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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF ACETATOBIS-(TRIPHENYLPHOSPHINE)DICARBONYLMANGANESE(I), $(CH_3CO_2)Mn(CO)_2[P(C_6H_5)_3]_2$: AN ORGANOMETALLIC COMPLEX CONTAINING A CHELATING ACETATE LIGAND*

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SUMMARY

The accidental but intriguing synthesis of acetatobis(triphenylphosphine)-dicarbonylmanganese(I), $(CH_3CO_2)Mn(CO)_2[P(C_6H_5)_3]_2$, has been accomplished by the reaction of $NaMn(CO)_5$ with $(CH_3)_3SiCl$ followed by the addition of triphenylphosphine and acetic acid. A three-dimensional single-crystal X-ray diffraction analysis has shown an octahedral-like molecule containing a symmetrically oxygen-chelating acetate group, the first such group to be reported in a metal carbonyl complex. The two triphenylphosphine ligands occupy mutually *trans* positions with the two carbonyl ligands possessing the remaining *cis* sites in the octahedral complex. The compound crystallizes with four molecules in a monoclinic unit cell of space group symmetry $P2_1/c$ and of dimensions $a = 17.744(2)$ Å, $b = 9.692(1)$ Å, $c = 20.004(2)$ Å, and $\beta = 106.195(4)°$. The relatively long Mn–O(acetate) bond lengths [2.066(6) and 2.069(7) Å] and the relatively short Mn–CO bond lengths [1.701(12) and 1.760(13) Å] and the relatively short $Mn–P(C_6H_5)_3$ bond lengths [2.260(3) and 2.275(3) Å], compared to the corresponding Mn–CO and $Mn–P(C_6H_5)_3$ bond lengths in other manganese carbonyl triphenylphosphine complexes, are rationalized on the basis that the acetate ligand in this molecule functions primarily as a σ-donor.

INTRODUCTION

A variety of carboxylate complexes of metals are known, and their chemistry has been extensively reviewed[1]. Examples are known of compounds in which the carboxylate group acts either as a monodentate ligand or as a chelating or bridging bidentate ligand.

In the field of transition metal organometallic chemistry, however, only a few scattered examples of carboxylate complexes are known. These include: (1) the *monodentate*-carboxylate complexes $(\pi\text{-}C_5H_5)M(CO)_3(O_2CCF_3)$ (M = Mo, W)[2], $(\pi\text{-}C_5H_5)Fe(CO)_2(O_2CCF_3)$, $Mn(CO)_5(O_2CCF_3)$, $(\pi\text{-}C_3H_5)Fe(CO)_3(O_2CCF_3)$[3], and the

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$[M(CO)_5(O_2CR)]^-$ anions ($M = Cr, Mo, W$; $R = CF_3, C_2F_5, C_6H_5, CH_3, H$)[4]; (2) the acetate-bridged complex $[(\pi\text{-}C_3H_5)Pd(O_2CCH_3)]_2$[5]; and (3) the carboxylate-chelated complexes $(\pi\text{-}C_5H_5)M(O_2CCH_3)_2$ ($M = Ti$[6], V[7]). In addition, a number of chelating dithiocarboxylate complexes of manganese and rhenium[8,9] have been reported.

The present compound, which to our knowledge appears to be the first reported example of a metal carbonyl compound containing a chelating acetate ligand, was synthesized fortuitously as the result of an unsuccessful attempt to prepare $(CH_3)_3SiMn(CO)_5$ by the reaction of $NaMn(CO)_5$ with $(CH_3)_3SiCl$ in tetrahydrofuran solvent. Berry and MacDiarmid[10] reported that although these reagents give the desired product when reacted without solvent, they yield only ill-defined red products when reacted in tetrahydrofuran[11,12]. Curtis[13] investigated the reaction of $NaMn(CO)_5$ with $(C_6H_5)_3SiCl$ in tetrahydrofuran and reported the isolation of $[(C_6H_5)_3Si]_2O$ and a compound later identified by X-ray crystallography as $[(C_2H_5)_4N]Mn_3(CO)_{14}$[14].

In our case, $(CH_3)_3SiCl$ was added to a solution of $NaMn(CO)_5$ in tetrahydrofuran, and a red solution was obtained as reported above. In an effort to stabilize the products of this reaction, a solution of triphenylphosphine and acetic acid (to protonate any anions present) in tetrahydrofuran was added. From the resulting mixture three compounds were isolated: $Mn_2(CO)_9P(C_6H_5)_3$, $Mn(CO)_3[P(C_6H_5)_3]_2Cl$, and $(CH_3CO_2)Mn(CO)_2[P(C_6H_5)_3]_2$. These products apparently result from attack by acetic acid and triphenylphosphine on the $[Mn_3(CO)_{14}]^-$ anion. The fact that both chloride [from $(CH_3)_3SiCl$] and acetate anions find their way into the final products suggests the possibility that the $[Mn_3(CO)_{14}]^-$ anion may have utility in the synthesis of a variety of manganese carbonyl complexes, by reaction with various anionic and/or neutral reagents.

The compound $(CH_3CO_2)Mn(CO)_2[P(C_6H_5)_3]_2$ was characterized by elemental analysis and by IR and NMR spectroscopy; however, since some doubt remained as to its constitution, particularly with regard to the mode of attachment of the acetate ligand, a determination of the crystal structure was carried out.

EXPERIMENTAL

Synthesis of $(CH_3CO_2)Mn(CO)_2[P(C_6H_5)_3]_2$

A solution of $NaMn(CO)_5$ was prepared by reduction of 11.7 g (30 mmol) of $Mn_2(CO)_{10}$ with 1% sodium amalgam in 200 ml of tetrahydrofuran (previously distilled over lithium aluminum hydride). A solution of 6.5 g (60 mmol) of $(CH_3)_3SiCl$ in 50 ml of tetrahydrofuran was added, and the resulting solution was stirred for 24 h during which the solution color became red. A solution of 31.5 g of $P(C_6H_5)_3$ (120 mmol) and 50 ml of acetic acid in 100 ml of tetrahydrofuran was then added to the red solution. The mixture was stirred overnight, and the solvent removed. The residue was dissolved in chloroform and filtered, and the solvent was removed from the filtrate. Addition of ether to the residue yielded orange, air-stable crystals of $(CH_3CO_2)Mn(CO)_2[P(C_6H_5)_3]_2$, which were recrystallized from a dichloromethane/heptane mixture. Yield, 2.02 g (2.91 mmol), 4.9% based on Mn; m.p. 185–186°. [Found*: C, 67.7; H, 4.74; P, 8.50; mol. wt. 700 (X-ray crystallography). $C_{40}H_{33}MnO_4P_2$ calcd.:

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C, 69.0; H, 4.75; P, 8.92%; mol. wt., 695.]

The ether was removed from the filtrate, and the residue was chromatographed over alumina. A yellow band of $Mn_2(CO)_9P(C_6H_5)_3$ was eluted with a 2/1 hexane/chloroform mixture. Yield, 3.44 g (5.52 mmol), 18.4% based on Mn. A second yellow band of $Mn(CO)_3[P(C_6H_5)_3]_2Cl$ was eluted with chloroform. Yield, 9.57 g (15.2 mmol), 25.4% based on Mn. Both $Mn_2(CO)_9P(C_6H_5)_3$ and $Mn(CO)_3[P(C_6H_5)_3]_2Cl$ were identified by comparison of their IR spectra with those given in the literature[15,16].

Similar reactions, performed with either $P(C_6H_5)(CH_3)_2$ or $P(OCH_3)_3$ used in place of $P(C_6H_5)_3$, yielded no acetate-containing products, although the expected $Mn_2(CO)_9L$ and $Mn(CO)_3L_2Cl$ products [$L=P(C_6H_5)(CH_3)_2$, $P(OCH_3)_3$] were obtained.

Spectroscopic data on $(CH_3CO_2)Mn(CO)_2[P(C_6H_5)_3]_2$

IR spectrum (Beckmann IR-10 Spectrometer): Carbonyl stretching frequencies, 1930 s, 1858 s cm^{-1} ($CHCl_3$ soln.). Other prominent peaks: 1520 w, 1437 m, 1187 m, 1092 s, 745 s, 691 m, 604 w, 570 w, 512 s cm^{-1} (Nujol mull).

NMR spectrum (Varian A-60 spectrometer, $CDCl_3$ soln.): τ 2.66, unresolved multiplet (30), (C_6H_5); τ 9.35, singlet (3), (CH_3).

Single crystal X-ray data

A single crystal of $(CH_3CO_2)Mn(CO)_2[P(C_6H_5)_3]_2$ with dimensions (each defined by the perpendicular distance between the opposite pair of crystal faces) of 0.25 mm ($10\bar{1}$), 0.19 mm ($10\bar{2}$), 0.54 mm (010), and 0.24 mm (001) was mounted about the 0.54 mm direction (corresponding to the *b*-axis) on a glass fiber with epoxy cement. Preliminary oscillation, Weissenberg, and precession photographs determined the crystal system as monoclinic. After optical and X-ray alignment[17] on a full-circle, Datex-controlled General Electric diffractometer equipped with a scintillation counter and pulse height analyzer designed to admit 90% of the Zr-filtered Mo-$K\alpha$ radiation ($\lambda=0.7107$ Å), twenty-three representative diffraction maxima were carefully centered and least-squares refined[18].

Intensity data were collected by the $\theta-2\theta$ scan technique with (stationary crystal)−(stationary counter) background counts of 15 sec taken at the beginning and end of each scan. Intensity data corresponding to four octants (hkl, $\bar{h}kl$, $\bar{h}\bar{k}l$, $h\bar{k}l$) were obtained for $3° \leqslant 2\theta \leqslant 45°$, with a scan speed of 2° per min. Because some of the peaks were quite broad, the following variable scan ranges for 2θ were used: 3.0° for $3° \leqslant 2\theta \leqslant 10°$, and 2.5° for $10° < 2\theta \leqslant 45°$.

Four standard reflections were monitored after every 100 reflections in order to check on electronic and crystal stability as well as the possibility of crystal movement. During the entire collection of the two independent data sets (*i.e.*, for monoclinic C_{2h} Laue symmetry the asymmetric reciprocal lattice of intensities consists of two octants hkl, $\bar{h}kl$, which are related to the other two measured octants $\bar{h}kl$, hkl by twofold symmetry), the intensities of the standard reflections varied by ±2%; hence, no corrections for crystal decay were made. For the 26 reflections which had intensities exceeding the linear limits of the pulse-height analyzer, intensity measurements were repeated with attenuators placed between the crystal and the counter. The proper scale factor necessary to merge these intensities with the other data was obtained by measurements with and without attenuation of the intensities of several sets of standard reflections.

The corrected intensities [*i.e.*, $I=S-[0.5(t_s/t_B)\cdot(B_1+B_2)]$ and $\sigma^2(I)=S+0.25(t_s/t_B)^2\cdot(B_1+B_2)+ISK\cdot I^2$, where S=the count associated with total scan in scan time t_s, B_1=initial background count, B_2=final background count, t_B=time taken for each background count, and ISK=instrument stability or "ignorance" factor empirically assigned a value of 0.0016] were used to calculate structure factor amplitudes, $|F_o|=(I/Lp)^{\frac{1}{2}}$, where Lp is the Lorentz-polarization factor, and their estimated standard deviations $\sigma^2(F)=\sigma^2(I)[4I\cdot Lp]^{-1}$. A given reflection was considered "unobserved" if I was less than 2.5 $\sigma(I)$. Subsequently, the corrected data of the two equivalent forms were merged[19] to give a single set of data; a $\sigma(F)$ value for each independent $|F|$, which was obtained as a weighted average with weights $1/\sigma^2(F)$, was computed as the arithmetic mean of the corresponding values for the symmetry-equivalent $|F|$'s. This procedure yielded 2624 observed and 1135 unobserved independent reflections (not including the systematic absences required by the space group); only the observed data were used in the structural determination and least-squares refinement. Based on the linear absorption coefficient[20] for Mo-$K\alpha$ radiation of 5.61 cm^{-1}, transmission factors were calculated and were found to vary in their extreme range from only 0.88 to 0.92[21]. Since this small range of values caused a maximum fluctuation of $<2\%$ in $|F_o|$'s, absorption corrections were neglected. No extinction corrections were made.

Unit cell and space group

The measured lattice constants ($\sim 23°$) with estimated precisions for the monoclinic unit cell of $(CH_3CO_2)Mn(CO)_2[P(C_6H_5)_3]_2$ are $a=17.744(2)$ Å, $b=9.692(1)$ Å, $c=20.004(2)$ Å, $\beta=106.195(4)°$; the volume of the unit cell is 3466.9 Å^3. The density of 1.332 $g\cdot cm^{-3}$, calculated on the basis of four formula species per unit cell, agrees well with the experimental value of 1.326 $g\cdot cm^{-3}$ measured by the flotation method in mixtures of carbon tetrachloride and heptane. The total number of electrons per unit cell, $F(000)$, is 1440. Systematic absences of intensity data uniquely defined the probable space group to be $P2_1/c$; substantiation of this centrosymmetric space group was subsequently provided by the determination and least-squares refinement of the crystal structure.

Determination of the structure

The crystal structure (which involved the location of one molecule as the independent unit) was solved by the heavy atom technique. A Fourier synthesis[22], phased on the independent manganese atom whose location was obtained from an interpretation of a three-dimensional Patterson map, yielded initial coordinates for both phosphorus atoms as well as two oxygen and two carbon atoms; all remaining non-hydrogen atoms were located from successive Fourier syntheses. The discrepancy factors at this point were $R_1=[\Sigma||F_o|-|F_c||/\Sigma|F_o|]\times 100=22.2\%$ and $R_2=[\Sigma w_i||F_o|-|F_c||^2/\Sigma w_i|F_o|^2]^{\frac{1}{2}}\times 100=32.6\%$. A single least-squares refinement cycle with isotropic thermal parameters was performed with a limited set of data (*viz.*, 1458 reflections for which $15°\leqslant 2\theta\leqslant 35°$). The computer program MIRAGE[23] was then used to calculate rigid-body parameters for the six phenyl groups (including the hydrogen atoms). Throughout the subsequent least-squares refinement[24], each phenyl group was constrained to an idealized geometry with only the orientation and position of the centroid of the ring allowed to vary. After three more isotropic least-squares

cycles, the discrepancy factors were $R_1 = 11.1\%$ and $R_2 = 15.0\%$. Three additional cycles, carried out with anisotropic thermal parameters for the manganese and phosphorus atoms, slightly reduced the discrepancy factors to $R_1 = 10.3\%$ and $R_2 = 14.0\%$. Finally, two cycles were performed with anisotropic thermal parameters utilized for the manganese, phosphorus, and the carbon and oxygen atoms of the carbonyl and acetate ligands. The phenyl carbon atoms were each allowed to vary only isotropically while the isotropic thermal parameter for each phenyl hydrogen atom was fixed at 3.0 Å^2. This final refinement included all data from $10° \leqslant 2\theta \leqslant 40°$, comprising 2201 observed reflections. The discrepancy factors for the last cycle were $R_1 = 8.6\%$ and $R_2 = 11.5\%$ with no parameter shifted by more than 0.2σ. A three-dimensional Fourier difference synthesis showed no positive residual electron density greater than 0.3 electrons/Å^3. The individual hydrogen atoms of the acetate methyl group were not discernible on this map. Because of the large number of additional parameters which would result either from the breaking of the rigid-body constraints imposed on each phenyl ring or the allowing of anisotropic thermal motion for each phenyl carbon atom, it was decided to terminate the least-squares refinement at this stage. Even though the rigid-body refinement of the phenyl rings does not appear to be a very good model in view of the 0.10 Å variation in the P–C bond lengths for the six phenyl rings, it was presumed that a somewhat better refinement of the structure with resulting lower discrepancy factors due to a releasing of the phenyl rings from their above-described constraints was not worth the additional estimated financial cost. Furthermore, the reasonable values obtained for the molecular parameters in the non-phenyl portion of the molecule are in accord with the observed correlations (found in the variance–covariance matrix) among the positional parameters of different non-phenyl atoms and among the positional parameters of the non-phenyl atoms and the orientational angles and origin-defining centroid of each phenyl ring being small (*i.e.*, less than 0.2) in the final least-squares refinement of this structure.

All least-squares refinements were based on the minimization of $\Sigma w_i ||F_o| - |F_c||^2$ with the individual weights assigned according to the usual relationship $w_i = 1/\sigma^2(F_o)$ where the $\sigma^2(F_o)$ were previously defined. The atomic scattering factors used for all non-hydrogen atoms are those compiled by Hanson *et al.*[25], while those used for the hydrogen atoms are from Stewart *et al.*[26]. Anomalous dispersion corrections were made for the atomic scattering factors of manganese (*viz.*, $\Delta f' = 0.4$, $\Delta f'' = 0.9$ for Mo-$K\alpha$ radiation)[27] during the last least-squares cycles.

The positional and thermal parameters obtained from the output of the last cycle of the anisotropic-isotropic least-squares refinement are presented in Table 1*. Interatomic distances and bond angles with estimated standard deviations, calculated with the Busing–Martin–Levy function and error program[28] from the full inverse matrix, are listed in Table 2. Equations of least-squares planes along with distances of selected atoms from these planes and dihedral angles are given in Table 3[29].

* The table of structure factors has been deposited as NAPS Document No. XXXXX, with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 Third Avenue, New York, New York 10022. A copy may be secured by citing the document number and by remitting $2.00 for microfiche or $5.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

TABLE 1

FINAL ATOMIC PARAMETERS[a]

Atom	*x*	*y*	*z*	*B*(Å^2)
Mn	0.7598(1)	0.5020(2)	0.2491(1)	[b]
P(1)	0.8618(2)	0.5186(3)	0.3461(1)	[b]
P(2)	0.6536(2)	0.4901(3)	0.1541(1)	[b]
O(1)	0.6952(4)	0.6152(8)	0.3012(3)	[b]
O(2)	0.7524(4)	0.7134(7)	0.2343(3)	[b]
O(3)	0.8643(5)	0.4204(9)	0.1705(4)	[b]
O(4)	0.7455(5)	0.2136(9)	0.2832(4)	[b]
C(1)	0.7091(7)	0.7253(13)	0.2727(6)	[b]
C(2)	0.6761(8)	0.8664(11)	0.2850(6)	[b]
C(3)	0.8227(6)	0.4541(12)	0.2028(5)	[b]
C(4)	0.7501(6)	0.3276(13)	0.2697(5)	[b]
C(1–1)[c]	0.8846	0.6892	0.3791	4.1(2)
C(1–2)	0.9012	0.7886	0.3344	6.5(3)
C(1–3)	0.9149	0.9248	0.3568	8.5(4)
C(1–4)	0.9140	0.9615	0.4240	7.4(3)
C(1–5)	0.8984	0.8620	0.4688	6.9(3)
C(1–6)	0.8837	0.7259	0.4463	5.0(3)
C(2–1)	0.8457	0.4243	0.4148	3.7(2)
C(2–2)	0.7696	0.4186	0.4215	5.1(3)
C(2–3)	0.7539	0.3403	0.4746	6.2(3)
C(2–4)	0.8142	0.2678	0.5209	6.0(3)
C(2–5)	0.8983	0.2735	0.5142	5.6(3)
C(2–6)	0.9061	0.3518	0.4611	4.3(2)
C(3–1)	0.9553	0.4496	0.3399	4.1(2)
C(3–2)	0.9588	0.3083	0.3278	5.3(3)
C(3–3)	1.0285	0.2491	0.3224	6.8(3)
C(3–4)	1.0947	0.3313	0.3290	7.5(4)
C(3–5)	1.0912	0.4726	0.3411	9.0(4)
C(3–6)	1.0215	0.5317	0.3465	6.7(3)
C(4–1)	0.6183	0.3174	0.1280	3.6(2)
C(4–2)	0.6735	0.2155	0.1271	4.7(2)
C(4–3)	0.6488	0.0824	0.1047	5.9(3)
C(4–4)	0.5689	0.0513	0.0833	6.3(3)
C(4–5)	0.5137	0.1533	0.0842	7.1(3)
C(4–6)	0.5384	0.2863	0.1065	5.2(3)
C(5–1)	0.5652	0.5818	0.1576	3.5(2)
C(5–2)	0.5364	0.5549	0.2144	4.9(3)
C(5–3)	0.4700	0.6243	0.2212	5.7(3)
C(5–4)	0.4326	0.7208	0.1711	6.0(3)
C(5–5)	0.4614	0.7478	0.1143	6.6(3)
C(5–6)	0.5278	0.6783	0.1076	4.5(2)
C(6–1)	0.6718	0.5630	0.0813	3.3(2)
C(6–2)	0.7075	0.6922	0.0857	5.2(3)
C(6–3)	0.7206	0.7522	0.0265	5.4(3)
C(6–4)	0.6980	0.6829	−0.0371	5.4(3)
C(6–5)	0.6623	0.5537	−0.0415	5.6(3)
C(6–6)	0.6492	0.4938	0.0176	4.6(2)
H(1–2)	0.9010	0.7598	0.2816	
H(1–3)	0.9272	1.0029	0.3217	

(continued)

TABLE 1 (*continued*)

Atom	*x*	*y*	*z*	$B(Å^2)$
H(1–4)	0.9255	1.0684	0.4416	
H(1–5)	0.8976	0.8908	0.5215	
H(1–6)	0.8714	0.6478	0.4814	
H(2–2)	0.7222	0.4755	0.3851	
H(2–3)	0.6941	0.3358	0.4799	
H(2–4)	0.8018	0.2064	0.5626	
H(2–5)	0.9377	0.2166	0.5506	
H(2–6)	0.9658	0.3563	0.4558	
H(3–2)	0.9068	0.2438	0.3226	
H(3–3)	1.0312	0.1382	0.3129	
H(3–4)	1.1495	0.2849	0.3248	
H(3–5)	1.1432	0.5371	0.3463	
H(3–6)	1.0187	0.6426	0.3560	
H(4–2)	0.7363	0.2399	0.1439	
H(4–3)	0.6922	0.0024	0.1040	
H(4–4)	0.5495	−0.0531	0.0657	
H(4–5)	0.4510	0.1288	0.0673	
H(4–6)	0.4951	0.3663	0.1072	
H(5–2)	0.5658	0.4791	0.2536	
H(5–3)	0.4474	0.6032	0.2657	
H(5–4)	0.3805	0.7754	0.1765	
H(5–5)	0.4320	0.8235	0.0751	
H(5–6)	0.5504	0.6995	0.0630	
H(6–2)	0.7252	0.7466	0.1356	
H(6–3)	0.7487	0.8536	0.0300	
H(6–4)	0.7083	0.7299	−0.0835	
H(6–5)	0.6446	0.4993	−0.0914	
H(6–6)	0.6212	0.3923	0.0142	

[a] The estimated standard deviation in the last digit is given in parentheses in this and the following Tables.
[b] Anisotropic temperature factors of the form exp $[-(\beta_{11}\cdot h^2+\beta_{22}\cdot k^2+\beta_{33}\cdot l^2+2\beta_{12}\cdot h\cdot k+2\beta_{13}\cdot h\cdot l+2\beta_{23}\cdot k\cdot l)]$ were used for the manganese and phosphorus atoms and for the carbon and oxygen atoms of the carbonyl and acetate ligands; the resulting thermal coefficients are as follows:

Atom	$10^5\ \beta_{11}$	$10^5\ \beta_{22}$	$10^5\ \beta_{33}$	$10^5\ \beta_{12}$	$10^5\ \beta_{13}$	$10^5\ \beta_{23}$
Mn	277(7)	876(23)	169(5)	−17(9)	38(4)	−53(8)
P(1)	272(11)	1000(40)	192(9)	24(17)	44(8)	79(16)
P(2)	292(12)	854(39)	168(9)	−31(17)	50(8)	−27(15)
O(1)	408(33)	1289(112)	150(22)	−182(48)	33(21)	26(41)
O(2)	498(36)	991(101)	199(23)	64(48)	87(25)	39(39)
O(3)	521(41)	237(153)	319(30)	−38(64)	183(30)	−124(54)
O(4)	653(45)	1112(120)	342(31)	−79(58)	72(27)	117(51)
C(1)	411(57)	1244(193)	184(39)	−64(84)	−21(37)	−37(72)
C(2)	1034(85)	1133(165)	381(48)	−602(94)	218(52)	−34(68)
C(3)	356(50)	1328(167)	195(36)	−60(73)	58(35)	−9(61)
C(4)	314(49)	999(163)	208(36)	19(70)	33(31)	−5(64)

[c] These individual atomic parameters are based on the refined rigid-body crystallographic coordinates for all six phenyl rings which were based on the following model. Each ring was presumed to have D_{6h} symmetry with a C–C bond length of 1.395 Å and a C–H bond length of 1.09 Å. The origin of each phenyl ring was chosen at the center of the carbon framework. An isotropic temperature factor was varied for each phenyl carbon atom, while for each phenyl hydrogen atom the isotropic temperature factor was fixed at 3.0 $Å^2$.

TABLE 2

INTERATOMIC DISTANCES AND BOND ANGLES

A. Intramolecular distances (Å)			
Mn–P(1)	2.260(3)	P(1)–C(1–1)	1.785
Mn–P(2)	2.275(3)	P(1)–C(2–1)	1.739
Mn–O(1)	2.066(6)	P(1)–C(3–1)	1.824
Mn–O(2)	2.069(7)	P(2)–C(4–1)	1.812
Mn–C(3)	1.701(12)	P(2)–C(5–1)	1.822
Mn–C(4)	1.760(13)	P(2)–C(6–1)	1.729
O(1)–C(1)	1.265(13)		
O(2)–C(1)	1.235(12)	Mn–C(1)	2.439(12)
C(1)–C(2)	1.534(15)		
C(3)–O(3)	1.156(11)		
C(4)–O(4)	1.146(11)		
B. Bond angles (°)			
P(1)–Mn–P(2)	177.4(1)	Mn–O(1)–C(1)	90.9(7)
P(1)–Mn–O(1)	87.3(2)	Mn–O(2)–C(1)	91.6(7)
P(1)–Mn–O(2)	93.2(2)	O(1)–C(1)–O(2)	115.8(10)
P(1)–Mn–C(3)	89.8(3)	O(1)–C(1)–C(2)	123.3(11)
P(1)–Mn–C(4)	88.5(3)	O(2)–C(1)–C(2)	120.9(12)
P(2)–Mn–O(1)	90.1(2)	Mn–P(1)–C(1–1)	115.4
P(2)–Mn–O(2)	85.8(2)	Mn–P(1)–C(2–1)	111.9
P(2)–Mn–C(3)	92.7(4)	Mn–P(1)–C(3–1)	116.2
P(2)–Mn–C(4)	92.0(3)	C(1–1)–P(1)–C(2–1)	105.3
O(1)–Mn–O(2)	61.6(3)	C(1–1)–P(1)–C(3–1)	104.4
O(1)–Mn–C(3)	163.7(5)	C(2–1)–P(1)–C(3–1)	102.3
O(1)–Mn–C(4)	106.7(4)	Mn–P(2)–C(4–1)	115.3
O(2)–Mn–C(3)	102.5(4)	Mn–P(2)–C(5–1)	117.7
O(2)–Mn–C(4)	168.1(4)	Mn–P(2)–C(6–1)	112.2
C(3)–Mn–C(4)	89.3(5)	C(4–1)–P(2)–C(5–1)	103.3
Mn–C(3)–O(3)	178.8(10)	C(4–1)–P(2)–C(6–1)	105.4
Mn–C(4)–O(4)	178.4(10)	C(5–1)–P(2)–C(6–1)	101.4

RESULTS AND DISCUSSION

General description of the crystal and molecular structure

The crystal structure of $(CH_3CO_2)Mn(CO)_2[P(C_6H_5)_3]_2$ consists of discrete molecules possessing the geometry depicted in Fig. 1. The coordination about the central Mn^I atom may be best described as distorted octahedral with the acetate anion acting as a chelating four-electron donor ligand. The two carbonyl groups occupy two coordination sites which are approximately coplanar with the acetate ligand, while the two phosphine ligands occupy the two remaining *trans*-sites perpendicular to the plane of the acetate and two carbonyl ligands. The architecture of the $(CH_3CO_2)Mn(CO)_2[P(C)_3]_2$ core (*i.e.*, with exclusion of the phenyl rings for clarity) together with the principal bond lengths and bond angles is presented in Fig. 2. An [010] projection of the unit cell is shown in Fig. 3. (These diagrams were computer-drawn[30]). The intermolecular packing is determined primarily by Van der Waals forces as suggested by the intermolecular distances which show no CO···C(phenyl) contacts shorter than 3.40 Å and no C(phenyl)···C(phenyl) separations shorter than 3.18 Å.

TABLE 3

EQUATIONS OF "BEST" LEAST-SQUARES PLANES, DISTANCES OF ATOMS FROM THESE PLANES, AND DIHEDRAL ANGLES BETWEEN THE NORMALS OF THESE PLANES[a,b]

A. Equations of planes and distances (Å) of selected atoms from these planes

(*a*) Plane through Mn, C(1), C(2), O(1), and O(2)

$0.617X + 0.145Y + 0.773Z - 11.895 = 0$

Mn	0.03	O(3)	−0.11
O(1)	−0.02	O(4)	−0.20
O(2)	−0.02	C(3)	−0.02
C(1)	0.00	C(4)	0.14
C(2)	0.02	P(1)	−2.22
		P(2)	2.29

(*b*) Plane through Mn, C(3), C(4), O(3), and O(4)

$0.569X + 0.099Y + 0.816Z - 11.267 = 0$

Mn	0.00	O(1)	−0.11
O(3)	−0.01	O(2)	−0.06
O(4)	−0.01	C(1)	0.00
C(3)	−0.01	C(2)	0.05
C(4)	0.01	P(1)	−2.26
		P(2)	2.27

(*c*) Plane through Mn, C(1), C(2), C(3), C(4), O(1), O(2), O(3), and O(4)

$0.577X + 0.107Y + 0.810Z - 11.376 = 0$

Mn	0.00	C(1)	0.00
O(1)	−0.10	C(2)	0.04
O(2)	0.04	C(3)	−0.02
O(3)	0.02	C(4)	0.03
O(4)	0.03	P(1)	−2.26
		P(2)	2.27

B. Dihedral angles (°) between normals to planes

(*a*) and (*b*)	4.6	(*b*) and (*c*)	0.8
(*a*) and (*c*)	3.8		

C. Dihedral angles (°) between Mn–P(1) and Mn–P(2) axes and normals to planes

Mn–P(1) and (*a*)	6.1	P(1)···P(2) and (*a*)	5.8
Mn–P(1) and (*b*)	1.7	P(1)···P(2) and (*b*)	2.2
Mn–P(1) and (*c*)	2.4	P(1)···P(2) and (*c*)	2.7
Mn–P(2) and (*a*)	174.2		
Mn–P(2) and (*b*)	176.8		
Mn–P(2) and (*c*)	176.6		

[a] The equations of the planes are given in an orthogonal Ångström coordinate system (X,Y,Z) which is related to fractional coordinates (x,y,z) of the monoclinic unit cell by the following transformation: $X = a \cdot x + c \cdot z \cdot \cos\beta$, $Y = b \cdot y$, and $Z = c \cdot z \cdot \sin\beta$. [b] Unit weights were used for all atoms in the application of the Smith least-squares planes program[29].

The acetate ligand is symmetrically linked to the manganese atom with experimentally-equivalent Mn–O bond lengths of 2.066(6) and 2.069(7) Å. The average value of 2.068 Å is significantly longer than the average value of 1.894 Å found[31] for the Mn–O bond lengths in tris(acetylacetonato)manganese(III). The non-bonding distance from the manganese atom to the central trigonal carbon atom, C(1), of the acetate ligand is 2.439(12) Å. The orientation of the acetate ligand with respect to the Mn^{I} is in agreement with that sterically expected for trigonal hybridization of each of the two acetate oxygen atoms thereby making it possible for the π-electron delocalization of the acetate ligand to include the Mn atom (*vide infra*). The two carbon and

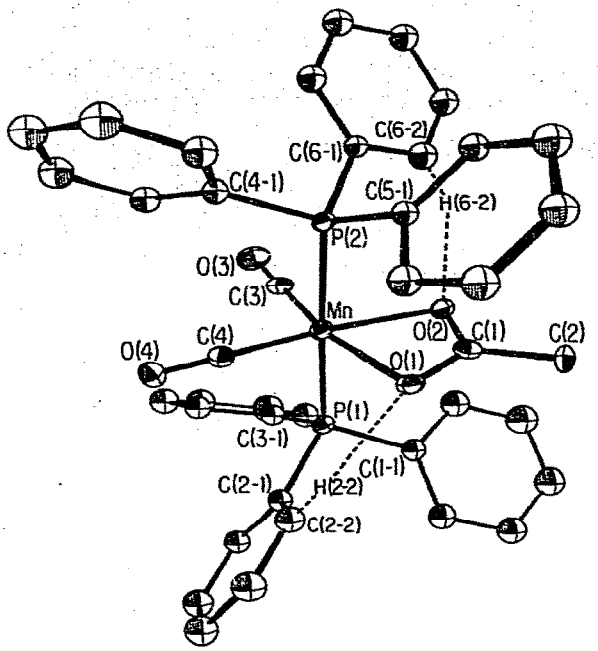

Fig. 1. Molecular configuration of $(CH_3CO_2)Mn(CO)_2[P(C_6H_5)_3]_2$.

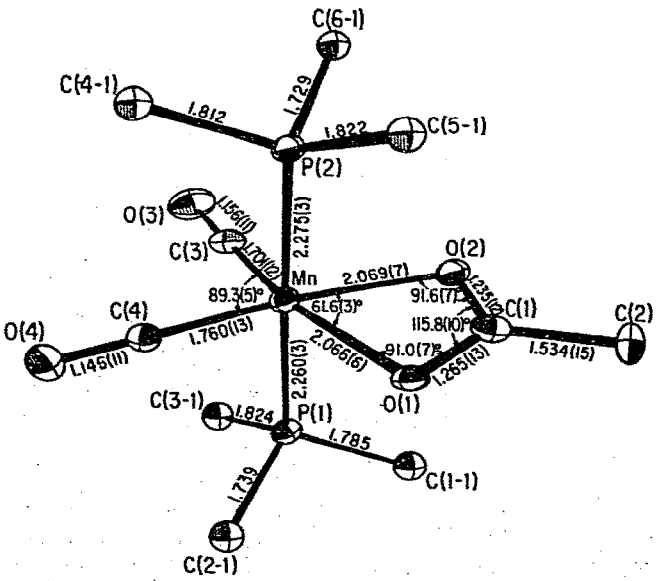

Fig. 2. Molecular parameters for the $(CH_3CO_2)Mn(CO)_2[P(C)_3]_2$ core (*i.e.*, the phenyl rings are omitted for clarity).

two oxygen atoms of the acetate ligand and the manganese atom are all within 0.03 Å of being co-planar [Table 3(a)]. The observation that the two Mn–O–C(1) bond angles of 91.0(7) and 91.6(7)° are considerably less than the idealized trigonal bond

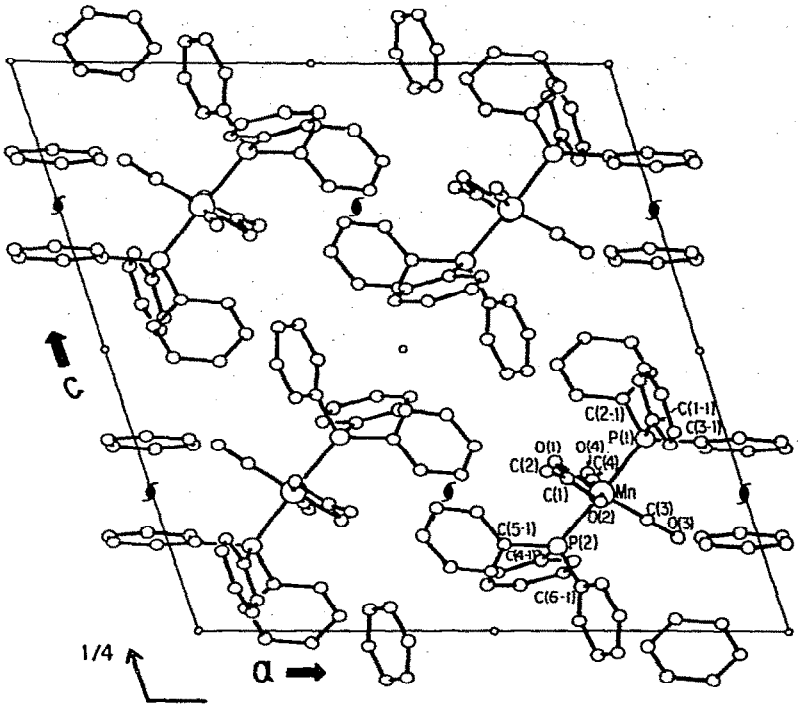

Fig. 3. [010] projection showing the four $(CH_3CO_2)Mn(CO)_2[P(C_6H_5)_3]_2$ molecules in the monoclinic unit cell of symmetry $P2_1/c$.

angle of 120° may be ascribed to the angular distortions imposed by the resulting four-membered MnO_2C ring system. The O(1)–C(1)–O(2) bond angle of 115.8(10)° is not appreciably smaller than the idealized value of 120° expected for a regular trigonal carbon atom. The two C(1)–O(1) and C(1)–O(2) bond lengths are 1.265(13) and 1.235(12) Å, respectively; the mean value of 1.25 Å is in accord with that contemplated for an electron-delocalized acetate ligand. The O(1)···O(2) "bite" of the acetate ligand is 2.12 Å.

The acetate carbon and oxygen atoms and the manganese atom lie very nearly in the same plane with the two carbonyl ligands, the maximum perpendicular displacement of the nine atoms from the "mean" plane being only 0.04 Å except for one acetate oxygen atom with a perpendicular deviation of 0.10 Å [Table 3(c)]. The approximately perpendicular orientation of the two phosphorus atoms to the "in-plane" carbonyl and acetate groups is evident from the vector defined by the two phosphorus atoms making an angle of 87.3° with the above "mean" plane.

The bond angles around the Mn are all reasonably close to 90° except for the expectedly acute bond angle of 61.6(3)° subtended at the Mn by the two acetate oxygen atoms and the "in-plane" O(1)–Mn–C(4) and O(2)–Mn–C(3) bond angles of 106.7(4) and 102.5(4)°, respectively; the diametrically opposite "in-plane" OC–Mn–CO bond angle is 89.3(5)°.

The two *trans* triphenylphosphine ligands in $(CH_3CO_2)Mn(CO)_2[P(C_6H_5)_3]_2$ are essentially equidistant from the Mn with one Mn–P bond length of 2.260(3) Å and

the other of 2.275(3) Å. As in other organometallic complexes containing triphenylphosphine ligands, the six Mn–P–C(phenyl) bond angles of range 111.9°–117.7° and of average value 114.8° are somewhat greater than the regular tetrahedral angle of 109.5°, while the six (phenyl)C–P–C(phenyl) bond angles of range 101.4°–105.4° and of average value of 103.7° are somewhat less. The six P–C(phenyl) distances vary from 1.729 to 1.824 Å with a mean value of 1.785 Å.

One prime structural feature of possible chemical significance is the indication from bond lengths that two *intramolecular* hydrogen bonds occur in the (CH_3CO_2)-$Mn(CO)_2[P(C_6H_5)_3]_2$ molecule (Fig. 1). These involve an *ortho*-hydrogen atom of one phenyl ring (*i.e.*, a hydrogen attached to one of the two carbon atoms adjacent to the phosphorus-attached carbon atom) of one triphenylphosphine ligand interacting with one acetate oxygen atom and an *ortho*-hydrogen atom of one phenyl ring of the other triphenylphosphine ligand interacting with the other acetate oxygen atom. One of these (phenyl)C–H–O(acetate) interactions is evidenced by a C(2–2)–O(1) distance of 3.07 Å, a H(2–2)–O(1) distance of 2.11 Å, and a C(2–2)–H(2–2)–O(1) angle of 144.6°, while the other is evidenced by a C(6–2)–O(2) distance of 2.86 Å, a H(6–2)–O(2) distance of 1.92 Å, and a C(6–2)–H(6–2)–O(2) angle of 141.4°. Despite there being some uncertainty in these calculated distances and angles due to a rigid-body model being assumed for each phenyl ring with idealized carbon and hydrogen positions, it is noteworthy that one possible manifestation of this indicated intramolecular hydrogen bonding for the two involved phenyl rings is that their Mn–P–C-(phenyl) bond angles of 111.9 and 112.2° are less obtuse than the other four Mn–P–C-(phenyl) bond angles which range from 115.3 to 117.7°.

The Mn–CO bond lengths are 1.701(12) and 1.760(13) Å; the mean value of 1.73 Å appears significantly shorter than the average values found for the Mn–CO bond lengths in a number of $Mn(CO)_5X$ and other manganese carbonyl complexes[32–34] {*i.e.*, the average values range from 1.79 to 1.87 Å[32] except for $Mn(CO)_5[Sn(C_6H_5)_3]$[33] where the mean value of 20 independent measurements is 1.76 Å}. The bonding implications of these short Mn–CO distances in $(CH_3CO_2)Mn(CO)_2[P(C_6H_5)_3]_2$ are discussed in the next section. The two C–O bond lengths of 1.146(11) and 1.156(11) Å are virtually identical and are within the terminal carbonyl bond length range found in highly precise structural analyses of certain metal carbonyl complexes. The essential linearity of the bonds is evident from the observed bond angles of 178.4 (10) and 178.8(10)°.

Stereochemistry and bonding implications in the $(CH_3CO_2)Mn(CO)_2[P(C_6H_5)_3]_2$ and related manganese carbonyl triphenylphosphine complexes

Salient structural features of $(CH_3CO_2)Mn(CO)_2[P(C_6H_5)_3]_2$ are the relatively long Mn–CO and Mn–$P(C_6H_5)_3$ bond lengths compared to the Mn–CO and Mn–$P(C_6H_5)_3$ bond lengths in other manganese carbonyl triphenylphosphine complexes. The Mn–O(acetate) bond lengths are ca. 0.2–0.3 Å longer than the terminal Mn–CO bond lengths in the same molecule as well as in all the other structurally determined manganese carbonyl complexes. In contrast to the short Mn–CO bond lengths being attributed primarily to the extensive π-acceptor ability of the carbonyl ligands (by virtue of their energetically available antibonding π^* orbitals), the much longer Mn–O(acetate) bond lengths indicate little multiple bond character for the oxygen-chelating acetate ligand either as a π-acceptor or as a π-donor. Further sup-

port for this hypothesis is given by the average Mn–O(acetate) bond length being 0.17 Å longer than the average Mn–O bond length found in tris(acetylacetonato)manganese(III)[31] (*vide supra*). This conclusion that the acetate ligand functions primarily as a σ-donor in $(CH_3CO_2)Mn(CO)_2[P(C_6H_5)_3]_2$ is in harmony with our belief that the acetate ligand energetically cannot compete with the carbonyl ligands as a π-acceptor and that the filled π-donor orbitals of the acetate ligand are too much lower in energy than either the π^*-acceptor orbitals of the carbonyls or the 3*d*-acceptor orbitals of the triphenylphosphine ligands for the MO's to allow much transmission of electron density from the acetate ligand to the other ligands through the π-orbital framework of the molecule.

The effect of considerable σ-donation by the acetate group is to increase the electron density on the central manganese atom. This accumulation of charge on the manganese may be reduced through greater π-backbonding onto both the carbonyl and triphenylphosphine ligands. An examination in Table 4 of relevant $Mn–P(C_6H_5)_3$ and Mn–CO bond lengths in this and other structurally determined manganese carbonyl triphenylphosphine molecules[35–38] (whose geometries with appropriate bond lengths are given in Fig. 4) indicates notable bond-length variations. These observable alterations may be correlated qualitatively on the basis of the expected σ- and π-bonding characteristics of the specific ligands comprising the octahedral-like or (trigonal bipyramidal)-like environment about the manganese atom. The shorter $Mn–P(C_6H_5)_3$ bond lengths are seen to occur for those complexes in Table 4 for which the triphenylphosphine ligand is *trans* to another triphenylphosphine ligand or *trans* to a $Sn(C_6H_5)_3$ ligand rather than *trans* to a carbonyl ligand which is a much better π-acceptor. The changes in Mn–CO bond lengths follow the same kind of pattern with the shortest distances detected for the carbonyl ligands *trans* to the acetate oxygen atoms in $(CH_3CO_2)Mn(CO)_2[P(C_6H_5)_3]_2$ and for the carbonyl groups *trans* to the triphenylphosphine and chlorine ligands (but not *trans* to another carbonyl group) in $Mn(CO)_4[P(C_6H_5)_3]Cl$. It is especially interesting that an indication in support of the Fenske premise[39] that the bonding characteristics are dependent upon the total molecular environment is given by comparison of the $Mn–P(C_6H_5)_3$ and Mn–CO

TABLE 4

$Mn–P(C_6H_5)_3$ AND Mn–CO BOND LENGTHS IN SEVERAL MANGANESE CARBONYL TRIPHENYLPHOSPHINE COMPLEXES

A. $Mn–P(C_6H_5)_3$ bond lengths (Å)	
$(CH_3CO_2)Mn(CO)_2[P(C_6H_5)_3]_2$[a]	(P *trans* to P) 2.260(3), 2.275(3)
$Mn(CO)_2[P(C_6H_5)_3]_2(NO)$[c]	(P *trans* to P) 2.278(5), 2.279(5)
$Mn(CO)_4[P(C_6H_5)_3][Sn(C_6H_5)_3]$[b]	(P *trans* to Sn) 2.267(19)
$Mn(CO)_3[P(C_6H_5)_3](NO)$[d]	(P *trans* to CO) 2.305(4)
$Mn(CO)_4[P(C_6H_5)_3]Cl$[e]	(P *trans* to CO) 2.398(4)
B. Mn–CO bond lengths (Å)	
$(CH_3CO_2)Mn(CO)_2[P(C_6H_5)_3]_2$[a]	[CO *trans* to O (acetate)] 1.701(12), 1.760(13)
$Mn(CO)_3[P(C_6H_5)_3](NO)$[d]	(CO *trans* to P) 1.833(11)
$Mn(CO)_4[P(C_6H_5)_3]Cl$[e]	(CO *trans* to P) 1.752(14)
	(CO *trans* to Cl) 1.752(15)
	(CO *trans* to CO) 1.819(15), 1.859(13)

[a] This work. [b] Ref. 35. [c] Ref. 36. [d] Ref. 37. [e] Ref. 38.

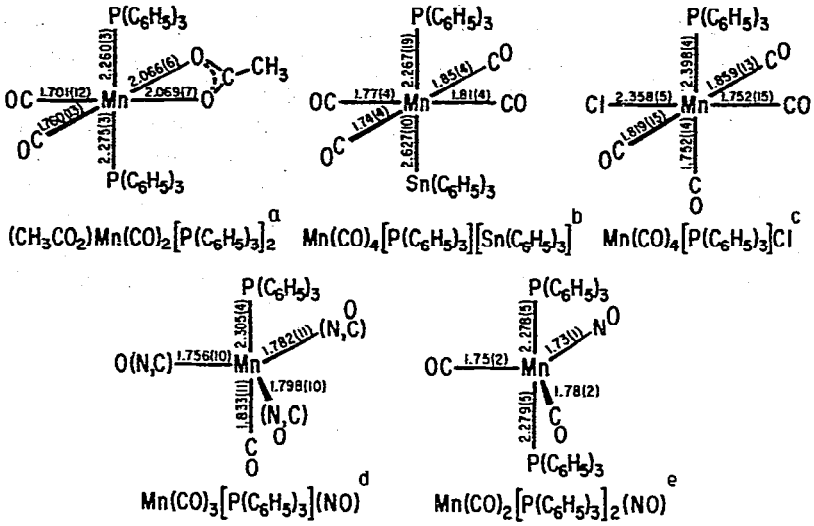

Fig. 4. Comparison of the configuration and appropriate bond lengths with those of related manganese carbonyl triphenylphosphine complexes ([a] this work; [b] ref. 35; [c] ref. 36; [d] ref. 37; [e] ref. 38). For the $Mn(CO)_3[P(C_6H_5)_3](NO)$ complex[37], the one equatorial nitrosyl ligand and two equatorial carbonyl ligands are not distinguishable.

bonds *trans* to each other in the octahedral-like $Mn(CO)_4[P(C_6H_5)_3]Cl$ molecule with the corresponding axial bonds in the (trigonal bipyramidal)-like $Mn(CO)_3[P(C_6H_5)_3](NO)$ molecule. Whereas the $Mn-P(C_6H_5)_3$ bond length is significantly longer by 0.095 Å in the former octahedral-like molecule, the Mn–CO bond length is significantly shorter by 0.081 Å. An explanation of these opposite trends in bond lengths is not obvious.

An unusual facet of the acetate ligand in $(CH_3CO_2)Mn(CO)_2[P(C_6H_5)_3]_2$ is the rather far-upfield position of the acetate methyl resonance in its NMR spectrum at 9.35τ, as compared with ca. 8.0τ for other metal acetate complexes[40,41]. From the previously described structural features and resulting interpretations, the higher shielding of the methyl protons of the acetate ligand in $(CH_3CO_2)Mn(CO)_2[P(C_6H_5)_3]_2$ is *not* deemed to be a consequence of greater π-backbonding from the metal to the acetate group. The most likely rationalization for the observed NMR chemical shift (kindly pointed out to us by one referee) would appear to be shielding effects due to ring currents from the phenyl rings proximate to the acetate ligand.

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