

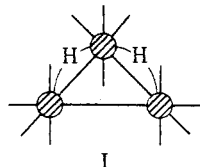
Preparation and Structure Determination of the $[\text{Mn}_3(\text{CO})_{14}]^-$ Anion. Comments on Staggered *vs.* Eclipsed Carbonyl Groups and Linear *vs.* Bent M-M-M and M-H-M Bonds

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Abstract: Treatment of $\text{H}_3\text{Mn}_3(\text{CO})_{12}$ with alcoholic base gives not the expected $[\text{H}_2\text{Mn}_3(\text{CO})_{12}]^-$ anion but the $[\text{Mn}_3(\text{CO})_{14}]^-$ anion in low yield. The structure of the $[\text{Mn}_3(\text{CO})_{14}]^-$ anion, isolated as its $[\text{Ph}_4\text{As}]^+$ salt, was determined *via* X-ray diffraction methods. Its geometry is shown to be essentially D_{3h} , with the three manganese atoms collinear, just as in the isoelectronic $\text{Mn}_2\text{Fe}(\text{CO})_{14}$. The equatorial CO groups on the terminal manganese are staggered with respect to those on the central manganese and are bent away from the axial CO groups. These observations are rationalized in terms of a model in which the interactions between a metal atom and carbonyl groups on a neighboring metal atom play a large part. Besides the staggered *vs.* eclipsed problem, the questions of linear *vs.* bent M-H-M linkages and linear *vs.* bent M-M-M skeletons are also discussed. Crystal data: unit cell triclinic; space group $P\bar{1}$; $a = 11.614(11)$, $b = 9.646(12)$, $c = 18.022(22)$ Å; $\alpha = 100.89(5)$, $\beta = 96.66(6)$, $\gamma = 90.96(5)^\circ$; $\rho_{\text{obsd}} = 1.60(1)$, $\rho_{\text{calcd}} = 1.587$ g cm⁻³ for $Z = 2$ and $V = 1968$ Å³; final R factor = 9.2% for 1414 nonzero reflections.

Our recent crystallographic determination of the hydrogen atom positions in $\text{H}_3\text{Mn}_3(\text{CO})_{12}$ ^{2a} prompted us to extend our studies to the anion $[\text{H}_2\text{Mn}_3(\text{CO})_{12}]^-$. In 1968 we had studied the structure of the analogous rhenium anion $[\text{H}_2\text{Re}_3(\text{CO})_{12}]^-$;^{2b} in that compound, the hydrogen atoms could not be detected directly but were inferred to exist in doubly bridging positions (as in I) because of certain molecular distor-



tions. It was our intention to extend this work to the $[\text{H}_2\text{Mn}_3(\text{CO})_{12}]^-$ anion in the hope that the hydrogen atom positions, if located, would provide confirmation for our earlier conclusions.

Since $[\text{H}_2\text{Re}_3(\text{CO})_{12}]^-$ was obtained by treatment of $\text{H}_3\text{Re}_3(\text{CO})_{12}$ with ethanolic KOH and isolated as its $[\text{Ph}_4\text{As}]^+$ salt by addition of $[\text{Ph}_4\text{As}]\text{Cl}$,^{2b} a similar reaction was run using $\text{H}_3\text{Mn}_3(\text{CO})_{12}$ in place of $\text{H}_3\text{Re}_3(\text{CO})_{12}$.³ This produced, in small yield, an air-sensitive red-orange crystalline material which turned out to be not the desired $[\text{Ph}_4\text{As}][\text{H}_2\text{Mn}_3(\text{CO})_{12}]^-$ but $[\text{Ph}_4\text{As}][\text{Mn}_3(\text{CO})_{14}]^-$. The structure determination of this compound is described here.

Experimental Section

All operations and manipulations were conducted under an atmosphere of nitrogen. All solvents were carefully dried and

degassed. Infrared spectra were obtained on a Perkin-Elmer 457 grating spectrophotometer. Conductivity measurements were made using a YSI Model 31 conductivity bridge.

Preparation⁵ of $[\text{Ph}_4\text{As}]^+[\text{Mn}_3(\text{CO})_{14}]^-$. To a stirred suspension of $\text{H}_3\text{Mn}_3(\text{CO})_{12}$ (0.5 g, 1.0 mmol) in 200 ml of absolute ethanol was added 10 ml of a 0.1 M solution of NaOH in ethanol. After 1 hr, the ethanol was evaporated under reduced pressure, the residue dissolved in the minimum amount of THF, and the solution filtered. $[\text{Ph}_4\text{As}]\text{Cl}$ (1.0 mmol) in a solution of 10 ml of ethanol was added, and the solution was concentrated and cooled to give several milligrams of the product as red crystals.⁷ Infrared data⁸ (acetone solution): 2073 (vw), 2037 (m), 1973 (vs), 1938 (m, br), 1884 (vw) cm⁻¹. Conductivity measurements (Table I) were consistent with the formulation of the compound as a 1:1 electrolyte.

Collection and Reduction of the X-Ray Data. The crystal used was a tiny parallelepiped, approximate dimensions 0.10 × 0.08 × 0.05 mm, mounted in a thin-walled glass capillary of diameter 0.1 mm. Weissenberg and precession photographs indicated a triclinic crystal system. The unit cell parameters, obtained by carefully measuring the setting angles of 28 reflections on a Nonius CAD-3 automated diffractometer, are given together with other relevant crystal data in Table II.

One hemisphere of data was collected by the $\theta/2\theta$ scan technique using Zr-filtered Mo K α radiation up to a 2θ limit of 40°. A total

(5) After it had become known that the anion in question was $[\text{Mn}_3(\text{CO})_{14}]^-$ and not $[\text{H}_2\text{Mn}_3(\text{CO})_{12}]^-$, it was found that much better yields could be obtained by using Curtis' method of treating $\text{NaMn}(\text{CO})_5$ with Ph_3SiCl .⁶ This yields a compound that was originally formulated as the bent (or cis) form of $[\text{Mn}_3(\text{CO})_{14}]^-$ but which is now known^{6c} to be the linear (or trans) form of $[\text{Mn}_3(\text{CO})_{14}]^-$.

(6) (a) M. D. Curtis, *Inorg. Nucl. Chem. Lett.*, **6**, 859 (1970); (b) M. D. Curtis, *Inorg. Chem.*, **11**, 802 (1972); (c) M. D. Curtis, submitted for publication.

(7) The chemical analyses were performed on the $[(\text{C}_2\text{H}_5)_4\text{N}][\text{Mn}_3(\text{CO})_{14}]^-$ crystals obtained in a completely analogous manner. *Anal.* Calcd: Mn, 23.98; C, 38.45; H, 2.91; N, 2.04. Found: Mn, 25.38; C, 38.66; H, 2.88; N, 2.03. The analyses were conducted by Schwarzkopf Microanalytical Laboratory and by PRC, Inc.

(8) The compound is extremely sensitive to air in solution, and decomposes in the ir cells even during the several minutes necessary to obtain the spectrum. Extraneous bands often appear at 2014, 1899, and 1861 cm⁻¹ which are probably due to $\text{Mn}_2(\text{CO})_{10}$ and $[\text{Mn}(\text{CO})_5]^-$. In the solid state and under N₂ the compound is indefinitely stable.

(9) The diffraction pattern was extremely weak, extending to a maximum $\sin \theta/\lambda$ value of only 0.45 Å⁻¹. This is due to the fact that the crystals were both small and mediocre in quality, an unavoidable consequence of the instability of the material, which necessitated a hurried crystal growth process. Consequently, (i) the data were taken only up to a maximum 2θ value of 40°, (ii) about half of the reflections were unobserved, and (iii) the final R factor is higher than what we would have preferred.

(1) (a) University of Southern California; (b) New College.
(2) (a) S. W. Kirtley, J. P. Olsen, and R. Bau, *J. Amer. Chem. Soc.*, **95**, 4532 (1973); (b) M. R. Churchill, P. H. Bird, H. D. Kaesz, R. Bau, and B. Fontal, *ibid.*, **90**, 7135 (1968).

(3) A photolytic preparation of $[\text{H}_2\text{Mn}_3(\text{CO})_{12}]^-$ had been reported earlier (see ref 4). We suspect, however, that this material may in fact be identical with the $[\text{Mn}_3(\text{CO})_{14}]^-$ anion described in this paper (see text).

(4) G. O. Evans, J. Slater, D. Giusto, and R. K. Sheline, *Inorg. Nucl. Chem. Lett.*, **7**, 771 (1971).

Table I. Conductivity Data for $[\text{Ph}_4\text{As}][\text{Mn}_3(\text{CO})_{14}]$

$C (M \times 10^6)$	$\sqrt{C} (\times 10^3)$	$L (\mu\text{mhos})$	$\Lambda (\times 10^{-2})$	$\Lambda_0 - \Lambda (\times 10^{-2})$
(a) $[\text{Ph}_4\text{As}][\text{Mn}_3(\text{CO})_{14}]$; Mol Wt = 940.4				
8.80	9.38	10.22	1.16	4.16
6.60	8.12	11.55	1.75	3.55
4.95	7.04	10.85	2.19	3.13
3.71	6.09	9.75	2.63	2.69
2.78	5.27	8.25	2.97	2.35
(b) $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{I}$; Mol Wt = 369.4 (used as standard)				
7.24	8.5	17.0	2.35	3.74
5.43	7.4	14.0	2.58	3.51
4.07	6.4	12.1	2.97	3.12
3.05	5.5	10.5	3.44	2.65
2.29	4.8	9.4	4.10	1.98

Table II. Crystal Data for $[\text{Ph}_4\text{As}][\text{Mn}_3(\text{CO})_{14}]$

$a = 11.614 (11) \text{ \AA}$	Mol wt = 940.4
$b = 9.646 (12) \text{ \AA}$	Space group = $P\bar{1}$
$c = 18.022 (22) \text{ \AA}$	$Z = 2$
$\alpha = 100.89 (5)^\circ$	$F(000) = 936$
$\beta = 96.66 (6)^\circ$	$\rho(\text{obsd})^a = 1.60(1) \text{ g cm}^{-3}$
$\gamma = 90.96 (5)^\circ$	$\rho(\text{calcd}) = 1.587 \text{ g cm}^{-3}$
$V = 1968 \text{ \AA}^3$	$\mu(\text{Mo K}\alpha) = 12.28 \text{ cm}^{-1}$

^a Obtained by flotation from a mixture of carbon tetrachloride and *o*-diiodobenzene.

of 2850 reflections (including 136 check reflections) was collected in the following manner: (1) a scan speed of $10^\circ/\text{min}$ was used; (2) the scan range was defined as $\Delta\theta = 1.2 + 0.15 \tan \theta$; (3) background counts were taken at the beginning and the end of each scan (the time taken for counting each background was precisely one-quarter of the time taken for the scan itself); (4) the number of scans for each reflection varied between two and ten, depending on the intensity of the reflection (weak reflections were scanned more often than strong ones); (5) zirconium-foil attenuators were automatically inserted if the counting rate exceeded 2500 counts/sec; (6) a takeoff angle of 4° was used.

Three check reflections which were monitored at 20-reflection intervals showed no significant variation in intensity. The standard deviation of each intensity reading, $\sigma(F_o^2)$, was estimated using the expression¹⁰

$$\sigma(F_o^2) = [(peak + background \text{ counts}) + 0.04(\text{net intensity})^2]^{1/2}$$

Reflections whose net intensities were less than 3σ were considered unobserved and were not included in the subsequent structure analysis. About half the collected data were removed because of this.⁹ The linear absorption coefficient for Mo K α radiation is 12.28 cm^{-1} , and from a calculation of transmission coefficients for selected reflections it was concluded that absorption corrections were unnecessary. This was confirmed by the observation that the intensity of an axial reflection (at $\chi = 90^\circ$) showed essentially no variation with ϕ . The intensities were further corrected for Lorentz and polarization effects and placed on an approximately absolute scale by means of a Wilson plot. At the end of data reduction, 1414 nonzero reflections were left.

Solution and Refinement of the Structure.¹¹ At the outset of the structure analysis, it was believed that the compound under study was $[\text{Ph}_4\text{As}][\text{H}_2\text{Mn}_3(\text{CO})_{12}]$. The close similarities between the ir spectrum of our compound (acetone solution) and the reported spectrum of $[\text{H}_2\text{Mn}_3(\text{CO})_{12}]^-$ (THF solution)⁴ certainly reinforced this belief. Consequently, the Patterson analysis was undertaken with the aim of locating four independent heavy-atom positions in the space group $P\bar{1}$ ($Z = 2$), three of the expected heavy atoms being clustered together in a triangular arrangement and the

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

(11) The major computations in this work were performed using CRYM, an amalgamated set of crystallographic programs developed by Dr. Richard Marsh's group at the California Institute of Technology.

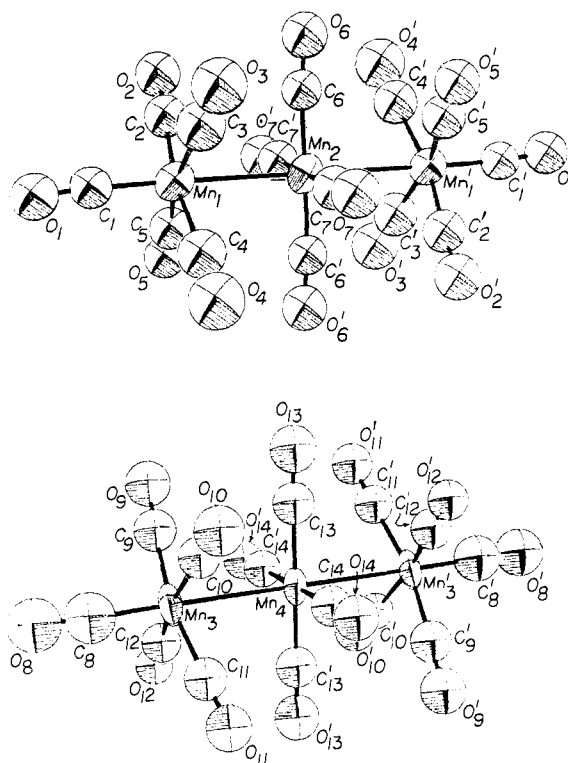


Figure 1. Separate ORTEP plots of the two independent $[\text{Mn}_3(\text{CO})_{14}]^-$ anions: (top) the $\text{Mn}_1\text{Mn}_2\text{Mn}_1'$ anion; (bottom) the $\text{Mn}_3\text{Mn}_4\text{Mn}_3'$ anion. Atoms $\text{Mn}_2 (0, 0, 0)$ and $\text{Mn}_4 (0, 0, 1/2)$ are crystallographic centers of symmetry (inversion centers).

fourth one (arsenic) substantially removed from the other three. A problem of this type is normally approached by searching the Patterson map in regions approximately 3 \AA from the origin for the presence of the three independent peaks characteristic of a triangular framework. To our surprise, there were not three, but only two independent peaks situated 3 \AA from the origin.

Other trinuclear models were then tried. An L-shaped skeleton [as in $\text{HRe}_2\text{Mn}(\text{CO})_{14}$]¹² would have predicted two Patterson peaks at $\sim 3 \text{ \AA}$ from the origin, plus a third at $\sim 4.2 \text{ \AA}$. This was rejected because a 4.2-\AA peak was not found. The idea of having a linear Mn_3 framework occurred to us for a while, but this was quickly rejected also because only one 3-\AA Patterson peak would have been expected with all three Mn atoms at general positions (positions $2i$ in $P\bar{1}$).

At this point, the alternative space group $P1$ was considered. Since the Patterson was clearly inconsistent with the original formulation $[\text{H}_2\text{Mn}_3(\text{CO})_{12}]^-$, we no longer felt it necessary to restrict the analysis solely to a consideration of Mn_3 species. We speculated that the compound might be a dimeric species, perhaps $[\text{Ph}_4\text{As}][\text{HMn}_2(\text{CO})_8] \cdot 3\text{THF}$. Consequently, a fresh attempt was made to solve the Patterson in space group $P1$, using a model containing two independent As atoms and two independent Mn_2 groups in the unit cell. This model fitted the Patterson very well. All the major peaks of the Patterson could be explained with the following atomic arrangement: Mn atoms at $(0.000, 0.000, 0.000)$, $(0.105, -0.186, 0.116)$, $(0.099, -0.149, 0.605)$, and $(-0.140, -0.069, 0.602)$; and As atoms at $(-0.332, -0.645, 0.348)$ and $(0.529, 0.329, 0.883)$. A structure factor calculation phased by this atomic arrangement gave a fairly respectable R factor of 36.2% .¹³ A difference Fourier map at this stage, however, revealed two more Mn atoms, each attached linearly to an Mn_2 group. Shifting the origin of the coordinate system to one of the central Mn atoms now revealed the true picture for the first time; the correct space group is the centrosymmetric $P\bar{1}$ after all, with one of the linear Mn_3 groups centered around the special position $(0, 0, 0)$, the other Mn_3 group centered around a different special position $(0, 0, 1/2)$, and

(12) (a) H. D. Kaesz, R. Bau, and M. R. Churchill, *J. Amer. Chem. Soc.*, **89**, 2775 (1967); (b) M. R. Churchill and R. Bau, *Inorg. Chem.*, **6**, 2086 (1967).

(13) $R = (\sum |F_o| - |F_c|) / (\sum |F_o|)$.

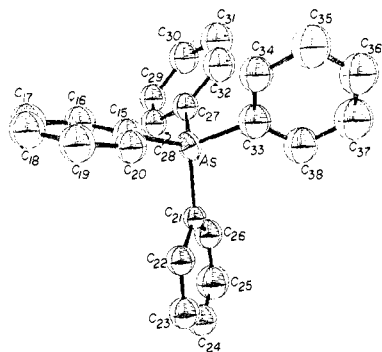


Figure 2. ORTEP plot of the Ph_4As^+ cation.

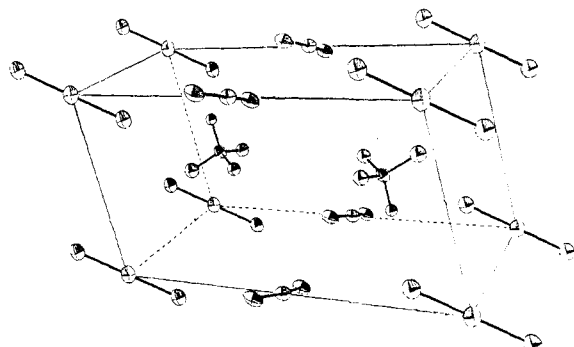


Figure 3. The arrangement of atoms in the unit cell of $[\text{Ph}_4\text{As}][\text{Mn}_3(\text{CO})_{14}]$ (for clarity, each anion is represented as an Mn-Mn-Mn group and each cation is drawn as an AsC_4 group). The $\text{Mn}_1\text{Mn}_2\text{Mn}_3$ anions sit at the corners (0, 0, 0) and the $\text{Mn}_3\text{Mn}_4\text{Mn}_3'$ anions at the edges (0, 0, $\frac{1}{2}$) of the unit cell. The two AsC_4 groups are completely contained within the unit cell. The net content of the unit cell is two cations and two anions.

the two As atoms occupying the general position (x, y, z), ($-x, -y, -z$). It was this unexpected feature of two independent Mn groups each lying in a different special position, plus the fact that the correct formulation of the compound was not originally known, that complicated earlier attempts at solving the Patterson map in space group $P\bar{1}$.

With the proper atomic arrangement, the remaining carbon and oxygen atoms were located without any difficulty from difference maps. Block-diagonal least-squares refinement¹⁴ (Mn, As anisotropic; C, O isotropic) resulted in a final agreement factor of $R = 9.2\%$.^{9, 13} A final difference Fourier map revealed 28 out of the 30 phenyl hydrogen atomic positions and no other extraneous peaks.

Discussion of the Structure

The two independent $[\text{Mn}_3(\text{CO})_{14}]^-$ anions are shown separately in Figure 1, and a picture of the $[\text{Ph}_4\text{As}]^+$ cation is given in Figure 2. Figure 3 shows the general arrangement of the ions within the unit cell. Final atomic parameters are listed in Table III, distances and angles of the $[\text{Mn}_3(\text{CO})_{14}]^-$ anions in Table IV, and molecular parameters of the $[\text{Ph}_4\text{As}]^+$ cation in Table V. A listing of the final observed and calculated structure factors is available.¹⁵

The geometry of the $[\text{Mn}_3(\text{CO})_{14}]^-$ anion is essentially identical with that of the isoelectronic neutral molecule $\text{Mn}_2\text{Fe}(\text{CO})_{14}$ synthesized by Schubert and Sheline,¹⁶ whose structure was elucidated by Agron, Ellison, and

(14) In the least-squares refinement, the parameters were blocked such that those associated with the $[\text{Mn}_3(\text{CO})_{14}]^-$ anions were put in one block and those associated with the $[\text{Ph}_4\text{As}]^+$ cations in the other.

(15) See paragraph at end of paper regarding supplementary material.

(16) E. H. Schubert and R. K. Sheline, *Z. Naturforsch. B*, **20**, 1306 (1965).

Table III. Final Atomic Parameters in $[\text{Ph}_4\text{As}][\text{Mn}_3(\text{CO})_{14}]$

Atom	x	y	z	B
As	0.4274 (2)	0.4856 (3)	-0.2341 (2)	a
Mn ₁	-0.0965 (4)	0.1565 (5)	-0.1139 (3)	a
Mn ₂ ^b	0.0000 (0)	0.0000 (0)	0.0000 (0)	a
Mn ₃	-0.2370 (4)	0.0855 (5)	0.4867 (3)	a
Mn ₄ ^b	0.0000 (0)	0.0000 (0)	0.5000 (0)	a
O ₁	-0.1844 (19)	0.3287 (24)	-0.2242 (13)	7.9 (6)
O ₂	-0.0315 (18)	-0.0805 (25)	-0.2258 (13)	8.1 (6)
O ₃	-0.3128 (24)	-0.0091 (28)	-0.1063 (14)	10.1 (7)
O ₄	-0.1446 (23)	0.3743 (31)	0.0206 (17)	10.9 (8)
O ₅	0.1442 (20)	0.2742 (22)	-0.0979 (11)	7.2 (6)
O ₆	0.1175 (19)	0.2614 (25)	0.0898 (12)	7.9 (6)
O ₇	-0.2035 (20)	0.0631 (22)	0.0827 (12)	8.1 (6)
O ₈	-0.4773 (24)	0.1675 (26)	0.4724 (14)	9.9 (7)
O ₉	-0.2298 (19)	0.0187 (22)	0.6437 (14)	8.1 (6)
O ₁₀	-0.1347 (19)	0.3740 (26)	0.5499 (12)	7.9 (6)
O ₁₁	-0.1831 (18)	0.1322 (21)	0.3368 (13)	7.3 (6)
O ₁₂	-0.2901 (16)	-0.2161 (22)	0.4240 (11)	5.8 (5)
O ₁₃	0.0421 (18)	0.1619 (23)	0.6586 (14)	8.1 (6)
O ₁₄	0.0701 (17)	0.2564 (23)	0.4453 (11)	6.7 (5)
C ₁	-0.1518 (28)	0.2548 (35)	-0.1823 (20)	6.3 (9)
C ₂	-0.0578 (28)	0.0136 (37)	-0.1796 (20)	7.1 (9)
C ₃	-0.2304 (35)	0.0587 (40)	-0.1082 (20)	8.4 (10)
C ₄	-0.1320 (32)	0.2908 (44)	-0.0279 (24)	8.2 (11)
C ₅	0.0557 (32)	0.2245 (35)	-0.1031 (18)	7.2 (9)
C ₆	0.0777 (28)	0.1543 (38)	0.0571 (18)	6.1 (8)
C ₇	-0.1215 (32)	0.0431 (34)	0.0517 (19)	7.0 (9)
C ₈	-0.3823 (38)	0.1317 (39)	0.4775 (21)	9.1 (11)
C ₉	-0.2355 (28)	0.0438 (34)	0.5818 (22)	6.9 (9)
C ₁₀	-0.1736 (27)	0.2633 (37)	0.5293 (18)	5.7 (8)
C ₁₁	-0.2041 (27)	0.1158 (33)	0.3952 (21)	6.4 (9)
C ₁₂	-0.2671 (26)	-0.0987 (36)	0.4488 (17)	6.1 (8)
C ₁₃	0.0250 (27)	0.0998 (35)	0.5970 (21)	6.6 (8)
C ₁₄	0.0424 (26)	0.1510 (37)	0.4657 (17)	5.8 (8)
C ₁₅	0.2697 (23)	0.5271 (27)	-0.2605 (16)	4.3 (7)
C ₁₆	0.2319 (23)	0.5291 (27)	-0.3345 (16)	4.7 (7)
C ₁₇	0.1103 (27)	0.5373 (30)	-0.3549 (17)	5.9 (8)
C ₁₈	0.0399 (24)	0.5549 (29)	-0.2997 (18)	5.3 (7)
C ₁₉	0.0761 (26)	0.5521 (30)	-0.2263 (18)	5.4 (7)
C ₂₀	0.1955 (24)	0.5356 (27)	-0.2051 (15)	4.3 (7)
C ₂₁	0.4357 (22)	0.2972 (26)	-0.2370 (14)	2.9 (6)
C ₂₂	0.3426 (23)	0.2178 (30)	-0.2166 (15)	4.5 (7)
C ₂₃	0.3485 (24)	0.0709 (31)	-0.2198 (16)	5.3 (7)
C ₂₄	0.4483 (27)	0.0020 (32)	-0.2431 (17)	5.8 (7)
C ₂₅	0.5374 (27)	0.0713 (35)	-0.2654 (17)	7.1 (8)
C ₂₆	0.5268 (23)	0.2153 (31)	-0.2630 (15)	4.9 (8)
C ₂₇	0.5307 (22)	0.5428 (29)	-0.2992 (16)	3.9 (7)
C ₂₈	0.5288 (22)	0.4690 (27)	-0.3723 (16)	4.0 (6)
C ₂₉	0.6043 (24)	0.5067 (29)	-0.4191 (15)	4.4 (7)
C ₃₀	0.6847 (25)	0.6211 (32)	-0.3900 (18)	5.8 (8)
C ₃₁	0.6889 (27)	0.6934 (33)	-0.3160 (19)	6.4 (8)
C ₃₂	0.6099 (27)	0.6529 (32)	-0.2692 (17)	5.9 (8)
C ₃₃	0.4827 (25)	0.5833 (31)	-0.1338 (16)	5.2 (8)
C ₃₄	0.4336 (23)	0.7103 (31)	-0.1040 (16)	4.9 (7)
C ₃₅	0.4799 (28)	0.7929 (33)	-0.0319 (19)	6.6 (8)
C ₃₆	0.5690 (28)	0.7395 (35)	0.0064 (17)	6.5 (8)
C ₃₇	0.6181 (27)	0.6185 (37)	-0.0205 (19)	7.2 (8)
C ₃₈	0.5699 (26)	0.5311 (31)	-0.0919 (18)	5.9 (8)

^a Anisotropic temperature factors are the following

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
As	45 (2)	115 (4)	30 (1)	-27 (5)	4 (3)	11 (4)
Mn ₁	64 (5)	185 (9)	41 (2)	0 (10)	19 (5)	26 (8)
Mn ₂	65 (7)	189 (13)	34 (3)	34 (15)	40 (7)	28 (10)
Mn ₃	40 (4)	133 (8)	56 (3)	-10 (9)	8 (6)	-3 (7)
Mn ₄	42 (6)	115 (11)	46 (4)	13 (13)	19 (7)	28 (10)

The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. ^b The positions of atoms Mn₂ and Mn₄ are fixed by symmetry.

Levy.¹⁷ Curiously, in $\text{Mn}_2\text{Fe}(\text{CO})_{14}$ it was also found that there are two crystallographically independent

(17) P. A. Agron, R. D. Ellison, and H. A. Levy, *Acta Crystallogr.*, **23**, 1079 (1967).

Table IV. Distances and Angles Associated with the $[\text{Mn}_3(\text{CO})_{14}]^-$ Anions

Anion 1		Anion 2	
(A) Bond Distances (in ångströms)			
Mn ₁ -Mn ₂	2.906 (5)	Mn ₃ -Mn ₄	2.883 (4)
Mn ₁ -C ₁	1.765 (35)	Mn ₃ -C ₈	1.751 (43)
Mn ₁ -C ₂	1.743 (36)	Mn ₃ -C ₉	1.832 (38)
Mn ₁ -C ₃	1.829 (41)	Mn ₃ -C ₁₀	1.844 (35)
Mn ₁ -C ₄	1.911 (42)	Mn ₃ -C ₁₁	1.809 (36)
Mn ₁ -C ₅	1.851 (37)	Mn ₃ -C ₁₂	1.793 (35)
Mn ₂ -C ₆	1.803 (35)	Mn ₄ -C ₁₃	1.818 (37)
Mn ₂ -C ₇	1.793 (36)	Mn ₄ -C ₁₄	1.771 (35)
C ₁ -O ₁	1.170 (42)	C ₈ -O ₈	1.160 (51)
C ₂ -O ₂	1.181 (43)	C ₉ -O ₉	1.181 (45)
C ₃ -O ₃	1.158 (49)	C ₁₀ -O ₁₀	1.130 (43)
C ₄ -O ₄	1.103 (52)	C ₁₁ -O ₁₁	1.146 (43)
C ₅ -O ₅	1.113 (43)	C ₁₂ -O ₁₂	1.151 (41)
C ₆ -O ₆	1.149 (43)	C ₁₃ -O ₁₃	1.150 (45)
C ₇ -O ₇	1.160 (43)	C ₁₄ -O ₁₄	1.195 (42)
(B) Bond Angles (in degrees)			
Mn ₁ -Mn ₂ -Mn ₁ '	180.0 (0) ^a	Mn ₃ -Mn ₄ -Mn ₃ '	180.0 (0) ^a
Mn ₁ -C ₁ -O ₁	175.0 (30)	Mn ₃ -C ₈ -O ₈	177.4 (35)
Mn ₁ -C ₂ -O ₂	178.0 (32)	Mn ₃ -C ₉ -O ₉	177.2 (28)
Mn ₁ -C ₃ -O ₃	176.6 (34)	Mn ₃ -C ₁₀ -O ₁₀	174.7 (28)
Mn ₁ -C ₄ -O ₄	174.2 (35)	Mn ₃ -C ₁₁ -O ₁₁	178.7 (29)
Mn ₁ -C ₅ -O ₅	175.0 (31)	Mn ₃ -C ₁₂ -O ₁₂	177.8 (27)
Mn ₂ -C ₆ -O ₆	172.1 (30)	Mn ₄ -C ₁₃ -O ₁₃	179.1 (28)
Mn ₂ -C ₇ -O ₇	175.7 (30)	Mn ₄ -C ₁₄ -O ₁₄	177.2 (27)
Mn ₂ -Mn ₁ -C ₁	178.4 (11)	Mn ₄ -Mn ₃ -C ₈	178.1 (13)
Mn ₂ -Mn ₁ -C ₂	85.1 (12)	Mn ₄ -Mn ₃ -C ₉	84.1 (10)
Mn ₂ -Mn ₁ -C ₃	83.3 (12)	Mn ₄ -Mn ₃ -C ₁₀	84.6 (10)
Mn ₂ -Mn ₁ -C ₄	84.2 (13)	Mn ₄ -Mn ₃ -C ₁₁	82.9 (10)
Mn ₂ -Mn ₁ -C ₅	81.7 (11)	Mn ₄ -Mn ₃ -C ₁₂	83.1 (10)
Mn ₁ -Mn ₂ -C ₆	92.6 (11)	Mn ₃ -Mn ₄ -C ₁₃	90.5 (10)
Mn ₁ -Mn ₂ -C ₇	89.8 (11)	Mn ₃ -Mn ₄ -C ₁₄	89.6 (10)
C ₁ -Mn ₁ -C ₂	95.3 (16)	C ₈ -Mn ₃ -C ₉	95.8 (16)
C ₁ -Mn ₁ -C ₃	98.2 (16)	C ₈ -Mn ₃ -C ₁₀	97.3 (16)
C ₁ -Mn ₁ -C ₄	95.4 (17)	C ₈ -Mn ₃ -C ₁₁	97.3 (16)
C ₁ -Mn ₁ -C ₅	96.8 (15)	C ₈ -Mn ₃ -C ₁₂	95.0 (16)
C ₂ -Mn ₁ -C ₃	89.1 (16)	C ₉ -Mn ₃ -C ₁₀	90.0 (15)
C ₃ -Mn ₁ -C ₄	87.7 (16)	C ₁₀ -Mn ₃ -C ₁₁	88.3 (14)
C ₄ -Mn ₁ -C ₅	92.6 (15)	C ₁₁ -Mn ₃ -C ₁₂	91.2 (14)
C ₅ -Mn ₁ -C ₂	87.7 (15)	C ₁₂ -Mn ₃ -C ₉	87.7 (15)
C ₂ -Mn ₁ -C ₄	169.2 (18)	C ₉ -Mn ₃ -C ₁₁	167.0 (14)
C ₃ -Mn ₁ -C ₅	164.8 (16)	C ₁₀ -Mn ₃ -C ₁₂	167.8 (14)
C ₆ -Mn ₂ -C ₇	88.9 (15)	C ₁₃ -Mn ₄ -C ₁₄	90.0 (15)
C ₆ -Mn ₂ -C ₆ '	180.0 (0) ^a	C ₁₃ -Mn ₄ -C ₁₃ '	180.0 (0) ^a
C ₇ -Mn ₂ -C ₇ '	180.0 (0) ^a	C ₁₄ -Mn ₄ -C ₁₄ '	180.0 (0) ^a

^a These angles are required by symmetry to be exactly 180°.

molecules each situated on a different special position.¹⁸ In $[\text{Mn}_3(\text{CO})_{14}]^-$, the two independent anions are centered on crystallographic centers of symmetry (inversion centers). Each anion has essentially D_{4h} symmetry, with the central $\text{Mn}(\text{CO})_4$ equatorial group staggered with respect to the other two sets of equatorial CO groups. Figure 4 shows this feature, and also the linearity of the seven-atom OCMMMCO backbone of the molecule, quite nicely. The average Mn-Mn distance (2.895 Å) agrees well with that found in $\text{Mn}_2(\text{CO})_{10}$ (2.923 (3) Å by X-ray diffraction¹⁹ and 2.977 (11) Å by electron diffraction^{20a}). As expected, the average axial M-C distance (1.758 Å) is significantly shorter than the average equatorial M-C distance (1.827 Å).

(18) In $\text{Mn}_2\text{Fe}(\text{CO})_{11}$, the two crystallographically independent molecules are situated at (0, 0, 0) and (0, $1/2$, $1/2$) in the monoclinic space group $C2/m$. Both of these special positions have $2/m$, or C_{2h} , symmetry.

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

(20) (a) A. Almenningen, G. G. Jacobsen, and H. M. Seip, *Acta Chem. Scand.*, **23**, 685 (1969); (b) N. I. Gapotchenko, N. V. Alekseev, K. N. Anisimov, N. E. Kolobova, and I. A. Ronova, *Zh. Strukt. Khim.*, **9**, 892 (1968); *J. Struct. Chem. USSR*, **9**, 784 (1968).

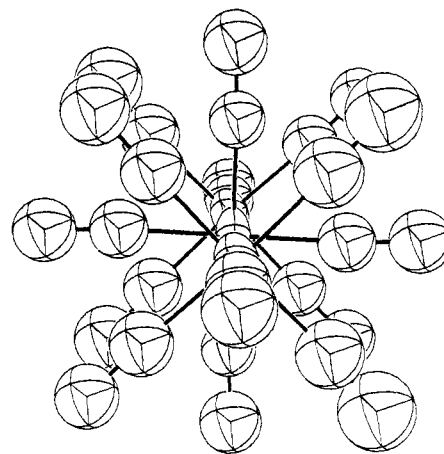


Figure 4. One of the $[\text{Mn}_3(\text{CO})_{14}]^-$ anions viewed from a point slightly off the fourfold axis. Note the linearity of the seven-atom OCMMMCO backbone and the staggered nature of the three sets of equatorial carbonyl groups.

Table V. Distances and Angles Associated with the $[\text{Ph}_4\text{As}]^+$ Cation

	Phenyl 1 (C ₁₅ -C ₂₀)	Phenyl 2 (C ₂₁ -C ₂₆)	Phenyl 3 (C ₂₇ -C ₃₂)	Phenyl 4 (C ₃₃ -C ₃₈)
Bond Distances (in ångströms)				
a	1.907 (27)	1.813 (26)	1.917 (27)	1.905 (29)
b	1.358 (40)	1.435 (37)	1.371 (39)	1.400 (42)
c	1.426 (42)	1.410 (42)	1.374 (38)	1.429 (44)
d	1.347 (43)	1.412 (42)	1.414 (41)	1.343 (46)
e	1.346 (45)	1.362 (45)	1.377 (46)	1.341 (49)
f	1.415 (41)	1.388 (46)	1.414 (45)	1.444 (46)
g	1.385 (39)	1.402 (38)	1.379 (41)	1.354 (43)
Bond Angles (in degrees)				
h	118.8 (21)	121.1 (19)	119.7 (20)	119.7 (21)
i	118.0 (21)	124.5 (20)	118.3 (21)	120.2 (23)
j	122.7 (25)	114.3 (24)	121.9 (25)	120.1 (27)
k	117.5 (25)	121.1 (24)	120.3 (25)	121.2 (26)
l	119.1 (27)	119.0 (26)	118.7 (25)	116.6 (29)
m	123.7 (28)	122.3 (29)	121.2 (28)	123.7 (31)
n	118.3 (27)	116.7 (28)	118.9 (29)	120.4 (30)
o	118.3 (26)	126.4 (26)	118.9 (27)	117.6 (29)
Angles around the As atom				
C ₁₅ -As-C ₂₁	108.6 (11)	C ₂₁ -As-C ₂₇	109.6 (12)	
C ₁₅ -As-C ₂₇	113.4 (12)	C ₂₁ -As-C ₃₃	108.9 (12)	
C ₁₅ -As-C ₃₃	110.5 (12)	C ₂₇ -As-C ₃₃	105.9 (12)	

This well-documented phenomenon has been discussed at great length elsewhere.²¹

The C(ax)-Mn-C(eq) Angle. The equatorial groups on the terminal manganese atoms are distinctly bent toward the central manganese atom, the average C(ax)-Mn-C(eq) angle being 96.4°.²² This, too, is a well-known phenomenon, having been previously noticed in $\text{Mn}_2(\text{CO})_{10}$,¹⁹ $\text{Mn}_2\text{Fe}(\text{CO})_{14}$,¹⁷ $\text{HR}_2\text{Mn}(\text{CO})_{14}$,¹² HR_3 -

(21) (a) S. J. LaPlaca, W. C. Hamilton, J. A. Ibers, and A. Davison, *Inorg. Chem.*, **8**, 1928 (1969); (b) B. A. Coyle and J. A. Ibers, *ibid.*, **11**, 1105 (1972); (c) G. L. Simon, A. W. Adamson, and L. F. Dahl, *J. Amer. Chem. Soc.*, **94**, 7654 (1972); (d) L. D. Brown, K. N. Raymond, and S. Z. Goldberg, *ibid.*, **94**, 7664 (1972).

(22) The carbonyl groups on the central Mn atom, however, are not inclined toward any particular terminal Mn atom.

(CO)₁₄,²³ [Cr₂(CO)₁₀]²⁻,²⁴ and [Mo₂(CO)₁₀]²⁻²⁴ and found to persist in the gaseous phase through electron diffraction studies on Mn₂(CO)₁₀ vapor.²⁰

This curious effect was initially attributed to steric repulsions between nonbonding carbon atoms (*i.e.*, interactions of the type C(ax)···C(eq)), but an accumulating body of structural evidence seems to indicate otherwise. A tabulation of the available results (Table VI(A)) shows that, in all cases, the C(eq)···

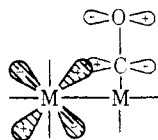
Table VI. A Comparison of the C-M-C Angles and Nonbonding C···C Contact Distances in Various Bi- and Trinuclear Metal Complexes

Molecule	Av	Av	Av	Av	Ref
	C(ax)-M-C(eq) angle	C(ax)···C(eq) distance	C(eq)-M-C(eq) angle	C(eq)···C(eq) distance	
(A) M-M Bonded Molecules					
Mn ₂ (CO) ₁₀	93.8	2.64	89.8	2.58	19
[Cr ₂ (CO) ₁₀] ²⁻	93.3	2.70	86.5	2.57	24
[Mo ₂ (CO) ₁₀] ²⁻	94.5	2.80	86.0	2.59	24
[Mn ₃ (CO) ₁₄] ⁻	96.4	2.68	89.3	2.58	This work
Mn ₂ Fe(CO) ₁₄	93.4	2.66	89.4	2.62	17
HRe ₃ (CO) ₁₄ ^a	94.5	2.75	89.7	2.65	23
HRe ₂ Mn(CO) ₁₄ ^a	94.7	2.67	89.6	2.58	12
(B) M-H-M Bonded Molecules					
[HCr ₂ (CO) ₁₀] ⁻	91.0	2.64	90.0	2.66	24
HRe ₃ (CO) ₁₄ ^b	90.0	2.78	90.0	2.87	23
HRe ₂ Mn(CO) ₁₄ ^b	90.8	2.80	89.9	2.83	12

^a Refers to the -(CO)₄M-M(CO)₅ portion of the molecule.
^b Refers to the -(CO)₄M-H-M(CO)₅ portion of the molecule.

C(eq) distances and the C(eq)-M-C(eq) angles are smaller than the C(ax)···C(eq) distances and the C(ax)-M-C(eq) angles, respectively. For example, in [Mo₂(CO)₁₀]²⁻ the average parameters are C(eq)···C(eq) = 2.59 Å, C(eq)-Mo-C(eq) = 86.0°, C(ax)···C(ax) = 2.80 Å, and C(ax)-Mo-C(ax) = 94.5°. Clearly, a C(ax)···C(eq) contact distance of 2.80 Å cannot be considered severe if a C(eq)···C(eq) distance of 2.59 Å is easily tolerated.

We tend to believe that the bending of the equatorial carbonyl groups away from the axial carbonyl group is due to bonding interactions between a metal atom and the equatorial CO's on the *opposite* metal atom (we will denote these as M···L' interactions)



This view is supported by recent molecular orbital calculations by Brown, *et al.*,²⁵ which indicate that the stability of M-M bonds is substantially strengthened by interactions of this type. Presumably, such interactions are of the conventional M (filled d orbital) → CO (π* orbital) back-bonding variety, except that in this case the M and CO are not directly bonded to each other.

(23) R. P. White, T. E. Block, and L. F. Dahl, submitted for publication.

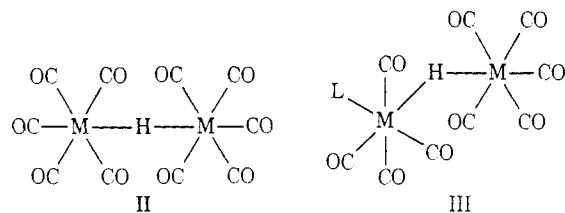
(24) L. B. Handy, J. K. Ruff, and L. F. Dahl, *J. Amer. Chem. Soc.*, **92**, 7312 (1970).

(25) D. A. Brown, W. J. Chambers, N. J. Fitzpatrick, and R. M. Rawlinson, *J. Chem. Soc. A*, 720 (1971).

This effect is related to Bennett and Mason's observation²⁶ that equatorial carbonyl groups in M(CO)₅L molecules are bent toward the weaker π acceptor (and thus could be used to gauge the relative π-acceptor abilities of various substituents). Also relevant is a study of the bonding in R₃SiCo(CO)₄ compounds by Berry, *et al.*,²⁷ where it was concluded that intramolecular Si···CO interactions are partially responsible for the bending of the equatorial carbonyl groups toward the silyl group. Additionally, an approximate but nonparameterized molecular orbital calculation by Hall and Fenske²⁸ has indicated that in the M(CO)_{6-z}L_z complexes (M = Cr, Mn, Fe; L = Cl, Br, I; x = 1, 2), the direct donation of electron density from the halogen's σ orbital to the cis carbonyl's π* orbital is the most important mechanism by which a change in the halogen affects a change in the carbonyl force constant.

Eclipsed vs. Staggered Conformations. Such M···L' interactions would lead the CO groups to seek regions of high d-electron density, which in polynuclear and binuclear complexes would be the regions between the metal atoms. By adopting a staggered conformation, the molecule maximizes the effect of M···L' interactions, for otherwise (in an eclipsed conformation) steric repulsions between the opposite sets of equatorial CO groups would prevent too much out-of-plane bending. These M···L' interactions would be substantially weakened if the M-M distance were appreciably lengthened; this is the situation in M-H-M bonded complexes such as [HCr₂(CO)₁₀]⁻²⁴ and the Re-H-Re portions of HRe₃Mn(CO)₁₄¹² and HRe₃(CO)₁₄.²³ In these cases, the M···L' interactions are reduced to the point where little out-of-plane bending occurs; the C(ax)-M-C(eq) angles are now close to 90° (see Table VI(B)). In the absence of other dominant interactions, the van der Waals attractive forces between equatorial CO groups now become important conformation-determining factors, and the molecule becomes eclipsed to maximize these. This is the situation in [HCr₂(CO)₁₀]⁻.²⁴ In HRe₃(CO)₁₄, however, steric factors arising from the bending of the main M···M-M backbone (*vide infra*) prevent the adoption of an eclipsed conformation.

Linear vs. Bent M-H-M Linkages. The preceding discussion leads to the conclusion that the d-electron distribution in metal carbonyls could, in certain cases, influence the molecular geometry of those compounds. This is further seen by examining the structures of a variety of M-H-M-bonded species. In cases where the distribution of equatorial ligands is radially symmetrical (II; as in [HCr₂(CO)₁₀]⁻²⁴ and HReCr(CO)₁₀²⁹), the



(26) M. J. Bennett and R. Mason, *Nature (London)*, **205**, 760 (1965).

(27) A. D. Berry, E. R. Corey, A. P. Hagen, A. G. MacDiarmid, F. E. Saalfeld, and B. B. Wayland, *J. Amer. Chem. Soc.*, **92**, 1940 (1970).

(28) M. B. Hall and R. F. Fenske, *Inorg. Chem.*, **11**, 1619 (1972).

(29) A. S. Foust, W. A. G. Graham, and R. P. Stewart, *J. Organometal. Chem.*, in press.

molecule adopts a linear M–H–M arrangement. However, introduction of some other ligand L in an equatorial position (III) perturbs the radial symmetry of d-electron density in the equatorial plane and triggers a bending of the M–H–M angle. This happens in $\text{HRe}_3(\text{CO})_{14}$ (L = $\text{Re}(\text{CO})_5$; M–H–M (est) = 159°),²³ $\text{HRe}_2\text{Mn}(\text{CO})_{14}$ (L = $\text{Mn}(\text{CO})_5$; M–H–M (est) = 164°),¹² and $\text{HW}_2(\text{CO})_9(\text{NO})$ (L = NO; M–H–M (est) = 151°).³⁰ Presumably, this effect is observed only if the central backbone is easily deformable, such as in M–H–M.

Linear vs. Bent M–M–M Linkages. It is interesting to note that $[\text{Mn}_3(\text{CO})_{14}]^-$ and $\text{Mn}_2\text{Fe}(\text{CO})_{14}$ are linear while $\text{HRe}_3(\text{CO})_{14}$ and $\text{HRe}_2\text{Mn}(\text{CO})_{14}$ are bent. We believe that steric reasons would make it quite impossible for $[\text{Mn}_3(\text{CO})_{14}]^-$ and $\text{Mn}_2\text{Fe}(\text{CO})_{14}$ to adopt a bent (or cis) configuration. In the structures of $\text{HRe}_3(\text{CO})_{14}$ and $\text{HRe}_2\text{Mn}(\text{CO})_{14}$, considerable steric strain arises from the close nonbonding contacts between the equatorial oxygens of the terminal metal atoms, so much so that the M–M···M angles are highly distorted (106.0° in $\text{HRe}_3(\text{CO})_{14}$ and 98.1° in $\text{HRe}_2\text{Mn}(\text{CO})_{14}$). Removal of a hydrogen atom from the M–H–M bond would decrease the M–M distance and further aggravate the already severe strain in the molecule. It would therefore be highly unlikely that a bent $\text{M}_3(\text{CO})_{14}$ -type molecule could exist.

Having established that $\text{M}_3(\text{CO})_{14}$ molecules should be linear (or trans), the question then arises of why the $\text{HM}_3(\text{CO})_{14}$ molecules are bent, even at the expense of incurring severe internal strain. Here again, we believe the key to be the importance of the M···L' interactions discussed earlier. The M–M–M bend disrupts the radial symmetry of the d-electron density distribution around the central metal atom, causing the M–H–M angle to bend (*vide ante*) and maximizing the M···L' attractions across the M–H–M bond. van der Waals attractive forces between the closely interlocked carbonyl groups on the terminal metal atoms might also contribute to the stability of the bent configuration.

Existence of Bent $[\text{Mn}_3(\text{CO})_{14}]^-$ and $[\text{H}_2\text{Mn}_3(\text{CO})_{12}]^-$. The synthesis of $[\text{Mn}_3(\text{CO})_{14}]^-$ was first reported by Curtis,⁶ who prepared it from the reaction of NaMn -

$(\text{CO})_5$ with Ph_3SiCl . However, Curtis formulated the structure of this compound as bent (or cis), a geometrical arrangement which we consider unlikely (see preceding section). In our hands,⁵ the same reaction yields a product whose ir spectrum is indistinguishable from the $[\text{Mn}_3(\text{CO})_{14}]^-$ prepared as described in this paper, *i.e.*, the linear (or trans) form. It is possible that Curtis' complex ir spectrum, on which his structural assignment is based, is made up of bands arising from the linear $[\text{Mn}_3(\text{CO})_{14}]^-$ plus decomposition products.⁸

The other question centers on the status of the originally sought-after material, $[\text{H}_2\text{Mn}_3(\text{CO})_{12}]^-$. Evans, *et al.*, reported the preparation of $[\text{H}_2\text{Mn}_3(\text{CO})_{12}]^-$ via irradiation of an acetone solution of $\text{Mn}_2(\text{CO})_{10}$, followed by precipitation as its $[(\text{C}_2\text{H}_5)_4\text{N}]^+$ salt.⁴ Although we did not repeat this particular reaction, we strongly suspect that this anion is also $[\text{Mn}_3(\text{CO})_{14}]^-$ (linear form), because the reported spectrum of $[\text{H}_2\text{Mn}_3(\text{CO})_{12}]^-$ closely resembles ours. Moreover, it was reported that the protons of $[\text{H}_2\text{Mn}_3(\text{CO})_{12}]^-$ could not be detected by nmr methods. The generation of $[\text{Mn}_3(\text{CO})_{14}]^-$ via photolytic methods (if indeed this was what happened) thus closely parallels the generation of $\text{Mn}_2\text{Fe}(\text{CO})_{14}$ via photolysis of $\text{Mn}_2(\text{CO})_{10}$ and $\text{Fe}(\text{CO})_5$ in acetone.¹⁶

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105×148 mm, $24\times$ reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-988.

(30) M. Andrews, D. Tipton, S. W. Kirtley, and R. Bau, *J. Chem. Soc., Chem. Commun.*, 181 (1973). Since this paper has appeared, we have revised our earlier assignment of the NO in the axial position. We now believe the NO to be in an equatorial position.