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Intramolecular Metalation with Methylmanganese and Methylrhenium Carbonyl Complexes. 9. The Crystal and Molecular Structure of Tetracarbonyl-2-(bis-*p*-tolylphosphino)-5-methylphenylmanganese, $(CH_3C_6H_4)_2\overline{PC_6H_3(CH_3)Mn}(CO)_4$, an Internal Aromatic Metalation Product Involving a Four-Membered Metallocycle[1]

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Abstract: The structure of $(p\text{-tolyl})_2\overline{PC_6H_3(CH_3)Mn}(CO)_4$ has been determined from data collected on an automated diffractometer with monochromatized Mo Kα radiation. The compound crystallizes in the monoclinic space group $P2_1/c$ with a = 10.865 (3) Å, b = 13.508 (3) Å, c = 16.571 (3) Å, β = 100.63 (2)°, and V = 2390.3 (10) Å^3. The density of 1.30 g cm^{-3} calculated on the basis of four molecules per unit cell agrees with the flotation value of 1.29 g cm^{-3}. The structure was solved by use of Patterson and Fourier summations and refined by use of full-matrix least-squares methods to a conventional R index of 6.0% based on 1459 independent observed reflections. Four carbonyl groups and a bidentate tris-*p*-tolylphosphine bound to manganese through the phosphorus atom and an ortho atom of one of the tolyl groups occupy essentially octahedral coordination sites on manganese. The carbon atoms of the metalated tolyl group are coplanar with manganese and phosphorus. The greatest distance to any of these atoms from the least-squares plane through them is 0.027 Å. Variations from standard bond lengths in the four-membered ring fused to the aromatic ring are found to be in the direction of electron delocalization in the metallocycle.

The cyclometalation reaction has been the subject of increasing attention[2] owing first to interest in its intrinsic properties, secondly to its relation to the activation of carbon–hydrogen bonds,[3] and thirdly to possibilities for organic synthesis.[4] This body of work of course has included a proportional number of crystallographic studies[5] on derivatives in which metals are bonded to a variety of aromatic rings or to a side chain of an aromatic ring also connected through a donor atom to the same metal. There have been only two communications, of structures for iridium compounds, in which the metal is part of a four-membered ring.[6] This type of system has proven to be somewhat elusive from the crystallographic point of view although compounds containing four-membered rings were among the earliest known examples of cyclometalation, e.g., $Ph_2\overline{PC_6H_4Ir}(H)(Cl)(PPh_3)_2$,[7] and $Ph_2\overline{PC_6H_4M}(PPh_3)_2$ M = Rh,[8a] Ir.[8b] For manganese, we observed a four-membered metallocyclic product in the complex tetracarbonyl-2-(bisphenylphosphino)phenylmanganese, $Ph_2\overline{PC_6H_4Mn}(CO)_4$[9] (OPMn).[10] Both we[11a] and other groups[11b,c] had earlier tried without success to obtain suitable single crystals of OPMn and we therefore turned to the title compound (TOPMn)[9,10] in hopes that the factors leading to twinning or other crystal growth problems would be overcome. This proved to be the case and we here report the first crystallographic study in full of an internal metalation product in which the metal is part of a four-membered ring.

Experimental Section

The preparation of the title compound is described elsewhere.[1b,10] Crystals suitable for x-ray study were grown from a diethyl ether/*n*-hexane solution. The compound was suspended in a few milliliters of *n*-hexane in an Erlenmeyer flask and enough ether was added to dissolve it. Nitrogen was carefully blown over the solution until crystals began to form on the sides of the flask. Approximately 0.5 mL of ether was added and the flask warmed to redissolve all the compound. The flask was sealed under nitrogen and placed in the low temperature compartment of a refrigerator at −20 °C overnight, and pale yellow, air-stable crystals of TOPMn were obtained in the shape of parallelepipeds.

Data Collection. A crystal of approximate dimensions 0.20 × 0.30 × 0.20 mm along the *a*, *b*, and *c* axial directions, respectively, was glued on the tip of a glass fiber with the *b* axis parallel to the goniometer axis of rotation. Preliminary photographs and all intensity data were collected by use of this crystal. Oscillation and Weissenberg (*h*0*l* and *h*1*l*) photographs revealed systematic absences for *h*0*l* of $l = 2n + 1$ and 0*k*0 of $k = 2n + 1$ leading to a space group assignment of $P2_1/c$ in the monoclinic system.

The crystal was transferred to a Syntex $P\bar{1}$-four-circle autodiffractometer equipped with a scintillation counter, a pulse height analyzer, and a graphite monochromatized Mo Kα radiation source (λ 0.710 69 Å). Fifteen reflections (2θ = 20–30°) were centered in order to obtain accurate lattice parameters. The refined unit cell parameters are a = 10.865 (3) Å, b = 13.508 (3) Å, c = 16.571 (3) Å, and β = 100.63 (2)°. The unit cell volume is 2390.3 (10) Å^3. The density at room temperature of 1.29 g/cm^3 was obtained by flotation in a mixture of dichloromethane and *n*-hexane. The crystallographic density, assuming four formula units in the unit cell, is 1.30 g/cm^3.

Intensities were collected at room temperature using the θ–2θ scan technique with a scan rate of 2°/min and a scan range from 1.0° below the Kα_1 peak to 1.0° above the Kα_2 peak. The takeoff angle was 4.0° and a background time to scan time ratio of 1.0 was employed. Intensity data were collected to a limit of 2θ = 50°. Three standard reflections (108, $52\bar{5}$, and $26\bar{3}$) were measured after every 97 reflections throughout the data collection to monitor crystal and diffractometer stability. The variations in the intensities of these standards were random; all were within 3.0% of their respective mean.

Of the 4812 reflections measured, 1459 reflections for which $I \geqslant 3.0\sigma(I)$ were used in the solution and refinement of the structure. Reduction and processing of the data were accomplished by utilizing the following equations:[12]

$$I = N - (t_s/2t_b)(B_1 + B_2)$$

$$\sigma(I) = [N + (t_s/2t_b)^2(B_1 + B_2) + (0.04I)^2]^{1/2}$$

$$|F_o| = K[I/(\mathrm{Lp})]^{1/2}$$

$$\sigma(F_o) = (K/2)\sigma(I)/[I(\mathrm{Lp})]^{1/2}$$

where N is the total scan count, B_1 and B_2 are the individual background counts on each side of the peak, t_s is the scan time (seconds), t_b is the time (seconds) of the background count on each side of the peak, and Lp is the correction for Lorentz and polarization effects. In this case, $t_b = 0.5t_s$. The absorption coefficient μ was calculated to be 6.77 cm^{-1}, which for the above-mentioned crystal leads to a transmission factor range of 0.85–0.91 within the 2θ range measured. From this it is estimated that absorption effects would cause fluctuations of no more than 3.5% in I or 2% in $|F_o|$ and no corrections for the effects of absorption were therefore undertaken.

Solution and Refinement. The initial positional coordinates of the Mn atom were determined from a three-dimensional Patterson summation. Three Fourier syntheses revealed the positions of all nonhydrogen atoms. Refinement was carried out by use of full-matrix, least-squares methods using atomic scattering factors for all nonhydrogen atoms as compiled by Hanson et al.[13] Hydrogen atomic scattering factors were obtained from Stewart et al.[14] Anomalous dispersion corrections ($\Delta f'$ and $\Delta f''$) were applied to the form factors for manganese and phosphorus.[15]

Two cycles of least-squares refinement for all nonhydrogen atoms utilizing isotropic temperature factors converged to a conventional R index[16] of 0.123 and weighted R index[16] of 0.131. Two cycles of refinement in which the temperature factors for manganese and phosphorus were allowed to vary anisotropically led to a conventional R index of 0.093. In all subsequent refinement, the phenyl carbons and hydrogens of the two nonmetalated tolyl groups were treated as rigid groups with d(C–C) = 1.395 Å and d(C–H) = 1.084 Å.[17]

Difference Fourier maps revealed the location of all nongroup hydrogen atoms. The final refinement of positional and anisotropic thermal parameters for all nonhydrogen nongroup atoms, positional and isotropic thermal parameters for group atoms, and positional parameters of the nongroup hydrogen atoms led to a final conventional R index of 0.060 and a final weighted R_w index of 0.061.

In the final least-squares cycle, the largest shift was 0.15σ (for a group positional parameter). The standard deviation in a reflection of unit weight was 1.57. The final difference Fourier map revealed two peaks greater than 0.30 e/Å^3 (0.41 and 0.35 e/Å^3) each of which was associated with (C–C) bonds in the nonmetalated tolyl groups.

A set of structure factors was calculated for all unique reflections on the basis of the final positional and thermal parameters. The structure factors for the 1459 reflections used in the solution of the structure are displayed in Table **I**; see paragraph at end of paper regarding supplementary material. Analysis of several portions of the molecule for possible rigid body motion was carried out by the program (ACA No. 1) written by Schomaker and Trueblood (1968)[18] which is based on the treatment presented in their paper on the rigid-body motion of molecules in crystals. No portion of the molecule was found to conform to the standards set therein for rigid body motion.

Description and Discussion of the Structure

The molecular structure and the numbering system are illustrated in Figure 1. There are no nonhydrogen intermolecular distances of less than 3.0 Å. The shortest nonhydrogen to hydrogen intermolecular distance is 2.67 Å and the shortest hydrogen–hydrogen distance is 2.57 Å, thus establishing that the molecule is a monomer.

Table II. Atomic Positional Parameters[a]

Atom	x	y	z
Mn	0.75559 (16)	0.10634 (11)	0.08355 (8)
P	0.8866 (2)	0.1432 (2)	0.2073 (1)
O_{21}	0.5777 (8)	0.0257 (7)	0.1845 (5)
O_{22}	0.9129 (8)	0.2178 (6)	−0.0141 (4)
O_{23}	0.8514 (11)	−0.0898 (7)	0.0472 (5)
O_{24}	0.5441 (11)	0.1261 (9)	−0.0540 (6)
C_1	0.8015 (8)	0.2563 (6)	0.2027 (5)
C_2	0.7177 (9)	0.2456 (7)	0.1294 (5)
C_3	0.6371 (9)	0.3229 (9)	0.1018 (5)
C_4	0.6382 (9)	0.4075 (8)	0.1496 (7)
C_5	0.7200 (11)	0.4155 (7)	0.2231 (6)
C_6	0.8035 (9)	0.3415 (7)	0.2500 (5)
C_{21}	0.6469 (11)	0.0544 (8)	0.1448 (6)
C_{22}	0.8573 (12)	0.1736 (8)	0.0249 (6)
C_{23}	0.8142 (13)	−0.0147 (10)	0.0608 (6)
C_{24}	0.6284 (14)	0.1155 (10)	−0.0013 (7)
C_{25}	0.5460 (10)	0.4927 (8)	0.1209 (6)
C_{26}	0.8335 (9)	−0.1015 (8)	0.5106 (6)
C_{27}	0.4458 (11)	0.2520 (9)	0.2535 (7)
H_3	0.573 (8)	0.316 (6)	0.059 (5)
H_5	0.727 (8)	0.477 (7)	0.255 (5)
H_6	0.862 (7)	0.350 (6)	0.303 (4)
H_{251}[b]	0.598 (9)	0.548 (8)	0.143 (6)
H_{252}[b]	0.496 (9)	0.491 (7)	0.166 (6)
H_{253}[b]	0.477 (9)	0.455 (7)	0.086 (6)
H_{261}[b]	0.785 (9)	−0.056 (7)	0.536 (6)
H_{262}[b]	0.910 (9)	−0.149 (7)	0.524 (5)
H_{263}[b]	0.773 (9)	−0.140 (7)	0.489 (6)
H_{271}[b]	0.484 (10)	0.228 (8)	0.303 (6)
H_{272}[b]	0.430 (9)	0.237 (8)	0.193 (7)
H_{273}[b]	0.426 (10)	0.320 (9)	0.227 (7)

[a] Values in parentheses in this and in following tables are the estimated standard deviations and refer to the last digit of the preceding number. [b] These hydrogen atoms are on methyl groups and their numbers correspond to that of the carbon atom to which each is bonded.

Table III. Atomic Thermal Parameters ($\times 10^4$)[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mn	184.5 (22)	78.5 (11)	35.9 (6)	−5.5 (15)	9.3 (9)	−10.1 (8)
P	126.8 (31)	53.7 (16)	32.3 (9)	3.9 (19)	17.3 (14)	−1.4 (11)
O_{21}	232 (13)	150 (8)	76 (5)	−61 (8)	41 (6)	−25 (5)
O_{22}	282 (14)	145 (8)	62 (4)	33 (8)	54 (6)	38 (5)
O_{23}	529 (23)	92 (7)	108 (6)	37 (11)	125 (9)	−26 (5)
O_{24}	396 (20)	225 (12)	87 (5)	−51 (13)	−94 (8)	4 (7)
C_1	116 (12)	64 (7)	35 (4)	−8 (7)	17 (6)	−5 (4)
C_2	115 (13)	65 (7)	40 (4)	−5 (8)	19 (6)	5 (5)
C_3	100 (12)	102 (9)	46 (5)	5 (9)	7 (6)	4 (5)
C_4	105 (13)	79 (8)	64 (6)	32 (9)	25 (7)	20 (6)
C_5	167 (15)	60 (8)	65 (6)	−9 (9)	27 (8)	−0 (6)
C_6	125 (12)	59 (7)	50 (5)	−5 (8)	12 (6)	−6 (5)
C_{21}	190 (18)	97 (9)	48 (5)	−35 (10)	5 (7)	−24 (6)
C_{22}	259 (20)	82 (9)	39 (5)	45 (10)	19 (8)	4 (5)
C_{23}	344 (24)	101 (10)	52 (5)	5 (13)	62 (9)	−10 (6)
C_{24}	324 (24)	147 (12)	52 (6)	−56 (16)	−15 (10)	−14 (8)
C_{25}	8.3 (3)[b]		H_{251}, H_{252}, H_{253}, 9.5[c]			
C_{26}	7.9 (3)[b]		H_{261}, H_{262}, H_{263}, 9.0[c]			
C_{27}	10.2 (3)[b]		H_{271}, H_{272}, H_{273}, 11.3[c]			
H_3	6.4[c]					
H_5	7.1[c]					
H_6	6.1[c]					

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$. [b] Isotropic temperature parameter B, of the form $\exp[-B \sin^2 \theta/\lambda^2]$. [c] Assigned isotropic thermal parameter.

Table IV. Group Positional Parameters[a]

Group	X	Y	Z	ϕ	θ	ρ
Tol 1	0.8717 (5)	0.0748 (4)	0.2985 (3)	0.721 (3)	−2.836 (3)	2.155 (3)
Tol 2	1.0527 (4)	0.1687 (4)	0.2198 (4)	−2.669 (7)	2.062 (3)	2.897 (7)

[a] C. Scheringer, *Acta Crystallogr.*, **16**, 546 (1963).

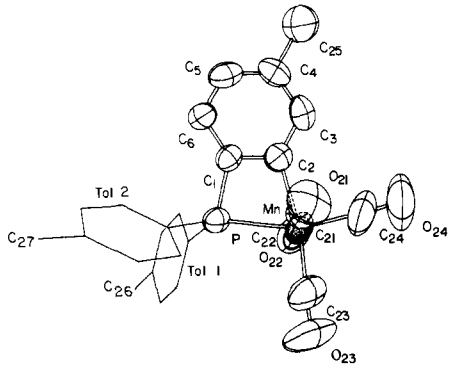


Figure 1. ORTEP plot of tetracarbonyl-2-(bis-*p*-tolylphosphino)-5-methylphenylmanganese, $(p\text{-tolyl})_2\overline{PC_6H_3(CH_3)Mn}(CO)_4$ (TOPMn), showing thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted.

Four carbonyl groups and a bidentate tris-*p*-tolylphosphine comprise the manganese coordination sphere in a distorted octahedral array. The chelating phosphine is bound to the manganese through the phosphorus atom and an ortho carbon atom of one of the tolyl groups. The phosphorus, manganese and metalated tolyl carbon atoms are coplanar. The greatest distance from one of these atoms to their least-squares plane is 0.027 Å (see Table VIII).

Observed bond lengths and bond angles are given in Tables VI and VII, respectively, and the direction cosines of the least-squares planes and the deviations of atoms therefrom are given in Table VIII.

Table V. Derived Positional and Isotropic Thermal Parameters for Group Atoms

Group	Atom	x	y	z	B, Å^2
Tol 1	C_1	0.8717	0.0748	0.2985	4.0 (2)
	C_2	0.8016	0.1103	0.3549	4.8 (2)
	C_3	0.7888	0.0532	0.4230	5.1 (2)
	C_4	0.8462	−0.0394	0.4347	5.1 (2)
	C_5	0.9163	−0.0749	0.3783	6.8 (2)
	C_6	0.9291	−0.0178	0.3102	5.8 (2)
	H_2	0.7570	0.1822	0.3458	5.8[a]
	H_3	0.7343	0.0807	0.4669	6.1[a]
	H_5	0.9609	−0.1469	0.3874	7.8[a]
	H_6	0.9836	−0.0454	0.2664	7.0[a]
Tol 2	C_1	1.0527	0.1687	0.2198	4.6 (2)
	C_2	1.1213	0.1441	0.1593	5.8 (2)
	C_3	1.2474	0.1702	0.1691	6.5 (2)
	C_4	1.3049	0.2207	0.2394	6.8 (2)
	C_5	1.2364	0.2453	0.2999	6.3 (2)
	C_6	1.1102	0.2192	0.2901	5.1 (2)
	H_2	1.0766	0.1049	0.1047	6.8[a]
	H_3	1.3007	0.1511	0.1220	7.5[a]
	H_5	1.2811	0.2846	0.3545	7.3[a]
	H_6	1.0569	0.2383	0.3372	6.3[a]

[a] Assigned isotropic thermal parameters.

Structural Features of the Four-Membered Ring. The ring involving Mn, P, C_1, and C_2 is planar. As expected for such a system all angles inside this ring are smaller than normal bond angles of the participating atoms (see Figure 1 and Table VII). The Mn–P–C_1 angle of 85.2 (3)° is considerably distorted from

Table VI. Observed Bond Lengths

Atoms	Distance (Å)	Atoms	Distance (Å)
Mn-P	2.324 (3)		
Mn-C_2	2.097 (9)	P-C_1	1.781 (9)
Mn-C_{21}	1.833 (13)	C_{21}-O_{21}	1.154 (11)
Mn-C_{22}	1.840 (13)	C_{22}-O_{22}	1.133 (11)
Mn-C_{23}	1.819 (14)	C_{23}-23	1.130 (12)
Mn-C_{24}	1.785 (14)	C_{24}-O_{24}	1.151 (13)
C_1-C_2	1.385 (10)	C_3-H_3	0.90 (9)
C_2-C_3	1.385 (12)	C_5-H_5	0.99 (9)
C_3-C_4	1.390 (12)	C_6-H_6	0.99 (9)
C_4-C_5	1.373 (12)	P-Tol 1(C_1)	1.803[a]
C_5-C_6	1.368 (12)	P-Tol 2(C_1)	1.812[a]
C_6-C_1	1.391 (11)	Tol 1(C_4)-C_{26}	1.538[a]
C_{25}-C_4	1.543 (13)	Tol 2(C_4)-C_{27}	1.563[a]
C_{25}-H_{251}	0.97 (11)	C_{26}-H_{261}	0.96 (10)
C_{25}-H_{252}	1.01 (11)	C_{26}-H_{262}	1.04 (10)
C_{25}-H_{253}	1.00 (11)	C_{26}-H_{263}	0.86 (10)
		C_{27}-H_{271}	0.92 (12)
		C_{27}-H_{272}	1.01 (12)
		C_{27}-H_{273}	1.03 (12)

[a] Distances involving tolyl group atoms are without esd's.

Table VII. Observed Bond Angles (deg)

Atoms	Angle	Atoms	Angle
P-Mn-C_2	67.5 (3)	Mn-P-C_1	85.2 (3)
P-Mn-C_{21}	86.9 (3)	Mn-P-Tol 1	120[a]
P-Mn-C_{22}	91.8 (3)	Mn-P-Tol 2	125[a]
P-Mn-C_{23}	101.2 (4)	C_1-P-Tol 1	110[a]
P-Mn-C_{24}	159.9 (5)	C_1-P-Tol 2	110[a]
C_2-Mn-C_{21}	87.3 (4)	Tol 1-P-Tol 2	104[a]
C_2-Mn-C_{22}	85.7 (4)		
C_2-Mn-C_{23}	168.7 (5)	Mn-C_{21}-O_{21}	177.1 (11)
C_2-Mn-C_{24}	92.7 (5)	Mn-C_{22}-O_{22}	175.4 (11)
C_{21}-Mn-C_{22}	172.9 (5)	Mn-C_{23}-O_{23}	179.4 (13)
C_{21}-Mn-C_{23}	93.3 (5)	Mn-C_{24}-O_{24}	176.2 (14)
C_{21}-Mn-C_{24}	88.8 (5)		
C_{22}-Mn-C_{23}	93.8 (5)		
C_{22}-Mn-C_{24}	90.2 (5)		
C_{23}-Mn-C_{24}	98.6 (6)		
P-C_1-C_2	101.5 (7)	Mn-C_2-C_1	105.7 (7)
P-C_1-C_6	137.0 (8)	Mn-C_2-C_3	135.3 (8)
C_2-C_1-C_6	121.4 (8)	C_1-C_2-C_3	118.9 (8)
C_2-C_3-C_4	119.6 (8)	C_3-C_4-C_5	120.4 (9)
C_2-C_3-H_3	122.0 (12)	C_3-C_4-C_{25}	120.1 (10)
C_4-C_3-H_3	117.0 (12)	C_5-C_4-C_{25}	119.5 (11)
C_4-C_5-C_6	121.0 (9)	C_5-C_6-C_1	118.6 (8)
C_4-C_5-H_5	121.0 (12)	C_5-C_6-H_6	119.0 (10)
C_6-C_5-H_5	117.0 (11)	C_1-C_6-H_6	123.0 (10)

[a] Angles involving the tolyl groups are without esd's. Angles involving phosphorus and the groups are to atom C_1 of that group.

the ideal angle of 109° but compares well with Ir-P-C_1 angles of 83.7 and 85.7° reported for $Ph_2\overline{PC_6H_4Ir}(PPh_3)L_2$ (L = C_2H_4, CO)[6a] and 83.8 (3) and 84.1 (2)° reported for $IrH[\overline{PPh_2(C_6H_4)}]_2PPh_3$.[6b] The P-$C_1$-$C_2$ angle is also reduced from the ideal 120° to 101.5 (7)° and again compares well with those of the above mentioned compounds, namely, 101.2° and 101.9°,[6a] and 100.3 (7)° and 101.0 (5)°.[6b] However, the most distorted angle is that of P-Mn-C_2, which at 67.5 (3)° is 25% smaller than the ideal 90° angle. The high degree of distortion in these angles probably accounts for the ease of ring expansion when in solution in the presence of donor ligands, giving in the case of OPMn the acyl derivative $Ph_2\overline{PC_6H_4C(O)}Mn(CO)_3L$.[10]

The Mn-P distance (2.324 (3) Å) is somewhat longer than observed in other compounds containing this bond in a metalocyclic ring; i.e., d(Mn-P) = 2.300 (4) Å for compound A[9a,19] shown below. It is appreciably longer than the separation between similarly bonded atoms reported by Robertson and Whimp[20] for compound B (2.279 (3) Å) or in the σ-oxobutyl derivative C d(Mn-P) = 2.295 (3) Å[21] and its isomeric

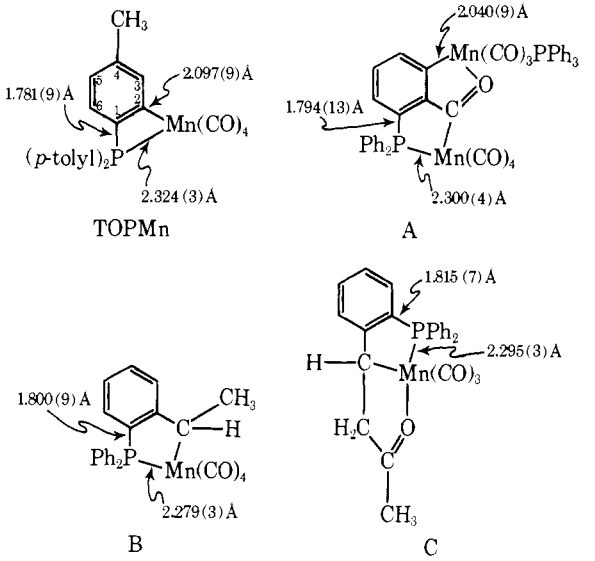
Table VIII. Least-Squares Planes

Plane no.	Direction cosines with respect to a	b	c*	Atoms involved
1	−0.7572	−0.4253	0.4958	Mn, P, C_1, C_2
2	−0.7782	−0.4065	0.4788	C_1-C_6
3	−0.7697	−0.4146	0.4854	Mn, P, C_1-C_6, C_{25}

Deviations of Atoms from Least-Squares Planes (Å × 10^3)

Atom	Plane no. 1	2	3	Atom	Plane no. 1	2	3
Mn	3[a]	−10	11[a]	C_{21}			1825
P	−3[a]	−63	−24[a]	C_{22}			−1829
O_{21}			2982	C_{23}	−22	−73	−36
O_{22}			−2935	C_{24}	114	150	152
O_{23}	−42	−119	−70	C_{25}	−79	47	9[a]
O_{24}	208	278	266	H_3		209	189
C_1	5[a]	−5[a]	14[a]	H_5		−50	−60
C_2	−5[a]	17[a]	23[a]	H_6		−44	−21
C_3	−81	−15[a]	−27[a]				
C_4	−76	1[a]	−16[a]				
C_5	−33	12[a]	7[a]				
C_6	−11	−9[a]	4[a]				

[a] Atoms used in defining least-squares plane.



π-oxopropenyl derivative[22] (D, not illustrated here) d(Mn-P) = 2.300 (1) Å. The Mn-P distance in TOPMn is thus elongated, close to or tending toward that found for the Mn-P separation for unmetalated ligands, i.e., 2.311 (18) Å in *cis*-$CH_3Mn(CO)_4PPh_3$,[23] 2.364 (4) Å for the unmetalated phosphine in compound A, or 2.382 (4) Å for the unmetalated phosphine in tricarbonyl[(methylsulfidomethyl)phenyl-*2,C,S*]triphenylphosphinemanganese.[5c]

The Mn-C_2 bond length in TOPMn of 2.097 (9) Å is similarly somewhat longer than other Mn-C(aromatic) bond lengths which are generally found in the range 2.03-2.07 Å (see ref 24 and others cited therein). That for compound A for instance at 2.040 (9) Å falls well in that range. The P-C_1 bond, on the other hand, does not show any unusual effects. At 1.781

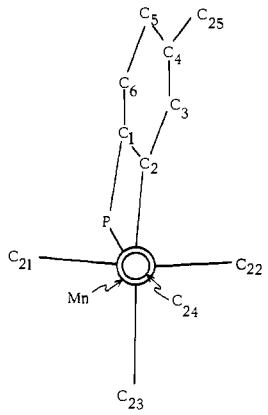


Figure 2. Schematic representation of disposition of least-squares plane system no. 3 ($Mn-P-C_1-C_6-C_{25}$, see Table VIII) with respect to the $Mn(CO)_4$ group.

Table IX. Selected Intramolecular Nonbonding Distances

Atoms	Distance (Å)	Atoms	Distance (Å)
C_{21}-P	2.88	C_{22}-C_3	3.54
C_{22}-P	3.01	C_{21}-C_{23}	2.66
C_{21}-C_2	2.72	C_{22}-C_{23}	2.67
C_{22}-C_2	2.69	C_{21}-C_{24}	2.53
C_{21}-C_3	3.69	C_{22}-C_{24}	2.57

(9) Å it is somewhat shorter than the corresponding P-C distances of P-tolyl(1) (1.803 Å) and P-tolyl(2) (1.812 Å) (see Table VI) but these differences fall within 3σ and 4σ and are of marginal if any significance. Furthermore, similar trends are observed in five-membered metallocycles.[24] Thus the most dramatic effects in the four-membered metallocycle are found around the manganese atom, namely, in the small $P-Mn-C_2$ angle (67.5 (3)°) and in a significant lengthening of the separation from that metal atom to those two bonded atoms. The disposition of carbonyl groups around the manganese atom is also affected, see below.

Structural Features in the Metalated Tolyl Group. No appreciable distortion of the tolyl group was found. The average C-C bond length is 1.382 Å (see Table VI) and the greatest distance from the least-squares plane through the six carbon atoms of the ring to one of the carbon atoms is 0.017 Å (see Table VIII).

Structural Features around Manganese. The principal distortion in the disposition of carbonyl groups around manganese is in the angle $C_{23}-Mn-C_{24}$ = 98.6 (6)° (see Table VII) which is the angle between carbonyl groups situated opposite to and in approximately the same plane as the metallocycle. This no doubt results from the narrowing in the angle $P-Mn-C_2$ of the metallocycle, discussed above. Further examination of some bond angles (Table VII), intramolecular nonbonding distances (Table IX), and deviations of the carbonyl atoms from the least-squares plane no. 3 (Table VIII) reveals that the metalated ring system is somewhat twisted with respect to the carbonyls as illustrated schematically in Figure 2. From the data listed in Table VIII it is evident that while C_{23} is only slightly below (0.036 Å) the least-squares plane no. 3, C_{24} is appreciably above (0.154 Å) this plane. Furthermore, bond angles and nonbonding distances show that C_{21} is very much closer to P than is C_{22} while C_{22} is slightly closer to C_2 than is C_{21} (See Table IX).

The mean Mn-C (carbonyl) distance is 1.819 Å with the greatest distances observed in the trans pair of carbonyls. The shortest such bond is $Mn-C_{24}$, trans to the phosphorus, which would be expected from the reduced electron-accepting properties of this ligand compared to carbonyl groups. The mean C-O distance is 1.142 Å.

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Supplementary Material Available: Table I, the observed and calculated structure factor amplitude (5 pages). Ordering information is given on any current masthead page.

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(5) Recent studies include: (a) hydridochloro(phenylazophenyl-*2-C,N'*)bis(triphenylphosphine)iridium(III)·*n*-hexane, J. F. van Baar, R. Meij, and K. Olie, *Cryst. Struct. Commun.*, **3**, 587 (1974); (b) tetracarbonyl-2-(acetyl)phenylmanganese, C. B. Knobler, S. S. Crawford, and H. D. Kaesz, *Inorg. Chem.*, **14**, 2062 (1975); and (c) tricarbonyl[(methylsulfidomethyl)phenyl-*2-C,S*]triphenylphosphinemanganese, R. J. Doedens, J. T. Veal, and R. G. Little, *ibid.*, **14**, 1138 (1975).

(6) (a) $Ph_2\overline{PC_6H_4}IrL_2PPh_3$, L = C_2H_4, CO, and $(i\text{-}Pr)_2\overline{PC_3H_6}IrL_2P(i\text{-}Pr)_3$, L = C_2H_4, G. Perego, G. Del Piero, M. Cesari, M. G. Clerici, and E. Perrotti, *J. Organomet. Chem.*, **54**, C51 (1973); (b) $IrH[PPh_2(\overline{C_6H_4})]_2PPh_3$, G. Del Piero, G. Perego, A. Zazzetta, and M. Cesari, *Cryst. Struct. Commun.*, **3**, 725 (1974).

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(10) This is the acronym we have found convenient to use as a trivial name for *o*rthometalated *p*hosphine *man*ganese complex. For the corresponding *p*-tolyl derivative named in the title, we added a "T" to the front of the acronym.

(11) (a) For OPMn,[9,10] white needle-like crystals were grown from ether-hexane solutions. Oscillation and Weissenberg (*hk*0 and *hk*1) photographs indicated either tetragonal space group $P4/n$ (no. 85) or $P4_2/n$ (no. 86) (see "International Tables for X-Ray Crystallography", Vol. III, Kynock Press, Birmingham, 1962). The unit cell parameters of these crystals were $a = b$ = 22.93 Å and c = 8.38 Å; these and others obtained using various solvent systems were unsuitable for x-ray data collection, which observations were corroborated in two other laboratories with whom we were in touch through private communications: (b) Professor J. A. Ibers, Northwestern University, Evanston, Ill., and (c) Dr. J. Bell, The Australian National University, Canberra.

(12) The programs used in this work included locally written data reduction programs: JBPATT, JBFOUR, and PEAKLIST, modified versions of Fourier programs written by J. Blount; local versions of ORFLS (Busing, Martin, and Levy), structure factor calculations and full-matrix least-squares refinement; ORTEP (Johnson) figure plotting; MGTL (Schomaker and Trueblood), analysis of possible rigid body, least-squares planes; and ORFEE (Busing, Martin, and Levy), distances, angles, and error computations. All calculations were performed on the IBM 360-91 computer operated by the UCLA Campus Computing Network.

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(16) The function $\Sigma w||F_o| - |F_c||^2$ was minimized in the least-squares refinement and the discrepancy indices were defined as $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, where $w = [1/\sigma(F_o)]^2$.

(17) After our refinement was completed we became aware of a revised value d(C-H) = 0.95 Å recommended for use in rigid body analyses; cf. M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973).

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(24) The relevant parameters are summarized below, using the letters from the diagrams and text to designate the compounds, and using "terminal" to designate aromatic rings on phosphorus not involved in cyclometalation:

	d[P-C(aromatic)], Å		
Cmpd	Metalocycle	Terminal	Terminal
A	1.794	1.830	1.825
B	1.800	1.820	1.820
C	1.815	1.848	1.831
D	1.795	1.823	1.823

Further Studies of the Electronic Spectra of $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$. Assignment of the Weak Bands in the 600–350-nm Region. Estimation of the Dissociation Energies of Metal–Metal Quadruple Bonds

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Abstract: Previously published evidence bearing on the polarizations and assignments for the strong bands in $Re_2Cl_8^{2-}$ and related species is synthesized and it is shown that work from our two laboratories gives a consistent picture. New polarized spectra of thick crystals of $(n\text{-}Bu_4N)_2[Re_2Cl_8]$ and $(n\text{-}Bu_4N)_2[Re_2Br_8]$, measured at 15 K, are reported and discussed. Four new regions of weak absorption between the more intense $\delta \rightarrow \delta^*$ (14 700 cm^{-1}) and $\pi(Cl) \rightarrow \delta^*$ (32 600 cm^{-1}) bands of $Re_2Cl_8^{2-}$ have been characterized. The first weak band of $(n\text{-}Bu_4N)_2[Re_2Cl_8]$ maximizes at 17 675 cm^{-1} and consists of three progressions in a 225-cm^{-1} excited state a_{1g}(ReRe) stretching vibration built on three origins. Two of the progressions are polarized parallel and one perpendicular with respect to the ReRe molecular axis. The band red shifts by only 200 cm^{-1} in $(n\text{-}Bu_4N)_2[Re_2Br_8]$. The results indicate that the band is attributable to the electric-dipole-forbidden, metal-localized transition $\delta \rightarrow \pi^*(^1A_{1g} \rightarrow {}^1E_g)$. A second absorption at 20 940 cm^{-1} exhibits only perpendicularly polarized progressions on several vibronic origins with a common vibrational spacing of ca. 400 cm^{-1} (a_{1g}(ReCl) stretch). This band also intensifies and red shifts upon warming (15 to 300 K). The 1790-cm^{-1} red shift of this band in $(n\text{-}Bu_4N)_2[Re_2Br_8]$ pinpoints it as a $\delta \rightarrow d_{x^2-y^2}(b_{2u})(^1A_{1g} \rightarrow {}^1A_{1u})$ transition. The third band, which is at 23 645 cm^{-1}, is extremely weak and only one perpendicularly polarized progression in the a_{1g}(ReReCl) skeletal bending mode was detected. A $\pi \rightarrow \delta^*(^1A_{1g} \rightarrow {}^1E_g)$ assignment is suggested. The fourth absorption system is comprised of two sharp peaks at 27 000 and 28 100 cm^{-1}, which are parallel polarized. These peaks shift to 21 290 and 22 080 cm^{-1} in $(n\text{-}Bu_4N)_2[Re_2Br_8]$, consistent with a ligand to metal charge transfer (LMCT) assignment. As the LMCT transitions to a^1E_u and b^1E_u states are not split appreciably in $Re_2Cl_8^{2-}$, it is suggested that the fourth weak band system is derived from the corresponding $e_g\pi(Cl) \rightarrow \delta^*(^1A_{1g} \rightarrow A_{2u}(a,b^3E_u))$ excitations. Dissociation energies of Re–Re and Mo–Mo quadruple bonds have been estimated from a Birge–Sponer extrapolation, giving values of 115–130 kcal/mol for the former and 110–160 kcal/mol for the latter.

The earliest, tentative suggestions[1,2] as to how to assign the electronic spectrum of $Re_2Cl_8^{2-}$, the species in which the existence of quadruple bonds was discovered,[1,3] as well as the extension of such assignments to the spectra of closely related complexes, have not withstood recent experimental[4-10] and theoretical[6,10-12] scrutiny. Work done within the past few years[4-12] has provided new spectral assignments that seem certain to be correct in their essentials and bring us to a point of departure for delving more deeply into the details of the spectra and bonding in the entire class of compounds[13] containing quadruple M–M bonds and other multiple bonds between metal atoms. One purpose of this paper is to present some new and pertinent facts concerning the spectra of the $Re_2X_8^{2-}$ (X = Cl, Br) ions.

In the past it has appeared that there have been disagreements between publications from our two laboratories as to observations and interpretations regarding the electronic structural properties of $Re_2Cl_8^{2-}$ and related species containing quadruple bonds. In actual fact, we are in essentially complete agreement as to the observations and their interpretation. In view of the importance of establishing a clear picture of the situation regarding the prototypal[1,3] quadruple bond, i.e., that in $Re_2Cl_8^{2-}$, we also present in this report a synthesis of some isolated observations recorded in earlier publications, as well as a needed critique of our previous estimates of the bond dissociation energies (BDE's) of quadruple bonds.

Contrary to the impression created in a recent publication[5] from one of our laboratories, there was in fact a sound basis for the claim, which was advanced[4,6] first by Cowman and Gray, that the 14 000-cm^{-1} absorption band in $Re_2Cl_8^{2-}$ is polarized parallel to the Re–Re axis. The crystallographic results, showing as they do the existence of a disorder in the crystals, taken together with the earlier crystal spectra,[4,7] confirmed in the most direct way the aforementioned assignment of polarization. The misunderstanding between our laboratories was in large part attributable to the fact that the logic of the Cowman–Gray argument was not presented in full form in either of the two published documents.[4,6] To set the record straight, we shall now outline the main parts of the argument.

It should be recalled that each of the three complexes, (*n*-