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

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

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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, $Ph_2P[C_6H_3(\overline{CO})\overline{Mn}(CO)_3PPh_3]Mn(CO)_4$, and a Phosphine Substituted Derivative. Interconversions of Secondary Metalation Products

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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, $\beta = 115.90$ (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 $P\overline{1}$ with $a = 10.847$ (2) Å, $b = 13.782$ (3) Å, $c = 19.570$ (4) Å, $\alpha = 97.79$ (2)°, $\beta = 96.77$ (2)°, $\gamma = 103.03$ (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

$$Ph_2P[C_6H_3(\overline{CO})\overline{Mn}(CO)_3L]Mn(CO)_3L' \quad (L = CO, L' = PPh_3, \mathbf{3}; L = PPh_3, L' = CO, \mathbf{4}; L = L' = PPh_3, \mathbf{5}; L = L' = CO, \mathbf{6})$$

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

Recently we reported that the thermolysis of *cis*-CH₃Mn(CO)₄PPh₃ (**1**) yielded a primary metalation product, $Ph_2\overline{PC_6H_4Mn}(CO)_4$[3] (**2**), as well as three secondary metalation products,[4]

$$Ph_2P[C_6H_3(\overline{CO})Mn(CO)_3L]Mn(CO)_3L'$$
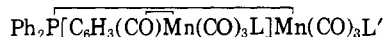
(L = CO, L' = PPh$_3$, **3**; L = PPh$_3$, L' = CO, **4**; L = L' = PPh$_3$, **5**)

Even after a single crystal x-ray diffraction study established the structure of **3**,[1,5] it was not clear that compounds **4** and **5** had similar structures. The highest observable ion in the mass spectrum of **4**[4] appeared at m/e 772, accompanied by peaks for loss of five carbonyl groups. This contrasted with the mass spectrum of **3** which revealed a parent ion at m/e 856 and peaks corresponding to the loss of eight carbonyl groups. The involatility of product **5**, on the other hand, prevented us from obtaining a mass spectrum and the other spectroscopic and analytic data did not lead to an unambiguous structure assignment.[4] We therefore undertook single crystal x-ray studies on both **4** and **5**.[6] The details of this study are reported here together with observations concerning the chemical interrelationships among the secondary metalation products. A comparison of the parameters of the structure of **3** with those of **4** and **5** is given in a companion paper in which the structure determinations of **3** and of a related mixed metal derivative are presented.

Experimental Details of the Structure Determination

X-Ray Data for Compound 4. The preparation of **4** has been described elsewhere.[3,4] Crystals suitable for an x-ray study were grown from a dichloromethane/hexane solution as described previously.[1] The crystals obtained were air and x-ray stable orange parallelepipeds.

Weissenberg photographs revealed the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$, compatible with space group $P2_1/c$.[7] A crystal bounded by {100}, {010}, and {001} with crystal dimensions normal to these faces of 0.21 × 0.18 × 0.21 mm was chosen for intensity measurements and mounted with a close to the ϕ axis of a Syntex P$\overline{1}$ four-circle autodiffractometer equipped with a scintillation counter, pulse height analyzer, and a graphite monochromatized Mo Kα radiation source (λ = 0.71069 Å). Fifteen reflections (2θ = 20–40°) were centered in order to obtain accurate lattice parameters. The refined unit cell parameters are a = 11.185 (2)[8] Å, b = 26.922 (4) Å, c = 14.606 (3) Å, β = 115.90 (1)°. The unit cell volume is 3956 Å^3. The density at room temperature of 1.42 g cm^{-3} was obtained by flotation in bromoform and hexane. The crystallographic density, assuming four formula units in the unit cell, is 1.44 g cm^{-3}.

Intensities were measured as previously described,[9] except that a constant scan rate of 2.4°/min was used. Three check reflections (0, 5, −2; 1, 4, 1; 1, 11, −4) were measured after each 97 intensity measurements. These standards showed no significant variations or decline in intensity. Intensities were corrected for Lorentz and polarization effects by the use of PIBAR,[10a] and the data were processed as previously described.[9] Of 5357 unique reflections measured, for which 2θ $\leq$ 45°, 2183 with $I \geq 3\sigma(I)$ were considered observed.

The absorption coefficient μ was calculated to be 8.07 cm^{-1}, which for the above-mentioned crystal leads to a transmission factor range of 0.85–0.90 within the 2θ range measured. It is estimated that absorption effects would cause fluctuations of no more than 2.5% in I; no corrections for the effects of absorption were made.

Determination and Refinement of the Structure of 4. Trial positions for the two Mn atoms were found from a three-dimensional Patterson summation.[10a] A Fourier synthesis phased on these Mn positions yielded the positions of the two P atoms and of several light atoms. Additional Fourier syntheses yielded the positions of the remaining nonhydrogen atoms. It became clear at this point that **4** is an isomer of **3** with the same empirical formula.

Refinement was carried out by use of full matrix least-squares procedures[10a] using atomic scattering factors as described previously; anomalous dispersion corrections were applied to the form factors for Mn and P.[1,9] The phenyl rings were treated as rigid groups with d(C-C) = 1.395 Å and d(C-H) = 1.084 Å;[10b] carbon atoms in the groups were assigned individual isotropic thermal parameters and group H atoms were assigned B values of 6.0 Å^2.

One cycle of least-squares refinement in which all atoms were assigned isotropic thermal parameters led to discrepancy indices R_F = 0.089 and R_w = 0.116.[11] One cycle in which the heavy atoms were assigned anisotropic thermal parameters led to values R_F = 0.083 and R_w = 0.111.

The positions of the three hydrogen atoms on the trisubstituted benzene ring were calculated using the program HPOSN.[10] These H atoms were assigned isotropic thermal parameters of 5.0 Å^2 in subsequent refinement; their positions were also held constant. Four cycles of refinement, with anisotropic temperature parameters for Mn and P and isotropic temperature parameters for all other atoms, converged with discrepancy factors R_F = 0.075 and R_w = 0.077. The largest

Table I. Atomic Positional and Thermal Parameters for **4**

Atoms	x	y	z	B, Å^2
Mn1	−0.02628 (19)	0.33797 (7)	0.58449 (15)	a
Mn2	0.20622 (20)	0.44919 (8)	0.87054 (15)	a
P2	0.2419 (4)	0.3857 (1)	0.9853 (3)	a
P3	−0.2353 (4)	0.3700 (1)	0.5592 (3)	a
C1	0.1460 (11)	0.3355 (5)	0.9065 (9)	2.9 (3)
C2	0.0903 (11)	0.3457 (4)	0.8028 (9)	2.3 (2)
C3	0.0232 (12)	0.3099 (5)	0.7263 (9)	2.6 (3)
C4	0.0120 (13)	0.2627 (5)	0.7625 (10)	3.4 (3)
C5	0.0643 (14)	0.2530 (5)	0.8666 (11)	4.2 (3)
C6	0.1311 (13)	0.2881 (5)	0.9377 (10)	3.8 (3)
C7	0.1042 (11)	0.3962 (4)	0.7689 (9)	2.5 (3)
C11[b]	−0.0494 (13)	0.3640 (5)	0.4624 (11)	3.8 (3)
C12	0.1336 (14)	0.3185 (5)	0.6078 (11)	4.3 (3)
C13	−0.0896 (14)	0.2811 (6)	0.5350 (11)	4.1 (3)
C21	0.3088 (16)	0.4918 (6)	0.9667 (13)	5.6 (4)
C22	0.3391 (14)	0.4254 (5)	0.8447 (11)	4.2 (3)
C23	0.1634 (15)	0.4919 (6)	0.7681 (12)	5.1 (4)
C24	0.0578 (15)	0.4678 (5)	0.8839 (11)	4.4 (3)
O7	0.0539 (8)	0.4002 (3)	0.6727 (6)	3.1 (2)
O11	−0.0641 (10)	0.3759 (4)	0.3833 (8)	5.3 (2)
O12	0.2410 (11)	0.3050 (4)	0.6215 (8)	6.5 (3)
O13	−0.1328 (10)	0.2401 (4)	0.5106 (8)	5.7 (3)
O21	0.3770 (11)	0.5198 (4)	1.0286 (9)	6.4 (3)
O22	0.4164 (11)	0.4080 (4)	0.8221 (8)	6.3 (3)
O23	0.1321 (10)	0.5205 (4)	0.7014 (9)	6.4 (3)
O24	−0.0357 (11)	0.4798 (4)	0.8924 (8)	6.5 (3)
H4[c]	−0.035	0.236	0.712	5.0
H5	0.048	0.220	0.885	5.0
H6	0.167	0.280	1.007	5.0

^{a} Anisotropic thermal parameters for the Mn and P atoms are given in Table II. ^{b} Hydrogen atoms and carbonyl groups are numbered to correspond to the carbon or metal atoms to which they are bonded. ^{c} Hydrogen atom positional and temperature parameters included but not refined in least-squares cycles.

Table II. Atomic Anisotropic Thermal Parameters for **4** ($\times 10^5$)

Atom	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mn1	731 (24)	95 (4)	352 (14)	−21 (8)	193 (15)	−22 (6)
Mn2	836 (26)	100 (4)	385 (14)	−48 (8)	257 (15)	−29 (7)
P2	802 (45)	113 (7)	315 (25)	−28 (14)	216 (28)	18 (10)
P3	720 (44)	129 (7)	367 (26)	12 (15)	190 (27)	18 (11)

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

Table III. Group Parameters for Nonmetalated Phenyl Groups of **4**

Groups	x	y	z	ϕ^a	θ^a	ρ^a
Ph 4	0.4138 (7)	0.3643 (4)	1.0480 (7)	−0.058 (7)	−2.595 (6)	0.491 (7)
Ph 5	0.1841 (11)	0.3919 (4)	1.0843 (7)	1.997 (8)	2.412 (6)	1.146 (8)
Ph 6	−0.2690 (11)	0.4335 (3)	0.5067 (8)	−1.284 (7)	2.599 (7)	−2.684 (7)
Ph 7	−0.2600 (8)	0.3737 (4)	0.6739 (6)	3.154 (6)	−3.120 (6)	0.973 (5)
Ph 8	−0.3845 (8)	0.3366 (3)	0.4701 (6)	−1.773 (7)	2.530 (6)	−0.974 (7)

^{a} The definitions of these parameters are given in ref 17; measurements in radians.

final shift for a group parameter was 0.15σ; no individual atom parameter shifted more than 0.01σ. The standard deviation in an observation of unit weight is 1.86.

A final difference map showed residuals in the range from −0.4 to +0.5 e/Å^3; all peaks with |maxima| > 0.3 e/Å^3 were associated with the phenyl rings that had been treated as rigid groups.

The final atomic positional and thermal parameters and group positional parameters are given in Tables I, II, and III. Table IV presents the positional and thermal parameters of the individual group atoms. The final values of $|F_o|$ and $|F_c|$ are shown in Table V (supplementary material).

X-Ray Data for Compound 5. The preparation of **5** has been described elsewhere.[3,4] Suitable crystals were obtained from dichloromethane/hexane by the method previously described.[1] Compound **5** crystallized as air and x-ray stable irregularly shaped orange crystals.

Since Weissenberg and rotation photographs showed no symmetry, one of the triclinic space groups, $P1$ or $P\bar{1}$, was indicated.[7] The crystal used for data collection was a parallelepiped bounded by {100}, {010}, and {001}. Crystal dimensions normal to these faces were $0.10 \times 0.20 \times 0.24$ mm. The crystal was mounted with b close to the ϕ axis of the Syntex $P\bar{1}$ autodiffractometer. Unit cell parameters, determined from a least-squares fit of 15 accurately centered high-order reflections, are $a = 10.847$ (2) Å, $b = 13.782$ (3) Å, $c = 19.570$ (4) Å, $\alpha = 97.79$ (2)°, $\beta = 96.77$ (2)°, and $\gamma = 103.03$ (2)°. The unit cell volume is 2790 Å^3. The density at room temperature of 1.39 g cm^{-3} was obtained by flotation in bromoform and hexane. The crystallographic density, assuming two formula units per unit cell, is 1.40 g cm^{-3}.

Intensities were measured as previously described,[9] except that a constant scan rate of 2.4°/min was used. Three check reflections (1, 6, −7; −1, 0, −1; 0, −2, 4) were measured after each 97 intensity measurements. These standards showed only a slight (less than 2σ) decline in intensity. The data were corrected for Lorentz and polarization effects[10] and processed as previously described.[9] Of 7350 reflections measured, for which $2\theta \leq 45°$, 2112 with $I > 3\sigma(I)$ were considered observed.

The calculated minimum and maximum transmission factors, based on $\mu = 7.12$ cm^{-1} and the above-mentioned crystal dimensions, are 0.87 and 0.95. Since absorption effects could have caused errors of no more than ~2% in the values of $|F_o|$, no corrections for the effects of absorption were made.

Determination and Refinement of the Structure of 5. The original space group determination was ambiguous ($P1$ or $P\bar{1}$); a statistical study using CENACEN[12] indicated a centrosymmetric space group; see ref 1a for details.

The structure was solved using Patterson and Fourier methods.[1a] After a Fourier synthesis phased on the complete molecule $C_{61}O_7Mn_2P_3$, the discrepancy indices were $R_F = 0.224$ and $R_w = 0.268$. The electron density map thus produced showed, along with the input atoms, weak and diffuse peaks which were attributed to the C and 2 Cl atoms of a dichloromethane (DCLM) molecule.

Atomic scattering factors for nonhydrogen atoms were taken from ref 13; hydrogen scattering factors were obtained from Stewart, Davidson, and Simpson[14] and anomalous dispersion corrections ($\Delta f'$ and $\Delta f''$) were applied to the form factors for

Table IV. Derived Parameters for Group Atoms of **4**

Group	Atom	x	y	z	B, Å^2
Ph 4	C1	0.4138	0.3643	1.0480	3.1 (3)
	C2	0.4474	0.3183	1.0216	4.9 (4)
	C3	0.5799	0.3030	1.0644	7.2 (5)
	C4	0.6787	0.3336	1.1336	6.5 (4)
	C5	0.6450	0.3796	1.1600	5.7 (4)
	C6	0.5126	0.3949	1.1172	4.9 (4)
	H2	0.3707	0.2946	0.9678	6.0^a
	H3	0.6060	0.2673	1.0439	6.0
	H4	0.7816	0.3217	1.1668	6.0
	H5	0.7218	0.4034	1.2138	6.0
	H6	0.4865	0.4306	1.1378	6.0
Ph 5	C1	0.1841	0.3919	1.0843	3.8 (3)
	C2	0.2679	0.4089	1.1816	6.8 (5)
	C3	0.2188	0.4154	1.2538	7.4 (5)
	C4	0.0860	0.4048	1.2286	7.1 (5)
	C5	0.0023	0.3877	1.1312	9.1 (6)
	C6	0.0513	0.3813	0.0591	7.1 (5)
	H2	0.3711	0.4172	1.2013	6.0
	H3	0.2839	0.4286	1.3294	6.0
	H4	0.0479	0.4098	1.2846	6.0
	H5	−0.1010	0.3795	1.1116	6.0
	H6	−0.0138	0.3680	0.9834	6.0
Ph 6	C1	−0.2690	0.4335	0.5067	4.4 (4)
	C2	−0.3984	0.4465	0.4392	8.9 (5)
	C3	−0.4258	0.4945	0.3990	9.2 (6)
	C4	−0.3236	0.5293	0.4263	7.5 (5)
	C5	−0.1942	0.5162	0.4939	6.0 (4)
	C6	−0.1669	0.4683	0.5341	5.3 (4)
	H2	−0.4778	0.4195	0.4179	6.0
	H3	−0.5264	0.5046	0.3465	6.0
	H4	−0.3449	0.5665	0.3951	6.0
	H5	−0.1148	0.5433	0.5151	6.0
	H6	−0.0662	0.4581	0.5865	6.0
Ph 7	C1	−0.2600	0.3737	0.6739	3.2 (3)
	C2	−0.2725	0.4188	0.7158	4.8 (4)
	C3	−0.2927	0.4194	0.8035	7.1 (5)
	C4	−0.3004	0.3749	0.8494	6.2 (4)
	C5	−0.2879	0.3297	0.8075	5.7 (4)
	C6	−0.2677	0.3291	0.7198	4.6 (4)
	H2	−0.2666	0.4535	0.6802	6.0
	H3	−0.3025	0.4545	0.8361	6.0
	H4	−0.3161	0.3753	0.9176	6.0
	H5	−0.2938	0.2951	0.8432	6.0
	H6	−0.2579	0.2940	0.6873	6.0
Ph 8	C1	−0.3845	0.3366	0.4701	3.7 (3)
	C2	−0.4976	0.3322	0.4870	5.2 (4)
	C3	−0.6108	0.3086	0.4150	6.1 (4)
	C4	−0.6108	0.2895	0.3263	6.9 (5)
	C5	−0.4977	0.2939	0.3095	6.7 (5)
	C6	−0.3846	0.3174	0.3814	4.8 (4)
	H2	−0.4976	0.3471	0.5559	6.0
	H3	−0.6986	0.3052	0.4281	6.0
	H4	−0.6987	0.2712	0.2704	6.0
	H5	−0.4978	0.2790	0.2405	6.0
	H6	−0.2967	0.3208	0.3683	6.0

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

chlorine as well as those of manganese and phosphorus.[15] Two cycles of least-squares refinement in which all atoms were

Table VI. Atomic Positional and Thermal Parameters for **5**

Atom	x	y	z	B, Å^2
Mn1	0.6088 (3)	0.2486 (2)	0.6613 (2)	a
Mn2	0.8010 (4)	0.0343 (3)	0.7971 (2)	a
P1	0.7885 (7)	0.1424 (5)	0.8965 (3)	a
P2	0.8016 (6)	−0.0732 (4)	0.6982 (3)	a
P3	0.7999 (6)	0.3679 (4)	0.6546 (3)	a
C1	0.7574 (20)	−0.0060 (16)	0.6287 (11)	3.4 (5)
C2	0.7206 (18)	0.0797 (15)	0.6515 (10)	2.3 (5)
C3	0.6619 (20)	0.1342 (16)	0.6081 (12)	3.5 (5)
C4	0.6496 (22)	0.0954 (18)	0.5357 (13)	4.8 (6)
C5	0.6944 (24)	0.0107 (19)	0.5103 (13)	5.4 (6)
C6	0.7487 (21)	−0.0401 (17)	0.5580 (12)	4.3 (6)
C7	0.7407 (20)	0.1187 (17)	0.7268 (12)	3.8 (6)
C11^b	0.5505 (22)	0.3424 (17)	0.7082 (12)	4.2 (6)
C12	0.4726 (25)	0.1588 (19)	0.6692 (12)	4.9 (6)
C13	0.5262 (26)	0.2727 (19)	0.5842 (15)	6.2 (7)
C21	0.8618 (23)	−0.0448 (18)	0.8470 (12)	4.8 (6)
C22	0.6351 (25)	−0.0274 (18)	0.7950 (12)	4.4 (6)
C24	0.9541 (24)	0.1151 (17)	0.7905 (12)	4.1 (6)
O7	0.7128 (13)	0.2023 (10)	0.7425 (7)	3.2 (3)
O11	0.5063 (15)	0.4037 (12)	0.7383 (8)	5.8 (4)
O12	0.3836 (17)	0.0966 (13)	0.6748 (9)	6.7 (5)
O13	0.4664 (17)	0.2792 (13)	0.5320 (10)	7.2 (5)
O21	0.9103 (16)	−0.0978 (13)	0.8808 (9)	6.7 (5)
O22	0.5286 (16)	−0.0690 (11)	0.7885 (8)	5.0 (4)
O24	1.0564 (17)	0.1642 (13)	0.7858 (8)	6.1 (4)
H4^c	0.610	0.131	0.503	5.0
H5	0.683	−0.015	0.460	5.0
H6	0.784	−0.096	0.541	5.0

^{a} Anisotropic thermal parameters for Mn and P atoms are given in Table VII. ^{b} Hydrogen atoms and carbonyl groups are numbered to correspond to the carbon or metal atoms to which they are bonded. ^{c} Hydrogen atom positional and temperature parameters included but not refined in least-squares cycles.

Table VII. Atomic Anisotropic Thermal Parameters for **5** ($\times 10^4$)

Atom	$\beta_{11}{}^a$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mn1	72 (5)	34 (3)	25 (1)	17 (3)	3 (2)	9 (2)
Mn2	95 (5)	34 (3)	20 (1)	19 (3)	4 (2)	9 (2)
P1	114 (10)	54 (6)	21 (3)	21 (6)	10 (4)	7 (3)
P2	89 (9)	34 (5)	22 (3)	15 (3)	15 (5)	8 (3)
P3	67 (8)	38 (5)	31 (3)	22 (5)	8 (4)	12 (3)

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

assigned isotropic thermal parameters decreased the conventional R index to 0.096.

At this point the eight phenyl rings were described as rigid groups: d(C–C) = 1.395 Å, d(C–H) = 1.084 Å. The dichloromethane previously located was also described as a rigid group (d(C–Cl) = 1.772 Å, d(C–H) = 1.068 Å, ∠(H–C–H) = 117.1°, ∠(Cl–C–Cl) = 105.7°) and the positions of the three remaining H atoms on the trisubstituted benzene ring were calculated using the program HPOSN.[10] These three H atoms

were assigned isotropic thermal parameters of 5.0 Å^2 in subsequent refinement; those in the eight phenyl rings were assigned 6.0 Å^2; and those in the dichloromethane, 20 Å^2. These values approximate the thermal motion of the various portions of the structure.

Three further cycles of refinement converged with discrepancy factors $R_F = R_w = 0.088$. The largest final shift for a group positional parameter was 0.39σ and for a nongroup atom positional parameter, 0.15σ. The standard deviation in an observation of unit weight is 1.88.

A final difference map showed residuals in the range from −0.6 to +0.7 e/Å^3. Peaks with $|\text{maxima}| > 0.5$ e/Å^3 are associated with the dichloromethane molecule; all other peaks with $|\text{maxima}| > 0.4$ e/Å^3 are associated with the other rigid groups.

The final least-squares parameters are given in Tables VI, VII, and VIII, with the standard deviations of these parameters as derived from the inverse matrix. Table IX represents the parameters of the individual atoms derived from the data in Table VIII. The final values of $|F_o|$ and $|F_c|$ are given in Table X (supplementary material).

Description of the Structures. The molecular structure of **5** is shown in Figures 1 and 2. That of **4** is similar except that the triphenylphosphine group (P$_1$) on Mn$_2$ has been replaced by a carbonyl group (CO$_{23}$), see Figure 3. The systematic name for **4** is given in the title; that for **5**, which is a triphenylphosphine substitution product of **4**, is abd-tricarbonyl-c-triphenylphosphine-$efgk$ [μ-[carbonyl[6-(diphenylphosphine)-o-phenylene]]]-hjl-tricarbonyl-i-triphenylphosphinemanganese)manganese.

The structures of **4** and **5** are both very similar to that of **3**.[1] Each contains two manganese atoms bridged by the same novel quadridentate ligand which form a planar metallotricyclic ring system. Compound **4** is actually an isomer of **3** in which an equatorial phosphine (P$_1$) on Mn$_2$ and an *axial* carbonyl on Mn$_1$ have replaced each other. Compound **5** is a substitution product of **3**; CO$_{14}$ of **3** has been replaced by a triphenylphosphine group. The root mean square amplitudes of vibration along the three principal axes of the vibrational ellipsoids of the heavy atoms for both **4** and **5** are given in Table XI (supplementary material). Bond lengths and angles are similar to those of **3**; these are shown in Tables XII-XV. It is interesting to note that replacement of the triphenylphosphine on Mn$_2$ (in **3** and **5**) with a carbonyl (in **4**) leads to a significantly longer distance for the chelate Mn$_2$-P$_2$ bond, i.e., 2.304 (4) Å in **4** vs. 2.276 (2) Å in **3** and 2.274 (8) Å in **5**. Further comparisons of some relevant bond lengths of **3**, **4**, **5** and other related derivatives have been discussed in the previous part of this series.[1]

It should be pointed out that both **4** and **5** deviate from planarity more than **3**. This is probably due to steric interaction involving the *axial* triphenylphosphine group. Least-squares plane data are given in Tables XVI and XVIII, and deviations therefrom in Tables XVII and XIX.

No very close intermolecular contacts were found in these

Table VIII. Group Parameters for **5**

Groups	x	y	z	ϕ^a	θ	ρ
Ph 1	0.7479 (14)	0.0841 (12)	0.9726 (7)	2.922 (11)	2.529 (10)	1.447 (10)
Ph 2	0.9428 (12)	0.2297 (11)	0.9279 (8)	0.460 (12)	2.597 (9)	2.297 (11)
Ph 3	0.6730 (14)	0.2222 (12)	0.8963 (9)	−0.587 (15)	−2.352 (9)	3.112 (14)
Ph 4	0.9380 (14)	−0.1214 (12)	0.6777 (8)	2.541 (14)	2.368 (8)	−2.765 (13)
Ph 5	0.6734 (14)	−0.1890 (8)	0.6858 (7)	0.904 (13)	2.336 (8)	−3.025 (12)
Ph 6	0.7802 (13)	0.4336 (9)	0.5797 (6)	−1.922 (9)	2.648 (8)	−2.133 (9)
Ph 7	0.8514 (13)	0.4714 (9)	0.7269 (7)	2.587 (10)	−2.521 (9)	1.272 (10)
Ph 8	0.9468 (12)	0.3258 (11)	0.6494 (8)	−0.380 (18)	−2.166 (8)	−0.087 (17)
DCLM^b	0.5751 (17)	0.2940 (8)	0.1279 (19)	−3.104 (18)	3.054 (36)	2.723 (8)

^{a} The definitions of these parameters are given in ref 17. ^{b} Dichloromethane.

Table IX. Derived Parameters for Group Atoms of **5**

Group	Atom	x	y	z	B, Å²	Group	Atom	x	y	z	B, Å²
Ph 1	C1	0.7479	0.0841	0.9726	3.8 (5)	Ph 5	C1	0.6734	−0.1890	0.6858	3.2 (5)
	C2	0.7833	0.1444	1.0384	7.2 (7)		C2	0.6912	−0.2597	0.7284	3.7 (5)
	C3	0.7526	0.1037	1.0975	7.5 (8)		C3	0.5976	−0.3496	0.7225	5.5 (6)
	C4	0.6866	0.0027	1.0909	6.8 (7)		C4	0.4862	−0.3689	0.6741	5.1 (6)
	C5	0.6512	−0.0576	1.0250	6.8 (7)		C5	0.4684	−0.2983	0.6315	5.9 (7)
	C6	0.6819	−0.0169	0.9659	5.1 (6)		C6	0.5620	−0.2083	0.6374	4.6 (6)
	H2	0.8346	0.2229	1.0436	6.0		H2	0.7778	−0.2447	0.7660	6.0
	H3	0.7801	0.1506	1.1487	6.0		H3	0.6115	−0.4045	0.7556	6.0
	H4	0.6628	−0.0289	1.0198	6.0		H4	0.4135	−0.4388	0.6695	6.0
	H5	0.5999	−0.1361	1.0198	6.0		H5	0.3818	−0.3132	0.5939	6.0
	H6	0.6543	−0.0637	0.9148	6.0		H6	0.5482	−0.1534	0.6043	6.0
Ph 2	C1	0.9428	0.2297	0.9279	4.1 (6)	Ph 6	C1	0.7802	0.4336	0.5797	2.6 (5)
	C2	1.0363	0.2000	0.9697	6.2 (7)		C2	0.6939	0.4948	0.5825	4.0 (5)
	C3	1.1597	0.2627	0.9879	9.9 (10)		C3	0.6729	0.5480	0.5282	5.4 (6)
	C4	1.1896	0.3550	0.9643	7.6 (8)		C4	0.7382	0.5400	0.4712	4.7 (6)
	C5	1.0961	0.3847	0.9225	7.3 (8)		C5	0.8245	0.4789	0.4685	5.7 (6)
	C6	0.9728	0.3220	0.9043	7.6 (8)		C6	0.8456	0.4257	0.5227	4.0 (5)
	H2	1.0131	0.1283	0.9880	6.0		H2	0.6431	0.5009	0.6267	6.0
	H3	1.2323	0.2396	1.0203	6.0		H3	0.5955	0.5955	0.5303	6.0
	H4	1.2855	0.4037	0.9784	6.0		H4	0.7219	0.5814	0.4291	6.0
	H5	1.1194	0.4565	0.9041	6.0		H5	0.8753	0.4727	0.4242	6.0
	H6	0.9001	0.3451	0.8718	6.0		H6	0.9127	0.3782	0.5206	6.0
Ph 3	C1	0.6730	0.2222	0.8963	4.4 (6)	Ph 7	C1	0.8514	0.4714	0.7269	3.0 (5)
	C2	0.5557	0.1866	0.8523	5.4 (6)		C2	0.9267	0.5642	0.7185	4.2 (5)
	C3	0.4636	0.2427	0.8539	5.8 (6)		C3	0.9668	0.6432	0.7751	5.8 (7)
	C4	0.4888	0.3344	0.8994	6.8 (7)		C4	0.9318	0.6293	0.8401	6.2 (7)
	C5	0.6061	0.3700	0.9434	8.8 (9)		C5	0.8565	0.5365	0.8485	6.4 (7)
	C6	0.6982	0.3139	0.9418	8.0 (8)		C6	0.8164	0.4576	0.7919	4.5 (6)
	H2	0.5361	0.1154	0.8169	6.0		H2	0.9540	0.5750	0.6680	6.0
	H3	0.3724	0.2151	0.8197	6.0		H3	1.0253	0.7153	0.7686	6.0
	H4	0.4172	0.3780	0.9006	6.0		H4	0.9630	0.6907	0.8841	6.0
	H5	0.6257	0.4412	0.9787	6.0		H5	0.8292	0.5258	0.8990	6.0
	H6	0.7894	0.3416	0.9760	6.0		H6	0.7579	0.3855	0.7984	6.0
Ph 4	C1	0.9380	−0.1214	0.6777	3.8 (5)	Ph 8	C1	0.9468	0.3258	0.6494	3.3 (5)
	C2	1.0620	−0.0763	0.7122	5.9 (6)		C2	0.9516	0.2501	0.5954	5.1 (6)
	C3	1.1646	−0.1135	0.6930	7.7 (8)		C3	1.0640	0.2177	0.5918	6.9 (7)
	C4	1.1432	−0.1959	0.6394	8.4 (8)		C4	1.1715	0.2611	0.6423	6.7 (7)
	C5	1.0192	−0.2411	0.6049	6.0 (7)		C5	1.1667	0.3368	0.6962	6.6 (7)
	C6	0.9166	−0.2038	0.6240	5.3 (6)		C6	1.0544	0.3691	0.6998	5.4 (6)
	H2	1.0787	−0.0122	0.7538	6.0		H2	0.8680	0.2164	0.5562	6.0
	H3	1.2610	−0.0784	0.7198	6.0		H3	1.0677	0.1589	0.5499	6.0
	H4	1.0230	−0.2248	0.6245	6.0		H4	1.2589	0.2360	0.6395	6.0
	H5	1.0025	−0.3051	0.5632	6.0		H5	1.2503	0.3705	0.7354	6.0
	H6	0.8202	−0.2390	0.5972	6.0		H6	1.0507	0.4280	0.7418	6.0
						DCLM[b]	C1	0.5751	0.2940	0.1279	16.8 (15)
							Cl1	0.7230	0.3817	0.1626	18.5 (5)
							Cl2	0.4680	0.3674	0.1029	23.6 (6)
							H1	0.5410	0.2562	0.1686	20.0
							H2	0.5880	0.2480	0.0820	20.0

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

structures. The closest contacts for **4** are Ph4H4-Ph5H4 (1 + x, y, z), 2.391 Å and O_{11}-Ph5H3 ($x, y, z − 1$), 2.461 Å. The closest contacts for **5** are Ph2H4-Ph3H4 ($1 + x, y, z$), 2.255 Å, and O_{13}-Ph6H3 ($x − 1, 1 − y, z − 1$), 2.458 Å. The contacts involving the dichloromethane are particularly long. The shortest intermolecular chlorine–hydrogen contact is DCLM Cl_2-Ph2H3 ($x − 1, y, z − 1$), 2.911 Å, but thermal parameters for the dichloromethane are very large. All other intermolecular contacts in either structure are greater than the sum of the van der Waals radii for the atoms involved.[16]

The solid state structure of **4** does not clarify the absence of a parent ion in the mass spectrum. In fact several of the secondary metalation products show a relatively easy loss of these carbonyl groups in their mass spectra.[4]

Interconversions of Secondary Metalation Products. Previously we postulated two paths by which the isomeric secondary metalation products **3** and **4** were formed.[4] In the absence

of information to the contrary, we assumed that parallel and competing reactions were responsible for the production of these isomers.[4] In an effort to shed light on this and related questions, a series of reactions were carried out with the derivatives **3**, **4**, **5**, and **8** which are summarized in Scheme I.

Thermal activation of **3** was found to give predominantly its isomer, **4**, and the primary metalation product, **2**, with traces of **5** and **8**. However, thermal activation of the isomer **4** gave only small amounts of **8** with 80% of **4** recovered. This established **4** as the thermodynamically more stable product and indicates that it may be formed from **3** as well as directly from the initial starting materials in the reaction.

When **4** was reacted with carbon monoxide at elevated temperatures, **8** was formed exclusively, which indicates that the trace of **8** found in the thermal activation of **4** was probably due to reaction of **4** with CO liberated through decomposition. However, when its isomer, **3**, was reacted with CO under
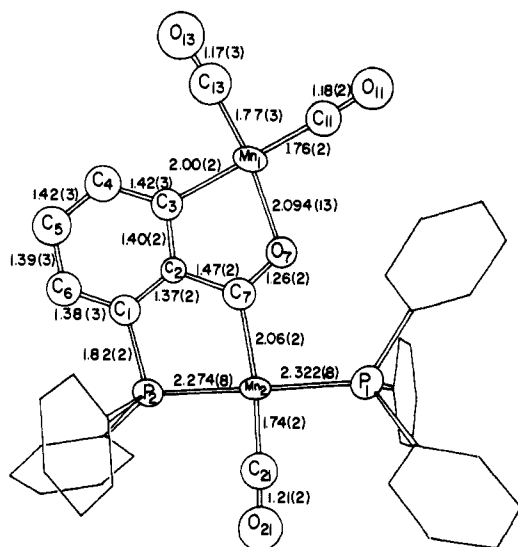
Figure 1. ORTEP plot of the molecular structure of **5**. The thermal ellipsoids are shown at the 50% probability level.
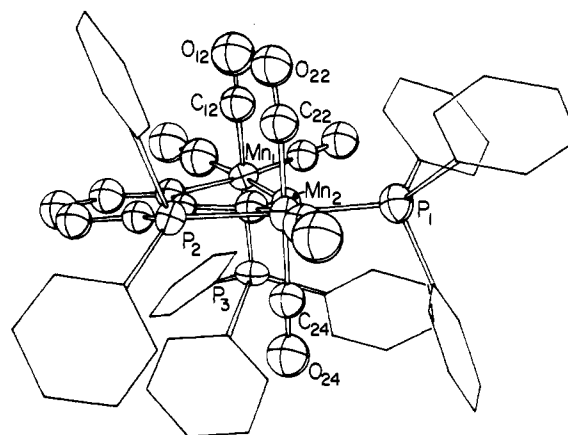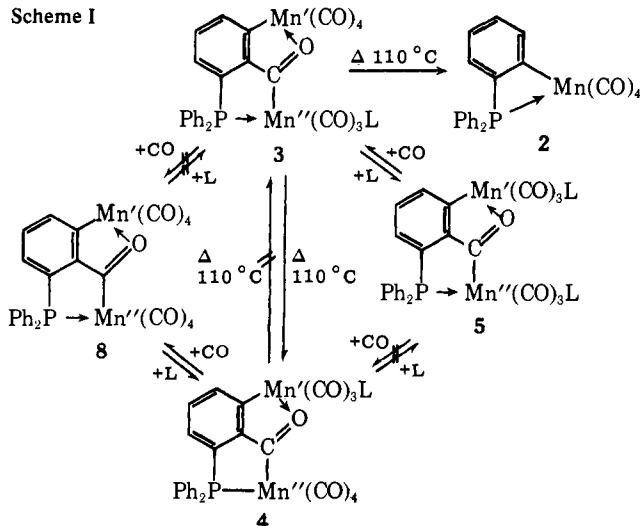

Figure 2. ORTEP plot of the molecular structure of **5** showing the disposition of the axial ligands. Thermal ellipsoids are shown at the 50% level.

Table XII. Interatomic Distances (Å) in **4**

	Distance		Distance
Mn1–C11	1.826 (15)	P2–C1	1.794 (13)
Mn1–C12	1.749 (15)	C1–C2	1.391 (15)
Mn1–C13	1.708 (15)	C2–C3	1.415 (15)
Mn1–P3	2.364 (4)	C3–C4	1.403 (16)
Mn1–C3	2.041 (12)	C4–C5	1.395 (18)
Mn1–O7	2.064 (8)	C5–C6	1.362 (17)
Mn1–C7	2.899 (12)	C6–C1	1.389 (16)
Mn1–O11	2.962 (11)	C2–C7	1.479 (15)
Mn1–O12	2.933 (12)	C7–O7	1.270 (13)
Mn1–O13	2.989 (11)	C11–O11	1.140 (14)
		C12–O12	1.184 (15)
Mn2–C21	1.789 (17)	C13–O13	1.195 (15)
Mn2–C22	1.803 (16)	C21–O21	1.168 (16)
Mn2–C23	1.779 (17)	C22–O22	1.152 (15)
Mn2–C24	1.824 (16)	C23–O23	1.168 (16)
Mn2–C7	2.016 (12)	C24–O24	1.153 (16)
Mn2–P2	2.304 (4)		
Mn2–O7	2.948 (8)	P2–Ph4C1	1.830[a]
Mn2–O21	2.957 (12)	P2–Ph5C1	1.825
Mn2–O22	2.952 (12)		
Mn2–O23	2.946 (12)	P3–Ph6C1	1.842
Mn2–O24	2.976 (12)	P3–Ph7C1	1.817
		P3–Ph8C1	1.842

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

Scheme I

Table XIII. Bond Angles for **4**

Atoms	Angle, deg	Atoms	Angle, deg
C11–Mn1–C12	90.1 (6)	Mn1–P3–Ph6	114.3
C11–Mn1–C13	94.3 (7)	Mn1–P3–Ph7	114.5
C11–Mn1–P3	89.9 (4)	Mn1–P3–Ph8	117.5
C11–Mn1–C3	173.2 (5)	Ph6–P3–Ph7	104.3
C11–Mn1–O7	97.7 (5)	Ph6–P3–Ph8	101.6
C12–Mn1–C13	90.8 (7)	Ph7–P3–Ph8	102.8
C12–Mn1–P3	175.7 (5)		
C12–Mn1–C3	83.7 (6)	Mn1–C11–O11	173.6 (13)
C12–Mn1–O7	89.6 (5)	Mn1–C12–O12	178.6 (13)
C12–Mn1–P3	93.5 (5)	Mn1–C13–O13	172.9 (13)
C13–Mn1–C3	88.6 (6)	Mn2–C21–O21	178.9 (15)
C13–Mn1–O7	167.9 (6)	Mn2–C22–O22	174.5 (13)
P3–Mn1–C3	96.0 (4)	Mn2–C23–O23	177.9 (14)
P3–Mn1–O7	86.1 (2)	Mn2–C24–O24	179.6 (14)
C3–Mn1–O7	79.4 (4)	Mn1–O7–C7	118.9 (8)
		Mn1–C3–C2	111.4 (9)
C21–Mn2–C22	94.0 (7)	Mn1–C3–C4	133.5 (9)
C21–Mn2–C23	95.2 (7)	Mn2–C7–O7	126.1 (9)
C21–Mn2–C24	92.4 (7)	Mn2–C7–C2	120.9 (8)
C21–Mn2–C7	174.5 (6)	C2–C7–O7	112.9 (10)
C21–Mn2–P2	93.3 (5)	P2–C1–C2	114.2 (10)
C22–Mn2–C23	89.8 (7)	P2–C1–C6	127.2 (10)
C22–Mn2–C24	172.6 (6)	C7–C2–C1	118.8 (11)
C22–Mn2–C7	81.2 (6)	C7–C2–C3	117.3 (10)
C22–Mn2–P2	89.6 (5)	C1–C2–C3	123.9 (11)
C23–Mn2–C24	89.4 (7)	C2–C3–C4	115.0 (11)
C23–Mn2–C7	88.9 (6)	C3–C4–C5	121.2 (12)
C23–Mn2–P2	171.6 (5)	C4–C5–C6	122.0 (14)
C24–Mn2–C7	91.4 (6)	C5–C6–C1	119.6 (13)
C24–Mn2–P2	91.1 (5)	C6–C1–C2	118.4 (12)
C7–Mn2–P2	82.7 (4)		
Mn2–P2–Ph4	119.9		
Mn2–P2–Ph5	114.1		
Mn2–P2–C1	103.1 (4)		
Ph4–P2–Ph5	106.9		
Ph4–P2–C1	104.9		
Ph5–P2–C1	106.7		

similar conditions, only trace amounts of **8** were found along with a small amount of **4** and **2** which, as shown above, is expected from the thermal decomposition of **3**. Derivative **5** reacted with CO to give predominantly **3** and small amounts of the products expected from the thermal decomposition of **3** were also found.

Reaction of PPh₃ with **3** and **4** showed reactivity reversing that observed with CO; namely, **3** yielded **5** and **8** yielded **4**. Treatment with PPh₃ of **4** led to its recovery unchanged. A pattern of reactivity is thus established between adjacent pairs

Table XIV. Interatomic Distances for **5**

	Distance, Å		Distance, Å
Mn1–C11	1.762 (24)	P2–C1	1.823 (21)
Mn1–C12	1.738 (27)	C1–C2	1.366 (24)
Mn1–C13	1.773 (29)	C2–C3	1.397 (24)
Mn1–P3	2.367 (7)	C3–C4	1.424 (26)
Mn1–C3	2.001 (21)	C4–C5	1.416 (28)
Mn1–O7	2.094 (13)	C5–C6	1.393 (27)
Mn1–C7	2.871 (21)	C6–C1	1.384 (26)
Mn1–O11	2.945 (17)	C2–C7	1.473 (25)
Mn1–O12	2.901 (18)	C7–O7	1.264 (21)
Mn1–O13	2.936 (19)	C11–O11	1.185 (22)
		C12–O12	1.164 (24)
Mn2–C21	1.743 (24)	C13–O13	1.168 (26)
Mn2–C22	1.801 (26)	C21–O21	1.213 (24)
Mn2–C24	1.808 (25)	C22–O22	1.151 (23)
Mn2–C7	2.058 (21)	C24–O24	1.183 (23)
Mn2–P1	2.322 (8)		
Mn2–P2	2.274 (8)	P2–Ph4C1	1.818[a]
Mn2–O7	2.975 (14)	P2–Ph5C1	1.832
Mn2–O21	2.955 (18)		
Mn2–O22	2.950 (17)	P1–Ph1C1	1.838
Mn2–O24	2.990 (18)	P1–Ph2C1	1.810
		P1–Ph3C1	1.844
		P3–Ph6C1	1.840
		P3–Ph7C1	1.805
		P3–Ph8C1	1.824

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

Table XV. Bond Angles for **5**

Atoms	Angle, deg	Atoms	Angle, deg
C11–Mn1–C12	89.4 (11)	Mn2–P2–Ph4	124.7
C11–Mn1–C13	87.7 (11)	Mn2–P2–Ph5	112.2
C11–Mn1–P3	91.3 (8)	Mn2–P2–C1	103.3 (8)
C11–Mn1–C3	175.4 (10)	Ph4–P2–Ph5	102.2
C11–Mn1–O7	100.9 (8)	Ph4–P2–C1	107.9
C12–Mn1–C13	89.4 (11)	Ph5–P2–C1	105.0
C12–Mn1–P3	177.2 (8)		
C12–Mn1–C3	86.0 (10)	Mn1–P3–Ph6	111.4
C12–Mn1–O7	89.8 (9)	Mn1–P3–Ph7	115.2
C12–Mn1–P3	93.3 (9)	Mn1–P3–Ph8	119.2
C13–Mn1–C3	91.8 (10)	Ph6–P3–Ph7	102.2
C13–Mn1–O7	171.4 (9)	Ph6–P3–Ph8	105.6
P3–Mn1–C3	93.3 (6)	Ph7–P3–Ph8	101.4
P3–Mn1–O7	87.4 (4)		
C3–Mn1–O7	79.5 (7)	Mn1–C11–O11	177.3 (21)
		Mn1–C12–O12	178.0 (23)
Mn2–P1–Ph1	116.7	Mn1–C13–O13	173.8 (24)
Mn2–P1–Ph2	109.7	Mn2–C21–O21	176.6 (22)
Mn2–P1–Ph3	121.8	Mn2–C22–O22	175.0 (21)
Ph1–P1–Ph2	104.0	Mn2–C24–O24	177.1 (21)
Ph1–P1–Ph3	97.8	Mn1–O7–C7	115.3 (14)
Ph2–P1–Ph3	104.8	Mn1–C3–C2	112.9 (16)
		Mn1–C3–C4	133.6 (17)
C21–Mn2–C22	95.5 (11)	Mn2–C7–O7	125.4 (17)
C21–Mn2–C23	91.6 (8)	Mn2–C7–C2	119.8 (16)
C21–Mn2–C24	96.4 (11)	C2–C7–O7	114.7 (19)
C21–Mn2–C7	171.9 (10)	P2–C1–C2	114.0 (18)
C21–Mn2–P2	89.9 (8)	P2–C1–C6	125.2 (17)
C22–Mn2–C23	88.3 (8)	C7–C2–C1	119.3 (19)
C22–Mn2–C24	168.1 (10)	C7–C2–C3	116.0 (19)
C22–Mn2–C7	87.8 (9)	C1–C2–C3	124.7 (21)
C22–Mn2–P2	88.8 (8)	C2–C3–C4	113.5 (19)
C23–Mn2–C24	89.9 (8)	C3–C4–C5	123.1 (22)
C23–Mn2–C7	96.0 (7)	C4–C5–C6	118.8 (24)
C23–Mn2–P2	176.9 (3)	C5–C6–C1	119.1 (22)
C24–Mn2–C7	80.7 (9)	C6–C1–C2	120.5 (21)
C24–Mn2–P2	92.6 (7)		
C7–Mn2–P2	82.7 (7)		

Table XVI. Least-Squares Planes in **4**

	Direction cosines ($\times 10^5$) with respect to			Description	$\Sigma(D),^2$
Plane	a	b	$c*$	of plane	$\text{Å}^2 \times 10^4$
A	96 179	−27 361	−995	Benzene ring	5
B	96 519	−25 725	4727	Mn1, C2, C3, C7, O7	30
C	95 484	−28 774	−7407	Mn2, P2, C1, C2, C7	42
D	95 876	−28 403	−977	11-atom tricyclic system	435

Interplanar Angles	
Planes	Angle, deg
A and B	176.6
A and C	176.2
B and C	172.8

Table XVII. Distances from Least-Squares Planes in **4** ($\text{Å} \times 10^3$)[a]

Atom	A	B	C	D
Mn1	156	26*	374	124*
Mn2	46	182	−25*	120*
P2	177	371	36*	131*
C1	10*	120	−42*	−21*
C2	−14*	23*	17*	−48*
C3	6*	−32*	117	−17*
C4	6*	−26	108	−3*
C5	−11*	31	7	−16*
C6	3*	114	−55	−13*
C7	−24	11*	14*	−73*
O7	8	−28*	126	−43*
C11	481	271	787	439
O11	737	469	1098	685
C13	204	9	487	188
O13	194	−38	516	190
C21	233	462	61	154
O21	371	660	134	284
C23	−88	−9	−90	−166
O23	−217	−176	−175	−304

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

Table XVIII. Least-Squares Planes in **5**

	Direction cosines ($\times 10^5$) with respect to			Description	$\Sigma(D)^2,$
Plane	a	b	$c*$	of plane	$\text{Å}^2 \times 10^4$
A	−80 305	−59 647	2271	Benzene ring	21
B	−78 586	−60 858	10 981	Mn1, C2, C3, C7, O7	176
C	−87 412	−48 570	144	Mn2, P2, C1, C2, C7	70
D	−83 025	−55 706	1922	11-atom tricyclic system	1317

Interplanar Angles	
Planes	Angle, deg
A and B	174.9
A and C	172.4
B and C	169.3

of derivatives in the parallelogram defined by **3**, **5**, **4**, and **8**; solid arrows indicate observed interconversions while the dashed arrows indicate that no interconversion was observed. This pattern shows that the manganese atom (Mn′) bearing the acyl group coordinated through oxygen is substitutionally more labile than the other (Mn″). The substitutions furthermore occur exclusively in the axial position of Mn′, i.e., cis to the oxygen-coordinated acyl group.

The isomerization of **3** to **4** accompanied by formation of **2** illustrates some further interesting transformations possible

Table XIX. Distances from Least-Squares Planes in **5** (Å × 10³)[a]

| Atom	A	B	C	D
Mn1	61	58*	504	182*
Mn2	139	448	−11*	57*
P2	306	472	32*	172*
C1	28*	57	−56*	−44*
C2	−26*	14*	50*	−39*
C3	3*	−53*	243	46*
C4	18*	−153	245	51*
C5	−15*	−200	49	−43*
C6	−7*	−90	−99	−87*
C7	−97	64*	−15*	−101*
O7	−247	−84*	−11	−195*
P1	74	522	57	48
C11	253	296	871	441
O11	428	499	1166	662
C13	323	170	916	493
O13	588	335	1270	786
C21	255	677	−106	101
O21	267	767	−242	63

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

for the secondary metalation products. The transformations are summarized in Scheme II in the form of postulated intermediates.

The loss of PPh₃ from Mn″ in **3** would create a coordinatively unsaturated center on this metal atom. This is indicated by the asterisk in the intermediate **3** minus L (3-L) at the left-hand side of Scheme II. There are two possible ways in

Scheme II

iso-4

3-L

iso-3-L
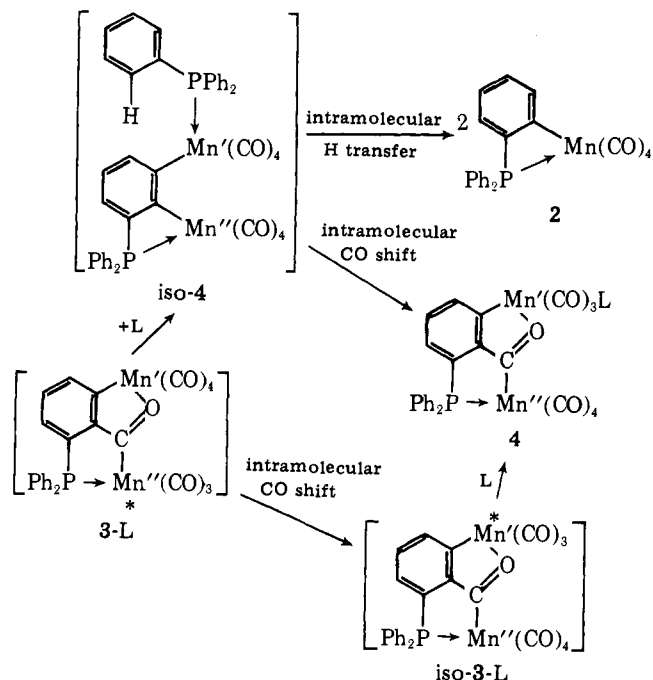
which this intermediate might react to give the accounted products. The first is illustrated by the upper pathway in Scheme II. A migration by Mn″ from acyl carbon to the phenyl ring would restore coordinative saturation at Mn″ and open a position on Mn′ to attack by L giving the species labeled iso-4. An intramolecular shift of hydrogen in this intermediate analogous to that observed by Cheney et al.[18] in complexes of platinum containing cyclometalation rings would bring Mn′ into bonding at the second phenyl ring. This would produce 2 mol of the cyclometalation product **2**, as indicated. Parallel or sequential pathways are possible for the formation of **4**. A parallel independent pathway could involve isomerization of the intermediate **3-L** through intramolecular transfer of CO

from Mn′ to Mn″. This is shown on the lower path of Scheme II. Attack by L at Mn′ would give **4**. Alternatively, the intramolecular shift of CO could occur in the intermediate iso-**4**, leading to **4** in competition with intramolecular H transfer which leads to 2 mol of **2**. These intermediates indicate the interesting intramolecular exchange pathways possible for the secondary metalation products which will be the subject of further studies in our group.

Experimental Details for the Interconversion Reactions

All reactions were carried out under nitrogen. General reaction conditions and reagents as well as spectroscopic instrumentation have been described previously.[3,4]

Thermal Isomerization and Degradation of 3. The title compound (0.058 g, 0.07 mmol) was refluxed under nitrogen in 15 mL of octane for 1 h. The solution was cooled under a stream of nitrogen and applied directly to a silica gel/hexane chromatography column. The products were eluted as described previously.[4] Identification of each product was by infrared spectroscopy. The products, in the order in which they were removed from the column, are as follows (relative yields based on 3 are shown in parentheses): **2** (12%), **8** (8%), unreacted **3** (25%), **4** (31%), and **5** (6%).

Attempted Thermal Isomerization of 4. The title compound (0.103 g) was refluxed in 15 mL of octane for 1.25 h. The solution was cooled and applied directly to a column. Unreacted **4** was recovered in 80% yield. The only other measurable product was **8** (11%). The balance was an insoluble brown material which is found in all of the reactions and has not been characterized. No trace either of **2** or **3** was found.

The Reversible Reaction of 4 with CO. The secondary metalated product, **4** (0.080 g), was brought to reflux in 15 mL of octane while bubbling CO through it. **4** did not completely dissolve until between 90 and 100 °C. Immediately upon dissolution, an infrared spectrum was taken showing considerable conversion to **8** at this point. However, over the next 1 h, no further change occurred, indicating that an equilibrium had been reached. Addition of CO was continued after the heater was removed; a precipitate began to form immediately. An infrared spectrum at this point showed only **8** present in solution.

The solution was purged with nitrogen and then heated to 80 °C for 4 h. Product **4** was recovered after column chromatography in 85% yield.

The Reaction of 8 with PPh₃. Product **8** stirred with an excess of PPh₃ for 24 h at room temperature showed no reaction. The mixture was then heated to 100 °C for 1 h and chromatographed yielding 90% of the theoretical yield of **4**.

The Reversible Reaction of 5 with CO. Product **5** (0.080 g) was suspended in 15 mL of octane and maintained at 105 °C while bubbling CO through it. After 0.5 h the solution cleared and an infrared spectrum showed complete conversion to **3**. The resulting solution was purged with nitrogen and stirred at 80 °C for 2 h and then overnight at room temperature. Column chromatography revealed a small amount of **4** (10%) but mostly **5** (70%). Traces of products derived from thermal degradation of **3** were also found.

Reaction of 4 with PPh₃. Product **4** (0.55 g) and PPh₃ (0.019 g) were heated at 105 °C in xylene (15 mL) for 3 h. An infrared spectrum showed no change in **4**.

Reaction of 3 with CO. Product **3** (0.074 g) was refluxed in 15 mL of toluene while bubbling CO through it. After 1.5 h, the solution was allowed to cool while the CO still bubbled through it. Column chromatography gave **8** (6%), unreacted **3** (55%), **4** (14%), plus traces of other compounds not measured.

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 furnished by the UCLA Campus Computing Network.

References and Notes

(1) (a) Taken in part from the Dissertation of B. T. Huie, UCLA, 1975. (b) Part 10: B. T. Huie, C. B. Knobler, G. Firestein, R. J. McKinney, and H. D. Kaesz, *J. Am. Chem. Soc.*, preceding paper in this issue.
(2) In order to preserve continuity and facilitate correlation of the results reported in the present work with that of the two preceding relevant publications, ref 3 and 4, the numbering of these derivatives in those papers has been retained in the present work. Since the present paper refers only to the unsubstituted derivatives, the letter index *a* following the compound number has been omitted; this was used in the earlier papers to differentiate these derivatives from the fluoro (letter index *b*) or methyl derivatives (letter index *c*).
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(8) The numbers given in parentheses throughout this paper are the estimated standard deviations, and refer to the last digit given.
(9) Part 9: R. J. McKinney, C. B. Knobler, B. T. Huie, and H. D. Kaesz, *J. Am. Chem. Soc.*, **99**, 2988 (1977).
(10) (a) 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; 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. (b) 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).
(11) The function $\Sigma||F_o| - |F_c||^2$ was minimized in the least-squares refinement and the discrepancy indices were defined as

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

where

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

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Isolation and Structural Characterization of Bis(η^5-cyclopentadienyl)bis(carbonyl)-μ-(o-phenylene)-diiridium(Ir–Ir), $(C_5H_5)_2(CO)_2Ir_2(C_6H_4)$: A Product Formally Derived from the Double Oxidative Addition of Benzene to Iridium

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Abstract: During a study of the reaction of $(\eta^5\text{-}C_5H_5)Ir(CO)_2$ and photo-2-pyrone in benzene solution, a yellow, crystalline compound was isolated in low yield. Subsequent studies have shown that this substance can also be obtained in the absence of photo-2-pyrone in comparable yields. The product has been identified as bis(η^5-cyclopentadienyl)bis(carbonyl)-μ-(o-phenylene)-diiridium(Ir–Ir) (**1**) by means of ^{1}H NMR, IR, and mass spectral analyses as well as by x-ray diffraction techniques. The complex crystallizes in the monoclinic system, space group $P2_1/n$. Crystal parameters are $a = 9.734$ (4), $b = 9.468$ (4), $c = 17.224$ (7) Å, $\beta = 94.20$ (4)°, $Z = 4$. The structure was solved by the heavy atom technique employing Fourier methods and was refined by full-matrix least-squares methods to final discrepancy factors of $R = 0.041$ and $R_w = 0.036$. The intensity data were collected on an Enraf-Nonius CAD-4 diffractometer and corrections were made for absorption and isotropic extinction. The two iridium atoms are symmetrically σ bonded to the phenylene ring, giving rise to an approximate (noncrystallographic) twofold axis bisecting the iridium-iridium bond and lying in the plane of the phenylene ring. The iridium-iridium bond distance is 2.7166 (2) Å, the two Ir–(C_5H_5) centroid distances are 1.907 (3) and 1.912 (3) Å, the two Ir–(CO) distances average 1.814 (3) Å, and the two iridium to phenylene ring carbon distances are both 2.045 (3) Å. The formation of **1** under these conditions is indicative of the double oxidative addition of one benzene molecule to two iridium atoms. Infrared, ^{1}H NMR, and chemical degradation studies indicate that a phenyliridium hydride intermediate such as $(\eta^5\text{-}C_5H_5)Ir(CO)(C_6H_5)(H)$ (**2**) is produced in the early stages of this reaction sequence. Possible reaction mechanisms are discussed.

The homogeneous catalytic activation of carbon-hydrogen bonds has become the subject of intense research efforts in recent years, since it relates to a new type of homogeneous catalysis, and offers some potentially important new pathways, at least involving arenes, for organic synthesis.[1] This activation is usually postulated to occur as a result of cleavage of the C–H bond by a highly reactive, coordinatively unsaturated transition metal species, and concomitant formation of a C–M–H intermediate. At the present time, however, bona fide examples of this important process which involve *unactivated* C–H bonds