Finally, this study has confirmed one of the three modes of metal coordination proposed for 2,3-diazabicyclo[2.2.1]hept-2-ene. It will be of interest to examine this bicyclic azo compound in other types of metal-coordinated configurations.

Acknowledgments.—The support of this work by the National Science Foundation is gratefully acknowledged. We thank Dr. R. P. Bennett for providing the sample used in this study and also thank Professor J. A. Ibers for providing a preprint of ref 12b.

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The Crystal and Molecular Structure of $[Mn(CO)_4(C_2P(C_6H_5)_3)Br]$. A Coordination Compound of the Unusual Carbonyl–Ylide Reaction Product $(C_6H_5)_3P^+—C{\equiv}C:^-$

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The crystal and molecular structure of the unusual compound $[Mn(CO)_4(C_2P(C_6H_5)_3)Br]$ has been determined from single-crystal, three-dimensional X-ray data collected by counter methods. The material crystallizes as yellow-orange needles in the monoclinic space group $P2_1/c$ ($C_{2h}{}^5$). The lattice constants are $a = 9.564$ (3), $b = 12.019$ (3), $c = 21.237$ (8) Å, and $\beta = 107.02$ (2)°. The calculated density for four molecules per unit cell is 1.52 g/cm^3, as compared with an observed density of 1.47 (2) g/cm^3. Full-matrix least-squares refinement on F for 1214 independent reflections with $F^2 > 3\sigma(F^2)$ converged to a weighted R factor of 6.33%. The structure consists of discrete molecular units of octahedrally coordinated manganese with the $C_2P(C_6H_5)_3$ ligand cis to Br. The C–C distance in the MnC_2 group is 1.216 (14) Å; the Mn–C–C angle is 176.3 (12)° and the P–C–C angle is 164.0 (12)°. These values indicate that the $C_2P(C_6H_5)_3$ ligand may be best represented as a phosphonium molecule, $(C_6H_5)_3P^+—C{\equiv}C:^-$, in which one of the organic groups is the acetylide anion. There is partial disorder between the bromine and one of the carbonyl groups. This disorder is satisfactorily treated in the model refined.

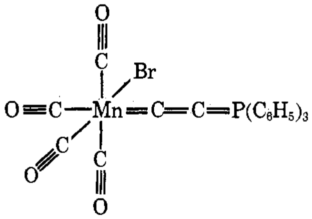
Introduction

In their studies of the reactions of transition metal complexes with ylides, Mitchell, Korte, and Kaska[2] observed that $Mn(CO)_5Br$ reacts readily with the bis ylide hexaphenylcarbodiphosphorane[3,4] according to eq 1. The yellow-orange manganese complex comes

$$Mn(CO)_5Br + (C_6H_5)_3P{=}C{=}P(C_6H_5)_3 \longrightarrow [Mn(CO)_4(C_2P(C_6H_5)_3)Br] + (C_6H_5)_3P{=}O \quad (1)$$

out of benzene solution as an oil which may be separated as crystalline needles from the accompanying triphenylphosphine oxide by repeated crystallization from toluene–pentane or methylene chloride–pentane solutions. Reaction 1 is formally analogous to the Wittig reaction of ylides with carbonyl-containing organic molecules.[5] This, however, appears to be the first instance of the reaction of an ylide with a coordinated carbonyl group in a transition metal complex.

In the original formulation of the manganese complex the cumulene structure



was suggested. Infrared evidence was used to support the formulation of the complex as the cis isomer.[2] The crystal structures of triphenylphosphoranylideneketene, $(C_6H_5)_3PC_2O$, and its sulfur analog have been reported previously and they have been considered as cumulene molecules.[6,7] As a first step in establishing the structural chemistry of the new class of compounds, of which $[Mn(CO)_4(C_2P(C_6H_5)_3)Br]$ is the first member, we have determined the crystal and molecular structure of this complex by X-ray diffraction methods. A preliminary report of the structure determination has already been published.[8] We now present the complete details and the results of the final refinement of the structure.

Experimental Section

Crystals of $[Mn(CO)_4(C_2P(C_6H_5)_3)Br]$ were provided by Professor W. C. Kaska. The yellow-orange needles darken upon prolonged exposure to air, so crystals for this study were mounted in thin-walled capillaries under an argon atmosphere. Precession photographs showed monoclinic symmetry with systematic absences $h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$. The space group was thus uniquely determined as $P2_1/c$ ($C_{2h}{}^5$).

The crystal orientation and unit cell constants were determined by a least-squares refinement of 12 carefully centered reflections with 2θ angles in the range 20–30°.[9] Since the Mo $K\alpha_1$ and $K\alpha_2$ peaks are not well resolved in this range, the reflections were centered on Mo $K\bar{\alpha}$ (λ 0.71069 Å). The lattice parameters at 22° are $a = 9.564$ (3), $b = 12.019$ (3), $c = 21.237$ (8) Å, and $\beta = 107.02$ (2)°. The calculated density for four molecules in the unit cell is 1.54 g/cm^3. The observed density as determined by flotation in solutions of hexafluorobenzene and pentane is 1.47 (2) g/cm^3.

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[1] (a) National Institutes of Health Predoctoral Fellow. (b) Fellow of the Alfred P. Sloan Foundation.

[2] D. K. Mitchell, W. D. Korte, and W. C. Kaska, *J. Chem. Soc. D*, 1384 (1970).

[3] F. Ramirez, N. B. Desai, B. Hansen, and N. McKelvie, *J. Amer. Chem. Soc.*, **83**, 3539 (1961).

[4] G. H. Birum and C. N. Mathews, *ibid.*, **88**, 4198 (1966).

[5] A. W. Johnson "Ylid Chemistry," Academic Press, New York, N. Y., 1966.

[6] J. J. Daly and P. J. Wheatley, *J. Chem. Soc. A*, 1703 (1966).

[7] J. J. Daly, *ibid.*, 1913 (1967).

[8] S. Z. Goldberg, E. N. Duesler, and K. N. Raymond, *J. Chem. Soc. D*, 826 (1971).

[9] The programs for refinement of lattice constants and automated operation of the diffractometer are those of Busing and Levy as modified by Picker Corp. for the PDP 8/I.

TABLE I

POSITIONAL AND THERMAL PARAMETERS AND STANDARD DEVIATIONS[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	.32474(26)	.31188(22)	.07834(11)	.01600(43)	.01368(30)	.00298(8)	-.00462(29)	.00184(14)	.00123(12)
Mn	.06751(23)	.24808(20)	.06351(10)	.01314(33)	.00706(20)	.00222(6)	.00112(26)	.00165(11)	.00069(12)
P	.32435(37)	-.01087(31)	.23067(16)	.00912(54)	.00729(40)	.00184(11)	.00072(39)	.00165(20)	.00029(18)
O_1	.1354[b]	.0678[b]	-.0185[b]	9.55(78)[c]					
C_1	.1095(9)	.1368(5)	.0129[d]	2.76(40)[c]					
O_2	.9797(13)	.4018(10)	.9505(5)	.0291(25)	.0123(14)	.0028(4)	.0024(14)	.0008(8)	.0014(6)
C_2	.0119(17)	.3473(14)	-.0055(7)	.0151(26)	.0118(20)	.0016(4)	.0013(19)	-.0006(9)	.0007(8)
O_3	.0334(14)	.4151(10)	.1609(6)	.0334(26)	.0094(14)	.0045(5)	.0019(16)	.0038(9)	-.0015(6)
C_3	.0455(18)	.3496(14)	.1243(8)	.0164(28)	.0067(19)	.0036(6)	-.0003(19)	.0011(11)	.0005(8)
O_4	-.2327(12)	.1637(10)	.0423(6)	.0138(18)	.0152(15)	.0064(5)	-.0018(15)	.0023(9)	.0010(7)
C_4	-.1188(17)	.1949(13)	.0500(8)	.0146(27)	.0052(14)	.0043(6)	.0002(18)	.0023(12)	.0016(8)
C_5	.1500(14)	.1428(11)	.1368(6)	.0117(23)	.0064(15)	.0024(5)	.0006(15)	.0027(9)	.0002(7)
C_6	.2076(13)	.0779(11)	.1806(6)	.0091(22)	.0059(14)	.0027(5)	.0025(14)	.0029(8)	.0020(7)
Br_d	.1186(9)	.1146(8)	-.0178[e]	5.78(23)[c]					
O_{1d}	.3851[f]	.2905[f]	.0893[f]	9.55(78)[c,g]					
C_{1d}	.2636[f]	.2743[f]	.0794[f]	2.76(40)[c,g]					
C_{11}	.5332(10)	.4540(9)	.3047(5)	.0101(24)	.0054(14)	.0015(4)	-.0008(15)	.0014(8)	.0004(7)
C_{12}	.5412(10)	.4881(8)	.3685(5)	.0119(25)	.0095(18)	.0023(5)	-.0003(17)	.0022(9)	-.0006(8)
C_{13}	.4340(14)	.4546(10)	.3971(4)	.0141(31)	.0175(25)	.0033(6)	-.0030(23)	.0043(12)	-.0018(10)
C_{14}	.3190(11)	.3871(10)	.3620(6)	.0142(29)	.0119(20)	.0033(6)	-.0002(20)	.0053(11)	.0004(9)
C_{15}	.3110(9)	.3530(8)	.2982(6)	.0133(28)	.0093(19)	.0038(7)	-.0042(18)	.0038(11)	-.0011(9)
C_{16}	.4182(12)	.3865(9)	.2696(4)	.0123(26)	.0081(17)	.0021(5)	-.0010(18)	.0032(10)	-.0011(8)
C_{21}	.7665(13)	.3632(7)	.2611(6)	.0085(23)	.0072(16)	.0018(5)	-.0007(17)	.0010(9)	.0001(8)
C_{22}	.8932(13)	.3349(10)	.3108(4)	.0135(28)	.0084(19)	.0023(5)	-.0012(18)	.0026(10)	.0013(8)
C_{23}	.9616(9)	.2332(13)	.3085(6)	.0096(26)	.0131(26)	.0046(8)	.0025(23)	.0026(11)	.0018(12)
C_{24}	.9035(16)	.1597(8)	.2566(8)	.0167(34)	.0083(20)	.0052(8)	.0030(23)	.0056(13)	.0024(11)
C_{25}	.7760(16)	.1880(10)	.2069(6)	.0241(38)	.0056(18)	.0038(7)	-.0011(21)	.0051(13)	-.0015(9)
C_{26}	.7084(10)	.2898(12)	.2092(5)	.0119(26)	.0099(20)	.0028(6)	-.0041(19)	.0029(10)	-.0012(8)
C_{31}	.4026(13)	.0472(8)	.3097(4)	.0084(23)	.0079(16)	.0023(5)	.0026(17)	.0021(9)	.0014(7)
C_{32}	.5359(12)	.1034(10)	.3256(6)	.0114(29)	.0095(19)	.0033(6)	-.0012(19)	.0025(10)	-.0015(8)
C_{33}	.5913(10)	.1523(9)	.3875(7)	.0096(26)	.0135(23)	.0045(7)	-.0043(19)	.0017(12)	-.0021(11)
C_{34}	.5133(16)	.1449(10)	.4335(4)	.0228(38)	.0126(22)	.0024(6)	.0009(25)	.0001(13)	-.0014(9)
C_{35}	.3799(15)	.0887(10)	.4176(5)	.0208(37)	.0118(22)	.0035(7)	.0020(24)	.0036(13)	-.0007(10)
C_{36}	.3245(9)	.0398(9)	.3557(6)	.0123(27)	.0097(18)	.0026(5)	-.0030(18)	.0017(10)	-.0013(9)

[a] The form of the thermal ellipsoid is $\exp -\left[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell\right]$. Numbers in parentheses, here and in succeeding tables, are the estimated standard deviations in the least significant digits.

[b] Determined by constraining C_1O_1 to be linear with a bond length equal to the C_3O_3 distance.

[c] Isotropic thermal parameter, B.

[d] Determined by constraining the Mn-C_1 bond length to be equal to the Mn-C_3 distance.

[e] Determined by constraining the Mn-Br_d bond length to be equal to the Mn-Br distance.

[f] Determined by applying mirror operation described in the text to C_1O_1.

[g] Thermal parameter, B, constrained to value for corresponding atom in C_1O_1.

Data Collection and Reduction

Intensity data were collected on an automated Picker four-circle diffractometer using Mo Kα radiation. Data were collected in the θ–2θ scan mode to a 2θ angle of 45°. A scan rate of 1°/min was used with a scan from 0.60° below the Kα_1 peak to 0.60° above the Kα_2 peak. Stationary 10-sec background counts were taken at the start and end of each scan. The takeoff angle for the X-ray tube was 2.0° and the Bragg angle for the graphite monochrometer crystal was 12.02°. The detector was located 33 cm from the source and had a 7 × 7 mm receiving aperture.

Data were collected for the octants $\pm h$, $+k$, $+l$. The stability of the crystal and diffractometer was checked by measuring the 020, 300, and 006 reflections after every 60 reflections. These reflections showed constant intensity within 1–2% throughout data collection. Our program UCFACS was used to reduce and process the data.[10] Corrections for Lorentz and polarization effects were applied. The parameter p used to prevent overweighting strong reflections was chosen as 0.04.[10] A total of 3347 reflections was observed of which there were 1214 independent reflections with $F^2 > 3\sigma(F^2)$.

The data crystal had maximum point-to-point distances of 0.086 × 0.163 × 0.383 mm and was mounted approximately along the 010 axis (the longest direction). The linear absorption coefficient, μ, is 25.1 cm^{-1}. The value of $e^{-\mu t}$ ranged from a minimum of 0.65 to a maximum of 0.81. The actual range in integrated transmission factors is much smaller than this and so no absorption correction was applied.

Solution and Refinement of the Structure

The structure was solved by the application of heavy-atom techniques.[11] Full-matrix, least-squares refinements were carried out on F for 1214 independent reflections with $F^2 > 3\sigma(F^2)$. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting factor, w, is $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for neutral Br, Mn, P, O, and C were taken from the tabulation of Cromer and Mann,[12] while those for hydrogen are from Stewart, *et al.*[13] Corrections for anomalous dispersion effects for Mn,

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[10] E. N. Duesler and K. N. Raymond, *Inorg. Chem.*, **10**, 1486 (1971).

[11] In addition to local programs for the CDC 6400 computer, modifications of the following programs were used: Ibers' NUCLS, a group least-squares version of the Busing–Levy ORFLS program; Zalkin's FORDAP Fourier program; ORFFE, a function and error program by Busing, Martin, and Levy; Johnson's ORTEP thermal ellipsoid plot program.

[12] D. T. Cromer and B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

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

Br, and P using both f' and f'' were included in the calculations. Values for f' and f'' are those of Cromer.[14]

The Mn and Br atoms were easily located from a three-dimensional Patterson map. A difference Fourier clearly showed the phosphorus atom and indicated the positions of several carbonyl groups. Further cycles of least squares and difference Fourier syntheses located the phenyl rings and carbonyl groups with the exception of the carbonyl group denoted as C_1O_1 in Figure 1, in which the carbon and oxygen atoms were unresolved.

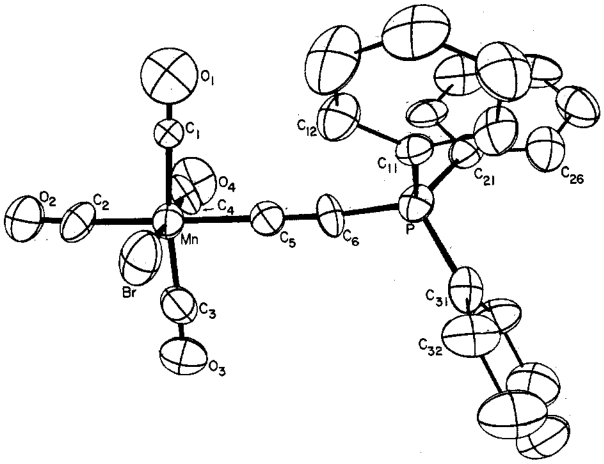

Figure 1.—A perspective drawing of $Mn(CO)_4(C_2P(C_6H_5)_3)Br$.

At this point R_1 = 13.5% and R_2 = 15.0%[15] for a model in which the thermal motion for all of the atoms was treated isotropically and in which the phenyl carbons were considered as part of planar, rigid groups with a C–C bond length of 1.395 Å.[16] Each rigid group was assigned a single isotropic temperature factor. Introduction of anisotropic temperature factors for the nongroup atoms and individual isotropic temperature factors for the group atoms resulted in R_1 = 9.8% and R_2 = 12.2% after three cycles of refinement but atoms C_1 and O_1 did not refine. A region of large electron density roughly between the expected C_1 and O_1 positions was observed in the Fourier map. This is due to a partial disorder between the bromine atom and the carbonyl group C_1O_1. The disordered atoms in the predominant form are denoted Br, C_1, and O_1, while those in the subordinate form are called Br_d, C_{1d}, and O_{1d}. A model was chosen in which the Br occupancy was varied and the position of Br_d was constrained such that the Mn–Br_d distance was the same as the Mn–Br distance. The Mn–C_1O_1 group was constrained to be linear with the Mn–C_1 distance equal to the Mn–C_3 distance, and the C_1O_1 distance equal to the C_3O_3 distance. Atoms C_{1d} and O_{1d} were related to C_1 and O_1 by applying a mirror operation. This mirror plane bisects the angle formed by the $Mn\rightarrow Br$ and $C_3\rightarrow Mn$ vectors. These constraints were applied to the derivatives in the least-squares refinements using the formalism described by Raymond.[17] The hydrogen contributions were calculated based on the ideal geometry of the phenyl rings and a CH bond length of 0.9 Å. The fixed isotropic contributions of the hydrogen atoms to the structure factors were calculated from these positions and an average isotropic temperature factor for each ring, which was chosen as the average value for the carbon atoms plus 1. Thus the hydrogen temperature factors were 5.50, 5.60, and 6.10 Å^2 for rings 1, 2, and 3 respectively. A difference Fourier showed evidence of anisotropic thermal motion for the phenyl carbon atoms. The model was revised to allow anisotropic motion for these atoms (which were still constrained to be rigid groups) and isotropic motion for the disordered atoms. This final model converged after five cycles to R_1 = 6.49% and R_2 = 6.33%.[18]

The final error in an observation of unit weight, defined as

$$\left(\frac{\sum w(|F_o| - |F_c|)^2}{N_o - N_v}\right)^{1/2}$$

is 1.81, where N_o and N_v are the number of observations and the number of variables, respectively. A final difference Fourier showed no peaks larger than 0.8 e/Å^3, or roughly 15% of a carbon atom. The largest peaks appeared in the region of the disordered bromine or as ripple near the other heavy atoms.

Discussion

The positional and thermal parameters for the nonhydrogen atoms are given in Table I. The root-mean-square amplitudes of vibration along the principal axes are given in Table II. The phenyl carbon positions were obtained from the group parameters for the rings as given in Table III. The positional and thermal pa-

TABLE II

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION ALONG PRINCIPAL AXES (Å × 10^3)

Atom	Axis 1	Axis 2	Axis 3
Br	214 (4)	251 (3)	350 (3)
Mn	200 (4)	228 (4)	247 (4)
P	180 (6)	200 (6)	235 (6)
O_1	348 (14)[a]		
C_1	187 (13)[a]		
O_2	223 (18)	312 (16)	372 (15)
C_2	165 (28)	286 (22)	297 (25)
O_3	235 (19)	322 (16)	381 (15)
C_3	219 (31)	252 (23)	298 (26)
O_4	237 (16)	326 (16)	380 (15)
C_4	176 (29)	247 (23)	312 (21)
C_5	187 (25)	214 (26)	244 (21)
C_6	156 (31)	166 (28)	281 (20)
Br_d	271 (5)[a]		
O_{1d}	348 (14)[a,b]		
C_{1d}	187 (13)[a,b]		
C_{11}	162[c]	196	217
C_{12}	197	230	267
C_{13}	181	265	372
C_{14}	144	293	302
C_{15}	183	247	314
C_{16}	152	224	269
C_{21}	187	194	232
C_{22}	164	246	272
C_{23}	190	274	345
C_{24}	212	220	361
C_{25}	179	252	336
C_{26}	183	223	303
C_{31}	166	188	271
C_{32}	210	226	296
C_{33}	179	284	350
C_{34}	204	298	348
C_{35}	236	295	314
C_{36}	201	230	291

[a] Thermal motion is isotropic. [b] Thermal parameter, B, constrained to value for corresponding atom in C_1O_1. [c] Estimated standard deviations were not calculated for group atoms but are expected to be in the range 10–30.

TABLE III

GROUP PARAMETERS[a]

	Group 1	Group 2	Group 3
x_c	0.4261 (7)	0.8350 (8)	0.4579 (8)
y_c	0.4205 (5)	0.2615 (6)	0.0960 (6)
z_c	0.3333 (3)	0.2589 (4)	0.3716 (4)
δ	1.961 (8)	−2.668 (9)	−0.711 (12)
ϵ	−2.433 (8)	2.969 (8)	−2.160 (9)
η	−1.866 (8)	−0.760 (6)	1.982 (12)

[a] x_c, y_c, z_c are the fractional coordinates of the group center; δ, ϵ, η (in radians) have been defined previously: R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965); S. J. La Placa and J. A. Ibers, *J. Amer. Chem. Soc.*, **87**, 2581 (1965); *Acta Crystallogr.*, **18**, 511 (1965).

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

(15) $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

(16) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1969.

(17) K. N. Raymond, *Acta Crystallogr., Sect. A*, **28**, 163 (1972)

(18) A listing of structure factors 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, by referring to code number INORG-72-1397. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

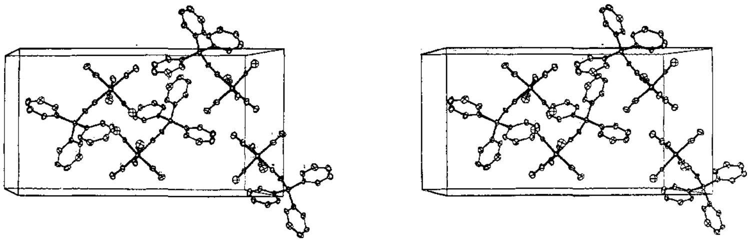

Figure 2.—A stereoscopic view of the unit cell for $Mn(CO)_4C_2P(C_6H_5)_3Br$. The origin is at the front lower left. The vertical axis is *b* and the horizontal axis *c*.

rameters used in calculating the fixed hydrogen contributions are presented in Table IV.

TABLE IV

CALCULATED HYDROGEN COORDINATES AND ISOTROPIC TEMPERATURE FACTORS

Atom	*x*	*y*	*z*	*B*, Å^2
H_{12}	0.6154	0.5312	0.3902	5.50
H_{13}	0.4392	0.4759	0.4373	
H_{14}	0.2495	0.3654	0.3794	
H_{15}	0.2358	0.3101	0.2743	
H_{16}	0.4120	0.3654	0.2272	
H_{22}	0.9302	0.3802	0.3439	5.60
H_{23}	0.0404	0.2118	0.3399	
H_{24}	0.9436	0.0920	0.2540	
H_{25}	0.7365	0.1405	0.1722	
H_{26}	0.6263	0.3089	0.1762	
H_{32}	0.5880	0.1076	0.2961	6.10
H_{33}	0.6798	0.1881	0.3939	
H_{34}	0.5518	0.1767	0.4737	
H_{35}	0.3319	0.0848	0.4478	
H_{36}	0.2401	0.0043	0.3461	

The structure consists of discrete molecular units of $Mn(CO)_4(C_2P(C_6H_5)_3)Br$. Figure 1 is a perspective drawing of a single molecule and Figure 2 is a stereoscopic view of the contents of the unit cell. The coordination about the manganese is essentially octahedral with the $C_2P(C_6H_5)_3$ ligand cis to the bromine atom. Such a geometry is to be expected if the ligand is a poorer π acceptor than CO and maximum π stabilization of the carbonyl groups is to be attained.[19] The disorder in the structure consists of partial bromine occupancy at the position of the carbonyl group C_1O_1. The occupancy factor for Br as determined in the least-squares refinement is 0.723 (4); hence there is an interchange of the bromine and carbonyl sites in 28% of the molecules.

TABLE V

BONDED DISTANCES IN $Mn(CO)_4(C_2P(C_6H_5)_3)Br$

Atoms	Distance, Å	Atoms	Distance, Å
$Mn-C_1$	1.833 (18)[a]	C_4-O_4	1.118 (15)
$Mn-C_2$	1.844 (17)	C_5-C_6	1.216 (14)
$Mn-C_3$	1.833 (18)	$P-C_6$	1.679 (13)
$Mn-C_4$	1.835 (16)	$P-C_{11}$	1.788[c]
$Mn-C_5$	1.981 (14)	$P-C_{21}$	1.778[c]
C_1-O_1	1.135 (16)[b]	$P-C_{31}$	1.769[c]
C_2-O_2	1.108 (14)	Br–Mn	2.507 (8)
C_3-O_3	1.135 (16)		

[a] Constrained to be equal to the $Mn-C_3$ distance. [b] Constrained to be equal to the C_3-O_3 distance. [c] Estimated standard deviations for bonds involving the group atoms were not calculated but are expected to be in the range 10–20.

The bonded distances within a molecule are given in Table V. Of the four independent manganese–carbon bonds (one bond was constrained in the model) the $Mn-C_5$ bond, 1.981 (14) Å, is significantly longer than the others, which have an average value of 1.847 (10) Å. The average carbon–oxygen distance is 1.120 (9) Å. These values for the carbonyl groups are virtually identical with those found in $HMn(CO)_5$, where the respective averages are 1.836 (4) and 1.130 (5) Å.[20] The C_5-C_6 bond length in the $C_2P(C_6H_5)_3$ ligand, 1.216 (14) Å, is within 1σ of the standard acetylenic triple-bond length of 1.204 (2) Å but differs by 8σ from the standard ethylenic double-bond length of 1.337 (6) Å.[16] This bond length is also shorter than the C–C bond in cumulene systems.[21–24] It is the same as the C–C distance found in $(C_6H_5)_3PC_2O$[6] and $(C_6H_5)_3PC_2S$.[7]

Coordination about the phosphorus atom is essentially tetrahedral. The $P-C_6$ bond length of 1.679 (13) Å is significantly shorter than the average for the $P-C_{i1}$ (i = 1, 3) bonds, which is 1.778 (9) Å. The three phenyl carbon atoms bonded to the phosphorus lie in a plane perpendicular to the $P-C_6$ bond and are nearly at the vertices of an equilateral triangle. The phosphorus is no more than 0.125 Å from any of the phenyl planes. This corresponds to an out-of-plane bending of less than 4°. It is within 0.05 Å (excluding the out-of-plane distortion) of each of the three axes defined by the bonded and para carbon atoms for the three rings, so there is at most a 1.5° distortion from perfect linearity. These distortions are certainly not chemically significant. The bond angles are given in Table VI. It is of

TABLE VI

BOND ANGLES IN $Mn(CO)_4(C_2P(C_6H_5)_3)Br$

Atoms	Angle, deg	Atoms	Angle, deg
$Br-Mn-C_1$	85.5 (3)	C_4-Mn-C_5	92.6 (6)
$Br-Mn-C_2$	86.9 (5)	$Mn-C_1-O_1$	180[a]
$Br-Mn-C_3$	91.1 (5)	$Mn-C_2-O_2$	175.6 (16)
$Br-Mn-C_4$	176.8 (5)	$Mn-C_3-O_3$	177.7 (16)
$Br-Mn-C_5$	86.9 (4)	$Mn-C_4-O_4$	179.0 (17)
C_1-Mn-C_2	93.9 (5)	$Mn-C_5-C_6$	176.3 (12)
C_1-Mn-C_3	171.6 (5)	C_5-C_6-P	164.0 (12)
C_1-Mn-C_4	91.3 (6)	C_6-P-C_{11}	109.3[b]
C_1-Mn-C_5	83.6 (4)	C_6-P-C_{21}	110.5
C_2-Mn-C_3	93.7 (7)	C_6-P-C_{31}	111.6
C_2-Mn-C_4	93.4 (7)	$C_{11}-P-C_{21}$	107.1
C_2-Mn-C_5	173.5 (6)	$C_{11}-P-C_{31}$	109.2
C_3-Mn-C_4	92.0 (7)	$C_{21}-P-C_{31}$	109.1
C_3-Mn-C_5	88.5 (6)		

[a] Constrained in the model for disorder. [b] Estimated standard deviations were not calculated for angles involving the group atoms but may be expected to be in the range 4–15.

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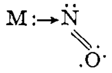
interest that the angles around the phosphorus which involve C_6 tend to be larger than those which involve only phenyl carbon atoms. The angles of most interest, however, are the $Mn–C_5–C_6$ angle of 176.3 (12)° and the $P–C_6–C_5$ angle of 164.0 (12)°. These values are very close to those found in triphenylphosphoranylidenethioketene.[7]

There are three resonance forms which may be used to describe the bonding in the compounds $(C_6H_5)_3PC_2X$ ($X = O, S, Mn(CO)_4Br$)

$$(C_6H_5)_3P{=}C{=}C{=}X \longleftrightarrow (C_6H_5)_3P^{+}{-}C{\equiv}C{-}X^{-} \longleftrightarrow (C_6H_5)_3P^{+}{-}\underset{\cdot\cdot}{C}^{-}{=}C{=}X$$

I II III

Form I has been considered as the predominant one and the unusual angles observed in the oxygen (145.5°) and sulfur (168.0°) compounds have been explained in terms of $d_\pi–\Pi_\pi$ bonding between atoms X and C.[6,7] Such an explanation is rather unsatisfactory; the bond angles may be explained more easily in terms of the relative contributions of forms I–III. In form III, the carbon bonded to the phosphorus may be thought of as having sp^2 hybridization and a bent P–C–C bond is expected. In forms I and II the P–C–C linkage would be linear. This situation is analogous to the case of nitrosyl complexes in which NO^+ may function as either a σ donor, $M{\leftarrow}:N{\equiv}O:$, and coordinate linearly or as a σ acceptor



and adopt a bent geometry.[25,26] Of the three resonance forms for $(C_6H_5)_3PC_2X$, I and III will be most important for X = oxygen because of the pronounced tendency of first-period elements to form double bonds. We therefore expect the greatest deviation from linearity for the oxygen compound. Evidence for the contribution of resonance form I can be found in all three compounds in the shortness of the phosphorus bond to the ligand carbon compared to those to the phenyl carbons, as well as in the bond angles about phosphorus. Once again, the oxygen compound shows the effect to the greatest extent and this is completely consistent with the relatively important contribution of resonance form I. For all three compounds the shortness of the carbon–carbon bond is evidence for an important contribution by form II, but it is a general property of acetylene, cyanide, and carbonyl bonds that the bond distance is constant to within experimental error even though there may be large changes in bond order in adjacent bonds.

It appears that the major difference between $(C_6H_5)_3PC_2O$ and $(C_6H_5)_3PC_2Mn(CO)_4Br$ is that for the latter resonance form II predominates. The metal–ligand bond is much longer than that found for the carbonyl groups and this indicates that there is less double-bond character than in the metal carbonyl bond. When it is formulated as $(C_6H_5)_3P^{+}{-}C{\equiv}C:^{-}$ the ligand can be considered as a phosphonium molecule in which one of the organic groups is the acetylide anion. It is to be expected that the ligand is a good σ donor. It is expected to be a poorer π acceptor than CO (in which formal positive charge resides on the β atom, oxygen, in the triple-bond resonance structure) but better than the acetylide anion (in which there is no formal positive charge on the β atom). This formulation should prove useful in explaining and predicting the subsequent coordination chemistry of $(C_6H_5)_3PC_2$ and similar ligands.

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