bonding planes belonged to the {010}, {101}, {130}, and {212} forms. The average full width at half-maximum of peak profiles obtained by narrow-source open-counter ω scans for this crystal was ~0.10°. The general procedures employed in data collection paralleled those previously described.¹⁶ The takeoff angle was 2.1° and the diffracted beam was filtered through 3.0-mil Nb foil. A 4 × 4 mm counter aperture was positioned 28 cm from the crystal. The pulse height analyzer was set to admit ~95% of the Mo K α peak. A scan range of -0.55° to +0.65° in 2θ from the calculated scattering angle was used for reflections with $2\theta \leq 30^\circ$. This scan range was increased by 0.10° for reflections with $30^\circ < 2\theta < 42.5^\circ$ and by an additional 0.10° for higher angle reflections. A scan rate of 1°/min in 2θ was employed and stationary-background counts of 20 sec were taken at each end of the scan. Four standard reflections were measured at intervals of 100 reflections throughout data collection; the intensities of these reflections showed an average variation of $\pm 1.4\%$, substantially less than their estimated standard deviations. Owing to instrumental problems, several weeks elapsed between collection of data with 2θ