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Photochemical Synthesis of η-Acetylene Complex of an Orthometalated Manganesecarbonyl Derivatives, $(PhO)_2P(OC_6H_4)Mn(CO)_3(PhC{\equiv}CPh)$, and Its Structural Study by ^{13}C and ^{31}P NMR Spectroscopies

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Synopsis. Photochemical reaction of an orthometalated manganesecarbonyl derivative, $(PhO)_2P(OC_6H_4)Mn(CO)_4$ with $PhC{\equiv}CPh$ in benzene yielded $(PhO)_2P(OC_6H_4)Mn(CO)_3(PhC{\equiv}CPh)$ and its structure was studied by ^{13}C and ^{31}P NMR spectroscopy based on ^{13}C and ^{31}P NMR data for relevant orthometalated metal carbonyl derivatives including $(o\text{-}CH_3C_6H_4O)_2P[OC_6H_3(CH_3)]Mn(CO)_3P[OC_6H_4(CH_3)]_3$ which was first synthesized in this study.

Previous reports from this labolatory revealed that orthometalated triphenyl phosphite manganesecarbonyl derivatives, $(PhO)_2P(OC_6H_4)Mn(CO)_4$ (**1**) and $(PhO)_2P(OC_6H_4)Mn(CO)_3P(OPh)_3$ (**2**) dissociate the ligand CO or L ($L{=}P(OPh)_3$) quite easily upon photolysis in solutions.[1,2]

$$(PhO)_2P(OC_6H_4)Mn(CO)_4 \xrightarrow{h\nu} (PhO)_2P(OC_6H_4)Mn(CO)_3\ (\mathbf{3}) + CO \qquad (1)$$

$$(PhO)_2P(OC_6H_4)Mn(CO)_3L \xrightarrow{h\nu} (PhO)_2P(OC_6H_4)Mn(CO)_3\ (\mathbf{3}) + L \qquad (2)$$

This observation prompted us to "trap" the 16 electron intermediate, $(PhO)_2P(OC_6H_4)Mn(CO)_3$ (**3**) by reacting with other nucleophiles such as diphenylacetylene. Present paper reports isolation of $(PhO)_2P(OC_6H_4)Mn(CO)_3(PhC{\equiv}CPh)$ (**4**) and its structural study by ^{13}C and ^{31}P NMR spectroscopies based on the spectral data for relevant orthometalated triphenyl phosphite metal carbonyl derivatives. Synthesis of $(o\text{-}CH_3C_6H_4O)_2P[OC_6H_3(CH_3)]Mn(CO)_3P[O(o\text{-}CH_3C_6H_4)]_3$ is also reported.

Experimental

Photolysis was performed under an argon atmosphere with a Riko 100 W high pressure Hg lamp. Solvent was purged with argon gas sufficiently before use. The sample of **1** was prepared according to the literature method[3] and other samples of **2** and $(PhO)_2P(OC_6H_4)Mn(CO)_2L_2$ (**5**) were obtained as was described in the previous papers.[1,2] IR spectra were measured with a Jasco 701G spectrometer for Nujol mull samples and ^{13}C and ^{31}P NMR were measured for ca. 0.5 mol dm^{-3} chloroform-*d* solutions at 30 °C on a Varian XL-200 spectrometer operated at 50.309 and 80.984 MHz respectively with Fourier transform mode for naturally abundant levels. The spectra were recorded using a 10 mm o.d. sample tube. Chemical shifts were referenced to internal Me_4Si standard for ^{13}C nucleus and to external H_3PO_4 standard contained in a 1 mm capillary for ^{31}P nucleus. A positive chemical shift designates a resonance to a lower field than that of the resonance of the respective standard.

Synthesis of $(C_6H_5O)_2P(OC_6H_4)Mn(CO)_3(C_6H_5C{\equiv}CC_6H_5)$ (4). A 0.996 g (2.1 mmol) sample of **1** and 0.372g (2.1 mmol) of diphenylacetylene, **dpa**, were dissolved into 50 ml of benzene and the mixture was photolyzed for 8 h. From the resulting yellow solution, the solvent was vacuum-stripped to leave an yellow oil. This oil was dissolved into a minimum amount of benzene and was loaded on a Florisil column. Unreacted starting materials (**1** and **dpa**) were eluted with petroleum ether. Then, mixed solvent of benzene and hexane (1 : 1) eluted a white product, which was recrystallized from mixed solvent of benzene and petroleum ether (1 : 1) to yield 200 mg of $(PhO)_2P(OC_6H_4)Mn(CO)_3(PhC{\equiv}CPh)$ (**4**). (Yield 15%). Retention of the orthometalated ring was exemplified by detection of three weak peaks at 1105, 960, and 795 cm^{-1} in IR which are characteristic of the orthometalated triphenyl phosphite.[1,2] Found: C, 66.76; H, 3.57; P, 4.70%. Calcd for $(PhO)_2P(OC_6H_4)Mn(CO)_3(PhC{\equiv}CPh)$, $C_{35}H_{24}O_6MnP$: C, 67.10; H, 3.86; P, 4.95%. IR ν(CO) (Nujol mull) 2080 (vs), 1995 (vs), and 1961(s) cm^{-1}.

Synthesis of $BrMn(CO)_3L'_2$ ($L'{=}(o\text{-}CH_3C_6H_4O)_3P$) (6). A 1.56 g (5.7 mmol) sample of $BrMn(CO)_5$ and 10 g (28 mmol) of $(o\text{-}CH_3C_6H_4O)_3P$, L′, (hereafter L′ denotes $(o\text{-}CH_3C_6H_4O)_3P$ and L denotes $P(OPh)_3$) were dissolved into 80 ml of choloroform and the mixture was stirred at 55 °C for 18 h. Then the solvent was almost vacuum-stripped and 50 ml of hexane was added to precipitate yellow crystals of $BrMn(CO)_3L'_2$ (**6**): Yield 2.6 g (53%). IR ν(CO) (Nujol mull) 2065 (m), 1990 (vs), and 1932 (vs) cm^{-1}.

Synthesis of $MeMn(CO)_3L'_2$ (7). A 2.0 g (2.2 mmol) sample of **6** in 40 ml of THF was reduced to $NaMn(CO)_3L'_2$ by stirring over Na amalgam for 3 h. To the supernatant THF solution of $NaMn(CO)_3L'_2$, 0.5 g (3.5 mmol) of CH_3I in 20 ml of THF was added and the mixture was stirred at room temperature overnight. Solvent was distilled off at reduced pressure to leave cleam yellow solid. This solid was extracted three times with each 20 ml of benzene. Then the benzene was almost distilled off at reduced pressure from the combined extracts and 10 ml of petroleum ether was added. The mixture was stored in a refrigerator to give pale yellow crystals of $MeMn(CO)_3L'_2$ (**7**). Yield 1.1 g (62%). IR ν(CO) (benzene solution) 2030 (w), 1953 (vs), and 1929 (s) cm^{-1}. Found: C, 64.30; H, 5.31%. Calcd for $CH_3Mn(CO)_3L'_2$, $C_{46}H_{45}MnO_9P_2$: C, 64.34; H, 5.28%.

Synthesis of $(o\text{-}CH_3C_6H_4O)_2P[OC_6H_3(CH_3)]Mn(CO)_3L'$ (8). A 0.9g (1 mmol) sample of **7** was dissolved into 50 ml of benzene and the solution was photolyzed for 4 h. The solution was concentrated to about 5 ml at reduced pressure and it was loaded on a Florisil column. After elution of unknown products and unreacted **7** with petroleum ether, pale yellow product of **8** was eluted with benzene. After

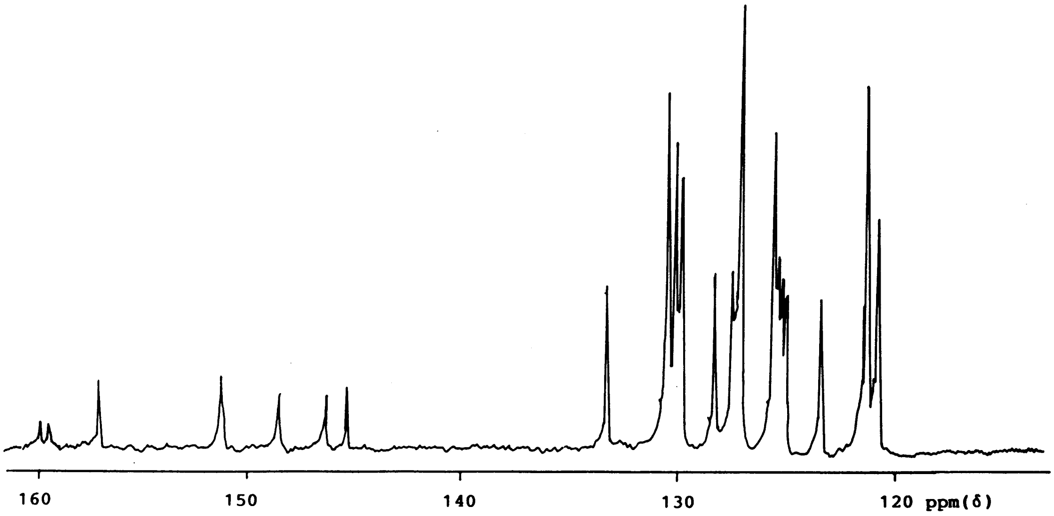


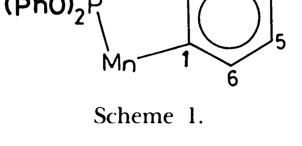
Fig. 1. ^{13}C NMR spectrum of $(PhO)_2\overline{P(OC_6H_4)Mn}(CO)_3(PhC\equiv CPh)$ in $CDCl_3$.

recrystallization from mixed solvent of benzene-petroleum ether (1 : 1), 100 mg of pure product **8** was obtained. (Yield 12%) Found: C, 64.00; H, 5.09%. Calcd for $(o\text{-}CH_3C_6H_4O)_2\overline{P[OC_6H_3(CH_3)]Mn}(CO)_3L'$, $C_{45}H_{41}MnO_9P_2$: C, 64.14; H, 4.90%. IR ν(CO) (benzene solution) 2040 (w), 1970 (vs), and 1940 (s) cm^{-1}.

X-Ray Data Collection. A colorless crystal of **4** with approximate dimensions 0.30×0.35×0.70 mm^3, which was grown-up from cyclohexane-petroleum ether, was mounted on a Rigaku AFC-5 automated four circle diffractometer equipped with Mo $K\alpha$ radiation (λ=0.71073 Å). The crystal belongs to triclinic system with unit cell dimensions a=22.904(8), b=22.918(8), c=12.795(5) Å, α=106.32(3), β=106.28(3), γ=85.53(3)°, and V=6187(4) Å^3. A total of 8639 independent reflections with $|F_o|>3\sigma(|F_o|)$ were obtained at room temperature using the $\omega-2\theta$ scan technique up to 2θ=50°. The structure has so far been solved neither by the standard heavy atom method nor direct method based on $P\bar{1}$ space group (UNICS-III program package, MULTAN 78 program and a HITAC M-200H computer).

Spectral Assignments

As is shown in Fig. 1, ^{13}C NMR spectrum of **4** is very complex. Therefore, the assignment of each peak is rather laborious without the aid of ^{13}C NMR data of relevant orthometalated triphenyl phosphite derivatives. When the ^{13}C NMR spectrum of **4** is compared with those of $(PhO)_2\overline{P(OC_6H_4)Fe}(CO)Cp$ (**9**) and $(PhO)_2\overline{P(OC_6H_4)Fe}(L)Cp$ (L=$P(OPh)_3$) (**10**),[4] we are tempted to opt following assignments of peaks observed in the lower field than 140 ppm; the doublet at 159.6 ppm is assignable to C_2 carbon and the singlet at 151.2 ppm is assigned to P–O–C carbon of unmetalated benzene rings.[4,5] The doublet at 145.7 ppm is assignable to C_1 carbon and the signlet at 148.4 ppm to C_6 carbon (Scheme 1). The alkyne carbon resonance at 89.2 ppm for free $PhC\equiv CPh$ disappears in **4** and a new resonance appears at 157.0 ppm instead, which is assignable to coordinated alkyne carbons to the Mn atom.[6,7] ^{13}C NMR spectrum of **4** is devoid of the doublet at around 111 ppm due to C_3 carbon resonance which is detected at 110.9 and 110.2 ppm in the spectra of **9** and **10**;[4,8] the doublet is not strong in **9** and **10** and this doublet is presumably hidden behind strong resonances around 120 ppm in **4**. The strong resonances between 120 and 133 ppm are so complex that it seems prudent to leave the assignment unsettled except just describing that these resonances are originated from phenyl carbon atoms of **dpa**, unmetalated phenyl carbons of P–O–Ph groups and phenyl carbons of metalated P–O–C_6H_4–groups. Thus, resonances due to C_4 and C_5 are not assigned but just pointing out that these resonances may be located at around 125 ppm.[4] Table 1 collates selected ^{13}C and ^{31}P NMR data of **4** together with those of relevant orthometalated manganesecarbonyl derivatives.



Scheme 1.

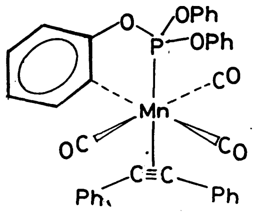
Results and Discussion

It is well recognized that ^{31}P NMR spectroscopy is very convenient and useful structural probe to discriminate between metalated and unmetalated triphenyl phosphite ligands;[9,10] that is, orthometalation of the ligand causes a large downfield chemical shift (≈30 ppm) compared to unmetalated coordinated $P(OPh)_3$. This criterion holds for present series of orthometalated manganese-carbonyl derivatives, **1**, **2**, **5**, and **8** except **4**, as is seen from Table 1; the internal ^{31}P-chemical shift between metalated and unmetalated phosphite ligands ranges from 30.5 to 36.5 ppm and the resonance of metalated phosphite ligand is detected at lower field than 190 ppm. However, ^{31}P chemical shift of **4** is observed at about 20—30 ppm upfield as for metalated phosphite and is close to those of unmetalated ligand(s) in **7**, **11**, and **12**. According to the ^{31}P NMR studies by Stewart's group,[10] the chemical shift of coordinated triphenyl phosphite is very sensitive to the nature of the trans ligand. Therefore, 21.4 ppm upfield shift for **4** compared to **1** seems to reflect the different trans effect of $PhC\equiv CPh$ from that of CO. These lines of evidence prompt us to postulate the trans structure for **4** as is illustrated in Scheme 2, although definitive evidence of this issue must wait for future success of single crystal X-ray structure analysis.

Table 1. Selected ^{13}C and ^{31}P NMR Data

Compound	^{13}C Resonances (δ, ppm)					^{31}P Resonances (δ, ppm)	
	-C≡C-	C_1	C_2	C_3	C_6	Orthometalated	Unmetalated
$(PhO)_2\overline{P(OC_6H_4)Mn}(CO)_3(PhC\equiv CPh)$ (**4**)	157.0	145.7	159.6		148.4	171.7	
$(PhO)_2\overline{P(OC_6H_4)Fe}(CO)Cp$ (**9**)[4]		141.6	161.7	110.9	144.2	203.4	
$(PhO)_2\overline{P(OC_6H_4)Fe}(L)Cp$ (**10**)[4]		143.0	163.2	110.2	146.0	200.0	166.4
$(PhO)_2\overline{P(OC_6H_4)Mn}(CO)_4$ (**1**)						193.1	
$(PhO)_2\overline{P(OC_6H_4)Mn}(CO)_3L$ (**2**)						194.4[a]	157.9[a]
$(PhO)_2\overline{P(OC_6H_4)Mn}(CO)_2L_2$ (**5**)						196.5[b]	162.6[b]
$(o\text{-}MeC_6H_4O)_2\overline{P[OC_6H_3(Me)]Mn}(CO)_3L'$ (**8**)						197.4[c]	166.9[c]
$MeMn(CO)_4L$ (**11**)							167.4
$MeMn(CO)_3L_2$ (**12**)							171.3
$MeMn(CO)_3L'_2$ (**7**)							169.9

a) $J_{pp}=100.7$ Hz. b) $J_{pp}=103$ Hz. c) $J_{pp}=121$ Hz. L denotes $P(OPh)_3$; L′ denotes $(o\text{-}CH_3C_6H_4O)_3P$; Cp denotes $\eta\text{-}(C_5H_5)$.



Scheme 2.

According to the previous report,[2] photolysis of $MeMn(CO)_3L_2$ yielded three kinds of orthometalated products, that is **1** (1 : 1), **2** (1 : 2), and **5** (1 : 3).[11] However, photolysis of $MeMn(CO)_3L'_2$ afforded only 1 : 2 type orthometalated compound **8**. Steric crowdness due to the methyl group located at another ortho position may partly be responsible for the lack of 1 : 3 type metalation product. However, the reason of the lack of 1 : 1 type metalation product is not clear at present. Presumably the yield of 1 : 1 type product is low and eluded isolation.

Carbonyl stretching pattern in IR of **8** is very close to that of **2**. This resemblance suggests that **8** has a similar cis structure to that of **2**.[1]

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8) Indeed, this doublet is detected at around 111 ppm for **1**, **2**, and **5**.

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10) R. P. Stewart, Jr., L. R. Isbrandt, and J. J. Benedict, *Inorg. Chem.*, **15**, 2011 (1976) and references therein.

11) These abbreviation denote following metal to phosphite ligand ratios in orthometalated products; 1 : 1 means that Mn: phosphite is 1 : 1, 1 : 2 means Mn: phosphite is 1 : 2, and 1 : 3 means Mn: phosphite is 1 : 3.