Figure 4[42] and the torsional angles in Table VII indicate puckering of the carbon portion of the chelate ring relative to cyclohexane, where the tilt angle is 49.6°, and the torsional angles are 54.6°. This puckering is in response to the long Co–N bond and the small ring angle at cobalt of 90°. The terminal angle C(5)–C(6)–C(7) is 116.5°, considerably larger than in cyclohexane.

The molecular packing is illustrated in Figure 3 and some nonbonding distances are given in Table VIII. There are two N–H···Br hydrogen bonds, of lengths 3.37 and 3.40 Å, linking the bromide ion to the same cation. The resulting ion pair is linked by an N–H···O hydrogen bond to a screw-related ion pair, the distance N(1)···O(21) being 3.04 Å

(42) J. B. Lambert, R. E. Carhart, and P. W. R. Corfield, *J. Amer. Chem. Soc.*, 91, 3567 (1969).

and the angle at the hydrogen atom being 145°. The distance between C(2) and O(11) of the molecule related by a translation along b is quite short at 3.03 Å, but there is no evidence for C–H···O hydrogen bonding, the distances H(3)···O(11) and H(4)···O(11) being 2.42 and 2.78 Å, respectively. The shortest contact within the cation is between H(10) and H(17), at 2.15 Å.

Registry No. Δ-β-*cis*-Dinitro(5-methyl-1,4,8,11-tetraazaundecane)cobalt(III) bromide, 39561-37-0.

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Crystal and Molecular Structure of a Stable π-Oxopropenylmanganese Tricarbonyl Complex

G. B. ROBERTSON and P. O. WHIMP*

The crystal and molecular structure of a stable π-oxopropenyl complex 2-(1′,2′-dimethyloxopropenyl)phenyldiphenylphosphinomanganese tricarbonyl, $[\pi\text{-}\{O\cdots C(CH_3)\cdots C(CH_3)\}C_6H_4P(C_6H_5)_2Mn(CO)_3]$, has been determined from three-dimensional X-ray data collected by counter methods. Crystals are triclinic, space group $P\bar{1}$ (C_i^1, No. 2), with a = 9.303 (5), b = 11.689 (6), c = 10.654 (6) Å, α = 81.90 (2), β = 96.64 (2), γ = 83.71 (2)°, Z = 2. The measured and calculated densities are 1.38 (1) and 1.38 g cm^{-3}, respectively. The structure was solved by conventional heavy-atom techniques and was refined by block-diagonal least-squares methods to weighted and unweighted R factors of 0.053 and 0.038, respectively, for the 2953 independent reflections with $I/\Delta(I) \geqslant 3.0$. The coordination at the manganese atom is essentially a distorted octahedron, with three carbonyl ligands occupying mutually cis sites. The remaining sites are occupied by the phosphorus atom and the delocalized pseudo-π-allylic oxopropenyl substituent of the 2-(1′,2′-dimethyloxopropenyl)phenyldiphenylphosphine ligand. The π-oxopropenyl group is asymmetrically coordinated to the manganese atom, the Mn–C distances being 2.219 (3) and 2.126 (3) Å. The Mn–O distance is 2.058 (2) Å. Within the π-oxopropenyl moiety, the C–C and C–O distances [1.427 (5) and 1.295 (4) Å, respectively] are intermediate between their respective single- and double-bond distances, confirming the formulation as a delocalized π-bonded system.

Introduction

Methylmanganese pentacarbonyl, $[CH_3Mn(CO)_5]$, reacts with a variety of ligands to give acyl derivatives of general formula $[(CH_3CO)Mn(CO)_4(\text{ligand})]$.[1-10] These acyl complexes are thought to result from migration of the methyl group from the manganese atom to a coordinated carbonyl ligand.

(1) F. Calderazzo and F. A. Cotton, *Chim. Ind. (Milan)*, 46, 1165 (1964).

(2) R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 86, 3994 (1964).

(3) R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 86, 5043 (1964).

(4) C. S. Kraihanzel and P. K. Marples, *J. Amer. Chem. Soc.*, 87, 5267 (1965).

(5) F. Calderazzo and K. Noak, *J. Organometal. Chem.*, 4, 250 (1965).

(6) F. Calderazzo and K. Noak, *Coord. Chem. Rev.*, 1, 118 (1966).

(7) F. Calderazzo, K. Noak, and U. Schaerer, *J. Organometal. Chem.*, 6, 265 (1966).

(8) K. Noak, M. Ruch, and F. Calderazzo, *Inorg. Chem.*, 7, 345 (1968).

(9) C. S. Kraihanzel and P. K. Marples, *Inorg. Chem.*, 7, 1806 (1968).

(10) C. S. Kraihanzel and P. K. Marples, *J. Organometal. Chem.*, 20, 269 (1969).

The reaction of $[CH_3Mn(CO)_5]$ with the potentially bidentate ligand 2-vinylphenyldiphenylphosphine $[o\text{-}CH_2=CHC_6H_4P(C_6H_5)_2, \mathbf{1} \text{ (sp)}]$ gives two yellow isomeric, air-stable crystalline complexes, **2** and **3**, of empirical formula $C_{25}H_{20}MnO_4P$.[11] Crystal structure analyses together with

1

2

3
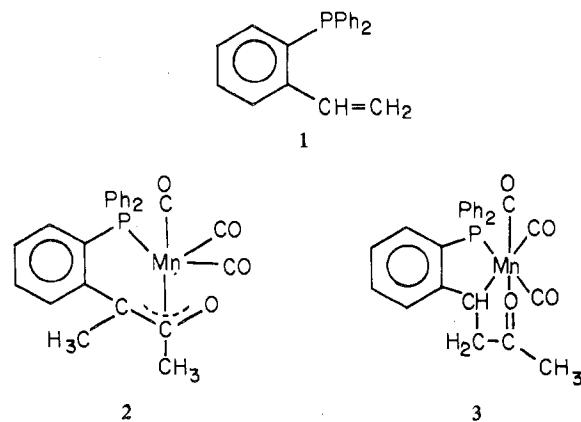
(11) M. A. Bennett and R. Watt, *Chem. Commun.*, 95 (1971).

infrared and ^{1}H nmr data indicate that **2** is a pseudo-π-allylic (three-electron) π-oxopropenyl complex, while **3** is a σ-bonded oxobutyl derivative.[12] Formation of both complexes can be readily understood in terms of attack, presumably *via* a manganese-acyl intermediate, on the vinyl substituent of the coordinated 2-vinylphenyldiphenylphosphine ligand. Thus, formation of **2** results from attack at the 1' carbon atom of the sp group (accompanied by hydride migration), while **3** results from attack at the 2' carbon atom. Similar alternate modes of addition have been observed in the isomerization of HMn(CO)$_4$(sp) to [{o-(CH$_3$)CHC$_6$H$_4$}P(C$_6$H$_5$)$_2$Mn(CO)$_4$] and [(o-CH$_2$CH$_2$C$_6$H$_4$)P(C$_6$H$_5$)$_2$Mn(CO)$_4$] *via* hydride attack at the 1' and 2' carbon atoms, respectively.[13]

It has been suggested that the reduction of α,β-unsaturated aldehydes and ketones by HCo(CO)$_4$ proceeds *via* an unstable cobalt-π-oxopropenyl intermediate. While no such complex has, hitherto, been isolated,[11,14] we now describe, in detail, the three-dimensional single-crystal X-ray structural analysis of the π-oxopropenyl complex [2-(1',2'-dimethyloxopropenyl)phenyldiphenylphosphinomanganese tricarbonyl], **2**. Preliminary accounts of this work have appeared previously.[11,12]

Experimental Section

Crystal Data. Crystals of 2-(1',2'-dimethyloxopropenyl)phenyldiphenylphosphinomanganese tricarbonyl, **2**, of suitable size and quality for X-ray structural analysis were supplied by Dr. M. A. Bennett and Dr. R. Watt of this school. *Anal.* Calcd for C$_{25}$H$_{20}$MnO$_4$P: C, 63.84; H, 4.29; P, 6.58. Found: C, 63.4; H, 4.5; P, 6.4.[15]

Preliminary Weissenberg (Cu Kα radiation; 0kl and 1kl data) and precession (Mo Kα radiation; h0l, h1l, hk0, and hk1 data) photographs showed neither systematic absences nor diffraction symmetry higher than C_i ($\bar{1}$). The crystals were, therefore, assumed to be triclinic. The possible space groups are $P1$ and $P\bar{1}$, but the latter was considered more likely.[16,17] The successful solution and subsequent refinement of the structure confirms the choice of the centrosymmetric space group $P\bar{1}$ (C_i^1, No. 2).

The crystal, of dimension 0.037 × 0.016 × 0.019 cm (elongated in the a direction), was transferred to a computer-controlled Picker FACS-I fully automatic four-circle diffractometer and aligned so that the arbitrarily assigned crystallographic a axis and the instrumental Φ axis were approximately coincidental. The unit cell dimensions and the crystal orientation matrix were obtained from the least-squares refinement[18] of the 2θ, ω, χ, and Φ values obtained from 12 carefully centered high-angle reflections using graphite crystal monochromated Cu Kα_1 radiation (λ 1.5405 A; takeoff angle 3.0°; temperature 20 ± 1°). The unit cell parameters are $a = 9.303 \pm 0.005$, $b = 11.689 \pm 0.006$, $c = 10.654 \pm 0.006$ A; $\alpha = 81.90 \pm 0.02$, $\beta = 96.64 \pm 0.02$, $\gamma = 83.71 \pm 0.02°$; cell volume 1129.9 A^3. The "reduced cell," obtained from a Delaunay reduction,[19] is $a' = 15.965$, $b' = 11.689$, $c' = 9.303$ A; $\alpha' = 96.29$, $\beta' = 115.18$, $\gamma' = 125.06°$; cell volume 1129.3 A^3. The observed density ($\rho_{obsd} = 1.38 \pm 0.01$ g cm^{-3}; by flotation in aqueous KI solution) is in excellent agreement with the value calculated for a molecular weight of 470.34 and $Z = 2$ ($\rho_{calcd} = 1.38$ g cm^{-3}). With $Z = 2$, no crystallographic symmetry constraints are placed on the molecule. The structure was solved and refined in terms of the nonreduced cell, and the subsequent atomic positional parameters refer to this cell.

(12) M. A. Bennett, G. B. Robertson, R. Watt, and P. O. Whimp, *Chem. Commun.*, 752 (1971).

(13) M. A. Bennett and R. Watt, *Chem. Commun.*, 94 (1971).

(14) R. W. Goetz and M. Orchin, *J. Amer. Chem. Soc.*, 85, 2782 (1963).

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(16) W. Nowacki, T. Matsumoto, and A. Edenharter, *Acta Crystallogr.*, 22, 935 (1967).

(17) J. D. H. Donnay, G. Donnay, E. G. Cox, O. Kennard, and M. V. King, "Crystal Data, Determinative Tables," Monograph No. 5, 2nd ed., American Crystallographic Association, Washington, D. C., 1963.

(18) The Busing and Levy programs for four-circle diffractometers [*Acta Crystallogr.*, 22, 457 (1967)] were used for all phases of diffractometer control and data collection.

(19) B. Delaunay, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, 84, 109 (1933).

Data Collection. Graphite crystal monochromated Cu Kα radiation was used to collect 4119 reflections (including "standards"; *vide infra*) of the type hkl, $\bar{h}kl$, $hk\bar{l}$, and $\bar{h}k\bar{l}$ within the range 3° ⩽ 2θ ⩽ 125°. The θ-2θ scan technique was used, with a 2θ scan speed of 1°/min, and an asymmetric scan range from (2θ − 1.1)° to (2θ + 1.1 + Δ)° [Δ is the 2θ separation (in degrees) of the Cu Kα_1 and Kα_2 peaks at the 2θ value of the reflection concerned]. The takeoff angle was 3.0°. The pulse height analyzer was set to admit 95% of the Cu Kα peak, and the counter was 30 cm from the crystal. Backgrounds were measured for 20 sec on either "side" of each reflection, at the scan range limits, and were assumed to be linear between these two points. The intensities of three reflections, in diverse areas of reciprocal space, were monitored after each 40 reflections had been measured. None showed any significant variation during data collection.

Data were reduced to values of $|F_o|$ using the program SETUP. The Lorentz-polarization factor is given by LP = $(\cos^2 2\theta + \cos^2 2\theta_m)/$ [$\sin 2\theta(1 + \cos^2 2\theta_m)$] where θ and θ_m (=13.25°) are the Bragg angles for the reflection and the monochromator, respectively. The corrected intensities were assigned individual standard deviations

$$\sigma(F_o) = [(LP)^2 \Delta I^2 + (\rho|F_o|^2)^2]^{1/2}/2F_o$$

where $\Delta I = [CT + (t_p/t_b)^2(B1 + B2)]^{1/2}$, LP is the Lorentz-polarization factor, CT is the integrated reflection intensity, B1 and B2 are the individual background counts, and ρ (=0.001$^{1/2}$) is an arbitrarily assigned factor to account for instrumental "unknowns."[20,21] Reflections for which the individual background measurements differed significantly [*i.e.*, if $|B1 - B2|/(B1 + B2)^{1/2}$ ⩾ 4.0] were discarded. The data were sorted to the order required for efficient operation of subsequent programs, using the program SORTIE. At the same time, equivalent reflection forms were averaged, and those reflections for which $I/\Delta I < 3.0$ {where $I = [CT - (t_p/t_b)(B1 + B2)]$} were discarded as being unobserved. A total of 2965 unique reflections were used for the initial solution and refinement of the structure. The statistical R factor, defined as $\Sigma\sigma_s(F_o)/\Sigma|F_o|$, is 0.018 [$\sigma_s(F_o) = (LP)\Delta I^2/2|F_o|$].

Solution and Refinement of the Structure. Atom coordinates, other than for hydrogen, were obtained *via* conventional Patterson and Fourier syntheses. Preliminary full-matrix least-squares refinement of overall scale factor, individual isotropic temperature factors for all atoms, rigid-body parameters for the phenyl rings [C(201)–C(206)] and [C(301)–C(306)] (see Figure 1), and individual atomic positional parameters for the remaining nonhydrogen atoms converged in three cycles with R_1 [=Σ ||F_o| − |F_c||/Σ |F_o|] = 0.090 and R_2 {=[Σw(|F_o| − |F_c|)^2/Σw|F_o|^2]$^{1/2}$}= 0.100 [using equal (unit) weights]. Atomic scattering factors, with those for Mn and P corrected for the real and imaginary parts of anomalous scattering,[22,23] were taken from ref 24.

At this point, the data were corrected for absorption effects (μ = 58.72 cm^{-1}), using a grid size of 10 × 4 × 6 points, parallel to a, b, and c, respectively. Transmission factors varied from 0.300 to 0.471. The data were sorted, and equivalent forms were again averaged (as above). Refinement was continued, with 2953 unique reflections, using block-diagonal least-squares methods. Three cycles of refinement, in which the scale factor, individual atomic coordinates, and individual isotropic temperature factors were varied, converged with $R_1 = 0.085$ and $R_2 = 0.097$ (unit weights). Anisotropic thermal parameters of the form exp[−($\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl$] were introduced for all atoms. With this model and individual reflection weights [$w = 1/\sigma^2(F_o)$], parameter convergence was achieved with $R_1 = 0.048$ and $R_2 = 0.070$. A subsequent difference Fourier synthesis showed maxima attributable to the phenyl hydrogen atoms but accurate map coordinates could not be obtained. In consequence, calculated phenyl hydrogen atom coordinates (assuming C–H = 1.10 A) were included, as fixed contributions to F_c, in all subsequent cycles of least-squares refinement. These coordinates, together with fixed isotropic temperature factors ($B_H = B_C + 1.0$ A^2 assumed), were recalculated after each cycle of least-squares refinement. No attempt was made to include the six methyl hydrogen atoms in the scattering model. Four further cycles of least-

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

(22) C. T. Prewitt, Ph.D. Thesis, Massachusetts Institute of Technology, 1962, p 163.

(23) D. T. Cromer, *Acta Crystallogr.*, 18, 17 (1965).

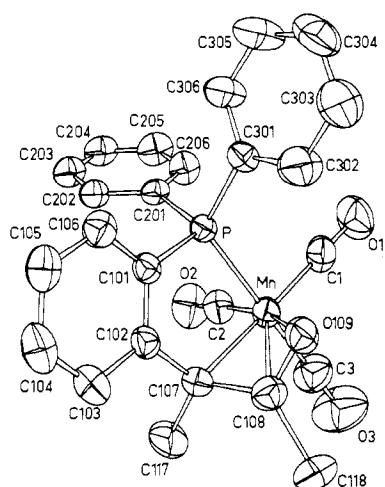(24) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 202.

Figure 1. One molecule of [{π-O$\overline{\cdots}$C(CH$_3$)$\overline{\cdots}$C(CH$_3$)}C$_6$H$_4$P-(C$_6$H$_5$)$_2$Mn(CO)$_3$] showing the overall stereochemistry and the atom numbering scheme.

squares refinement converged with $R_1 = 0.038$ and $R_2 = 0.053$. On the final cycle, no individual parameter shift was greater than 0.2 of the estimated parameter standard deviation (*vide infra*).

A final difference Fourier map showed six very diffuse peaks (of maximum density *ca.* 0.6–0.8 e/Å^3) attributable to the six methyl hydrogen atoms omitted from the scattering model. No other positive maxima of density greater than 0.3 e/Å^3 were observed. An examination of $|F_o|$ and $|F_c|$ showed no evidence of serious extinction effects, and, consequently, no correction was applied. Likewise, a weighting scheme analysis revealed no serious dependence of $w[|F_o| - |F_c|]^2$ on either $|F_o|$ or $(\sin\theta)/\lambda$. The standard deviation of an observation of unit weight, defined as $\{\Sigma w[|F_o| - |F_c|]^2/(m-n)\}^{1/2}$ [where m is the number of observations and n (=280) is the number of parameters varied], is 2.24; *cf.* 1.00 for ideal weighting, indicating that a larger value of ρ, the instrumental "uncertainty factor," should have been chosen.

The final atomic positional and thermal parameters, together with their estimated standard deviations, obtained by inversion of the block-diagonal matrices, are listed in Table I. A list of observed and calculated structure factors ($\times 10$) is available.[25]

Computer Programs. The data reduction programs SETUP and SORTIE were written by Dr. B. M. Foxman, who also modified the Fourier program MUFR-3, which was originally written by J. D. White, University of Melbourne. Least-squares refinement was performed using SFLS-5 originally by Prewitt[22] but modified for rigid-body refinement by Bennett and Foxman.[26] The block-diagonal modification, by Foxman, uses either 4 × 4 or 3 × 3 and 6 × 6 matrices but does not include the rigid-body option. The absorption correction program ACACA[27] was modified by Foxman to suit the geometry of the Picker diffractometer. Molecular geometries were calculated using MGEOM by J. S. Wood, while PUBTAB, by R. C. Elder, was used to produce the table of structure factor amplitudes. Figures 1 and 2 were produced by ORTEP.[28] Calculations were carried out on the CDC3600 computer of the CSIRO Division of Computing Research, Canberra, and the IBM 360/50 computer of the Australian National University Computer Centre.

Results

Description of the Structure. The crystal structure, as defined by the cell parameters, symmetry operations, and atom coordinates of Table I, consists of discrete monomeric units possessing neither crystallographic nor virtual symmetry

higher than C_1. The stereochemical arrangement of one such unit, along with the atom numbering scheme, is shown in Figure 1, while Figure 2 presents a stereoscopic view of the molecule. The thermal ellipsoids are drawn to enclose 50% of the probability distribution and for clarity, the phenyl hydrogen atoms have been omitted. The coordination at the manganese atom approximates to a distorted octahedron, with three carbonyl groups occupying mutually cis sites. The three remaining sites are occupied by the phosphorus atom and the delocalized π-oxopropenyl moiety. Principal intramolecular distances and interbond angles, together with their estimated standard deviations, are listed in Table II. For convenience, certain bond lengths and bond angles relating to the "chelate" ring [Mn-P-C(101)-C(102)-π-oxopropenyl] are presented schematically in Figure 3. The results of least-squares calculations, defining some important planes through the molecule, are collected in Table III.[29]

Discussion. Bond length and bond angle data given in Figure 3 and Table II, together with the disposition of the oxopropenyl moiety relative to the remaining ligands (*vide infra*), confirm its formulation as a pseudo-π-allylic three-electron donor system. Moreover, comparison of the metal–ligand distances [Mn-C(107), 2.219 (3); Mn-O(109), 2.058 (2) Å] with the appropriate covalent radii sums [Mn-C, 2.21; Mn-O, 2.10 Å; Mn(I) covalent radius = 1.44 Å assumed][30] shows the manganese–π-oxopropenyl bonding to be essentially "symmetric," in the sense commonly applied to metal-π-allyl systems.[31] There are, however, small deviations from the totally symmetric situation. In particular, Mn-C(107) is 0.01 Å greater than the covalent radii sum, while Mn-O(109) is some 0.04 Å less than the corresponding Mn-O covalent radii sum. The difference [0.01 + 0.04 Å] is statistically significant ($\Delta/\sigma \approx 14$) but is, nevertheless, very much smaller than that of *ca.* 0.14 Å characteristic of "asymmetric" metal-π-allyl bonding.[31] Likewise, both C(107)–C(108) [1.427 (5) Å] and C(108)–O(109) [1.295(4) Å] show nearly equivalent contractions [0.11 and 0.13 Å, respectively] *vis a vis* the accepted single-bond distances [C–C = 1.541 (3) Å;[32a] C–O = 1.43 (1) Å[32b]]. Though not statistically significant, the sense of this difference [0.11–0.13 Å] corresponds with that expected in the free ligand but is contrary to that which might be expected in an equivalent simple asymmetric metal–allyl system. Clearly, the π-allyl–π-oxopropenyl comparison has some limitations, albeit relatively minor. Thus, the dihedral angle between the weighted π-oxopropenyl plane [C(107), C(108), O(109)] and the weighted manganese coordination plane [Mn, C(1), C(2)] is 118.7°. This agrees well with previous observations in the metal-π-allyl systems, *e.g.*, 111.5° for [(π-C$_3$H$_5$)PdCl]$_2$,[33] 114.5° for [(π-C$_3$H$_5$)Pd-(PPh$_3$)SnCl$_3$],[34] and an average value of 125° for [(π-1,3-dimethylallyl)PdCl]$_2$.[35] The methyl substituents C(117) and C(118) are each displaced from the plane of the π-oxopropenyl skeleton. C(117), the π-oxopropenyl substituent which approximates to the terminal methyl groups in 1,3-dimethylallyl complexes, is (+)0.28 Å out of plane and directed toward the metal atom. In contrast, C(102) is displaced ($-$)1.03 Å from this plane, while C(118) is aplanar by only

(25) A listing of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-1740.

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(29) The method for calculating weighted least-squares planes is outlined in ref 24, Vol. II, p 93.

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(31) E. M. McPartlin and R. Mason, *Chem. Commun.*, 16 (1967).

(32) *Chem. Soc., Spec. Publ.*, **No. 11** (1958): (a) p S12; (b) p S17.

(33) A. E. Smith, *Acta Crystallogr.*, **18**, 331 (1965).

(34) R. Mason and P. O. Whimp, *J. Chem. Soc. A*, 2709 (1969).

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Table I. Fractional Atomic Positional and Thermal Parameters for [{π-O.⁻⁻.C(CH₃).⁻⁻.C(CH₃)}C₆H₄P(C₆H₅)₂Mn(CO)₃]ᵃ

(a) Refined Positional and Anisotropic Thermal Parameters

Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mn	0.18539(5)	0.31549(4)	0.33424(5)	0.00870(7)	0.00639(4)	0.00646(5)	-0.00111(4)	0.00044(4)	-0.00111(4)
P	0.13346(8)	0.16902(7)	0.21961(7)	0.00614(9)	0.00506(6)	0.00638(7)	-0.00064(6)	0.00032(7)	-0.00025(5)
C(1)	0.1627(4)	0.2204(3)	0.4760(3)	0.0105(5)	0.0110(4)	0.0069(4)	-0.0025(4)	0.0005(3)	-0.0009(3)
O(1)	0.1496(4)	0.1590(3)	0.5668(3)	0.0218(6)	0.0182(4)	0.0086(3)	-0.0066(4)	0.0016(3)	0.0025(3)
C(2)	0.0017(4)	0.3829(3)	0.2934(3)	0.0132(6)	0.0077(3)	0.0091(4)	0.0006(3)	0.0013(4)	-0.0021(3)
O(2)	-0.1162(3)	0.4297(3)	0.2635(3)	0.0139(5)	0.0135(3)	0.0167(4)	0.0055(3)	0.0002(3)	-0.0034(3)
C(3)	0.2142(5)	0.4301(4)	0.4268(4)	0.0181(7)	0.0117(4)	0.0105(4)	-0.0049(4)	0.0031(4)	-0.0045(4)
O(3)	0.2211(4)	0.5050(3)	0.4872(3)	0.0357(9)	0.0173(5)	0.0194(5)	-0.0104(5)	0.0086(5)	-0.0127(4)
C(101)	0.2104(3)	0.2039(3)	0.0742(3)	0.0068(4)	0.0056(3)	0.0062(3)	-0.0007(2)	0.0003(3)	-0.0001(2)
C(102)	0.2511(3)	0.3151(3)	0.0532(3)	0.0080(4)	0.0061(3)	0.0062(3)	-0.0007(3)	0.0001(3)	0.0001(2)
C(103)	0.3005(4)	0.3513(3)	-0.0633(3)	0.0152(6)	0.0079(3)	0.0078(4)	-0.0024(4)	0.0019(4)	0.0009(3)
C(104)	0.3120(5)	0.2758(4)	-0.1518(3)	0.0201(7)	0.0119(4)	0.0065(4)	-0.0026(5)	0.0029(4)	-0.0003(3)
C(105)	0.2786(5)	0.1641(4)	-0.1281(3)	0.0170(7)	0.0104(4)	0.0073(4)	-0.0019(4)	0.0022(4)	-0.0023(3)
C(106)	0.2263(4)	0.1275(3)	-0.0148(3)	0.0113(5)	0.0071(3)	0.0080(4)	-0.0011(3)	0.0010(3)	-0.0016(3)
C(107)	0.2558(4)	0.3944(3)	0.1531(3)	0.0108(5)	0.0050(3)	0.0074(3)	-0.0020(3)	0.0003(3)	-0.0001(2)
C(117)	0.2063(5)	0.5237(3)	0.1009(4)	0.0215(8)	0.0044(3)	0.0121(5)	-0.0008(4)	0.0001(5)	0.0006(3)
C(108)	0.3733(4)	0.3648(3)	0.2553(3)	0.0095(5)	0.0076(3)	0.0084(4)	-0.0028(3)	0.0013(3)	-0.0015(3)
C(118)	0.4764(5)	0.4495(4)	0.2974(4)	0.0170(7)	0.0116(4)	0.0130(5)	-0.0091(5)	-0.0012(5)	-0.0019(4)
O(109)	0.3974(2)	0.2583(2)	0.3138(2)	0.0073(3)	0.0075(2)	0.0079(2)	-0.0009(2)	-0.0001(2)	0.0002(2)
C(201)	-0.0601(3)	0.1622(3)	0.1740(3)	0.0062(4)	0.0052(3)	0.0090(4)	-0.0008(2)	0.0003(3)	-0.0010(2)
C(202)	-0.1258(4)	0.1837(3)	0.0483(3)	0.0080(4)	0.0060(3)	0.0102(4)	-0.0005(3)	-0.0009(3)	-0.0005(3)
C(203)	-0.2772(4)	0.1842(3)	0.0204(4)	0.0089(5)	0.0082(3)	0.0136(5)	-0.0003(3)	-0.0030(4)	-0.0011(3)
C(204)	-0.3596(4)	0.1644(3)	0.1182(4)	0.0064(4)	0.0092(4)	0.0172(6)	-0.0010(3)	-0.0005(4)	-0.0019(4)
C(205)	-0.2950(4)	0.1436(4)	0.2444(4)	0.0082(5)	0.0114(4)	0.0158(6)	-0.0020(4)	0.0038(4)	-0.0026(4)
C(206)	-0.1455(4)	0.1427(3)	0.2720(4)	0.0078(5)	0.0102(4)	0.0108(4)	-0.0013(3)	0.0018(3)	-0.0013(3)
C(301)	0.2072(3)	0.0184(3)	0.2836(3)	0.0082(4)	0.0054(3)	0.0070(3)	-0.0004(3)	0.0010(3)	0.0001(2)
C(302)	0.3530(4)	-0.0054(3)	0.3374(4)	0.0099(5)	0.0071(4)	0.0182(6)	0.0005(3)	-0.0028(4)	-0.0003(4)
C(303)	0.4139(5)	-0.1191(4)	0.3872(5)	0.0143(7)	0.0094(4)	0.0194(7)	0.0026(4)	-0.0059(5)	-0.0004(4)
C(304)	0.3300(5)	-0.2082(3)	0.3854(4)	0.0219(8)	0.0069(4)	0.0131(5)	0.0030(4)	0.0013(5)	0.0014(3)
C(305)	0.1864(5)	-0.1859(3)	0.3318(4)	0.0183(8)	0.0060(3)	0.0191(7)	-0.0012(4)	0.0039(6)	0.0010(4)
C(306)	0.1257(4)	-0.0726(3)	0.2800(4)	0.0113(5)	0.0063(3)	0.0145(5)	-0.0012(4)	0.0015(4)	0.0003(3)

(b) Calculated Hydrogen Atom Coordinates and Isotropic Thermal Parameters

Atom	X	Y	Z	B, Å²	Atom	X	Y	Z	B, Å²
H(103)	0.330	0.440	-0.082	5.3	H(205)	-0.362	0.128	0.322	6.1
H(104)	0.352	0.305	-0.243	6.3	H(206)	-0.093	0.126	0.372	5.2
H(105)	0.289	0.105	-0.199	5.7	H(302)	0.420	0.067	0.340	6.3
H(106)	0.197	0.039	0.004	4.7	H(303)	0.529	-0.138	0.430	7.5
H(202)	-0.059	0.199	-0.029	4.5	H(304)	0.378	-0.298	0.426	6.9
H(203)	-0.330	0.201	-0.079	5.6	H(305)	0.120	-0.258	0.330	7.0
H(204)	-0.478	0.165	0.096	5.9	H(306)	0.010	-0.054	0.237	5.6

ᵃ Estimated standard deviations (in parentheses) in this and the following tables and also in the text refer to the last significant digit(s) in each case.
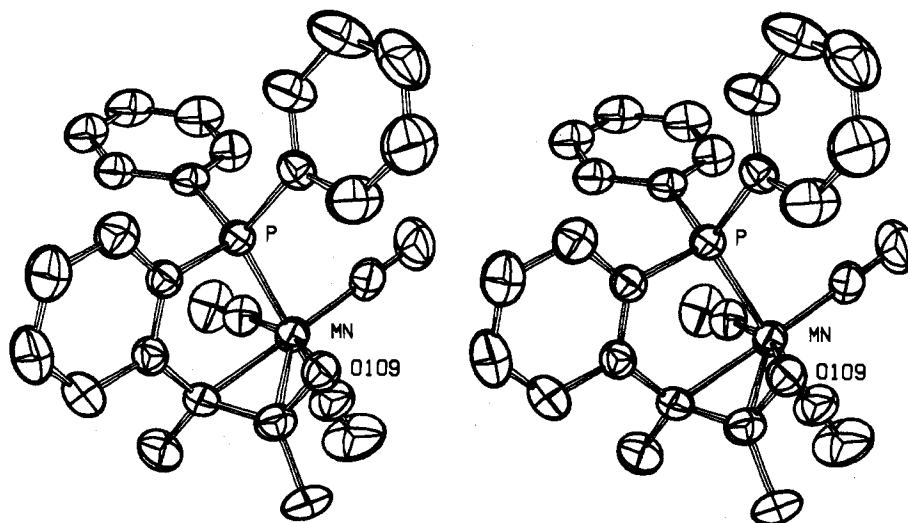

Figure 2. A stereoscopic view of the molecule.

Table II. Principal Intramolecular Distances and Angles

(a) Bond Distances, Å

Atoms	Distance	Atoms	Distance
Mn–P	2.300 (1)	Mn–C(1)	1.793 (4)
Mn–C(2)	1.780 (4)	Mn–C(3)	1.797 (4)
Mn–C(107)	2.219 (3)	Mn–C(108)	2.126 (3)
Mn–O(109)	2.058 (2)	C(1)–O(1)	1.147 (5)
C(2)–O(2)	1.158 (5)	C(3)–O(3)	1.160 (6)
P–C(101)	1.795 (3)	P–C(201)	1.823 (3)
P–C(301)	1.823 (3)	C(101)–C(102)	1.388 (4)
C(101)–C(106)	1.401 (5)	C(102)–C(103)	1.399 (5)
C(103)–C(104)	1.385 (5)	C(104)–C(105)	1.371 (6)
C(105)–C(106)	1.383 (5)	C(102)–C(107)	1.506 (4)
C(107)–C(108)	1.427 (5)	C(107)–C(117)	1.536 (5)
C(108)–O(109)	1.295 (4)	C(108)–C(118)	1.527 (6)
C(201)–C(202)	1.383 (3)	C(201)–C(206)	1.392 (5)
C(202)–C(203)	1.404 (5)	C(203)–C(204)	1.372 (6)
C(204)–C(205)	1.384 (6)	C(205)–C(206)	1.387 (5)
C(301)–C(302)	1.393 (5)	C(301)–C(306)	1.375 (5)
C(302)–C(303)	1.391 (6)	C(303)–C(304)	1.369 (6)
C(304)–C(305)	1.373 (7)	C(305)–C(306)	1.391 (5)

(b) Interbond Angles, Deg

| Atoms	Angle	Atoms	Angle
P–Mn–C(1)	88.06 (12)	P–Mn–C(2)	90.11 (12)
P–Mn–C(3)	176.25 (14)	P–Mn–C(107)	83.46 (9)
P–Mn–C(108)	100.13 (9)	P–Mn–O(109)	83.25 (7)
C(1)–Mn–C(2)	98.29 (17)	C(1)–Mn–C(3)	90.22 (18)
C(1)–Mn–C(107)	164.94 (15)	C(1)–Mn–C(108)	132.54 (14)
C(1)–Mn–O(109)	100.68 (13)	C(2)–Mn–C(3)	86.84 (18)
C(2)–Mn–C(107)	94.17 (14)	C(2)–Mn–C(108)	128.05 (15)
C(2)–Mn–O(109)	159.66 (13)	C(3)–Mn–C(107)	98.93 (16)
C(3)–Mn–C(108)	83.49 (17)	C(3)–Mn–O(109)	100.34 (15)
C(107)–Mn–C(108)	38.28 (12)	C(107)–Mn–O(109)	66.03 (10)
C(108)–Mn–O(109)	36.01 (11)	Mn–C(1)–O(1)	179.3 (3)
Mn–C(2)–O(2)	177.5 (3)	Mn–C(3)–O(3)	174.6 (4)
Mn–C(107)–C(102)	112.6 (2)	Mn–C(107)–C(108)	67.3 (2)
Mn–C(107)–C(117)	119.6 (2)	Mn–O(109)–C(108)	74.8 (2)
Mn–P–C(101)	104.16 (10)	Mn–P–C(201)	115.27 (10)
Mn–P–C(301)	119.86 (10)	C(101)–P–C(201)	106.85 (14)
C(101)–P–C(301)	106.00 (14)	C(201)–P–C(301)	103.78 (14)
P–C(101)–C(102)	115.0 (2)	P–C(101)–C(106)	123.6 (2)
C(102)–C(101)–C(106)	121.3 (3)	C(101)–C(102)–C(103)	117.9 (3)
C(102)–C(103)–C(104)	120.1 (4)	C(103)–C(104)–C(105)	121.8 (4)
C(104)–C(105)–C(106)	119.0 (4)	C(101)–C(106)–C(105)	119.8 (3)
P–C(201)–C(202)	123.0 (2)	P–C(201)–C(206)	117.4 (2)
C(202)–C(201)–C(206)	119.4 (3)	C(201)–C(202)–C(203)	120.0 (3)
C(202)–C(203)–C(204)	119.8 (4)	C(203)–C(204)–C(205)	120.7 (4)
C(204)–C(205)–C(206)	119.6 (4)	C(201)–C(206)–C(205)	120.5 (3)
P–C(301)–C(302)	118.4 (3)	P–C(301)–C(306)	123.0 (3)
C(302)–C(301)–C(306)	118.6 (3)	C(301)–C(302)–C(303)	120.3 (3)
C(302)–C(303)–C(304)	120.1 (4)	C(303)–C(304)–C(305)	120.0 (4)
C(304)–C(305)–C(306)	120.1 (4)	C(301)–C(306)–C(305)	120.8 (4)
C(101)–C(102)–C(107)	123.3 (3)	C(103)–C(102)–C(107)	118.6 (3)
C(102)–C(107)–C(108)	116.1 (3)	C(102)–C(107)–C(117)	114.6 (3)
C(117)–C(107)–C(108)	118.5 (3)	C(107)–C(108)–O(109)	118.0 (3)
C(107)–C(108)–C(118)	124.3 (3)	C(118)–C(108)–O(109)	117.6 (3)
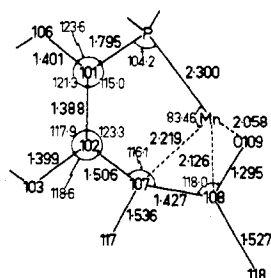
Figure 3. A schematic representation of the "chelate" ring about the Mn atom, showing more important geometrical aspects.

(–)0.05 Å. In the present complex, the relative aplanarity of the substituent atoms clearly derives from the fundamental asymmetry of the ligand itself, rather than from the small degree of asymmetry in the metal–ligand bonding. The

differing electronegativities of the two terminal atoms of the π-oxopropenyl group ensure increased π-electron localization at C(108) and O(109) and hence a low p character in the C(108) σ orbitals and a concomitant high p character in the C(107) σ orbitals. The further observations (1) that the angle sum at C(107) is only 350° [*cf.* 360° at C(108)], (2) that the distance C(107)–C(108) [1.427 (5) Å] exceeds the values for both symmetrically [*ca.* 1.37 Å[33,34]] and asymmetrically [*ca.* 1.40 Å[31,36]] coordinated π-allyls, and (3) that C(108)–O(109) appears to have slightly more double-bond character than C(107)–C(108) (*vide supra*) are all consistent with this rationale. The distance C(102)–C(107) [1.506 (4) Å] is within experimental error (3.0σ) of its expected value of 1.50 Å. Similarly, the π-oxopropenyl-methyl distances C(107)–C(117) [1.536 (5) Å] and C(108)–

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Table III. Least-Squares Planes

Best Weighted Least-Squares Planes

Plane	Atoms defining plane	Equation[a]
1	Mn, C(1), C(2)	$0.1283X + 0.8259Y + 0.5491Z = 5.6940$
2	C(107), C(108), O(109)	$-0.7147X + 0.2614Y + 0.6488Z = 0.8353$
3	Phenyl ring C(101)–C(106)	$0.8869X - 0.1769Y + 0.4267Z = 1.5016$
4	Phenyl ring C(201)–C(206)	$-0.1426X + 0.9891Y + 0.0380Z = 2.2596$
5	Phenyl ring C(301)–C(306)	$-0.3886X + 0.2359Y + 0.8907Z = 2.2465$

Distances (Å) of Atoms from Mean Planes

Atoms	Plane 1	Atoms	Plane 2	Atoms	Plane 3	Atoms	Plane 4	Atoms	Plane 5
Mn	0.0	C(107)	0.0	C(101)	-0.017	C(201)	-0.003	C(301)	0.006
C(1)	0.0	C(108)	0.0	C(102)	0.017	C(202)	0.004	C(302)	0.0
C(2)	0.0	O(109)	0.0	C(103)	-0.005	C(203)	-0.002	C(303)	-0.009
P	-2.299	Mn	1.686	C(104)	-0.018	C(204)	-0.001	C(304)	0.009
O(1)	-0.002	P	0.631	C(105)	0.016	C(205)	0.001	C(305)	0.003
O(2)	0.010	C(117)	0.282	C(106)	0.006	C(206)	0.002	C(306)	-0.009
O(3)	2.942	C(118)	-0.051	P	-0.133	P	0.110	P	0.015
O(109)	-0.261	C(102)	-1.030	C(107)	0.186				
C(3)	1.794			C(108)	1.491				
C(107)	-0.327			O(109)	2.078				
C(108)	0.320								

[a] The equations of the planes, $LX + MY + NZ = D$, refer to orthogonal coordinates. The matrix to transform from triclinic to orthogonal coordinates is

$$\begin{pmatrix} 9.2100 & 1.0187 & 0.0 \\ 0.0 & 11.6890 & 0.0 \\ -1.4043 & 1.5001 & 10.4536 \end{pmatrix}$$

$X = ax; Y = by; Z = cz.$

C(118) [1.527 (6) Å] are very close to the expected value of *ca.* 1.51-1.52 Å.

The Mn-P distance [2.300 (1) Å] is in excellent agreement with that observed for the isomeric σ-oxobutyl derivative **3** [2.295 (3) Å][12] but is longer than the value [2.279 (3) Å] observed for [{o-(CH₃)CHC₆H₄}P(C₆H₅)₂Mn(CO)₄][30] In each of these complexes, however, the Mn-P distance is very much shorter than the 2.54 Å estimated from covalent radii sums [1.44 + 1.10 Å assumed], and implies substantial π-bond character in the Mn-P bond.

The phosphorus-carbon distances P-C(201) and P-C(301), *i.e.*, to the unsubstituted phenyl groups, are each 1.823 (3) Å and are in excellent agreement with values reported for other metal-triphenylphosphine complexes. They also agree well with the average value of 1.828 Å observed for free triphenylphosphine.[37] In contrast, the remaining distance, P-C(101) [1.795 (3) Å], is significantly shorter [Δ = 0.28 Å, Δ/σ = 8]. The origin of this contraction is not clear, but there is some indication of a similar effect in the σ-oxobutyl isomer.[12] Possibly it is a consequence of the severe and apparently strain-induced deformation of the angle Mn-P-C(101) [104.16 (10)°]. This deformation [*ca.* 12° from the value of *ca.* 116° normally expected for the M-P-C angle in metal-triphenylphosphine complexes] clearly implies a substantial modification of the phosphorus σ-bonding orbital mixing coefficients compared with the situation in, for example, free triphenylphosphine. Additional evidence of strain in the "chelate" ring system (Figure 3) is provided by the deviation of P-C(101)-C(102) [115.1 (2)°] from its expected value of 120°. As is usual in both free and coordinated triphenylphosphine, the C-P-C angles are all significantly less than the tetrahedral value of 109° 27'. Carbon-

carbon distances within the phenyl rings vary from 1.369 (6) to 1.404 (5) Å with an average value of 1.386 Å. The C-C-C angles range from 117.9 (3) to 121.8 (4)° and average 120.0°.

The Mn-C(carbonyl) distances average 1.790 Å, and no individual distance differs significantly from the mean. This value is in good agreement with that observed for [{o-(CH₃)-CHC₆H₄}P(C₆H₅)₂Mn(CO)₄][30] [average 1.80 (1) Å] and with the two longer distances [average 1.805 Å] found in the σ-oxobutyl derivative.[12] For a Mn(I) σ-orbital radius of 1.44 Å, the implicit bond length contraction due to the synergic effect is *ca.* 0.35 Å. Virtually identical Mn-C(carbonyl) distances have also been reported for the apical bonds in Mn₂-(CO)₁₀.[38,39] The C-O(carbonyl) distances average 1.155 Å, and each is within experimental error of this mean. The observed distance is only slightly longer than that found for carbon monoxide. The Mn-C-O angles range from 179.3 (3) to 174.6 (4)°. Reasons for the nonlinearity of M-C≡O groupings have been discussed elsewhere.[40]

There are no unusually short intermolecular atom-atom contacts.

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