

Photochemically Induced Orthometalations. Isolation of $(\text{PhO})_2\text{P}(\text{OC}_6\text{H}_4)\text{Mn}(\text{CO})_4$, $(\text{PhO})_2\text{P}(\text{OC}_6\text{H}_4)\text{Mn}(\text{CO})_3\text{P}(\text{OPh})_3$, and $(\text{PhO})_2\text{P}(\text{OC}_6\text{H}_4)\text{Mn}(\text{CO})_2[\text{P}(\text{OPh})_3]_2$ from $\text{RMn}(\text{CO})_3[\text{P}(\text{OPh})_3]_2$ ($\text{R}=\text{CH}_3$ and H) and $\text{MeMn}(\text{CO})_4\text{P}(\text{OPh})_3$

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Photochemical reactions of $\text{RMn}(\text{CO})_3\text{L}_2$ ($\text{R}=\text{H}$ and CH_3 ; $\text{L}=\text{P}(\text{OC}_6\text{H}_5)_3$) and $\text{CH}_3\text{Mn}(\text{CO})_4\text{L}$ in benzene gave several kinds of orthometalated products, $(\text{PhO})_2\text{P}(\text{OC}_6\text{H}_4)\text{Mn}(\text{CO})_{4-x}\text{L}_x$ ($x=0, 1$, and 2). The reactions have been shown to proceed *via* ligand dissociation, CO and/or L, from the parent compounds and the resulting 16-electron intermediates activate a C–H bond of phenyl groups in triphenyl phosphite intramolecularly to yield orthometalated products. The results of photochemical reactions for $\text{MeMn}(\text{CO})_3\text{L}_2$ and $\text{MeMn}(\text{CO})_4\text{L}$ are compared with those of thermal reactions for these compounds. $\text{HMn}(\text{CO})_4\text{L}$ was left intact by photochemical and thermal reactions.

Photochemical reactions of manganese or rhenium carbonyls with phosphines or phosphites have been a subject of recent intensive scrutiny.^{1–8)} The reactions have been shown to proceed *via* metal centered radicals and to terminate in intermolecular reactions by abstracting X from RX such as CCl_4 and/or by coupling of two 17-electron metal carbonyl radicals, but the importance of intramolecular reaction pathway of metal carbonyl radicals or unstable intermediates with phosphines or phosphites has not yet been well explored to our knowledge. In the previous paper, we have demonstrated that manganese carbonyl radicals with triphenyl phosphite(s) which were produced by photochemical degradation of $\text{Me}_3\text{Sn–Mn}(\text{CO})_3\text{L}_2$ (**1**) (hereafter L denotes triphenyl phosphite) underwent intramolecular reactions by abstracting hydrogen from a benzene ring in the triphenyl phosphite moieties to afford orthometalated products⁹⁾ and the key role of 15-electron manganese carbonyl radicals with triphenyl phosphite ligand(s) was suggested to attain orthometalation. In this regard, $\text{MeMn}(\text{CO})_3\text{L}_2$ (**2**) and $\text{HMn}(\text{CO})_3\text{L}_2$ (**3**), which are isostructural and isoelectronic about the manganese atom with that of **1**, are attractive compounds to deepen our understanding on the intramolecular reactivity and/or orthometalation reaction mechanisms of unstable manganese carbonyl triphenyl phosphite intermediates which may be produced by photochemical excitation of these compounds. This paper reports isolation of orthometalated products from photochemical reactions of **2**, **3**, and $\text{MeMn}(\text{CO})_4\text{L}$ (**4**) and some suggestions on the photochemically induced orthometalation mechanisms of these compounds.

Experimental

$\text{CH}_3\text{Mn}(\text{CO})_3\text{L}_2$ (**2**),¹⁰⁾ $\text{HMn}(\text{CO})_3\text{L}_2$ (**3**),¹⁰⁾ and $\text{CH}_3\text{Mn}(\text{CO})_4\text{L}$ (**4**),¹¹⁾ and $\text{HMn}(\text{CO})_4\text{L}$ (**5**)¹²⁾ were prepared via reported methods under a nitrogen atmosphere. The photolysis was carried out under an argon atmosphere with a Riko 100 W high-pressure Hg lamp which was inserted in a 300 cm³ Pyrex reaction vessel. IR spectra were obtained on a JASCO-701G infrared spectrometer with 0.1 mm NaCl windowed liquid cells or for Nujol mulls. Molecular weight was determined by a Corona 114 molecular weight apparatus with a vapor pressure osmometry; benzene was employed as a solvent.

Photolysis of 2. A 0.9 g sample of **2** was dissolved in 50 cm³ of benzene and the solution was irradiated for 5 h. The solvent was vacuum-stripped to leave a pale yellow oil. The oil was dissolved in a minimum amount of benzene and was loaded on a Florisil column (60–100 mesh). The products were eluted with petroleum ether, cyclohexane, benzene, and chloroform successively. A colorless oil (**6**) (175 mg), three kinds of colorless crystals (**7**) (25 mg), (**8**) (50 mg), (**9**) (25 mg), and yellow crystals (**10a**) (15 mg) were obtained by carefully repeated recrystallizations of each fraction from benzene–cyclohexane. These products were characterized by IR, elemental analyses on C, H, and P, molecular weight determination and/or X-ray diffraction methods; the products **6**–**9** exhibited three IR bands (Nujol mulls) with medium intensities at around 1100, 950, and 800 cm^{−1} which are characteristic of an orthometalated triphenyl phosphite ligand.⁹⁾ The IR spectra in $\nu(\text{CO})$ region of **6**, **7**, and **9** are consistent with those of authentic $(\text{PhO})_2\text{P}(\text{OC}_6\text{H}_4)\text{Mn}(\text{CO})_4$ (**6**), *fac-cis*-($\text{PhO})_2\text{P}(\text{OC}_6\text{H}_4)\text{Mn}(\text{CO})_3\text{L}$ (**7**), and $(\text{PhO})_2\text{P}(\text{OC}_6\text{H}_4)\text{Mn}(\text{CO})_2\text{L}_2$ (**9**).⁹⁾ C, H, and P analyses on **8** suggested that this crystal has the same composition as that of **7** and molecular weight measurements indicated a monomeric property; elemental analyses of **8**. Found C, 61.86; H, 3.79; P, 8.02%. Calcd for $\text{C}_{39}\text{H}_{29}\text{MnO}_9\text{P}_2$: C, 61.75; H, 3.85; P, 8.17%. Molecular weight: Found 787. Calcd 759. The crystal of **8** showed two $\nu(\text{CO})$ peaks at 2055 (m) and 1975 (vs) cm^{−1}, while the isomer **7** showed three $\nu(\text{CO})$ peaks at 2030 (vs), 1965 (s), and 1941 (vs) cm^{−1} in benzene. This result indicates that **8** has a higher symmetry than that of **7** around the manganese atom and thus a mer-trans structure is assigned to **8** (Fig. 1). The yellow crystals of **10a** are the same product as that obtained by the photolysis of **1** from all respects. The final characterization of this yellow crystal is described below.

Photolysis of 3. A 0.9 g sample of **3** was dissolved in 50 cm³ of benzene and the solution was irradiated for 5 h. After similar work up as the case of **2**, the product were separated by column chromatography over Florisil. The first fraction was eluted with petroleum ether to afford 300 mg of the starting material after recrystallization from benzene–petroleum ether. The second fraction was eluted with cyclohexane and the third fraction was eluted with benzene. By recrystallization from benzene–petroleum ether, 60 mg of **9** and 10 mg of **7** were obtained. The final fraction was eluted with chloroform to afford 15 mg of yellow crystals **10a**.

Photolysis of 4. A 0.8 g sample of **4** was dissolved in 50 cm³ of benzene and the solution was irradiated for 8 h. Similar work up and purification as above gave 360 mg of **6**, 40 mg of

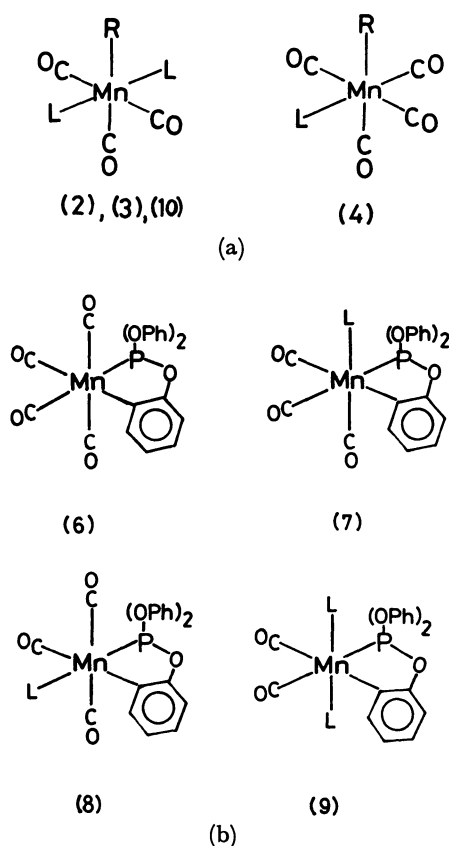


Fig. 1. Schematic pictures of starting materials (1(a)) and photochemical reaction products (1(b)).

7, 10 mg of 8, 5 mg of 9, and 15 mg of 10a.

Photolysis of 5. A 0.9 g sample of 5 was dissolved in 50 cm³ of benzene and the solution was photolyzed for 8.5 h. However, IR monitoring of the solution did not show any significant sign of reaction except slight decomposition.

Photolysis of 2 with $\text{P}(\text{OPh})_3$. To a benzene solution (50 cm³) containing 0.77 g (1 mmol) of 2, 310 mg of $\text{P}(\text{OPh})_3$ (1 mmol) was added and the solution was photolyzed for 5 h. After similar procedure of purification as above gave 20 mg of 7, 20 mg of 8, and 270 mg of 9.

Photolysis of 4 with $\text{P}(\text{OPh})_3$. A 0.88 g (1.8 mmol) of 4 and 0.83 g (2.7 mmol) of $\text{P}(\text{OPh})_3$ were dissolved in 50 cm³ of benzene and the mixture was photolyzed for 8 h. Through similar method of purification as above, 30 mg of 6, 280 mg of 7, 190 mg of 8, 510 mg of 9, and 15 mg of 10a were obtained.

Photolysis of 2 in CCl_4 . A carbon tetrachloride solution (40 cm³) which contained 0.63 g of 2 was photolyzed for 1 h. With similar procedure of purification, about 200 mg of *mer-trans*- $\text{ClMn}(\text{CO})_3\text{L}_2$ (10) was isolated.

Photolysis of 3 in CCl_4 . A 1.0 g sample of 3 was dissolved in 50 cm³ of carbon tetrachloride and the solution was irradiated for 1.5 h. The reaction mixture was similarly treated as above to give 200 mg of 10 and small amounts of unidentified products.

Photolysis of 4 in CCl_4 . A 1.1 g sample of 4 was dissolved in 50 cm³ of CCl_4 and the mixture was photolyzed for 3 h. Similar work up as above gave 20 mg of 2, 50 mg of 6, 100 mg of 7, and 90 mg of 10.

Thermolysis of 2 in Toluene. A 1.0 g sample of 2 was dissolved in 50 cm³ of toluene and the mixture was refluxed for 3.5 h. The solvent was distilled off under a reduced pressure and the resulting pale brown oil was subjected to column chromatography over Florisil. By similar procedure of purifi-

TABLE 1. PHOTOCHEMICAL AND THERMAL REACTION PRODUCTS OF 2, 3, AND 4 AND THEIR PROPORTIONS

| Reactant | Products (Molar ratio) |
|---|--|
| Photolysis | |
| $\text{CH}_3\text{Mn}(\text{CO})_3\text{L}_2$ (2) | 6 : 7 : 8 : 9 = 10 : 1 : 2 : 1 |
| $\text{HMn}(\text{CO})_3\text{L}_2$ (3) | 7 : 9 = 1 : 5 |
| $\text{CH}_3\text{Mn}(\text{CO})_4\text{L}$ (4) | 6 : 7 : 8 : 9 = 160 : 10 : 4 : 1 |
| Thermolysis | |
| $\text{CH}_3\text{Mn}(\text{CO})_3\text{L}_2$ (2) | 6 : 7 : 8 : 9 = \approx 0 : 10 : 5 : 1 |
| $\text{CH}_3\text{Mn}(\text{CO})_4\text{L}$ (4) | 6 : 7 = 16 : 1 |

cation as the case of photolysis, trace amount of 6, 280 mg of 7, 140 mg of 8, and 35 mg of 9 were obtained.

Thermolysis of 3 in Toluene. A 0.4 g sample of 3 was dissolved in 30 cm³ of toluene and the solution was refluxed for 5 h. However, no detectable change was observed by IR except decomposition.

Thermolysis of 4 in Toluene. A toluene solution (50 cm³) which contained 0.8 g of 4 was refluxed for 3 h. Similar work up as the thermolysis of 2 afforded 400 mg of 6 and 40 mg of 7.¹³⁾

Thermolysis of 5. A *p*-xylene solution which contained 0.71 g of 5 was refluxed for 1 h. However, no appreciable change was observed by IR except decomposition.

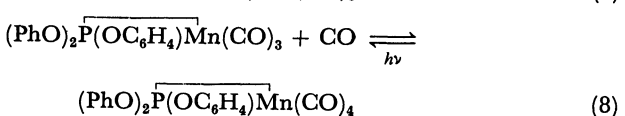
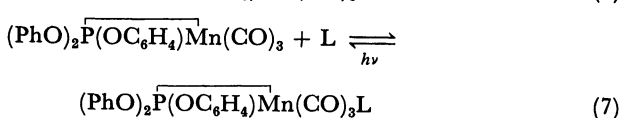
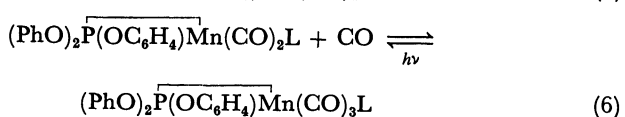
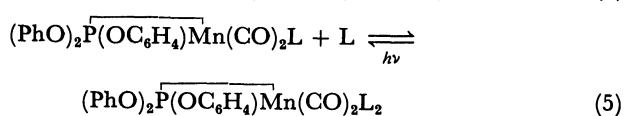
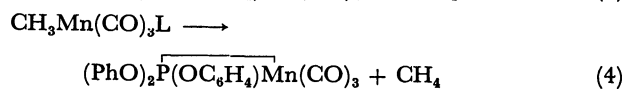
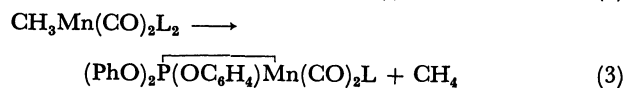
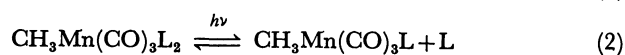
The yields were averaged for several runs and molar ratios of the products are collected in Table 1.

Characterization of Yellow Crystals 10a. Attempts for characterizing this yellow crystalline compound, 10a, was not rewarded in the previous study.⁹⁾ After publication of the paper, various experiments were added to the previous efforts; fluorescent X-ray analysis¹⁴⁾ revealed that chlorine atom was contained as a main component in these crystals and FD mass indicated the parent peak at $m/e=795$ ($\text{ClMn}(\text{CO})_3\text{L}_2=795$). These evidences established that the crystalline compound is $\text{ClMn}(\text{CO})_3\text{L}_2$, 10. Next experiment was performed to clarify the origin of the chlorine atom; photolysis of relevant compounds in spectral grade benzene (Dojin Chemistry Co.) did not yield yellow crystals, 10a. Therefore, the chlorine atom should come from HCl contained as a trace amount of impurity¹⁵⁾ in the benzene used as a solvent for photolysis.

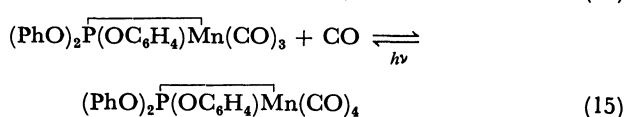
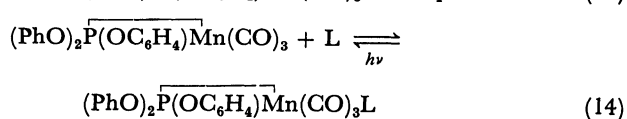
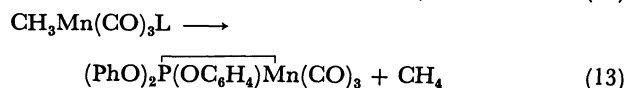
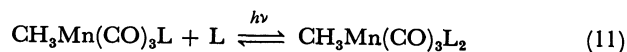
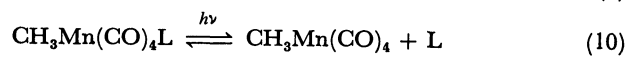
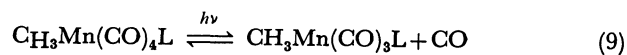
Results and Discussion

As was described in the Experimental section, several kinds of orthometalated products were obtained from photodegradation of mononuclear manganese carbonyl triphenyl phosphite derivatives. Among the data on photochemically induced orthometalation reactions including those of the previous paper,⁹⁾ a few points merit description; first, the absorption spectra for 2–5 are essentially identical with that of 1 in the region of 230–700 nm. However, the yields of the orthometalated products and molar ratios among the products depend not only on the number of triphenyl phosphite groups of the starting materials, but also on the kind of the sixth ligand, L', of the manganese atom for $\text{L}'\text{Mn}(\text{CO})_x\text{L}_y$. Therefore, a comparison of the results for a series of isoelectronic and isostructural compounds, $\text{Me}_3\text{Sn}-\text{Mn}(\text{CO})_3\text{L}_2$ (1), $\text{MeMn}(\text{CO})_3\text{L}_2$ (2), and $\text{HMn}(\text{CO})_3\text{L}_2$ (3) is interesting; 1 and 3 give the products of the same components, 7 and 9, with somewhat different molar ratio, but 2 affords two extra products, that is 6 and a new compound 8, in addition to 7 and 9. In this regard,

2 is rather close to **4** which has one triphenyl phosphite group if the components of the products alone are considered. In order to get a clue on the photochemical reaction pathways of this series of compounds, following types of experiments were performed; (i) photolysis in CCl_4 , (ii) photolysis with $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ in C_6H_6 , (iii) photolysis in C_6H_6 which was saturated with air, (iv) photolysis in C_6H_6 with the presence of triphenyl phosphite, and (v) photolysis in C_6H_6 with constant bubbling of argon to purge out evolved gaseous products, especially CO. The first three experiments (i), (ii), and (iii) were made to check whether a radical process, that is, homolytic cleavage of the $\text{L}'\text{-Mn}$ bond, is a main route or not. For **2**, we obtained following results; *mer-trans*- $\text{ClMn}(\text{CO})_3\text{L}_2$, **10** and *fac-cis*- $\text{ClMn}(\text{CO})_3\text{L}_2$, **10'** were yielded from the experiment (i). However, bibenzyl which should be produced if the initial step is a radical process, could not be detected from the experiment (ii). The products **6**–**9** were harvested with similar total amounts, but with somewhat different molar ratios from those of the normal photolysis in the experiment (iii). For experiment (iv), **6** which contains only one triphenyl phosphite group was not isolated, instead the yield of **9** which contains three triphenyl phosphite groups was about tenfolded. For experiment (v), the yield of **9** was considerably increased, but **6** eluded isolation. The result of the second and third experiment (ii) and (iii) indicated that the radical process of homolytic cleavage of the $\text{CH}_3\text{-Mn}$ bond is not a main process, although the result of experiment (i) suggested some contribution of the radical process (this issue will be discussed later based on the results for **4**). The experiment (iv) and (v) provided evidence that the ligand dissociation L and/or CO was photochemically induced to afford 16-electron intermediates and the dissociated ligand(s) was incorporated again into the 16-electron intermediates or orthometalated 16-electron intermediates. Before we advance our discussion on **2**, it seems appropriate to assess some results on **4** which behaved similarly to **2** in the normal photolysis; photolysis of **4** in CCl_4 produced $\text{CH}_3\text{Mn}(\text{CO})_3\text{L}_2$ (**2**), two kinds of orthometalated products, **6** and **7**, and $\text{ClMn}(\text{CO})_3\text{L}_2$ (**10**). As the photolysis of **10** in benzene did not yield any kind of orthometalated products, isolation of **6** and **7** indicates that these products are obtained from **4** and especially isolation of **2** is a clear evidence that the ligand dissociation is an important photochemical process for **4**. Another evidence to support this contention comes from the comparison of the result with that of $\text{Me}_2\text{Sn}[\text{Mn}(\text{CO})_4\text{L}]_2$; according to the previous paper,⁹⁾ irradiation of this compound in benzene brought homolytic cleavage of the Sn-Mn bond to afford $\cdot\text{Mn}(\text{CO})_4\text{L}$ radical and from this radical only one kind of orthometalated product **6** was isolated with low yield. From these observations, we are tempted to the assertion that the preponderant process of photoexcitation of **4** is ligand dissociation L or CO from the manganese atom to leave coordinatively unsaturated metal site, that is, 16-electron intermediates and these 16-electron intermediates activate a C–H bond in the phenyl groups of triphenyl phosphite(s) intramolecularly to yield orthometalated products, although some



Scheme 1.



Scheme 2.

contribution of radical process to the orthometalation should not be overlooked as was described in the previous study.⁹⁾ (Schemes 1 and 2)

Scheme 2 is devoid of the mechanism for the formation of **9**. However, we would like to suggest that **9** is produced by secondary photochemical degradation of **7** and/or **8** as was clarified in the previous study⁹⁾ and the reason for low yield of **9** from **4** is also accounted for by this mechanism. $\text{CH}_3\text{Mn}(\text{CO})_5$ eluded isolation.

For **3**, the experiment (i) afforded **10** and a few kinds of unidentified products in low yields. Although these results suggested that radical process was predominant, we could not isolate bibenzyl in the experiment (ii) and the yields of **7** and **9** were not suppressed in the

experiment (iii). In the experiment (v), the yield of **7** was suppressed, but the yield of **9** was doubled. The result of the experiment (v) indicates that the process of carbonyl dissociation and its uptake is also included in the mechanisms of the formations of **7** and **9**. Although general patterns of the photochemical reactions of **3** are quite close to those of **1**, it may be appropriate to postpone our conclusion on the orthometalation reaction mechanisms for **3** until we can get affirmative evidence in the future experiment.

Kaesz *et al.* isolated two kinds of orthometalated products, **6** and **7** by thermal reaction of $\text{CH}_3\text{Mn}(\text{CO})_4\text{L}$ (**4**).¹³⁾ However, photochemical reaction of **4** in the present study afforded four kinds of orthometalated products instead. The ramification appeared to suggest that the intermediates produced thermally from **4** are not the same as those produced photochemically. This idea prompted us to investigate thermal reaction of **2**. As was described in the Experimental section, thermolysis of **2** in toluene yielded the same products as in the case of photolysis. However, the molar ratios of the orthometalated products were significantly different from those of photolysis and especially the yield of **6** was quite low. In the thermolysis, the solvent was refluxed and gaseous products such as CO should be purged out easily with this reflux. Thus, the situation is quite similar to the photolysis of **2** with constant bubbling of argon (experiment (v)); in experiment (v) of **2**, **6** was not isolated. Therefore, quite low yield of **6** in thermolysis of **2** may not be considered to imply that the intermediates produced from **2** by thermal reaction is different from those produced photochemically.

Photochemical reaction of **4** yielded extra two orthometalated products in addition to two compounds **6** and **7** which are obtained by thermolysis. The low yield of **9** in photolysis suggests that this product is generated by secondary photodegradation of orthometalated products **7** and **8**. Indeed, it was clarified in the previous study that photolysis of **7** gave **8** and **9**⁹⁾ and further, thermolysis of **7** did not yield **8** and **9**; IR monitoring of thermal reaction of **7** in refluxed toluene for 3.5 h did not exhibit significant spectral change in carbonyl stretching region. Therefore, we can suggest at present that the intermediates from **4** by thermal reaction are not essentially different from those by photochemical

reaction.

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- 15) The content of HCl is described to be less than 0.0004% on the label, but real content of HCl seems greater than 0.0004% judging from the yield of **10**.