Intramolecular Metalation with Methylmanganese and Methylrhenium Carbonyl Complexes. 10. The Crystal and Molecular Structures of the Secondary Metalation Products *abd*-Tricarbonyl-*c*-triphenylphosphine-*efgk*-[μ-[carbonyl[6-(diphenylphosphino)-*o*-phenylene]]](*hijl*-tetracarbonylmanganese)manganese, $Ph_2P[C_6H_3(CO)Mn(CO)_4]Mn(CO)_3PPh_3$, and a Rhenium-Containing Derivative[1]

B. T. Huie, C. B. Knobler, G. Firestein, R. J. McKinney, and H. D. Kaesz*

Contribution No. 3729 from the Department of Chemistry, University of California, Los Angeles, California 90024. *Received October 26, 1976*

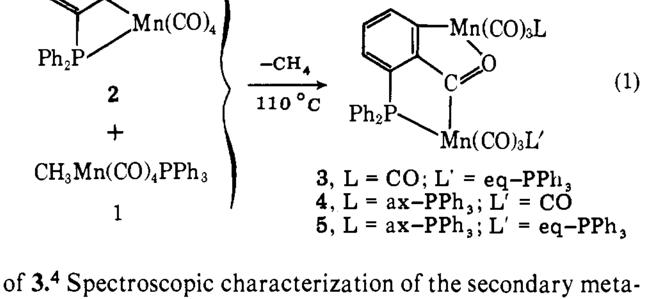
Abstract: The structures of *abd*-tricarbonyl-*c*-triphenylphosphine-*efgk*-[μ-[carbonyl[6-(diphenylphosphino)-*o*-phenylene]]]-(*hijl*-tetracarbonylmanganese)manganese (**3**) and *abcd*-tetracarbonyl-*efgk*-[μ-[carbonyl[6-(diphenylphosphino)-*o*-phenylene]]](*hijl*-tetracarbonylmanganese)rhenium (**6**) have been determined from data collected on an automated diffractometer with monochromatized Mo Kα radiation. Compound **3** crystallizes in the monoclinic space group $C2/c$ with a = 10.763 (2) Å, b = 34.713 (5) Å, c = 21.479 (3) Å, and β = 92.93 (1)°. The density of 1.42 g cm^{-3} calculated on the basis of eight molecules per unit cell agrees with the flotation value of 1.44 g cm^{-3}. Compound **6** crystallizes in the monoclinic space group $P2_1/c$ with a = 12.357 (6) Å, b = 11.258 (6) Å, c = 21.443 (5) Å, and β = 111.40 (3)°. The density of 1.80 g cm^{-3} calculated on the basis of four molecules per unit cell agrees with the flotation value of 1.77 g cm^{-3}. The structures were solved by use of Patterson and Fourier summations and refined by use of full matrix least-squares methods to conventional R indices of 5.7 (**3**) and 4.1% (**6**) based on 3211 and 3064 independent observed reflections, respectively. The molecular structure of **3** contains two manganese atoms each with an essentially octahedral arrangement of ligands. One manganese atom is coordinated to four carbonyl groups while the other is coordinated to three carbonyl groups and a triphenylphosphine. The two manganese atoms are bridged by a novel quadridentate ligand which is bidentate to each metal atom. The molecule contains an extended planar tricyclic ring system which includes the bridging ligand and both metal atoms. The molecular structure of **6** is very similar to that of **3**, differing by the replacement of the $Mn(CO)_3PPh_3$ moiety of **3** by $Re(CO)_4$. Examination and comparison of bond distances in these and related compounds suggests that the π electrons of the planar ring system are delocalized.

Recently we reported that the thermolysis of *cis*-$CH_3Mn(CO)_4PPh_3$ (**1**) yielded a primary metalation product, $Ph_2PC_6H_4Mn(CO)_4$ (**2**),[2] as well as three secondary metalation products,

$$Ph_2P[C_6H_3(CO)Mn(CO)_3L]Mn(CO)_3L'$$

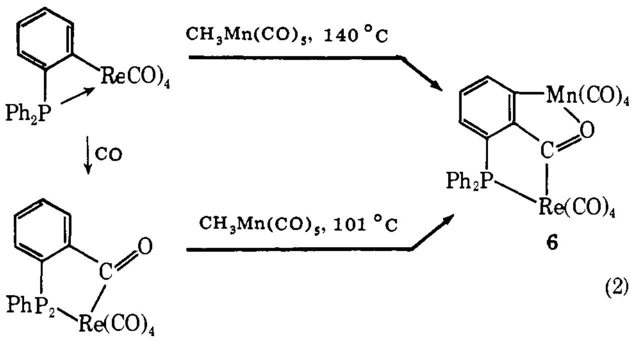
$$(L = CO, L' = PPh_3, \mathbf{3}; L = PPh_3, L' = CO, \mathbf{4}; L = L' = PPh_3, \mathbf{5})^3$$

Products **3** and **4** are empirical dimers of **2**, derived from the action of **1** on the primary metalation product, **2** (see reaction 1), while product **5** is a triphenylphosphine substitution product of **3**.[4] Spectroscopic characterization of the secondary metalation products, **3–5**, did not lead to unambiguous structural assignments[3] and the single-crystal x-ray diffraction studies which we undertook to determine their structures are described here and in a companion paper.[4]



(1)

In order unambiguously to establish the sequence of metal substitution during the formation of the secondary metalation products, the mixed metal derivative **6** was prepared by two parallel reaction paths.[3]



(2)

Here we report the crystal and molecular structures of the secondary metelation products, *abd*-tricarbonyl-*c*-triphenylphosphine-*efgk*-[μ[carbonyl[6-(diphenylphosphino)-*o*-phenylene]]](*hijl*-tetracarbonylmanganese)manganese (**3**), hereafter called DiMn,[5] and the closely related mixed metal derivative *abcd*-tetracarbonyl-*efgk*-[μ-carbonyl[6-(diphenylphosphino)-*o*-phenylene]]](*hijl*-tetracarbonylmanganese)-rhenium, (**6**), hereafter called ReMn.[5] The structures of **4** and **5** are described in a companion paper[4] and the data for this closely related set of derivatives are discussed and compared in the present work. A preliminary account of the structure of **3** (DiMn) has been reported.[6]

Experimental Section

The X-Ray Data for 3 (DiMn). The preparation of DiMn has been described elsewhere.[2,3] Crystals suitable for x-ray analysis were grown from an ether/hexane solution. The compound was dissolved in a minimum volume of ether and the solution diluted with an equal volume of hexane. The resulting solution was filtered and put into a Schlenk tube. Solvent was removed with a water aspirator until small

Table I. Atomic Positional Parameters of DiMn (**3**)

Atom	x	y	z
Mn1	0.44117 (11)	0.30407 (4)	0.60869 (5)
Mn2	0.19677 (10)	0.39180 (3)	0.47495 (5)
P1	0.06433 (17)	0.39361 (6)	0.55779 (9)
P2	0.33324 (17)	0.38648 (6)	0.39790 (8)
C1	0.4483 (7)	0.3521 (2)	0.4275 (3)
C2	0.4264 (6)	0.3393 (2)	0.4879 (3)
C3	0.5058 (6)	0.3139 (2)	0.5222 (3)
C4	0.6125 (7)	0.3019 (3)	0.4929 (4)
C5	0.6332 (8)	0.3130 (3)	0.4330 (4)
C6	0.5524 (9)	0.3378 (3)	0.3987 (4)
C7	0.3151 (6)	0.3533 (2)	0.5183 (3)
C11[a]	0.3695 (8)	0.3003 (3)	0.6833 (4)
C12	0.5376 (8)	0.3460 (3)	0.6352 (4)
C13	0.5662 (9)	0.2712 (3)	0.6299 (4)
C14	0.3512 (8)	0.2626 (3)	0.5770 (4)
C21	0.1100 (7)	0.4266 (3)	0.4268 (4)
C22	0.3009 (7)	0.4257 (2)	0.5176 (4)
C23	0.0986 (7)	0.3535 (2)	0.4392 (4)
O7	0.3067 (4)	0.3410 (1)	0.5730 (2)
O11	0.3276 (7)	0.2969 (2)	0.7311 (3)
O12	0.5983 (7)	0.3710 (2)	0.6507 (4)
O13	0.6448 (6)	0.2466 (2)	0.6404 (3)
O14	0.2984 (7)	0.2360 (2)	0.5594 (4)
O15	0.0586 (6)	0.4471 (2)	0.3923 (3)
O22	0.3698 (5)	0.4445 (2)	0.5462 (3)
O24	0.0332 (6)	0.3317 (2)	0.4156 (3)
H4	0.672 (7)	0.285 (2)	0.514 (4)
H5	0.698 (8)	0.312 (2)	0.413 (4)
H6	0.568 (8)	0.343 (2)	0.360 (4)

[a] Hydrogen atoms and carbonyl groups are numbered to correspond to the carbon or metal atoms to which they are bonded.

Table II. Atomic Thermal Parameters of DiMn (**3**) (×10^4)

Atom	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mn1	73.9 (12)	7.8 (1)	16.7 (3)	4.6 (3)	−1.3 (4)	1.6 (2)
Mn2	51.6 (11)	5.6 (1)	14.7 (3)	0.0 (3)	−0.7 (4)	0.0 (2)
P1	52.6 (19)	6.4 (2)	18.5 (5)	−0.1 (5)	3.4 (8)	0.4 (3)
P2	66.4 (20)	5.9 (2)	13.4 (4)	−1.2 (5)	0.4 (8)	0.4 (2)
C1	72 (8)	7 (1)	15 (2)	−3 (2)	5 (3)	−2 (1)
C2	49 (7)	6 (1)	15 (2)	2 (2)	−1 (3)	−1 (1)
C3	55 (7)	6 (1)	20 (2)	2 (2)	−2 (3)	0 (1)
C4	63 (8)	10 (1)	26 (2)	5 (2)	4 (4)	0 (1)
C5	96 (10)	11 (1)	28 (3)	10 (3)	21 (4)	2 (1)
C6	107 (10)	9 (1)	21 (2)	5 (3)	14 (4)	2 (1)
C7	47 (7)	5 (1)	17 (2)	0 (2)	−5 (3)	0 (1)
C11	114 (11)	12 (1)	27 (3)	10 (3)	−1 (4)	3 (1)
C12	88 (10)	11 (1)	24 (2)	5 (3)	−6 (4)	−1 (1)
C13	118 (11)	11 (1)	20 (2)	1 (3)	−3 (4)	2 (1)
C14	99 (10)	9 (1)	24 (2)	8 (3)	4 (4)	4 (1)
C21	67 (9)	10 (1)	23 (2)	3 (2)	2 (4)	1 (1)
C22	61 (8)	6 (1)	19 (2)	3 (2)	10 (3)	0 (1)
C24	72 (9)	9 (1)	19 (2)	−2 (2)	−1 (4)	1 (1)
O7	47 (7)	5 (1)	17 (2)	0 (2)	−5 (3)	0 (1)
O11	191 (10)	23 (1)	28 (2)	18 (3)	32 (4)	7 (1)
O12	197 (11)	17 (1)	43 (2)	−22 (3)	−19 (4)	−7 (1)
O13	130 (8)	13 (1)	39 (2)	21 (2)	−5 (3)	5 (1)
O14	179 (10)	9 (1)	49 (3)	−5 (2)	−20 (4)	−1 (1)
O21	121 (7)	13 (1)	35 (2)	15 (2)	−3 (3)	8 (1)
O22	104 (7)	11 (1)	28 (2)	−11 (2)	−7 (3)	−5 (1)
O24	112 (7)	12 (1)	38 (2)	−12 (2)	−20 (3)	3 (1)
	B, Å^2					
H4	5.1					
H5	5.7					
H6	5.4					

[a] The expression for the anisotropic temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

crystals started to form. The solution was then heated to redissolve all of the compound and sealed under nitrogen and the Schlenk tube immersed in a Dewar flask of hot (~60 °C) salt water. This entire assembly, wrapped in cheesecloth, was placed in the low-temperature compartment of a refrigerator at −20 °C overnight, yielding orange parallelepiped-shaped crystals.

Weissenberg and precession photographs revealed the systematic absences hkl for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$, compatible with space group Cc or $C2/c$.[7]

A crystal bounded by {100}, {010}, and {001} with dimensions normal to these faces of 0.24, 0.22, and 0.18 mm was chosen for intensity measurements and mounted with the b axis close to the ϕ axis of a four-circle computer-controlled diffractometer (Syntex P$\bar{1}$ autodiffractometer) equipped with a scintillation counter and a graphite monochromator. Lattice parameters, determined by a least-squares fit of 15 accurately centered reflections (2θ range 28–32°), are a = 10.763 (2) Å, b = 34.713 (5) Å, c = 21.479 (3) Å, β = 92.93 (1)°.[8] The unit cell volume is 8014 Å^3. The density at room temperature of 1.44 g cm^{-3} was obtained by flotation in a mixture of bromoform and hexane. The crystallographic density assuming eight formula units in the unit cell is 1.42 g cm^{-3}.

Intensities were measured using Mo Kα radiation and a θ–2θ scan method. The scan rate varied stepwise from 24°/min in 2θ for the strongest reflections to 2.4°/min for the weakest. The scan range was from 0.8° below the Kα_1 peak to 0.8° above the Kα_2 peak. The ratio of background time to scan time was 0.8. The pulse height analyzer was set at an 85% window for Mo Kα radiation.

The intensities of three reflections (3,−1,−5; 3,3,4; 1,−5,2) were measured after each 97 intensity measurements. The variations in the measured values of these standards were random and were not statistically significant. In all, 6266 unique reflections for which 2Å ≤ 50° were measured; 3211 with $I \geq 3\sigma(I)$ were considered observed.

The data reduction and processing were carried out by use of PIBAR[9] as described previously.[1]

The calculated value of the absorption coefficient μ is 8 cm^{-1} for Mo Kα radiation. The transmission factors range from 0.80 to 0.90 in the 2θ range involved. It is estimated that an absorption effect would cause fluctuations of no more than ±5% in I or ±2.5% in F_o. No corrections for the effects of absorption were made.

Determination and Refinement of the Structure of DiMn. The original space group determination was ambiguous (Cc or $C2/c$); statistical studies employing Wilson plot[10] and CENACEN[11] indicated a centrosymmetric space group, $C2/c$; the data are presented in ref 1a.

An inner sphere of 2518 reflections with $h \leq 9$, $k \leq 27$, and $|l| \leq 17$ was used for the solution and early refinement of this structure. Trial positions for the manganese atoms were found from a three-dimensional Patterson summation.[9] Fourier syntheses yielded possible positions for phosphorus, carbon, and oxygen atoms. Most of these could be fit into expected fragments: five phenyl rings and seven carbonyl groups. Eight peaks, however, could not be fit into previously predicted models. Another Fourier synthesis was carried out phased on the 2 Mn atoms, 2 P atoms, 37 C atoms, and 7 O atoms described above. This electron density map showed, in addition to the input atoms, the same eight peaks which had not been assigned. These were finally described as a benzoyl group, completing the structure.

Refinement was carried out by use of full matrix least-squares procedures[9] using atomic scattering factors for all nonhydrogen atoms as compiled by Hanson et al.[12] Hydrogen atomic scattering factors were those of Stewart et al.[13] Anomalous dispersion corrections ($\Delta f'$ and $\Delta f''$) were applied to the form factors for manganese and phosphorus.[14] Least-squares refinement of positional and isotropic thermal parameters for all nonhydrogen atoms led to a conventional discrepancy index, R,[15] of 0.075. Further refinement, with anisotropic thermal parameters for Mn and P, led to convergence at R = 0.070 (for 2518 reflections).

A difference Fourier map served to locate all 28 hydrogen atoms and these positions were verified by use of the program HPOSN.[9] The five phenyl rings were treated as rigid groups of D_{6h} symmetry for the C_6 skeleton, d(C–C) = 1.395 Å and d(C–H) = 1.00 Å, in all subsequent least-squares refinements.[16]

Refinement was continued using all 3211 observed reflections. All nongroup atoms (except hydrogen) were allowed to vibrate anisotropically and each hydrogen atom was assigned an isotropic tem-

Table III. Group Parameters of DiMn (**3**)

Groups	x	y	z	ϕ[a]	θ[a]	ρ[a]
Ph 1	0.0169 (5)	0.3491 (1)	0.5959 (2)	−2.453 (4)	2.377 (3)	0.691 (4)
Ph 2	0.1183 (5)	0.4217 (2)	0.6271 (2)	0.649 (4)	2.905 (3)	1.034 (4)
Ph 3	−0.0863 (4)	0.4156 (1)	0.5330 (2)	−0.528 (3)	2.959 (3)	−2.796 (3)
Ph 4	0.2749 (5)	0.3678 (2)	0.3234 (2)	−2.890 (4)	−2.845 (3)	−1.117 (4)
Ph 5	0.4169 (5)	0.4300 (1)	0.3747 (2)	0.881 (3)	−2.644 (3)	−0.319 (4)

[a] The definitions of these parameters are given in ref 16; measured in radians.

Table IV. Derived Parameters for Group Atoms of DiMn (**3**)

Group	Atom	x	y	z	B, Å^2
Ph 1	C1	0.0169	0.3491	0.5959	3.7 (2)
	C2	−0.0495	0.3518	0.6498	5.2 (2)
	C3	−0.0872	0.3184	0.6797	6.3 (2)
	C4	−0.0586	0.2823	0.6557	6.7 (2)
	C5	0.0078	0.2796	0.6018	6.4 (2)
	C6	0.0455	0.3130	0.5718	4.4 (2)
	H2	−0.0717	0.3798	0.6685	6.2[a]
	H3	−0.1388	0.3205	0.7216	7.3
	H4	−0.0879	0.2564	0.6789	7.7
	H5	0.0301	0.2516	0.5331	7.4
	H6	0.0971	0.3109	0.5299	5.4
Ph 2	C1	0.1183	0.4217	0.6271	3.4 (2)
	C2	0.2069	0.4042	0.6675	5.0 (2)
	C3	0.2494	0.4230	0.7218	6.1 (2)
	C4	0.2033	0.4594	0.7357	6.3 (2)
	C5	0.1148	0.4769	0.6954	6.9 (2)
	C6	0.0722	0.4580	0.6410	5.6 (2)
	H2	0.2427	0.3759	0.6566	6.0
	H3	0.3182	0.4094	0.7532	7.1
	H4	0.2364	0.4741	0.7780	7.3
	H5	0.0789	0.5052	0.7062	7.9
	H6	0.0034	0.4716	0.6097	6.6
Ph 3	C1	−0.0863	0.4156	0.5330	3.3 (1)
	C2	−0.1966	0.3945	0.5324	4.6 (2)
	C3	−0.3082	0.4114	0.5107	5.3 (2)
	C4	−0.3094	0.4494	0.4897	4.8 (2)
	C5	−0.1991	0.4705	0.4903	4.9 (2)
	C6	−0.0875	0.4536	0.5120	4.3 (2)
	H2	−0.1957	0.3649	0.5487	5.6
	H3	−0.3940	0.3950	0.5102	6.3
	H4	−0.3961	0.4626	0.4729	5.8
	H5	−0.2000	0.5001	0.4740	5.9
	H6	−0.0017	0.4700	0.5124	5.3
Ph 4	C1	0.2749	0.3678	0.3234	3.6 (2)
	C2	0.2204	0.3927	0.2789	5.0 (2)
	C3	0.1682	0.3781	0.2230	6.4 (2)
	C4	0.1705	0.3385	0.2116	6.4 (2)
	C5	0.2249	0.3136	0.2560	7.2 (3)
	C6	0.2772	0.3282	0.3119	5.5 (2)
	H2	0.2186	0.4234	0.2879	6.0
	H3	0.1258	0.3974	0.1885	7.4
	H4	0.1299	0.3272	0.1681	7.4
	H5	0.2267	0.2829	0.2471	8.2
	H6	0.3195	0.3088	0.3464	6.5
Ph 5	C1	0.4169	0.4300	0.3747	3.3 (1)
	C2	0.5210	0.4272	0.3389	5.3 (2)
	C3	0.5825	0.4605	0.3209	6.5 (2)
	C4	0.5399	0.4965	0.3389	5.5 (2)
	C5	0.4358	0.4995	0.3747	4.7 (2)
	C6	0.3743	0.4661	0.3926	3.8 (2)
	H2	0.5541	0.3991	0.3250	6.3
	H3	0.6634	0.4582	0.2931	7.5
	H4	0.5877	0.5224	0.3249	6.5
	H5	0.4027	0.5274	0.3886	5.7
	H6	0.2934	0.4783	0.4205	4.8

[a] No estimated standard deviations are given for the temperature parameters of the hydrogen atoms because their values have not been refined.

Table VII. Atomic Positional Parameters of ReMn (**6**)

Atom	*x*	*y*	*z*
Re	0.35135 (4)	0.23762 (3)	0.43245 (2)
Mn	0.54653 (13)	0.21944 (14)	0.68183 (7)
P	0.1976 (2)	0.3543 (2)	0.4486 (1)
O7	0.5087 (6)	0.2020 (6)	0.5800 (3)
O11	0.7533 (9)	0.0622 (9)	0.7090 (5)
O12	0.3761 (10)	0.0302 (10)	0.6790 (5)
O13	0.5714 (8)	0.2459 (9)	0.8235 (4)
O14	0.6783 (9)	0.4463 (8)	0.6964 (5)
O21	0.2407 (9)	0.2523 (10)	0.2762 (4)
O22	0.2162 (9)	0.0075 (8)	0.4393 (6)
O23	0.5661 (9)	0.0825 (9)	0.4447 (5)
O24	0.5010 (8)	0.4597 (8)	0.4309 (5)
C1	0.2513 (9)	0.3819 (9)	0.5377 (5)
C2	0.3517 (9)	0.3210 (8)	0.5752 (5)
C3	0.4023 (9)	0.3249 (9)	0.6446 (5)
C4	0.3476 (11)	0.4006 (11)	0.6756 (6)
C5	0.2543 (11)	0.4681 (12)	0.6404 (6)
C6	0.2056 (11)	0.4593 (12)	0.5720 (6)
C7	0.4148 (8)	0.2499 (9)	0.5414 (4)
C11	0.6744 (13)	0.1221 (12)	0.6990 (6)
C12	0.4407 (12)	0.1003 (11)	0.6770 (6)
C13	0.5651 (10)	0.2369 (11)	0.7690 (5)
C14	0.6308 (11)	0.3594 (11)	0.6883 (6)
C21	0.2831 (9)	0.2443 (12)	0.3335 (5)
C22	0.2676 (11)	0.0938 (11)	0.4376 (6)
C23	0.4859 (11)	0.1387 (10)	0.4394 (6)
C24	0.4438 (11)	0.3807 (10)	0.4311 (6)
H4[a]	0.377 (9)	0.412 (9)	0.729 (6)
H5	0.208 (10)	0.518 (10)	0.660 (6)
H6	0.140 (11)	0.504 (11)	0.551 (6)

[a] Hydrogen atoms are numbered to correspond to the carbon atoms to which they are bonded.

perature factor 1 Å^2 larger than that of the carbon atom to which it is attached. The positional (but not the thermal) parameters of the three nongroup hydrogen atoms were also allowed to vary. The agreement factors R and R_w[15] decreased to their final values of 0.057 and 0.062, respectively. The standard deviation in an observation of unit weight is 1.60.

A final three-dimensional difference Fourier synthesis showed residuals in the range from −0.4 to 0.6 e/Å^3; all peaks with |maxima| > 0.3 e/Å^3 are associated with the phenyl rings that had been treated as rigid groups.

The final least-squares parameters are given in Tables I-II with the standard deviations of these parameters as derived from the inverse matrix. Table IV represents the parameters of the carbon and hydrogen atoms derived from the data of Table III. The final values of $|F_o|$ and $|F_c|$ are shown in Table V (supplementary material).

Analysis of possible rigid-body motion of this molecule was carried out by use of the program (ACA no. 1) written by Schomaker and Trueblood (1968).[17] Some results of this analysis are shown in Table VI (supplementary material).

The X-Ray Data for 6 (ReMn). The preparation of ReMn has been described elsewhere.[3] 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 was warmed to redissolve all the solid material. The flask was sealed under nitrogen and placed in the low-temperature compartment of a refrigerator at −20 °C overnight. Yellow, air-stable crystals were obtained in the shape of parallelepipeds.

Data Collection. A crystal bounded by {100}, {010}, and {001} with crystal dimensions normal to these faces of 0.100, 0.275, and 0.100 mm, 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 using this crystal.

Oscillation and Weissenberg (*h*0*l* and *h*1*l*) photographs revealed

Table VIII. Atomic Thermal Parameters of ReMn (**6**) (×10^4)[a]

Atom	$\beta 11$	$\beta 22$	$\beta 33$	$\beta 12$	$\beta 13$	$\beta 23$
Re	60.4 (3)	51.7 (3)	12.6 (1)	−4.8 (4)	7.4 (1)	−2.6 (2)
Mn	70.2 (14)	70.5 (15)	13.8 (4)	−1.0 (11)	6.5 (6)	3.0 (6)
P	51 (2)	69 (2)	14 (1)	−4 (2)	3 (1)	−2 (1)
O7	78 (7)	72 (6)	14 (2)	4 (5)	10 (3)	0 (3)
O11	132 (12)	141 (12)	39 (4)	61 (10)	29 (5)	21 (5)
O12	155 (13)	137 (12)	41 (4)	−62 (10)	27 (6)	−2 (5)
O13	159 (11)	168 (12)	20 (2)	−12 (10)	25 (4)	−3 (5)
O14	128 (11)	98 (9)	29 (3)	−32 (8)	18 (5)	−5 (4)
O21	173 (12)	193 (13)	14 (2)	8 (12)	3 (4)	−4 (5)
O23	128 (12)	136 (11)	44 (4)	59 (9)	32 (6)	8 (5)
O24	105 (10)	105 (9)	37 (3)	−37 (8)	18 (5)	12 (4)
C1	63 (10)	65 (9)	18 (3)	−5 (8)	11 (4)	−3 (4)
C2	54 (8)	54 (8)	14 (2)	−3 (7)	5 (4)	0 (4)
C3	73 (10)	69 (9)	11 (3)	−8 (8)	8 (4)	1 (4)
C4	72 (11)	101 (12)	20 (4)	−19 (10)	17 (5)	−10 (5)
C5	75 (12)	131 (14)	27 (4)	24 (11)	21 (6)	−20 (6)
C6	61 (11)	115 (13)	24 (4)	6 (9)	11 (5)	−18 (6)
C7	65 (8)	56 (8)	13 (2)	−5 (8)	9 (4)	4 (4)
C11	105 (15)	100 (13)	16 (4)	7 (11)	10 (6)	14 (5)
C12	104 (14)	82 (11)	17 (3)	−16 (10)	7 (5)	0 (5)
C13	92 (10)	94 (11)	21 (3)	−1 (10)	13 (5)	5 (6)
C14	75 (12)	90 (12)	15 (3)	9 (9)	3 (5)	7 (5)
C21	73 (10)	120 (13)	22 (3)	4 (11)	9 (5)	−8 (7)
C22	85 (12)	77 (11)	28 (4)	8 (9)	15 (6)	4 (5)
C23	80 (13)	84 (11)	22 (4)	8 (10)	10 (6)	−4 (5)
C24	71 (12)	81 (11)	15 (3)	30 (9)	2 (5)	3 (5)
H4	5.0[b]					
H5	5.6[b]					
H6	5.4[b]					

[a] The expression for the anisotropic temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] These values were included but not refined in final least-squares cycles.

Table IX. Group Parameters of ReMn (**6**)

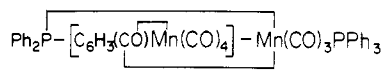
Group	x^a	y	z	ϕ	θ	ρ
Ph 1	0.1559 (7)	0.5002 (5)	0.4108 (4)	−1.140 (6)	−2.493 (5)	−2.638 (6)
Ph 2	0.0625 (6)	0.2735 (7)	0.4295 (4)	1.205 (15)	−1.956 (6)	−2.480 (15)

[a] The definitions of these parameters are given in ref 16.

Table X. Derived Positional and Isotropic Thermal Parameters for Group Atoms of ReMn (**6**)

Group	Atom	x	y	z	B, Å^2
Ph 1	C1 1	0.1559	0.5002	0.4108	4.0 (2)
	C1 2	0.0478	0.5213	0.3607	6.7 (4)
	C1 3	0.0195	0.6348	0.3339	8.3 (4)
	C1 4	0.0992	0.7273	0.3570	6.7 (3)
	C1 5	0.2072	0.7061	0.4071	6.3 (3)
	C1 6	0.2356	0.5926	0.4339	4.8 (3)
	H1 7	−0.0141	0.4495	0.3427	7.7[a]
	H1 8	−0.0645	0.6512	0.2950	9.3
	H1 9	0.0771	0.8155	0.3362	7.8
	H1 10	0.2692	0.7780	0.4251	7.3
	H1 11	0.3196	0.5762	0.4728	5.9
Ph 2	C2 1	0.0625	0.2735	0.4295	4.5 (2)
	C2 2	0.0103	0.2261	0.3653	6.4 (3)
	C2 3	−0.0918	0.1601	0.3492	9.2 (5)
	C2 4	−0.1417	0.1415	0.3972	9.6 (5)
	C2 5	−0.0895	0.1889	0.4614	8.9 (5)
	C2 6	0.0126	0.2549	0.4775	5.5 (3)
	H2 7	0.0490	0.2405	0.3279	7.4
	H2 8	−0.1324	0.1233	0.2993	10.2
	H2 9	−0.2210	0.0903	0.3847	10.5
	H2 10	−0.1282	0.1745	0.4988	9.9
	H2 11	0.0532	0.2917	0.5274	6.6

[a] No estimated standard deviations are given for the temperature parameters of the hydrogen atoms because their values have not been refined. These are assigned to be one unit greater than the value of the corresponding parameter of the carbon atom to which each is attached.



$Ph_2P-[C_6H_3(CO)Mn(CO)_4]-Mn(CO)_3PPh_3$

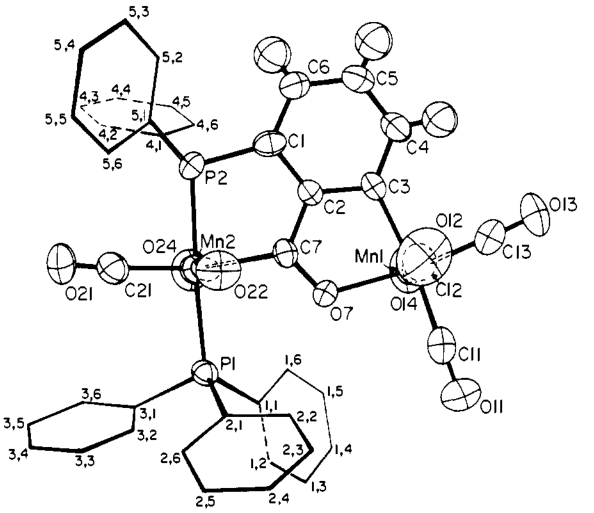


Figure 1. ORTEP plot of the DiMn molecule showing thermal ellipsoids at the 50% probability level. Carbon atoms of nonmetalated phenyl groups are indicated by numbers only and hydrogen atoms are omitted.

systematic absences for $h0l$ of $l = 2n + 1$ only. The crystal was transferred to a Syntex P$\bar{1}$ four-circle automated diffractometer equipped with a scintillation counter, a pulse height analyzer, and a graphite monochromatized Mo Kα radiation source (λ = 0.71069 Å). Diffractometer measurements indicated systematic absences in $0k0$ of $k = 2n + 1$ and a space group assignment in the monoclinic system, $P2_1/c$.[7]

Table XII. Least-Squares Planes of DiMn (**3**)

Plane	Direction cosines (×10^5) with respect to a	b	c^*	Description of plane
A	50 163	78 350	36 673	Benzene ring
B	51 013	78 094	36 042	Mn1, C2, C3, C7, O7
C	52 047	75 503	39 881	Mn2, P2, C1, C2, C7
D	51 400	77 112	37 574	11-atom tricycle system
E	52 327	76 669	37 198	Tricyclic system plus equatorial ligands

Interplanar Angles

Planes	Angle, deg
A and B	179.4
A and C	177.6
B and C	177.3

Lattice parameters, determined by a least-squares fit of 15 accurately centered reflections (2θ = 40–50°), are a = 12.357 (6) Å, b = 11.258 (6) Å, c = 21.443 (5) Å, and β = 111.40 (3)°. The density at room temperature of 1.77 g cm^{-3} was obtained by flotation in bromoform and n-hexane. The crystallographic density, assuming four formula units in the unit cell, is 1.80 g cm^{-3}.

Intensities were collected at room temperature using the θ–2θ scan method 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 (008, 332, and 108) were measured after every 97 reflections throughout the data collection to monitor crystal and diffractometer

Table XIII. Deviations of Atoms from Least-Squares Planes of DiMn (3) (Å × 10^3)[a]

Atom	*A*	*B*	*C*	*D*	*E*
Mn1	1	−2*	135	19*	7*
Mn2	89	78	−3*	13*	−25*
P1	30	−8	−36	−50	−110*
P2	118	128	7*	48*	31*
C1	21*	41	−12*	−13*	−16*
C2	−4*	6*	11*	−25*	−34*
C3	−16*	−2*	63	−9*	−9*
C4	21*	50	114	42*	57*
C5	−4*	36	43	4*	26*
C6	−17*	17	−35	−37*	−24*
C7	−3	−8*	−3*	−39*	−63*
C11	57	37	230	81	55*
C13	−62	−54	144	−9	−6*
C21	215	198	39	104	56*
O7	20	6*	66	−3*	−31*
O11	90	59	289	118	84*
O13	−142	−126	108	−68	−54*
O21	244	244	14	110	57*

[a] Asterisk indicates atoms used to define respective planes.

Table XIV. Interatomic Separations for DiMn (3)

Bond	Uncorrected, Å	Bond	Uncorrected, Å
P1-Ph1C1	1.834[a]	C6-H6	0.86(8)
P1-Ph2C1	1.847	Mn1-C11	1.818(10)
P1-Ph3C1	1.845	Mn1-C12	1.859(10)
P2-Ph4C1	1.810	Mn1-C13	1.805(10)
P2-Ph5C1	1.841	Mn1-C14	1.847(10)
P2-C1	1.812(8)	Mn1-C3	2.045(7)
C1-C2	1.403(9)	Mn1-O7	2.053(5)
C2-C3	1.410(9)	Mn1-C7	2.873(7)
C3-C4	1.400(10)	Mn1-O11	2.966(7)
C4-C5	1.374(11)	Mn1-O12	2.987(8)
C5-C6	1.404(12)	Mn1-O13	2.942(6)
C6-C1	1.399(10)	Mn1-O14	2.984(7)
C2-C7	1.474(9)	Mn2-C21	1.818(9)
C7-O7	1.257(8)	Mn2-C22	1.838(8)
C11-O11	1.149(9)	Mn2-C24	1.842(9)
C12-O12	1.128(10)	Mn2-C7	2.040(7)
C13-O13	1.138(9)	Mn2-P1	2.337(2)
C14-O14	1.139(10)	Mn2-P2	2.276(2)
C21-O21	1.149(8)	Mn2-O7	2.948(5)
C22-O22	1.142(8)	Mn2-O21	2.964(6)
C24-O24	1.135(8)	Mn2-O22	2.977(6)
C4-H4	0.98(8)	Mn2-O24	2.974(6)
C5-H5	0.92(8)		

[a] No estimated standard deviations are given for distances involving atoms treated as members of rigid groups.

stability. During the course of data collection, the intensities of the first and third reference reflections dropped about 2 and 5%, respectively, and the intensity of the second reference reflection varied within 2% of its mean. No corrections for decay were applied.

A total of 5618 reflections were measured; 176 of these were periodic checks of the standards, 233 were $0kl$, $0k\bar{l}$ pairs, 56 were space-group absences, and 3064 reflections for which $I \geq 3\sigma(I)$ were used in the solution and refinement of the structure. Reduction and processing of the data was accomplished as described previously.[1] In this case, $t_b = 0.5t_s$. The calculated value of μ for Mo Kα radiation is 51.8 cm^{-1}. Absorption corrections were made with the resulting transmission factors ranging from 0.75 to 0.82.

Determination and Refinement of the Structure of ReMn. A three-dimensional Patterson summation was used to locate the rhenium and manganese atoms. Because the rhenium atom is located approximately at $y = \frac{1}{4}$, there are two possible solutions; the Patterson vectors from equivalent positions related by $\bar{1}$ and those related by 2_1 both offer satisfactory interpretations. Electron density maps were computed based on each of these solutions and 25 atoms were located on one of them, while no additional atoms except a "split" phosphorus atom could be found on the other map. Two subsequent Fourier syntheses served to locate the remaining nonhydrogen atoms. Atomic scattering factors for all nonhydrogen atoms are those of Hanson et al.[12] Atomic scattering factors for hydrogen atoms are the values of Stewart et al.[13] Anomalous dispersion corrections ($\Delta f'$ and $\Delta f''$) were applied to the form factors for Re, Mn, and P.[14]

Full-matrix least-squares refinement for all nonhydrogen atoms, utilizing isotropic temperature parameters, converged to a conventional R index of 0.075. Introduction of anisotropic temperature parameters for Re, Mn, and P led to an R index of 0.048. In all subsequent refinement the two nonmetalated phenyl groups were treated as rigid groups[9] of D_{6h} symmetry with C-C bond distances of 1.395 Å and C-H distances of 1.084 Å.[18] The positional parameters of the three hydrogen atoms on the metalated phenyl ring were assigned based on the expected benzene hydrogen positions. Isotropic temperature parameters (of one unit greater than that of the C to which each is bonded) were assigned to these hydrogen atoms. All nonhydrogen atoms except for those in the phenyl rings constrained as rigid groups were allowed to vibrate anisotropically and finally the positional coordinates of the three hydrogen atoms were also allowed to

Table XV. Bond Angles of DiMn (**3**)[a]

Atoms	Angle, deg	Atoms	Angle, deg
C11-Mn1-C12	92.4 (4)	Mn1-C11-O11	177.5 (8)
C11-Mn1-C13	94.4 (4)	Mn1-C12-O12	178.5 (8)
C11-Mn1-C14	91.8 (4)	Mn1-C13-O13	176.6 (8)
C11-Mn1-C3	172.7 (3)	Mn1-C14-O14	176.9 (8)
C11-Mn1-O7	92.9 (3)	Mn2-C21-O21	174.6 (8)
C12-Mn1-C13	91.1 (4)	Mn2-C22-O22	175.0 (7)
C12-Mn1-C14	175.9 (4)	Mn2-C24-O24	175.6 (7)
C12-Mn1-C3	86.4 (3)	Mn1-O7-C7	118.5 (4)
C12-Mn1-O7	89.8 (3)	Mn1-C3-C2	110.7 (5)
C13-Mn1-C14	88.3 (4)	Mn1-C3-C4	133.2 (6)
C13-Mn1-C3	92.9 (3)	Mn2-C7-O7	125.1 (5)
C13-Mn1-O7	172.6 (3)	Mn2-C7-C2	121.1 (5)
C14-Mn1-C3	89.5 (3)	C2-C7-O7	113.7 (6)
C14-Mn1-O7	90.2 (3)	P2-C1-C2	112.9 (5)
C3-Mn1-O7	79.8 (2)	P2-C1-C6	128.8 (6)
		C7-C2-C1	118.9 (6)
C21-Mn2-C22	98.1 (3)	C7-C2-C3	117.3 (6)
C21-Mn2-C24	88.6 (3)	C1-C2-C3	123.7 (7)
C21-Mn2-C7	170.7 (3)	C2-C3-C4	116.1 (7)
C21-Mn2-P1	95.7 (3)	C3-C4-C5	121.0 (8)
C21-Mn2-P2	88.4 (3)	C4-C5-C6	122.5 (8)
C22-Mn2-C24	173.1 (3)	C5-C6-C1	118.3 (8)
C22-Mn2-C7	80.9 (3)	C6-C1-C2	118.2 (7)
C22-Mn2-P1	89.0 (2)	H4-C4-C3	120 (5)
C22-Mn2-P2	90.9 (2)	H4-C4-C5	119 (5)
C24-Mn2-C7	92.8 (3)	H5-C5-C4	119 (5)
C24-Mn2-P1	88.7 (2)	H5-C5-C6	118 (5)
C24-Mn2-P2	90.9 (2)	H6-C6-C5	118 (6)
C7-Mn2-P1	93.5 (2)	H6-C6-C1	123 (6)
C7-Mn2-P2	82.4 (2)		
P1-Mn2-P2	175.8 (1)		
Mn2-P1-Ph1	120.8		
Mn2-P1-Ph2	116.7		
Mn2-P1-Ph3	110.6		
Ph1-P1-Ph2	99.7		
Ph1-P1-Ph3	102.5		
Ph2-P1-Ph3	104.5		
Mn2-P2-Ph4	117.7		
Mn2-P2-Ph5	118.2		
Mn2-P2-C1	104.7 (2)		
Ph4-P2-Ph5	102.0		
Ph4-P2-C1	105.9		
Ph5-P2-C1	107.5		

[a] No estimated standard deviations are given for angles involving atoms treated as members of rigid groups.

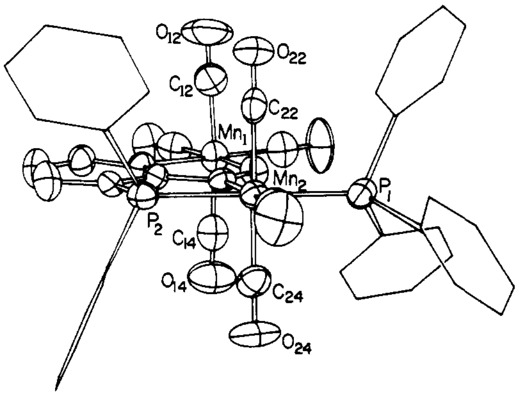


Figure 2. ORTEP plot of the DiMn molecule showing the disposition of axial carbonyl groups. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are omitted.

vary. Final values of R and R_w were 0.041 and 0.045 for 3064 unique reflections and 253 variables. In the final least-squares cycle, the largest shift for a group positional parameter was 0.10σ, for a nongroup nonhydrogen positional parameter 0.42σ, and for a nongroup nonhydrogen thermal parameter 0.21σ. The standard deviation in a reflection of unit weight was 1.19. A final difference Fourier showed two maxima and two minima of ± 1.4 e A^{-3}, all approximately 1 Å from the rhenium atom, and no other peaks larger than ± 0.7 e Å.

The final positional and thermal parameters are given in Tables VII-X. The final values of $|F_o|$ and $|F_c|$ are shown in Table XI (supplementary material).

Table XVII. Results of Least-Squares Planes Calculations for ReMn (**6**)

	Direction cosines (×10⁴) with respect to			Atoms determining
Plane	*a*	*b*	*c**	plane
A	−6635	−7437	818	Metalated benzene ring
B	−5987	−8008	190	Mn, O_7, C_7, C_2, C_3
C	−5687	−8197	683	Re, P, C1, C2, C7
D	−6136	−7896	73	11 atoms of E plus 4 equatorial carbonyl groups
E	−6224	−7799	658	11-membered 3-ring system

Description of the Structure of 3 (DiMn). The molecular structure of DiMn is shown in Figures 1 and 2. One manganese atom is coor-

Table XVIII. Distances of Atoms from Least-Squares Planes in ReMn (**6**) (Å × 10^3)[a]

Plane	*A*	*B*	*C*	*D*	*E*
Re	−296	55	−41*	69*	−102*
Mn	−46	35*	202	−19*	95*
P	96	221	55*	276*	154*
O7		−43*	38	−79*	−89*
O11		62	360	−52*	56
O13		326	603	256*	545
O21		−48	−306	7*	−344
O23		−72	−46	−118*	−315
C1	32*	25	−60*	64*	49*
C2	−27*	20*	14*	28*	43*
C3	−1*	−38*	26	−46*	49*
C4	23*	−161	−111	−154*	−6*
C5	−17*	−258	−283	−221*	−99*
C6	−10*	−163	−256	−110*	−69*
C7		26*	32*	17*	−25*
C11		54	302	−37*	73
C13		180	415	115*	337
C21		0	−197	40*	−246
C23		−13	−33	−36*	−225
H4					5
H5					−54
H6					−87

[a] Atoms used to define least-squares planes are indicated by asterisks.

Table XIX. Interatomic Distances for ReMn (**6**)

Atoms	Distance, Å	Atoms	Distance, Å
Re-P	2.438 (3)	Mn-C3	2.05 (1)
Re-C7	2.180 (8)	Mn-07	2.07 (1)
Re-C21	1.98 (1)	Mn-C14	1.87 (1)
Re-C22	1.95 (1)	Mn-C13	1.81 (1)
Re-C23	1.96 (1)	Mn-C12	1.85 (1)
Re-C24	1.98 (1)	Mn-C11	1.85 (1)
P-C1	1.81 (1)	O7-C7	1.27 (1)
P-C1 1	1.82[a]	O11-C11	1.14 (1)
P-C2 1[b]	1.81[a]	O12-C12	1.14 (1)
C1-C2	1.39 (1)	O13-C13	1.15 (1)
C1-C6	1.39 (1)	O14-C14	1.12 (1)
C2-C3	1.39 (1)	O21-C21	1.15 (1)
C3-C4	1.40 (1)	O22-C22	1.17 (1)
C4-C5	1.36 (2)	O23-C23	1.15 (1)
C5-C6	1.37 (2)	O24-C24	1.14 (1)
C2-C7	1.48 (1)	H4-C4	1.08 (11)
		H5-C5	1.00 (12)
		H6-C6	0.92 (12)

[a] No estimated standard deviations are given for distances involving atoms treated as members of rigid groups. [b] C2 1 refers to carbon atom 1 on phenyl group 2. All phenyl groups treated as rigid groups have been numbered in this way.

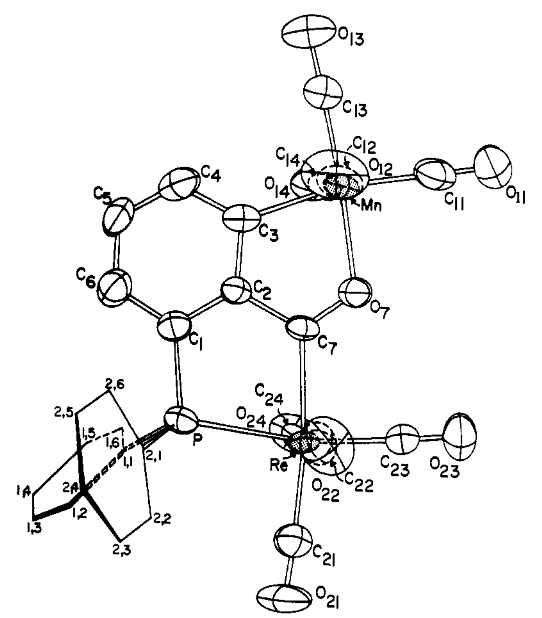


Figure 3. ORTEP plot of the ReMn molecule showing thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted. The numbering system is based on the system for DiMn.

Table XX. Interatomic Angles for ReMn (**6**)[a]

Atoms	Angle, deg	Atoms	Angle, deg
P-Re-C7	79.0 (3)	C3-Mn-O7	79.3 (3)
P-Re-C21	94.7 (3)	C3-Mn-C11	169.4 (5)
P-Re-C22	89.1 (4)	C3-Mn-C12	84.4 (5)
P-Re-C23	168.3 (4)	C3-Mn-C13	96.0 (5)
P-Re-C24	92.6 (3)	C3-Mn-C14	85.5 (5)
C7-Re-C21	173.1 (4)	O7-Mn-C11	90.2 (4)
C7-Re-C22	89.1 (4)	O7-Mn-C12	89.4 (4)
C7-Re-C23	89.5 (4)	O7-Mn-C13	174.6 (4)
C7-Re-C24	88.8 (4)	O7-Mn-C14	93.7 (4)
C21-Re-C22	93.7 (5)	C11-Mn-C12	96.6 (6)
C21-Re-C23	97.0 (5)	C11-Mn-C13	94.6 (5)
C21-Re-C24	88.7 (5)	C11-Mn-C14	94.2 (6)
C22-Re-C23	88.6 (5)	C12-Mn-C13	87.6 (5)
C22-Re-C24	177.0 (5)	C12-Mn-C14	168.7 (6)
C23-Re-C24	89.2 (5)	C13-Mn-C14	88.5 (5)
Re-C7-C2	120.7 (7)	Mn-O7-C7	116.5 (6)
Re-C7-O7	123.7 (7)	Mn-C11-O11	179.3 (11)
Re-C21-O21	177.1 (11)	Mn-C12-O12	174.5 (11)
Re-C22-O22	178.7 (11)	Mn-C13-O13	176.6 (11)
Re-C23-O23	178.4 (11)	Mn-C14-O14	174.1 (11)
Re-C24-O24	177.0 (10)	Mn-C3-C2	112.8 (7)
Re-P-C1	103.7 (4)	Mn-C3-C4	132.3 (8)
Re-P-C1 1	122.2[a]	C2-C1-C6	117.1 (10)
Re-P-C2 1	113.4[a]	C1-C2-C7	120.3 (9)
C1-P-C1 1	104.5[a]	C1-C2-C3	124.2 (9)
C1-P-C2 1	106.2[a]	C2-C3-C4	114.9 (10)
C1 1-P-C2 1	105.4[a]	C3-C4-C5	122.5 (11)
P-C1-C2	127.2 (9)	C4-C5-C6	120.5 (11)
P-C1-O2	115.7 (7)	C5-C6-C1	120.4 (12)
P-C1 1-C1 2	122.2[a]	C2-C7-O7	115.6 (8)
P-C11-C16	117.8[a]	C3-C2-C7	115.4 (9)
P-C2 1-C2 2	118.2[a]		
P-C2 1-C2 6	121.8[a]		

[a] See footnote *a* to Table XV.

dinated to four carbonyl groups, while the other manganese atom is coordinated to three carbonyl groups and a triphenylphosphine. These two manganese atoms are bridged by a novel quadridentate ligand which is bidentate to each metal atom. The molecule contains an extended planar tricyclic ring system involving the bridging ligand, both of the metal atoms, the three equatorial carbonyl groups (CO 11, 13, 21), and a phosphorus atom (P1). Least-squares plane data are given in Table XII and deviations therefrom in Table XIII. The internal skeleton is remarkably planar. The largest deviation of any atom of the tricyclic ring system from the least-squares plane through those atoms (Table XIII, plane D) is 0.05 Å (atom P2). The atoms of the equatorial ligands (CO 11, 13, 21, and P1) are as much as 0.12 Å away from this least-squares plane.

The rigid-body analysis of the 11-atom tricyclic ring system was quite satisfactory; the root mean square U_{ij} value was 0.0025 Å^2, which compares favorably with the average esd of the input β's which converts to 0.0045 Å^2 when put on the scale of U. Including the radial ligands in the rigid body triples the root mean square discrepancy between observed and calculated U_{ij} in the rigid-body analysis, indicating a great deal of independent motion on the part of these ligands.

Table XXI. Comparison of Selected Bond Lengths (Å)

Compd	Acyl C-O	Acyl C-C(Ph)	Phenyl C-Mn	Chelate Mn-P	Chelate P-C(Ph)	Other P-C(Ph) (av)	Mn-O	Ref
3	1.257 (8)	1.474 (9)	2.045 (7)	2.276 (2)	1.812 (8)	1.835	2.053 (7)	*a*
4	1.270 (13)	1.479 (15)	2.041 (12)	2.304 (4)	1.794 (13)	1.831	2.064 (8)	4
5	1.264 (21)	1.473 (25)	2.001 (21)	2.274 (8)	1.823 (21)	1.826	2.094 (13)	4
6	1.27 (1)	1.48 (1)	2.05 (1)		1.81 (1)	1.82	2.07 (1)	*a*
7	1.216 (2)	1.494 (2)						26
8	1.23 (1)			2.295 (3)	1.815 (7)	1.84	2.067 (7)	27
9	1.244 (3)	1.455 (3)	2.042 (2)				2.055 (2)	23
10	1.29	1.377 (9)	1.99					29
11				2.279 (3)	1.80 (1)	1.82		24

[a] This work.

The rigid-body librations are rather small, as would be expected of such a bulky group. The axis of the largest (4.1°) lies close to the least-squares plane; while the smallest (1.8°) is nearly perpendicular to that plane. The corrections applied to Mn-C bond lengths averaged 0.5σ (with a maximum of 0.75σ), but the corrections to Mn-P bonds were 0.5σ and 3.5σ (due primarily to lower values of σ). Corrections to the bond angles were in all cases less than 0.1° (0.5σ or less). The uncorrected intramolecular distances are given in Table XIV and uncorrected bond angles are given in Table XV. Uncorrected bond lengths will be used in subsequent discussion in order to facilitate comparison with other structures which have not undergone rigid body analysis. The root mean square thermal displacements of each atom are shown in Table XVI (supplementary material).

The geometry about the Mn atoms is best described as distorted octahedral. The greatest angular distortions are C3-Mn1-O7 (79.8 (2)°) and P2-Mn2-C7 (82.4 (2)°). Angles of 80 ± 3° at transition metals involved in five-membered rings are common.[19-24]

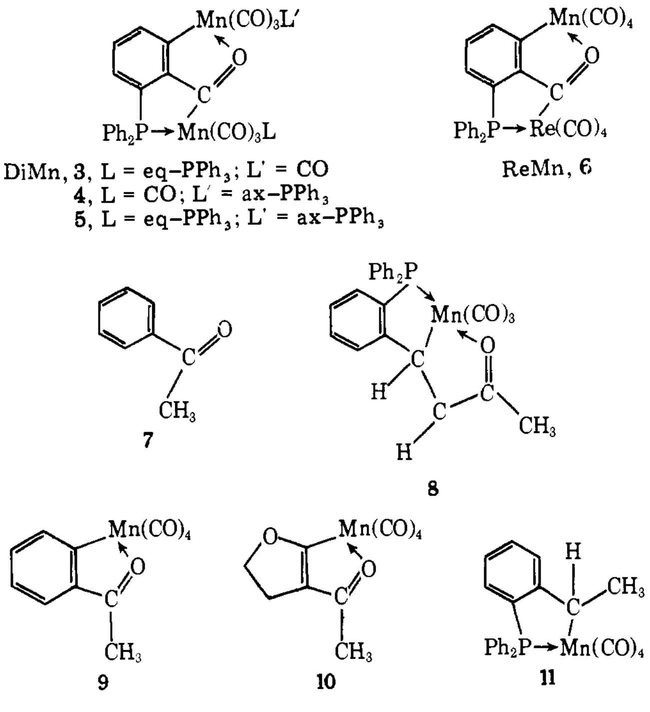
No significant intermolecular distances were found. The two closest contacts are Ph3H6-Ph3H6 ($-x$, $1-y$, $1-z$), 2.15 Å, and O24-Ph4H4 ($-x, y, \frac{1}{2}-z$), 2.45 Å.[25]

Description of the Structure of 6 (ReMn). In its essential features, the molecular structure of ReMn, shown in Figure 3, is very similar to that of DiMn. It differs by the replacement of the Mn2 and phosphine (P1) of DiMn with Re and a carbonyl group, CO(23), respectively.

The location of the Re and Mn atoms in their relative positions confirms the sequence of metalation proposed earlier.[3]

Least-squares plane data are given in Table XVII and deviations therefrom in Table XVIII. No rigid body analysis was undertaken; intramolecular distances (Table XIX) and bond angles (Table XX) are uncorrected. Again no significant intermolecular distances were found. The closest contact is O12-H1,9 ($-x$, $-y$, $1-z$), 2.34 Å.[25]

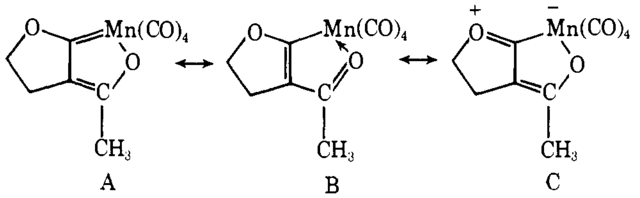
Scheme I


DiMn, **3**, L = eq-PPh$_3$; L' = CO
4, L = CO; L' = ax-PPh$_3$
5, L = eq-PPh$_3$; L' = ax-PPh$_3$
ReMn, **6**
7
8
9
10
11

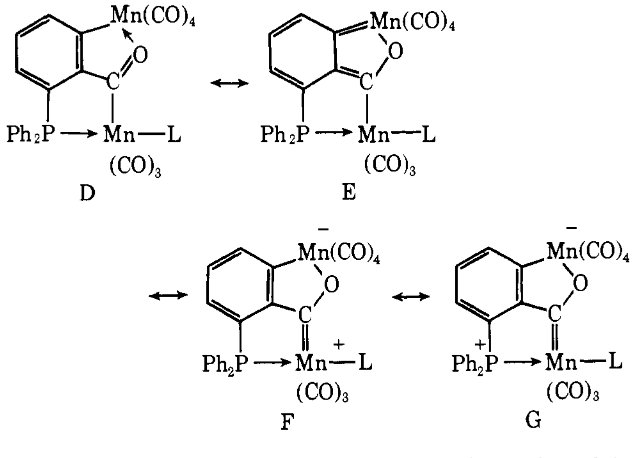
Discussion

The presence in these secondary metalation products of rigid extended planar ring systems suggests the possibility of π electron delocalization. Evidence for this phenomenon is provided by a careful examination and comparison of bond lengths of these and related derivatives. The compounds for which structural comparisons will be made are given in Scheme I, and the relevant bond lengths thereof are given in Table XXI.

Comparison of Acyl C-O Bond Lengths. The acyl C-O bond length in each of the secondary metalation products **3, 4, 5,** and **6** (Table XXI) is significantly longer than that found for a normal C-O double bond such as that of acetophenone (**7**).[26] An earlier structure of compound **8**[27] (Scheme I) shows only a marginal lengthening of the acyl C-O bond upon coordination of the oxygen to manganese. Any further lengthening may be an indication of the greater electron delocalization in the ring systems of the compounds in the present work.[28] The acyl C-O bond length of compound **9**[23] falls between that of **7** and the secondary metalation products. In contrast, compound **10**[29] has the longest acyl C-O distance, which has been explained in terms of contributions of canonical structures A and C.



Similar canonical structures for the secondary metalation products indicate greater possibilities of delocalization.



Comparison of C-C(Ph) Bond Lengths. A shortening of the C-C(Ph) bond length, adjacent to the acyl C-O, would also be expected of electron delocalization as in canonical structures

Table XXII. Comparison of Metal Carbonyl Bond Lengths (Å)

Compd	CO (av)	Chelate phenyl C	Chelate alkyl C	Acyl C	Chelate PPh_2	Acyl O	PPh_3
			Mn-C for Carbonyl Trans to				
3	1.85 (1)	1.818 (10)		1.818 (9)		1.805 (10)	
4	1.81 (2)	1.826 (15)		1.789 (17)	1.779 (17)	1.708 (15)	1.749 (15)
5	1.81 (2)	1.762 (24)		1.743 (24)		1.773 (29)	1.738 (27)
6	1.86 (1)	1.85 (1)				1.81 (1)	
8			1.805		1.805	1.763	
9	1.857 (3)	1.849 (3)				1.786 (3)	
10	1.87		1.87			1.77	
11	1.82		1.79		1.79		
			C-O for Carbonyl Trans to				
3	1.13 (1)	1.149 (9)		1.149 (8)		1.138 (9)	
4	1.15 (2)	1.140 (14)		1.168 (16)	1.168 (16)	1.195 (15)	1.184 (15)
5	1.14 (2)	1.185 (22)		1.2113 (24)		1.168 (26)	1.164 (25)
6	1.13 (1)	1.14 (1)				1.15 (1)	
8			1.16		1.16	1.14	
9	1.130 (3)	1.130 (3)				1.150 (3)	
10	1.13		1.13			1.16	

A, C, and E. As shown in Table XXI, the shortest C-C(Ph) bond in the related metallocycles is found in **10**, which has the longest C-O bond; correspondingly the longest C-C(Ph) bond is found in acetophenone (**7**), which has the shortest C-O bond.

Mn-P Bond Lengths. The Mn-P bond length within the ring systems of **3, 4, 5, 8,** and **11** (Table XXI) is shortened significantly compared to the Mn-P distance for terminal PPh_3, e.g., the Mn-PPh_3 bond trans to CO in **4.**

P-C Bond Lengths. In each of the six applicable cases discussed here the chelate P-C distance was slightly smaller than the average of the other P-C distances in the respective structures. Though each in itself is not sufficiently different to warrant notice, the consistency among the six compounds seems significant.

Trans Influence and Terminal Carbonyl Groups. The metal-carbon and carbon-oxygen bond lengths of the metal carbonyl group are influenced by the substitution in the position trans to it.[30] Among the compounds compared in this study there are seven different kinds of such trans groups on manganese; metal-carbonyl distances are shown in Table XXII. Though the sampling is small, the data reveal that the donor oxygen of the acyl group has substantially less π-acceptor capabilities than a carbonyl group, perhaps being somewhat similar to a triphenylphosphine ligand in that respect.

Conclusion

The structures presented in this and the companion work[4] establish a novel polycyclic construction for complexes containing two metals. These structures show extensive delocalization in the metallocyclic rings fused to the polysubstituted central phenyl ring, a feature which suggests possibilities for new materials possessing pseudo-one-dimensional electronic properties.[31] Such properties, of course, are not expected for the manganese or rhenium derivatives in the present structures owing to the presence of the axial CO or PPh_3 ligands extending above and below the planar portions of the molecule. Such axial ligands prevent the approach of metal atoms between adjacent molecules in the solid state. Analogues of the present derivatives, however, containing d^8 ions such as Rh(I), Ir(I), Pd(II), or Pt(II) in place of the d^6 Mn(I) or Re(I) ions could be expected to show interesting one-dimensional electric properties in the solid. Attempts to synthesize such analogues are presently in progress in our laboratory.

It would also be of interest to establish some spectroscopic means of characterizing the polycyclic constructions indicated here. We have earlier reported that these derivatives do not show sufficient ^{1}H NMR shifts although characteristic low-field ^{19}F NMR shifts are observed for fluorine atoms substituted ortho to the metal atoms in the polysubstituted central phenyl ring. Recent spectroscopic studies using ^{31}P[32] and ^{13}C NMR[33,34] indicate that these nuclei show characteristic chemical shifts associated with cyclometalation products; attempts to obtain such data for the compounds in our present study are underway.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also wish to thank Professor C. E. Strouse of this department for help and advice on the use of the Syntex diffractometer. Computer time was firnished by the UCLA Campus Computing Network.

Supplementary Material Available: Table V, observed and calculated structure factors for **6**; Table VI, results of rigid body analysis for **3**; Table XI, observed and calculated structure factors for **6**; and Table XVI, root mean square amplitudes of thermal motion in **3** (28 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Based in part on the Dissertation of B. T. Huie, UCLA, 1975. (b) For part 9 of this series, see R. J. McKinney, C. B. Knobler, B. T. Huie, and H. D. Kaesz, *J. Am. Chem. Soc.*, **99**, 2988 (1977).

(2) R. J. McKinney, R. Hoxmeier, and H. D. Kaesz, *J. Am. Chem. Soc.*, **97**, 3059 (1975).

(3) R. J. McKinney and H. D. Kaesz, *J. Am. Chem. Soc.*, **97**, 3066 (1975).

(4) B. T. Huie, C. B. Knobler, R. J. McKinney, and H. D. Kaesz, *J. Am. Chem. Soc.*, following paper in this issue.

(5) Owing to the complicated nature of the systematic names of these products we have used the abbreviations shown; DiMn refers to the presence of two manganese atoms in the molecule and ReMn refers to the presence of both a rhenium and a manganese atom.

(6) R. J. McKinney, B. T. Huie, C. B. Knobler, and H. D. Kaesz, *J. Am. Chem. Soc.*, **95**, 633 (1973); B. T. Huie and C. B. Knobler, Abstracts, American Crystallographic Association Meeting, Berkeley, Calif., March 1974, Paper I-11.

(7) "International Tables for X-Ray Crystallography", Vol. I, Kynoch Press, Birmingham, England, 1962.

(8) The numbers given in parentheses throughout this paper are the estimated standard deviations, and refer to the last digit given.

(9) 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; ABSN (Coppens), absorption correction; HPOSN (Hope) to calculate tentative hydrogen positions; ORTEP (Johnson), figure plotting; MGTL (Schomaker and Trueblood), analysis of possible rigid-body motion, least-squares planes; and ORFFE (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.

(10) A. J. C. Wilson, *Nature (London)*, **150**, 151 (1942).

(11) E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Crystallogr.*, **3**, 210 (1950).

(12) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

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

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

(15) The function $\Sigma w||F_o| - |F_c||^2$ was minimized in the least-squares refinement and the discrepancy indices were defined as

$$R = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|} \qquad R_w = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w|F_o|^2}\right]^{1/2}$$

where $w = \left[\frac{1}{\Sigma(F_o)}\right]^2$

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

(17) V. Schomaker and K. N. Trueblood, *Acta Crystallogr., Sect. B*, **24**, 63 (1968).

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

(19) (a) F. W. B. Einstein and D. Sutton, *J. Chem. Soc. Dalton Trans.*, 434 (1973); (b) G. Bombieri, L. Caglioti, L. Cattalini, E. Gasparrini, R. Graziani, and P. A. Vigato, *Chem. Commun.*, 1415 (1971).

(20) A. J. Cheney, W. S. McDonald, K. O. Flynn, B. L. Shaw, and B. L. Turtle, *J. Chem. Soc., Chem. Commun.*, 128 (1973).

(21) A. R. M. Clark, G. R. Knox, P. L. Pauson, R. J. Hoare, and O. S. Mills, *Chem. Commun.*, 168 (1971).

(22) R. G. Little and R. J. Doedens, *Inorg. Chem.*, **12**, 840, 844 (1973).

(23) C. B. Knobler, S. S. Crawford, and H. D. Kaesz, *Inorg. Chem.*, **14**, 2062 (1975).

(24) G. B. Robertson and P. O. Whimp, *J. Organomet. Chem.*, **49**, C27 (1973).

(25) All other contacts are longer than the sum of the van der Waals radii of the atoms involved. See L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, N.Y., 1960, p 224: r_{O-H} = 2.6 Å, r_{H-H} = 2.4 Å.

(26) Y. Tanimoto, H. Kobayashi, S. Nagakura, and Y. Saito, *Acta Crystallogr., Sect. B*, **29**, 1822 (1973).

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

(28) For comparison, averaged normal bond lengths are given as follows (Å, ±0.005): C–O, 1.426, C═O, 1.215; C–C, 1.537; C═C, 1.335 ["Interatomic Distances Supplement", *Chem. Soc., Spec. Publ.*, **No. 18** (1965)].

(29) C. P. Casey, R. A. Boggs, D. F. Martin, and J. C. Calabrese, *J. Chem. Soc., Chem. Commun.*, 243 (1973).

(30) A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc. A*, 1707 (1966).

(31) A. F. Garito and A. J. Heeger, *Acc. Chem. Res.*, **7**, 232 (1974).

(32) P. E. Garrou, *Inorg. Chem.*, **14**, 1435 (1975).

(33) A. R. Garber, P. E. Garrou, G. E. Hartwell, M. J. Smas, J. R. Wilkinson, and L. J. Todd, *J. Organomet. Chem.*, **88**, 219 (1975).

(34) R. P. Stewart, Jr., L. R. Isbrandt, J. J. Benedict, and J. G. Palmer, *J. Am. Chem. Soc.*, **98**, 3215 (1976).

Intramolecular Metalation with Methylmanganese and Methylrhenium Carbonyl Complexes. 11.[1] The Crystal and Molecular Structures of the Secondary Metalation Products *abcd*-Tetracarbonyl-*efgk*-[*μ*-[carbonyl[6-(diphenylphosphino)-*o*-phenylene]]](*hil*-tricarbonyl-*j*-triphenylphosphinemanganese)manganese, $Ph_2P[C_6H_3(CO)Mn(CO)_3PPh_3]Mn(CO)_4$, and a Phosphine Substituted Derivative. Interconversions of Secondary Metalation Products

B. T. Huie, C. B. Knobler, R. J. McKinney, and H. D. Kaesz*

Contribution No. 3720 from the Department of Chemistry
University of California, Los Angeles, California 90024.

Received October 26, 1976

Abstract: The structures of *abcd*-tetracarbonyl-*efgk*-[*μ*-[carbonyl[6-(diphenylphosphino)-*o*-phenylene]]](*hil*-tricarbonyl-*j*-triphenylphosphinemanganese)manganese (**4**)[2] and *abd*-tricarbonyl-*c*-triphenylphosphine-*efgk*-[*μ*-[carbonyl[6-(diphenylphosphine)-*o*-phenylene]]](*hjl*-tricarbonyl-*j*-triphenylphosphinemanganese)manganese (**5**)[2] have been determined from data collected on an automated diffractometer with monochromatized Mo Kα radiation. Compound **4** crystallizes in the monoclinic space group $P2_1/c$ with a = 11.185 (2) Å, b = 26.922 (4) Å, c = 14.606 (3) Å, β = 115.90 (1)°. The density of 1.44 g cm^{-3} calculated on the basis of four formula units per unit cell agrees with the flotation value of 1.42 g cm^{-3}. Compound **5** crystallizes in the triclinic space group $P\bar{1}$ with a = 10.847 (2) Å, b = 13.782 (3) Å, c = 19.570 (4) Å, α = 97.79 (2)°, β = 96.77 (2)°, γ = 103.03 (2)°. The density of 1.40 g cm^{-3} calculated on the basis of two molecules per unit cell agrees with the flotation value of 1.39 g cm^{-3}. The structures were solved by use of Patterson and Fourier summations and refined by use of full matrix least-squares methods to conventional R indices of 7.5 (**4**) and 8.8% (**5**) based on 2183 and 2112 independent observed reflections, respectively. The molecular structure of **4** contains two manganese atoms each with an essentially octahedral arrangement of ligands. One manganese atom is coordinated to three carbonyl groups and a triphenylphosphine while the other is coordinated to four carbonyl groups. The two manganese atoms are bridged by a novel quadridentate ligand which is bidentate to each metal atom. The molecule contains an extended planar tricyclic ring system which includes the bridging ligand and both metal atoms. The molecular structure of **5** is very similar to that of **4**, differing by the replacement of an *axial* carbonyl group of the Mn(CO)$_4$ unit by a triphenylphosphine. Thermolysis and substitution studies show that the tricyclic ring system is not easily disrupted. A method for the interconversion of the four secondary metalation products

$Ph_2P[C_6H_3(CO)Mn(CO)_3L]Mn(CO)_3L'$ (L = CO, L′ = PPh$_3$, **3**; L = PPh$_3$, L′ = CO, **4**; L = L′ = PPh$_3$, **5**; L = L′ = CO, **6**)

is described. Thermolysis of **3** is observed to give **4** along with some of the primary metalation product $Ph_2P(C_6H_4)Mn(CO)_4$.

Recently we reported that the thermolysis of *cis*-$CH_3Mn(CO)_4PPh_3$ (**1**) yielded a primary metalation product, $Ph_2PC_6H_4Mn(CO)_4$[3] (**2**), as well as three secondary metalation products,[4]