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cis-Tricarbonylbistriphenylphosphinemanganese and the Related Compounds[*1]

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Tricarbonyl-methylcyclopentadienylmanganese(I) (I) gives two manganese carbonyl triphenylphosphine compounds when treated with triphenylphosphine in the presence of a sodium dispersion, with tetrahydrofuran used as the solvent. One compound is a known diamagnetic $(CH_3C_5H_4)Mn(CO)_2(PPh_3)$(II) (38% yield) formed by a ligand substitution reaction without any change in the oxidation number of the central manganese(+1). The other compound is a novel paramagnetic manganese(0) compound, *cis*-$Mn(CO)_3(PPh_3)_2$ (III) (25% yield), which may be formed by a reductive phosphination reaction. A *cis* trigonal bipyramidal configuration, as in the case reported for $Fe(CO)_3(o\text{-}(AsMe_2)_2C_6H_4)$, is proposed for III on the basis of the results of infrared spectroscopy. The compound III gives the following derivatives: $BrMn(CO)_3(PPh_3)_2$, VI, $CH_3Mn(CO)_3(PPh_3)_2$, VII, and $Mn(CO)_3(PPh_3)_2\cdot 1/2\cdot CHCl_3$, VIII.

Manganese carbonyl compounds are generally prepared by reductive carbonylation methods,[1,2] in which compounds of manganese in its higher oxidation state are reduced in the presence of ligand carbon monoxide in ethereal solvents. By analogy with this, triphenylphosphine (PPh_3) can also be expected to react with the metal compounds in reductive phosphination reactions in appropriate solvents. In this experiment, methylcyclopentadienyltricarbonylmanganese(I) (I), a well-known starting material for the preparation of manganese carbonyl compounds,[2] was treated reductively with a sodium dispersion in the presence of triphenylphosphine in tetrahydrofuran(THF); a novel paramagnetic manganese(0) compounds, *cis*-tricarbonyl-bistriphenylphosphinemanganese(0) (III), and a known compound, methylcyclopentadienyldicarbonyltriphenylphosphinemanganese(I) (II), were thus obtained. The latter, II, was identical with the previously-reported compound prepared by the ultraviolet radiation reaction of I and PPh_3 in cyclohexane,[3] or by heating a mixture of I and PPh_3 without any solvent at a temperature higher than 250°C.[3] With regard to the former paramagnetic compound, III, paramagnetic pentacoordinated manganese carbonyl derivatives, which do not obey the inert gas rule, have scarcely been reported. Two examples are $Mn(CO)_4PR_3$[4] and $Mn(CO)_3$(Diphos).[*3,5]

Experimental[*4]

Reagents. Triphenylphosphine (PPh_3) was prepared by the method in the literature[6] and then recrystallized from ethanol. All the solvents used were distilled under a nitrogen atmosphere after ordinary purification procedures. A combustion Improver 2, Ethyl Corporation, containing a small amount of organic orange dyes, was used as methylcyclopentadienyltricarbonylmanganese(I) without any further purification. A sodium dispersion, 40% in toluene (Kawaken Fine Chemicals, Co., Ltd.), was employed.

Synthesis in THF Solvent. Compound I (9.6 g; 44 mmol) was treated with PPh_3 (23.0 g; 88 mmol) and a sodium dispersion (9.3 g, 40% in toluene; Na 160 mmol) in THF (150 m*l*) under a nitrogen atmosphere. When the mixture was shaken, gas evolution was observed. The shaking was continued for 7 hr, after which the sodium dispersion was filtered off. Then the filtrate and the washings were evacuated under nitrogen. The dark brown tarry residue was treated with concd. hydrochloric acid and heated on a water

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1) H. E. Podall, J. H. Dunn and H. Shapiro, *J. Amer. Chem. Soc.*, **82**, 1325 (1960); R. D. Closson, L. R. Buzbee and G. G. Ecke, *ibid.*, **80**, 6167 (1958).

2) H. E. Podall and A. P. Giraitis, *J. Org. Chem.*, **26**, 2587 (1961).

3) R. S. Nyholm, S. S. Sandhu and M. H. B. Stiddard, *J. Chem. Soc.*, **1963**, 5916.

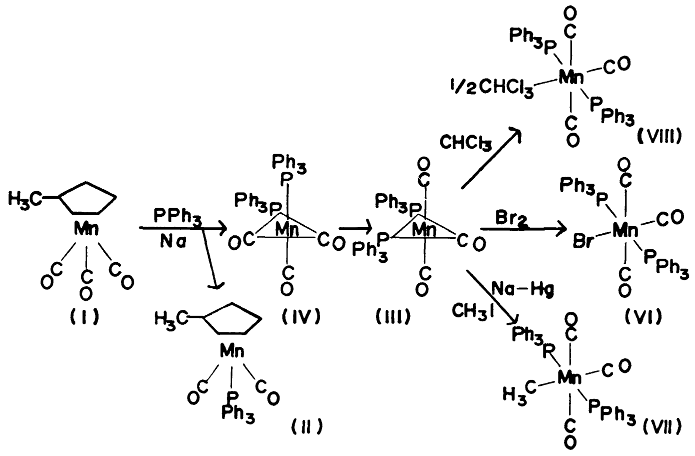
[*3] (Diphos) means $Ph_2PCH_2CH_2PPh_2$.

[*4] Mp uncorrected; the analytical results are shown in Table 1.

4) W. Hieber and W. Freyer, *Chem. Ber.*, **92**, 1765 (1959).

5) A. Sacco, *Gazz. Chim. Ital.*, **93**, 698 (1963).

6) J. Dodonow and H. Medox, *Chem. Ber.*, **61**, 907 (1928).



Scheme 1

bath. The residue turned into a brownish red viscous liquid; the phase of concd. hydrochloric acid was decanted away before cooling. Again concd. hydrochloric acid was added and decanted away. The residual viscous liquid was repeatedly treated with hot ethanol. Then a yellow precipitate and a brownish-red ethanol solution were obtained; they were separated by filtration. The precipitate was washed with water and then with ethanol. The crude product, tricarbonylbistriphenylphosphinemanganese, III (7.41 g, 25% yield), was recrystallized from benzene and then from acetone. The pale yellow crystals were dried *in vacuo*. A yellow chloroform adduct, $Mn(CO)_3(PPh_3)_2\cdot 1/2CHCl_3$, VIII, was obtained by the repeated recrystallization of III from chloroform-petroleum ether under nitrogen; it was then dried *in vacuo*. While the filtrate and the washings were combined and evaporated under reduced pressure. The crude product, methylcyclopentadienyldicarbonylmonotriphenylphosphinemanganese, II (7.75 g; 38% yield), was recrystallized from ethanol, and the resulting yellow needle crystals were measured after drying *in vacuo*. It sublimed at 100°C/10^{-4} mmHg and melted at 117°C (lit,[3] 119—20°C).

Synthesis in Dioxane Solvent. Compound I (3.35 g; 15.4 mmol) and PPh_3 (8.04 g; 30.7 mmol) were refluxed with a sodium lump (0.39 g; 17 mmol) in dioxane (55 m*l*) under a nitrogen atmosphere for 6 hr. The clear orange solution turned dark red after 30 min. After 70 min, the solution offered a clear brownish yellow color which did not change until the refluxing was stopped after 6 hr. After having been left nine days, the mixture was treated by a procedure similar to that used in the synthesis in THF. Yellow needle crystals of II were obtained in a yield of 69.4% (4.82 g), but III could not be separated in this procedure.

Synthesis in THF Solvent under Carbon Monoxide. Compound I (10.1 g; 46.1 mmol) was treated with PPh_3 (23.0 g; 88 mmol) and a sodium dispersion (16.5 g; 40% in toluene; Na 287 mmol) in THF (150 m*l*). The mixture was transferred into a 300-m*l* autoclave under a nitrogen atmosphere. The autoclave was purged twice with carbon monoxide at 60 atm and then vented to 10 atm at room temperature. It was heated to 130°C with rocking, the pressure being kept at 18 atm. When it was cooled after 6.5 hr, the barometer indicated 0 atm. The carbon monoxide was vented out, and the reaction mixture was filtered in air. The filtrate was treated by a procedure similar to that used in the synthesis under atmospheric pressure. Compound III was obtained as a yellow powder in a poor yield (44.1 mg, 0.14%); it was washed with hot ethanol, and then repeatedly with water and ethanol, and dried in air.

Reaction in THF Solvent under Atmospheric Pressure and at a Higher Temperature. Compound I (2.06 g; 9.45 mmol) and PPh_3 (5.20 g; 20 mmol) were refluxed with a sodium dispersion (1.58 g, 40% in toluene; Na 27.5 mmol) in THF (30 m*l*) under a nitrogen atmosphere for half an hour. The residual sodium was quenched with water after cooling, and phosphoric acid was added to the mixture. A suspension composed of aqueous and organic layers was thus obtained. The brown organic layer was extracted with petroleum ether; the aqueous layer was neutralized with sodium carbonate and extracted with THF. The THF extract was evacuated, and the residue was extracted with petroleum ether. The petroleum ether solution thus obtained was put together with the petroleum ether extract of the organic layer. The resulting petroleum ether solution was dried with calcium chloride and evaporated to deposit brown crystals. The crystals were dissolved with hot petroleum ether. Crystalline II was deposited instantaneously by cooling. Another brown crystal, IV, was obtained later on, although the main solute of the solution was confirmed to be II by a study of the infrared spectra.

Bromotricarbonylbistriphenylphosphinemanganese(I) (VI). Compound III (185.9 mg; 0.295 mmol) was treated with bromine (more than 29.5 mg; 0.184 mmol) in chloroform (50 m*l*). On occasional shaking, the red color turned orange, green, and at last yellow. White crystals were filtered off after 2 hr. The filtrate was evacuated to dryness. The residue was washed with diethyl ether and recrystallized from chloroform-petroleum ether. Yellowish brown crystals, VI, were thus obtained.

Methyltricarbonylbistriphenylphosphinemanganese(I) (VII). Compound III (98.5 mg; 0.149 mmol) was treated with a sodium amalgam (prepared by dissolving 1.2 g (52 mmol) of sodium metal in 13 m*l* of mercury) in THF (35 m*l*) under a nitrogen atmosphere. The mixture was left stand with occasional shaking. The yellow color turned brown during a 4-hr period. The mercury layer was then poured off, and the THF solution was filtered. The filtrate was treated with methyl iodide (8 m*l*; 130 mmol). The color gradually turned a greyish yellow green and then a transparent, yellowish brown on leaving still. The solution was filtered and evaporated. The residue was recrystallized from benzene-petroleum ether under a nitrogen atmosphere. Yellowish brown crystals, VII, were thus obtained.

Physical Measurements. *The Molecular Weights* were determined in benzene or in methylethylketone with a Mechrolab, model 301 A, osmometer.

The Magnetic Susceptibilities were measured with Gouy balances at room temperature.[*5] Cobalt(II) mercury(II) tetrathiocyanate ($\chi_g=16.44\pm0.08\times10^{-6}$ c.g.s.e.m.u., 20°C) was used as the standard substance for III and II, while water ($\chi_g=-0.722\times10^{-6}$ c.g.s.e.m.u., 25°C) was used for VIII diluted with NaCl.7)

The Infrared Spectra were recorded with Japan Optics DS-402G, Japan Optics IR-G, and Perkin Elmer model 137B Infracord recording spectrometers for the samples in the nujol mulls and KBr disks.

The ESR Spectra were recorded with a JEOL JES-118 spectrometer.

The ^1H NMR Spectra were recorded on a Varian HA-100 high-resolution spectrometer, using carbon tetrachloride as the solvent and tetramethylsilane as the internal reference.

Results and Discussion

Condition of the Synthesis. Ordinarily in the present experiment, the synthetic procedure was performed by shaking the THF solution of the reactants with a mechanical shaker at room temperature and at an atmospheric pressure of nitrogen. Two other conditions were investigated in an attempt to obtain III in a better yield and with more certainty. One of them was the reaction at so high a temperature that the sodium metal melted to react more completely with I. The THF solvent was replaced with dioxane for this purpose. Though this experiment was unsuccessful, purified II was obtained in a higher yield (69.4%) than that in the literature.3),[*6] The other reaction has at a higher temperature and at 10 atm of carbon monoxide in order to restrain the CO elimination. In this procedure, however, III was obtained in only a low yield (0.14%).

Tricarbonyl bistriphenylphosphine manganese(0) (III), $Mn(CO)_3(PPh_3)_2$. Compound III is composed of yellow, needle-like crystal readily air-oxidized in solution, although it is moderately stable against aereal oxidation in the solid state. The dilute chloroform solution of III gives no signal on an ESR spectrometer at temperature of liquid nitrogen under a nitrogen atmosphere, but it gives that of a high-spin manganese(II) compound after a short exposure to the air. Therefore, all the experiments, unless otherwise noted, were performed under a nitrogen atmosphere.

The results of the elementary analyses are listed in Table 1. The values observed on the pale yellow crystals recrystallized from benzene or from acetone do not agree well with those calculated in accordance with the formula noted above. This

Table 1

Compound	Mol wt Found (Calcd)	Elementary Analysis Found/(Calcd)%				μ_{eff}
		C	H	Mn c)	Cl	
II	449 a)	69.10	4.96	11.11		diamag.
$(CH_3C_5H_4)Mn(CO)_2(PPh_3)$	(452)	(69.00)	(4.87)	(12.17)		$\chi_g=-0.549$ $\times10^{-6}$ c. g. s. e. m. u.
III from benzene		65.86	4.27			
III from acetone	660 b)	65.74	4.52			1.81 BM
$Mn(CO)_3(PPh_3)_2$	(663)	(70.59)	(4.52)			
$Mn(CO)_3(PPh_3)_2\cdot(CH_3)_2CO$		(69.90)	(4.99)			
VIII		65.49	4.22		7.45	1.6 BM
$Mn(CO)_3(PPh_3)_2\cdot1/2\,CHCl_3$		(65.58)	(4.22)		(7.37)	
VI		62.04	4.45			
$BrMn(CO)_3(PPh_3)_2$		(62.99)	(4.04)			

a) in methylethylketone b) in benzene c) EDTA titration

[*5] The author's thanks are due to Professor Yukichi Yoshino, of the College of General Education, the University of Tokyo, and to Professor Yoshio Matsunaga, of the Faculty of Science of Hokkaido University, for the use of the Gouy balances.

[*6] 55% by the thermal method and 36% by the UV radiation method.

7) P. E. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, New York, N. Y. (1956).

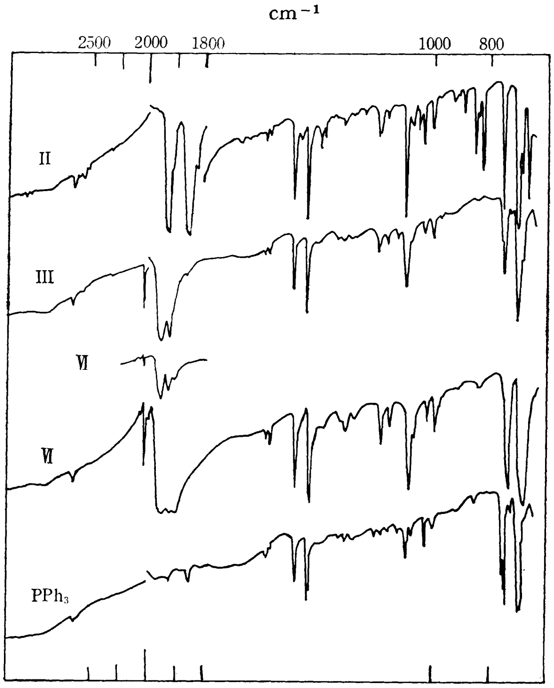


Fig. 1a. for KBr disk with DS-402 G spectrometer.

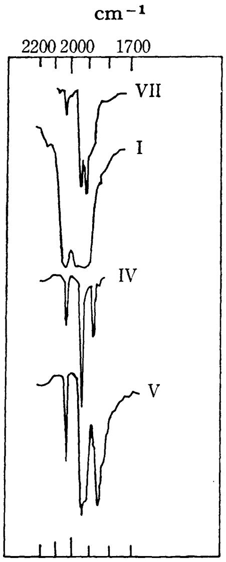


Fig. 1b. for Nujol mull with Infracord spectrometer.

cannot be attributed to the solvation of the compound (see Table 1). Though those on the yellow crystals recrystallized from chloroform-petroleum ether agree well with the solvated formula: Mn-$(CO)_3(PPh_3)_2 \cdot 1/2CHCl_3$, VIII, their infrared spectra are not identical with those of the crystals recrystallized from the former two solvents (see Table 2 and Fig. 1).

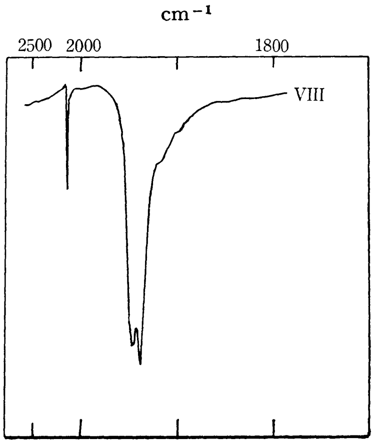
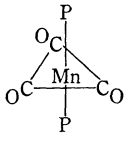


Fig. 1c. for Nujol mull with IR-G spectrometer.

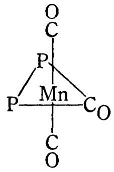
Fig. 1. Infrared spectra.

The molecular weight of III in a benzene solution (Table 1) agrees very well with that calculated according to the monomeric formula, Mn-$(CO)_3(PPh_3)_2$.

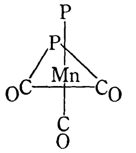
The infrared spectra and the wave numbers of III and VIII are shown in Fig. 1 and in Table 2. The absence of a band at about 840 cm^{-1}, characteristic of the methylcyclopentadienyl ligand, supports the idea that the $CH_3C_5H_4$ ligand of I is replaced in III. The absorption bands observed at from 760 cm^{-1} to 680 cm^{-1} can be assigned to the CH out-of-plane deformation bands of PPh_3. Three bands (one of them a doublet) in the C–O stretching region show that three CO ligands of I are not replaced. The C–O stretching pattern of pentacoordinated $M(CO)_3L_2$ was discussed by Cotton and Parish[8] and supplied by Manuel.[9] Only one infrared active band was observed for the D_{3h} symmetrical, *trans*-disubstituted trigonal bipyramidal (TBP) complexes (at 1930 cm^{-1} for rhenium[10]).



trans (D_{3h})



cis (C_{2v})



cis (C_s)

P: PPh_3

On the other hand, three bands like III were observed for most of the *cis*-$M(CO)_3L_2$, $M(CO)_3$-(Diphos),[*4] and $M(CO)_3$(Diars)[*7] (see Table 2). Since the (Diphos) and (Diars) ligands cannot form a monomeric *trans*-disubstituted complex, the C_{2v}

[*7] (Diars) means Me_2As *o*-$C_6H_4AsMe_2$.

8) F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, **1960**, 1440.

9) T. A. Manuel, *Inorg. Chem.*, **2**, 854 (1963).

10) M. Freni, D. Giusto and P. Romiti, *J. Inorg. Nucl. Chem.*, **29**, 761 (1967).

Table 2a

Number	Compound	Sample	color	CO stretching, cm^{-1}						
VIII	$Mn(CO)_3(PPh_3)_2\cdot 1/2\,CHCl_3$	b	yellow	2070 m	2055 sh	1948 s	1939 vs	1917 sh	1899 sh	
I	$CH_3C_5H_4Mn(CO)_3$	d	pale yellow		2033 s	1940 vs,	br			
II	$CH_3C_5H_4Mn(CO)_2(PPh_3)$	a	yellow				1927 vs	1855 vs	1827 sh	
III	$Mn(CO)_3(PPh_3)_2$	a *	pale yellow	2060 m	2050 m	1952 vs	1922 s	1863 sh		
IV	$Mn(CO)_3(PPh_3)_2$?	c	brown		2030 m	1950 vs		1870 m		
V	mixture	c	yellow		2030 s	1950 vs	1925 sh	1870 sh	1850 s	1830 sh
VI	$BrMn(CO)_3(PPh_3)_2$	a	yellowish brown		2040 m	1954 vs	1928 s	1908 sh		
VII	$CH_3Mn(CO)_3(PPh_3)_2$	c	yellowish brown		2035 w	1945 s	1920 vs	1880 sh		

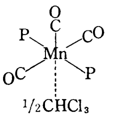
Compound	Sample	Reference	CO stretching, cm^{-1}			
$CH_3C_5H_4Mn(CO)_2(PPh_3)$	f	3			1934	1862
trans-$Re(CO)_3(PPh_3)_2$	g	10			1930	
$Mn(CO)_3$(Diphos)	e	5	1990 s		1900 vs	
cis-$Re(CO)_3(PPh_3)_2$	e	10	2000 w		1900 s	1820 m
$Fe(CO)_3$(Diars)	e	11	2009 vs		1916 vs	1880 sh
trans-$BrMn(CO)_3(PPh_3)_2$	f	13	2046	1955	1916	
cis-$Re(CO)_3$(Diphos)	e	10		1965	1905	1855

a) KBr disk, DS-402G. b) Nujol mull, IR-G. c) Nujol mull, Infracord. d) liquid, Infracord.
e) Nujol mull. f) chloroform solution. g) benzene solution. * recrystallized from benzene

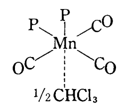
Table 2b

Compoun	Sample	C-H out of plane, cm^{-1}						
I	d		840 s					
II	a	851 s	842 m		751 s		701 s	687 s
III	a			758 s	751 s	748 s	698 s	686 s
VI	a			757 s	751 s	744 sh		693 s
PPh_3	a			758 s	752 s	746 s	701 s	694 s

or C_s symmetrical *cis*-disubstituted TBP structures were assigned to these complexes. The band pattern of III most resembles that of $Fe(CO)_3$(Diars),[11] for every band of the former is about 40 cm^{-1} higher than the corresponding band of the latter and the second bands of both compounds are more intensive than the lowest ones. Thus, the C_{2v} symmetrical TBP configuration is most likely for $Mn(CO)_3(PPh_3)_2$, much as with $Fe(CO)_3$(Diars). Now, for both $Mn(CO)_3$(Diphos) and I, two bands have been reported, but the lower intensive band might consist of two bands overlapping accidentally. $Mn(CO)_3(PPh_3)_2\cdot 1/2CHCl_3$, VIII, shows a C–O stretching absorption band pattern similar to those of these compounds (see Fig. 1). The structure of this adduct depends on whether the chloroform molecule is only a solvent of crystallization or a definite ligand. The appearance of the highest band suggests that a linear OC–Mn–CO skeleton is preserved.*[8] Therefore, two rectangular pyramidal (RP) structures, C_{2v} or C_s symmetrical, are very likely for the mother complex. The sixth coordination site of the octahedral configuration may be occupied by half-molar chloroform, though the existence of the chemical bond is uncertain. In other words, solvation may occur on the molecular plane in one of tow possible directions relative to the mother TBP complex.



C_{2v}



C_s

P: PPh_3

The magnetic susceptibilities and magnetic moments of III and VIII are listed in Table 1.*[9] The value of 1.86 BM has been reported[4] for Mn-

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[11] H. Nigam, R. S. Nyholm and D. V. Ramana Rao, *J. Chem. Soc.*, **1959**, 1397.

*[8] According to the explanation given by Angelici *et al.*[12] for the octahedral tricarbonyl complexes, the highest band can be assigned to the symmetric C–O vibration of linear OC–M–CO. C_{2v} structures (TBP and RP) and one of the RP C_s structures have this skeleton.

*[9] The corrections for PPh_3 and $CHCl_3$ have been calculated to be 166 and 69 respectively on the basis of Selwood's review.[7] For three CO it was reduced from the correction given by Hieber and Freyer[3] to $-(CO)_4(PPh_3)$, 219, to 40. (All the values are in units of 10^{-6} c.g.s.e.m.u.) The formula: $\mu_{\text{eff}}=2.83\times\sqrt{\chi_M^{\text{coor.}}\times T}$ was used.

[12] R. J. Angelici, F. Basolo and A. J. Poë, *J. Amer. Chem. Soc.*, **85**, 2215 (1963).

$(CO)_4(PPh_3)$, and that of 1.70 BM,[5] for $Mn(CO)_3$-(Diphos). The observed value agrees quite well with these, corresponding to one unpaired electron. This supports the idea that they are monomeric and zero valent manganese complexes, an idea which is also consistent with the observed molecular weight. In the chloroform adduct crystal VIII, the monomeric structure may be preserved for manganese because of its paramagnetism.

Two chemical reactions of III were investigated: one, its oxidation with bromine in chloroform, gave brown *trans*-$BrMn(CO)_3(PPh_3)_2$, VI, which is the usual hexa-coordinated complex. The results of CH analyses are listed in Table 1. The infrared spectra (see Table 2 and Fig. 1) are in good agreement with the results reported by Abel and Wilkinson[13] and corrected by Angelici *et al.*[14] with respect to structural assignment. The chemical shift value of the ^1H NMR spectrum (see Table 3) can be assigned to the protons of the phenyl group. The other reaction examined was the reduction of III with a sodium amalgam, followed by treatment with methyl iodide. Yellowish brown $CH_3Mn(CO)_3(PPh_3)_2$[*10] VII, was thus obtained; it was identified because its infrared spectra showed a pattern similar to that of isostructural VI. Thus, the mother complex is confirmed to be *cis*-$Mn(CO)_3(PPh_3)_2$.

Methylcyclopentadienyl dicarbonyl monotriphenylphosphinemanganese(I) (II), $(CH_3C_5H_4)Mn(CO)_2(PPh_3)$. All the results with II are consistent with the structure reported in the literature.[3] The chemical shifts of the ^1H NMR spectra are listed in Table 3, along with the assignment of the absorptions. In the preparative reaction, sodium metal may, in the present experiment, play the same role as the ultraviolet ray in those in the literature.[3,16]

TABLE 3

^1H NMR Spectra: Chemical shifts from TMS, ppm

assignments	II	VI	PPh_3
CH_3	1.42		
C_5H_4	3.39 3.54		
$P\text{-}C_6H_5$	6.77 6.88	7.29	7.15 7.19

The Unidentified Yellowish Brown Crystal (IV). This was obtained by a short reaction at a higher temperature. Yellow mixture, V, noticed in the course of synthesis in dioxane consisted of II and IV judging from its infrared spectra. Three almost equi-distant intensive C–O strethcing bands are characteristic of the infrared spectra of IV (see Table 2 and Fig. 1), and their intensities are about 1 : 2 : 1. No such feature is found in I, II, or III. Shoulders on the lower side of the lower two bands are assigned to absorptions of II mixing in. In comparison with the spectra of III, the bands of IV other than the strongest center one are relatively intensive. These facts lead to two hypothetical structures for IV. One is an octahedral $Mn(CO)_3(PPh_3)_2X$, where X may be a hydrido ligand or another ligand. The other is a structural isomer of III. Neither III nor IV has a D_{3h} structure. The C_{2v} structure may be assigned to III, and the C_s structure to IV, for the weakness of the highest band in the former spectra can be attributed to the strong coupling of *trans*-2CO vibrations.[*8] On the repeated recrystallization of the cruder III, the band at 1865 cm^{-1} became weak, and that at 1950 cm^{-1} intensive. This may be interpreted as resulting from the fact that the inpurity, II or IV, was taken off. However, another interpretation is possible, *i.e.*, an angular isomerization from the C_s structure to the C_{2v} one (see sheme). In the former there remains the original configuration of I for three CO, and the latter may be thermodynamically stable because of its higher symmetry. This rearrangement corresponds to the *cis-trans* isomerization of the octahedral complex for three CO ligands.[12]

The author wishes to express his hearty thanks to Professor Yukiyoshi Sasaki of the University of Tokyo for his helpful advice and encouragement throughout this work, and to Professor Shizuo Fujiwara of the University of Tokyo for his kind interest in this work.

[*10] This compound was prepared by Hieber *et al.*[15] from VI by an almost identical procedure.

13) E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, **1959**, 1501.

14) R. J. Angelici, F. Basolo and A. J. Poë, *Nature*, **195**, 993 (1962).

15) W. Hieber, M. Höfler and J. Muschi, *Chem. Ber.*, **98**. 311 (1965).

16) C. Barbeau, *Can. J. Chem.*, **45**, 161 (1967); W. Strohmeier and F. J. Müller, *Chem. Ber.*, **100**, 2812 (1967), and the literature cited therein.