

# Diene and Dienyl Complexes of Transition Elements. 8.<sup>1</sup>

## Addition and Substitution Reactions of Pentadienyltricarbonylmanganese with Phosphines, Phosphites, and Carbon Monoxide

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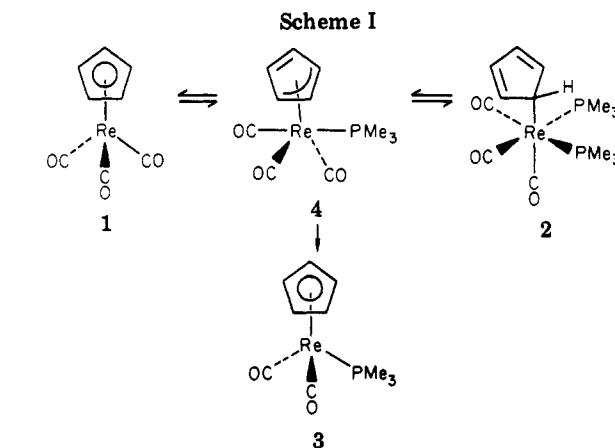
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Reactions between  $(\eta^5\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_3$  and tertiary phosphines and phosphites are described. Strongly basic phosphines ( $\text{L} = \text{PMe}_3$ ,  $\text{PMe}_2\text{Ph}$ , and  $\text{P-}n\text{-Bu}_3$ ) yield  $(\eta^3\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_3\text{L}$  in cyclohexane at room temperature. The crystal and molecular structure of  $(\eta^3\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_3\text{PMe}_3$  is reported. Crystal data are as follows: space group  $P2_1$ , monoclinic,  $a = 7.170$  (7) Å,  $b = 13.757$  (8) Å,  $c = 7.660$  (9) Å,  $\beta = 113.2$  (1)°. A total of 1041 independent reflections above background were measured on a diffractometer, and the structure was refined to  $R = 0.061$ . The molecule has an octahedral facial configuration, and the coordinated  $\eta^3$ -allyl group is unsymmetrically bonded [ $\text{Mn}-\text{C}(11) = 2.199$  (13) Å,  $\text{Mn}-\text{C}(12) = 2.124$  (10) Å,  $\text{Mn}-\text{C}(13) = 2.255$  (11) Å] with the longer bond to the carbon atom that bears the anti-vinyl substituent. In refluxing cyclohexane,  $(\eta^5\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_3$  is converted into the substitution products  $(\eta^5\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_2\text{L}$ , by a variety of tertiary phosphines and phosphites L. An associative mechanism via  $(\eta^3\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_3\text{L}$  is indicated. Some photochemical reactions are also reported, including evidence for the formation of  $(\eta^3\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_4$  both in solution and on irradiation in a carbon monoxide matrix at 20 K.

### Introduction

The open-chain  $\eta^5$ -pentadienyl complexes of manganese<sup>2</sup> and of rhenium<sup>3</sup>  $(\eta^5\text{-C}_5\text{H}_7)\text{M}(\text{CO})_3$  have recently been prepared by reaction of pentadienyltrialkyltin reagents with  $\text{M}(\text{CO})_5\text{Br}$  ( $\text{M} = \text{Mn, Re}$ ). Prior to these reports, the only examples of open-chain pentadienyl derivatives of these metals were a compound obtained from tropone and decacarbonyldimanganese<sup>4</sup> and (1-methylpentadienyl)-tricarbonylmanganese, prepared in low yield from 1,5-hexadienyl-3-trimethyltin and  $\text{Mn}(\text{CO})_5\text{Br}$ .<sup>5</sup> Recently an unusual pentadienyl trimetallic complex of formula  $\text{Mn}_3(3\text{-MeC}_5\text{H}_6)_4$  was synthesized from manganese(II) chloride and 2 equiv of 3-methylpentadienyl anion.<sup>6</sup>

Substitution of carbon monoxide in  $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$  by a wide variety of reagents has been studied in great detail.<sup>7</sup> This complex is quite inert to thermal substitution, requiring high temperature and long reaction times.<sup>8</sup> Consequently the majority of syntheses of the substitution products  $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{L}$  have been carried out by using photochemical procedures.<sup>9</sup> On photoexcitation<sup>10</sup> the tricarbonyl complex loses one molecule of carbon monoxide dissociatively, yielding the 16-electron fragment



$(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2$ . This fragment has a high affinity for two-electron ligands such as phosphines, phosphites, alkenes, alkynes, and dinitrogen. A common technique is to carry out the photolysis in tetrahydrofuran, which yields the labile complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{THF}$ .<sup>11</sup> Subsequently the solvent can be displaced by addition of the appropriate ligand L without further irradiation.<sup>12</sup> Alternatively direct irradiation of  $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$  in the presence of a photostable ligand may be performed in hydrocarbon solvents, but this method is prone to side reactions and decomposition during photolysis.<sup>13,14</sup>

Kinetic studies of CO exchange and substitution reactions of transition-metal carbonyl complexes have established two extreme types of mechanism, dissociative and

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Table I. Analytical Data for the Complexes  $(\eta^3\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_3\text{L}$ 

L	mp, °C	yield, <sup>a</sup> %	mol wt <sup>b</sup>	anal. found (calcd)		$\nu(\text{CO}),^c$ cm <sup>-1</sup>	$\nu(\text{C}=\text{C}),^c$ cm <sup>-1</sup>
				C	H		
PMe <sub>2</sub> Ph	78-79	46	344	56.04 (55.83)	5.58 (5.27)	2000, 1935, 1903	1612
PMe <sub>3</sub>	74-75	66	282	46.79 (46.82)	5.86 (5.72)	2000, 1937, 1905	1612
PBu <sub>3</sub>	42-43	31	408	58.51 (58.82)	8.26 (8.39)	1997, 1923, 1897	1612

<sup>a</sup> Yield of purified product. <sup>b</sup> Determined from mass spectrum. <sup>c</sup> Nujol mull.

associative.<sup>15,16</sup> For example,  $(\eta^3\text{-C}_3\text{H}_5)\text{Co}(\text{CO})_3$  shows rapid replacement of CO by phosphines by a dissociative path,<sup>17</sup> while the reactions of  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$  are somewhat slower, following, rather surprisingly, an associative mechanism. The latter observation has been explained by postulating slippage from  $\eta^5$  coordination of the  $\text{C}_5\text{H}_5$  group on attack of the nucleophile.<sup>18</sup>

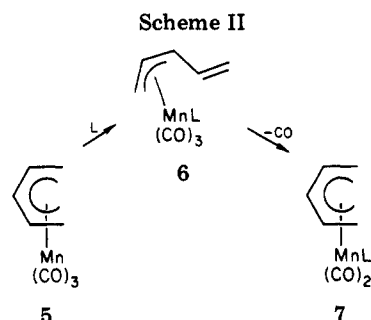
Casey and co-workers have studied the reactions of trimethylphosphine with  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3$ , 1.<sup>19</sup> When the two reactants were heated in hexane at 64 °C for 2.5 days, a high yield of the bis(phosphine) adduct 2, *fac*- $(\eta^1\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3(\text{PMe}_3)_2$ , was obtained. This reaction was shown to be reversible. Prolonged heating of the two reactants at 102 °C in toluene, however, afforded the substitution product  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2\text{PMe}_3$ .

It was suggested that the  $\eta^3\text{-C}_5\text{H}_5$  complex 4 acts as a common intermediate for formation of the bis(phosphine) adduct 2 and also for that of the substitution product 3. Prior to this work, similar formation of  $\eta^1\text{-C}_5\text{H}_5$  bis(phosphine) adducts had been observed for the nitrosyl complexes  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})(\text{NO})\text{Me}$ <sup>20</sup> and  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2(\text{NO})$  (M = Mo, W)<sup>21</sup> but had been explained in terms of a bent nitrosyl intermediate. Now the authors favor an  $\eta^3\text{-C}_5\text{H}_5$  intermediate in all cases.

Interconversion between  $\eta^5$ - and  $\eta^3$ -bonding modes should be much more favorable for open-chain pentadienyl ligands than for the closed cyclopentadienyl ligand.<sup>22</sup> Moreover, the ready replacement of ethene by other ligands in  $(\eta^5\text{-indenyl})\text{Rh}(\text{C}_2\text{H}_4)_2$ <sup>23</sup> compared with  $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{H}_4)_2$ <sup>24</sup> is considered to be due to the much easier  $\eta^5$  to  $\eta^3$  slippage in the former case. The salts  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\eta^5\text{-C}_5\text{H}_5\text{R})]^+\text{PF}_6^-$  on reaction with halide ion in acetone are readily and reversibly converted into complexes  $\text{Rh}(\eta^3\text{-RC}_5\text{H}_6)(\eta^5\text{-C}_5\text{H}_5)\text{X}$ .<sup>25</sup> It was therefore of interest to examine the reactions of  $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$  with donor ligands and to compare the results with similar reactions of  $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$  and of the allyl complex  $(\eta^3\text{-C}_3\text{H}_5)\text{Mn}(\text{CO})_4$ .<sup>26</sup>

## Results and Discussion

**Synthesis of  $(\eta^3\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_3\text{L}$  (L = PMe<sub>3</sub>, PMe<sub>2</sub>Ph, P-*n*-Bu<sub>3</sub>).** Reaction of the strong  $\sigma$ -donor phosphines, L = PMe<sub>3</sub>, PMe<sub>2</sub>Ph, or P-*n*-Bu<sub>3</sub> (1 mol), with  $(\eta^5\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_3$ , 5 (1 mol), in cyclohexane at room



temperature affords the  $\eta^3$ -pentadienyl adducts  $(\eta^3\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_3\text{L}$ . These were isolated in fair yield after recrystallization. Elemental analysis, NMR, IR, and mass spectroscopic data were all consistent with the suggested formulation (Table I).

The infrared spectra show three strong bands in the carbonyl stretching region (Table I) and a weaker band at 1612 cm<sup>-1</sup> assigned to the stretching mode of the free double bond of the  $\eta^3$ -pentadienyl ligand. The  $\nu(\text{CO})$  pattern is very similar to that observed for  $(\eta^3\text{-C}_3\text{H}_5)\text{Mn}(\text{CO})_3\text{L}$ .<sup>26,27</sup> The mass spectra show the familiar stepwise loss of three carbonyl groups.<sup>28</sup> In addition, however, the phosphine ligand is also lost, fragment ions  $[\text{C}_5\text{H}_7\text{Mn}(\text{CO})_n]^+$  ( $n = 1-3$ ) being observed in low relative intensity. This could be due to slight dissociation of phosphine from the adducts in the gas phase although we have no evidence of such dissociation in solution.

The <sup>1</sup>H NMR spectra reveal seven different signals for the protons of the  $\eta^3$ -pentadienyl group (Table II). The anti and syn protons H<sup>1a</sup> and H<sup>1b</sup> show very similar chemical shifts and overlap in the case of the PMe<sub>3</sub> and PPh<sub>3</sub> complexes. Coupling to phosphorus is observed for H<sup>1a</sup> [ $J(\text{P}-\text{H}) = 2.8$  Hz] and for H<sup>2</sup> [ $J(\text{P}-\text{H}) = 13$  Hz], but not to the syn protons H<sup>1b</sup> and H<sup>3</sup>. The protons H<sup>3</sup> resonate to low field of the protons H<sup>2</sup>, suggesting that they adopt a syn stereochemistry, thus placing the vinyl substituent in the anti position. This assignment is confirmed by double-resonance experiments on  $(\eta^3\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_3\text{PMe}_3$  and generalized for the other complexes on the basis of similar multiplicities and coupling constants. This assignment contrasts with observations on  $(\eta^3\text{-C}_5\text{H}_7)\text{RuCl}(\text{CO})(\text{PMe}_2\text{Ph})_2$ ,<sup>1</sup> in which the vinyl substituent is considered to be in the syn position.

The proton-decoupled <sup>13</sup>C NMR spectra of  $(\eta^3\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_3\text{L}$ , L = PMe<sub>2</sub>Ph and P-*n*-Bu<sub>3</sub>, were remarkable in that three sets of five signals were observed for the pentadienyl ligand, one set always more intense than the other two (Table III). Initially the spectrum of 6 (L = PMe<sub>3</sub>) showed only the five expected resonances, but after the sample had stood for several months two further peaks associated with each original resonance appeared. These anomalies may be due to the presence of geometrical isomers that slowly interconvert in solution. Geometrical

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Table II. <sup>1</sup>H NMR Data for Complexes (η<sup>3</sup>-CH<sup>1a</sup>(H<sup>1s</sup>)CH<sup>2</sup>CH<sup>3</sup>CH<sup>4</sup>=CH<sup>5</sup>H<sup>5</sup>)Mn(CO)<sub>3</sub>L

complex	chemical shifts, <sup>a</sup> δ						
	H <sup>1a</sup>	H <sup>2</sup>	H <sup>3</sup>	H <sup>4</sup>	H <sup>5</sup>	H <sup>5'</sup>	L
P- <i>n</i> -Bu <sub>3</sub>	2.37 (dt, J <sub>2</sub> = 12.8, J <sub>3</sub> = 7.8) J(PH <sup>1a</sup> ) = 2.75	3.63 (m) J(PH <sup>2</sup> ) = 12.5	4.24 (t, J = 9)	5.48 (dt, J <sub>4</sub> = 16.5, J <sub>5</sub> = 10)	4.84 (dd, J <sub>4</sub> = 10)	5.22 (dd, J <sub>5</sub> = 2)	0.84 and 1.22 (br m, 27 H)
PMe <sub>3</sub>	2.24 (m)	3.27 (m, J = 7.5) 12.8, J(PH <sup>2</sup> ) = 12.8	4.05 (t, J = 9)	5.41 (dt, J <sub>4</sub> = 16.8, J <sub>5</sub> = 10)	4.78 (dd, J <sub>4</sub> = 10)	5.15 (dd, J <sub>5</sub> = 2)	0.48 (d, J(PCH <sub>3</sub> ) = 9.8)
PMe <sub>2</sub> Ph <sup>b</sup>	2.26 (m)	3.44 (m, J = 7.5, J(PH <sup>2</sup> ) = 13)	3.77 (t, J = 8.6)	5.19 (dt, J <sub>4</sub> = 16.7, J <sub>5</sub> = 10)	4.64 (dd, J <sub>4</sub> = 10)	4.95 (dd, J <sub>5</sub> = 2)	1.49 (d, 3 H), 1.57 (d, 3 H), 7.44 (s, br, 6 H, J(PCH <sub>3</sub> ) = 9)

<sup>a</sup> In C<sub>6</sub>D<sub>6</sub>, relative to Me<sub>4</sub>Si (δ 0); 250 MHz; coupling constants in hertz. <sup>b</sup> In CDCl<sub>3</sub>, relative to Me<sub>4</sub>Si (δ 0); 250 MHz.

Table III. <sup>13</sup>C NMR Data for the Complexes Mn(η<sup>3</sup>-C<sub>5</sub>H<sub>7</sub>)(CO)<sub>3</sub>L

complex	chemical shifts <sup>a,c</sup>					
	C <sup>1</sup>	C <sup>2</sup>	C <sup>3</sup>	C <sup>4</sup>	C <sup>5</sup>	L
Mn(η <sup>3</sup> -C <sub>5</sub> H <sub>7</sub> )(CO) <sub>3</sub> PMe <sub>3</sub>	40.5	92.1	65.5	140.0	109.6	14.7 (m)
Mn(η <sup>3</sup> -C <sub>5</sub> H <sub>7</sub> )(CO) <sub>3</sub> PMe <sub>2</sub> Ph <sup>b</sup>	46.23, 39.99, (34.97)	100.32, (93.77), 89.47	(69.63), 68.44, 57.75	140.45, (137.96), 136.02	117.74, (111.42), 108.33	129 (m), 126.43, 15.98 (m)
Mn(η <sup>3</sup> -C <sub>5</sub> H <sub>7</sub> )(CO) <sub>3</sub> P- <i>n</i> -Bu <sub>3</sub>	(38.6), 35.2	94.6, 94.2, (90.1)	(70.3), 65.8, 64.9	141.6, 141.0, (139.0)	112.2, (108.5)	26.16, 25.65, 24.67, 13.80

<sup>a</sup> In C<sub>6</sub>D<sub>6</sub>, relative to Me<sub>4</sub>Si (δ 0); 100 MHz. <sup>b</sup> In CDCl<sub>3</sub>, relative to Me<sub>4</sub>Si (δ 0); 100 MHz. <sup>c</sup> Value in parentheses denotes high intensity signal.

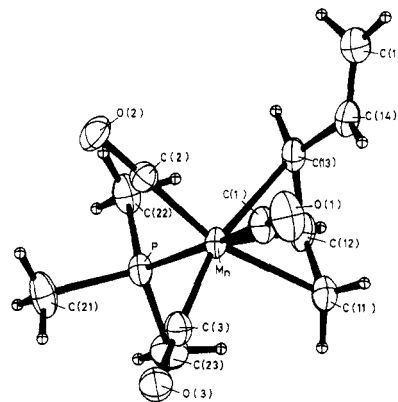


Figure 1. The molecular structure of (η<sup>3</sup>-C<sub>5</sub>H<sub>7</sub>)Mn(CO)<sub>3</sub>PMe<sub>3</sub> (ellipsoids at 30% probability). Hydrogen atoms are shown as small spheres for clarity.

Table IV. Atomic Coordinates (×10<sup>4</sup>) with Estimated Standard Deviations in Parentheses

atom	x	y	z	10 <sup>3</sup> U, Å <sup>2</sup>
Mn(1)	1118 (2)	0 (0)	2067 (2)	73 (1)
P(1)	1871 (4)	967 (2)	4707 (4)	77 (3)
C(1)	640 (19)	-600 (9)	-183 (15)	94 (13)
O(1)	417 (21)	-901 (8)	-1638 (13)	138 (15)
C(2)	-597 (15)	940 (8)	854 (13)	74 (11)
O(2)	-1732 (16)	1564 (7)	7 (16)	117 (12)
C(3)	3409 (18)	485 (9)	1982 (16)	102 (13)
O(3)	4890 (15)	766 (8)	1962 (17)	142 (13)
C(13)	-1205 (17)	-972 (8)	2485 (17)	99 (12)
C(12)	828 (20)	-1102 (8)	3886 (15)	105 (12)
C(11)	2465 (22)	-1372 (9)	3474 (23)	121 (16)
C(14)	-2178 (20)	-1650 (8)	943 (18)	107 (13)
C(15)	-4112 (25)	-1752 (11)	52 (24)	113 (18)
C(21)	2537 (28)	2215 (10)	4372 (22)	126 (20)
C(22)	-139 (23)	1156 (9)	5557 (19)	121 (16)
C(23)	4006 (22)	594 (13)	6817 (17)	89 (18)

isomers of (η<sup>3</sup>-enyl)Mn(CO)<sub>3</sub>L have been observed and separated by chromatography.<sup>29</sup>

**Discussion of the Structure of *fac*-(η<sup>3</sup>-C<sub>5</sub>H<sub>7</sub>)Mn(CO)<sub>3</sub>PMe<sub>3</sub>.** The molecular structure of (η<sup>3</sup>-C<sub>5</sub>H<sub>7</sub>)Mn(CO)<sub>3</sub>PMe<sub>3</sub> was determined by X-ray crystallography (Figure 1, Tables IV and V). The metal atom can be regarded as having slightly distorted octahedral coordination if the η<sup>3</sup>-pentadienyl ligand is considered to span two coordination positions on the manganese atom. The structure is similar to that found for the allyl complex (η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)Mn(CO)<sub>2</sub>(P(OMe)<sub>3</sub>)<sub>2</sub><sup>26</sup> but is considerably more distorted from ideal geometry.

In the present molecule, the manganese atom is bonded to a mutually trans phosphorus group (Mn-P = 2.300 (3) Å) and a carbonyl group (Mn-C(1) = 1.818 (11) Å), two mutually cis carbonyl groups (Mn-C(2) = 1.774 (11) Å and Mn-C(3) = 1.798 (12) Å) and the pentadienyl ligand. The bond lengths to the carbonyls and the phosphine are as expected.<sup>26</sup>

The η<sup>3</sup>-pentadienyl fragment is bonded to the metal in an asymmetric fashion (Mn-C(11) = 2.199 (13) Å, Mn-C(12) = 2.124 (10) Å, Mn-C(13) = 2.255 (11) Å). C(13) and C(14) are not bonded to the metal with Mn...C distances of over 3.0 Å. Indeed the two atoms are twisted out of the plane of C(11), C(12), C(13) by distances of -0.86 (1) Å and -1.22 (1) Å. This leaves the atoms on the opposite side of the plane from the metal which is 1.77 (1) Å from the plane.

This C(11), C(12), C(13) plane intersects the equatorial plane of Mn, C(2), C(3) at an angle of 70.7 (1)°. The

Table V

## Dimensions in the Coordination Sphere

Bond Lengths (Å)			
Mn(1)-P(1)	2.300 (3)	Mn(1)-C(13)	2.255 (11)
Mn(1)-C(1)	1.818 (11)	Mn(1)-C(12)	2.124 (10)
Mn(1)-C(2)	1.774 (11)	Mn(1)-C(11)	2.199 (13)
Mn(1)-C(3)	1.798 (12)		
Bond Angles (deg)			
P(1)-Mn(1)-C(1)	170.8 (3)	C(2)-Mn(1)-C(13)	96.1 (4)
P(1)-Mn(1)-C(2)	85.0 (3)	C(3)-Mn(1)-C(13)	164.2 (4)
C(1)-Mn(1)-C(2)	90.0 (5)	P(1)-Mn(1)-C(11)	99.2 (4)
P(1)-Mn(1)-C(3)	85.2 (3)	C(1)-Mn(1)-C(11)	87.7 (5)
C(1)-Mn(1)-C(3)	88.1 (5)	C(2)-Mn(1)-C(11)	164.1 (5)
C(2)-Mn(1)-C(3)	99.5 (5)	C(3)-Mn(1)-C(11)	96.1 (5)
P(1)-Mn(1)-C(13)	98.6 (3)	C(13)-Mn(1)-C(11)	68.2 (5)
C(1)-Mn(1)-C(13)	89.6 (4)		
Other Dimensions			
Bond Lengths (Å)			
C(13)-C(12)	1.440 (17)	C(12)-C(11)	1.381 (19)
C(13)-C(14)	1.450 (18)	C(14)-C(15)	1.289 (20)
Bond Angles (deg)			
Mn(1)-C(11)-C(12)	68.6 (6)	C(12)-C(13)-C(14)	123.0 (10)
Mn(1)-C(13)-C(12)	65.9 (5)	C(13)-C(12)-C(11)	124.4 (11)
Mn(1)-C(13)-C(14)	114.4 (7)	C(13)-C(14)-C(15)	125.1 (12)

comparable angle in the allyl complex is 71.0°. The carbon atoms C(11), C(12), and C(13) are respectively -0.09, 0.52, and -0.11 Å from the equatorial plane, again comparable to values found in the allyl complex.

The central Mn-C(12) bond is the shortest distance; with Mn-C(13), the carbon bonded to the vinyl substituent, being longer than Mn-C(11) by a significant 0.056 (17) Å. The C(12)-C(13) bond at 1.440 (17) Å is significantly longer than the C(11)-C(12) bond at 1.381 (19) Å, at the 95% confidence level.

There are no intermolecular contacts of less than the sum of van der Waals radii in the unit cell.

**Synthesis of  $(\eta^3\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_4$ .** (a) **Matrix Isolation Studies.** Low-temperature matrix isolation studies are useful in generating and characterizing species that might act as intermediates in reactions.<sup>30</sup> Irradiation of matrix-isolated metal carbonyls or their derivatives often leads to photodissociation of CO. Recently, however, species have been observed in which the mode of coordination of a polyene has changed. For example  $(\eta^3\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_3$  is formed from  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ ,<sup>31</sup>  $(\eta^2\text{-C}_4\text{H}_6)\text{Fe}(\text{CO})_3$  and  $(\eta^2\text{-C}_4\text{H}_6)\text{Fe}(\text{CO})_4$  are formed from  $(\eta^4\text{-C}_4\text{H}_6)\text{Fe}(\text{CO})_3$ ,<sup>32</sup> and  $(\eta^1\text{-C}_3\text{H}_5)\text{Co}(\text{CO})_4$  is formed from  $(\eta^3\text{-C}_3\text{H}_5)\text{Co}(\text{CO})_3$ <sup>33</sup> on photolysis in carbon monoxide matrices. Ring slip has also been observed in the reaction of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{ReH}$  with CO and N<sub>2</sub> in matrices.<sup>34</sup>

Preliminary photochemical studies of **5** isolated in frozen gas matrices at 20 K have been carried out. The infrared spectrum of the parent complex in a CO matrix (Figure 2) shows three strong bands in the carbonyl stretching region at 2027, 1959, and 1942 cm<sup>-1</sup>. After 3-min photolysis with a medium-pressure arc lamp using a CoSO<sub>4</sub>/NiSO<sub>4</sub> filter four new peaks at 2072, 1997, 1980, and 1965 cm<sup>-1</sup> were produced, unchanged starting material remaining. After 6-min irradiation a photostationary state was

reached. The spectrum after further irradiation (3 h) using a soda glass filter ( $\lambda > 325$  nm) showed complete consumption of starting material and conversion into essentially only one product. The band positions are almost identical with those observed in the spectrum of  $(\eta^3\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_4$ ,  $\nu(\text{CO})$  2075 (m), 1997 (s), 1979 (s), and 1964 (vs).<sup>35</sup> This provides strong evidence for the formation of  $(\eta^3\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_4$  in the photolysis experiments. On photolysis of **5** in N<sub>2</sub> matrices with  $\lambda > 325$  nm, there was considerable conversion to products, although very little growth was observed in the band at 2139 cm<sup>-1</sup> due to free CO. A product band in the  $\nu(\text{NN})$  region (2186 cm<sup>-1</sup>) and bands in the  $\nu(\text{CO})$  region at 2026, 1959, and 1935 cm<sup>-1</sup> are tentatively assigned to  $(\eta^3\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_3\text{N}_2$ .

(b) **Solution Reaction of **5** with CO.** We then sought to obtain evidence for the formation of the tetracarbonyl complex in solution. Photolysis of **5** in hexane under a carbon monoxide atmosphere (1 atm) was monitored by infrared spectroscopy over 31 h (the new bands produced correspond to the tetracarbonyl  $(\eta^3\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_4$ ,  $\nu(\text{CO})$  2070 (m), 1998 (s), and 1964 cm<sup>-1</sup>(s), and possibly also to the pentacarbonyl  $(\eta^1\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_5$ ,  $\nu(\text{CO})$  2047 (m), 2012 (s), 1985 cm<sup>-1</sup> (s); cf.  $(\eta^1\text{-C}_3\text{H}_5)\text{Mn}(\text{CO})_5$ , 2108 (m) 2046 (m), 2014 (vs), 1993 (s), and 1926 cm<sup>-1</sup> (vww)).<sup>35</sup>

**Substitution Reactions of  $(\eta^5\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_3$ .** Complexes  $(\eta^5\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_2\text{L}$ , **7** (L = PPh<sub>3</sub>, P(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>, PMe<sub>3</sub>, PMe<sub>2</sub>Ph, P(OMe)<sub>3</sub>, P(OEt)<sub>3</sub>, P(OPh)<sub>3</sub>, and AsPh<sub>3</sub>), have been prepared by thermal and/or photochemical methods, involving displacement of carbon monoxide from **5**. These complexes are slightly air-sensitive yellow crystalline materials or yellow liquids, but they can be stored for long periods under nitrogen at ambient temperature.

**Thermal Reactions.** The thermal reaction between **5** and phosphorus donor ligands in refluxing cyclohexane affords the substituted complexes **7**, which were isolated by chromatography on Florisil or sometimes by crystallization alone. When a stoichiometric ratio of reactants was used, the reaction rates monitored qualitatively by infrared spectroscopy were shown to depend on the entering ligand: PMe<sub>3</sub>  $\approx$  PMe<sub>2</sub>Ph > P(OPh)<sub>3</sub>  $\approx$  PPh<sub>3</sub>  $\approx$  P(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub> > P-

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Table VI. Frequencies of CO Stretching Modes ( $\text{cm}^{-1}$ ) for Complexes of Formula  $\text{Mn}(\eta^5\text{-C}_5\text{H}_7)(\text{CO})_2\text{L}^a$  and Related Cyclic Complexes  $\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{L}$ 

$\text{Mn}(\eta^5\text{-C}_5\text{H}_7)(\text{CO})_2\text{L}$	$\nu(\text{CO})$		$\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{L}$	$\nu(\text{CO})$ (cyclohexane)
	Nujol	$\text{CHCl}_3$		
$\text{PPh}_3$	1953, 1923 (sh), 1878, 1838 (sh)	1943, 1874	$\text{PPh}_3$	1945, 1884 <sup>b</sup>
$\text{P}(\text{C}_6\text{H}_{11})_3$	1939, 1927 (sh), 1887, 1858 (sh)		$\text{P}(\text{C}_6\text{H}_{11})_3$	1931, 1869 <sup>b</sup>
$\text{PMe}_3$	1948, 1881	1938, 1866	$\text{PMe}_3$	1939, 1876 <sup>b</sup>
$\text{PMe}_2\text{Ph}$	1944, 1878		$\text{PMe}_2\text{Ph}$	1932, 1867 <sup>c</sup>
$\text{P}(\text{OMe})_3$	1959, 1897	1955, 1887 <sup>d</sup>	$\text{P}(\text{OMe})_3$	1954, 1891 <sup>e</sup>
$\text{P}(\text{OEt})_3$	1958, 1896	1952, 1882 <sup>d</sup>	$\text{P}(\text{OEt})_3$	1949, 1886 <sup>e</sup>
$\text{P}(\text{OPh})_3$	<sup>f</sup>	1967, 1903	$\text{P}(\text{OPh})_3$	1970, 1909 <sup>e</sup>
$\text{AsPh}_3$	1933, 1859	1940, 1873	$\text{AsPh}_3$	1935, 1872 <sup>g</sup>

<sup>a</sup> All bands have strong intensity. <sup>b</sup> Reference 38. <sup>c</sup> Reference 39, in  $\text{CS}_2$  solution. <sup>d</sup> Broad peaks. <sup>e</sup> Reference 40. <sup>f</sup> Intermediate solubility in the mull giving broad signal. <sup>g</sup> Reference 41, in  $\text{CS}_2$  solution.

Table VII. Analytical Data for the Complexes  $(\eta^5\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_2\text{L}$ , 7

L	color	mp, °C	yield, <sup>a</sup> %	mol wt <sup>b</sup>	anal. found (calcd)	
					C	H
$\text{PPh}_3$	golden yellow	146-147 dec	44	440	68.97 (68.20)	5.08 (5.04)
$\text{P}(\text{C}_6\text{H}_{11})_3$	lemon yellow	173-175 dec	39	458	64.64 (64.49)	8.50 (8.79)
$\text{PMe}_3$	yellow	88.5-89.5	26 <sup>c</sup>	254	46.69 (47.26)	6.41 (6.36)
$\text{PMe}_2\text{Ph}$	yellow	liquid <sup>d</sup>	~10		(56.98)	(5.74)
$\text{P}(\text{OMe})_3$	pale yellow	81-83	51	302	38.98 (39.75)	5.48 (5.34)
$\text{P}(\text{OEt})_3$	pale yellow	liquid <sup>e</sup>	~20	344	(45.36)	(6.44)
$\text{P}(\text{OPh})_3$	pale yellow	55-57	40	488	61.62 (61.49)	4.54 (4.54)
$\text{AsPh}_3$	golden yellow	128-129 dec	39 <sup>f</sup>	484	61.69 (62.00)	4.88 (4.58)

<sup>a</sup> By thermal reactions. <sup>b</sup> These values were determined from the mass spectra. <sup>c</sup> 8% by photochemical reaction. <sup>d</sup> At  $-20^\circ\text{C}$  is a lemon yellow solid. <sup>e</sup> Very pale yellow crystals, melts at  $18^\circ\text{C}$ . <sup>f</sup> By photochemical reaction.

$(\text{OMe})_3 \approx \text{P}(\text{OEt})_3$ . (See Experimental Section.) Both  $\sigma$ -donor ability and steric effects apparently play a part. The faster reaction observed for  $\text{P}(\text{OPh})_3$  than for  $\text{P}(\text{OMe})_3$ , if significant, is surprising and cannot be explained from the existing evidence. The reaction rate was also shown to depend on the concentration of ligand,  $\text{P}(\text{OMe})_3$ ,  $\text{P}(\text{OEt})_3$ , or  $\text{P}(\text{OPh})_3$ . Pure products could not usually be obtained from reaction mixtures employing an excess of ligand. Comparison with other results<sup>26</sup> leads to the conclusion that the ease of replacement of a carbonyl group by phosphines and phosphites decreases in the order  $(\eta^3\text{-C}_3\text{H}_5)\text{Mn}(\text{CO})_4 > (\eta^5\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_3 > (\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ .

**Infrared Spectra.** The infrared frequencies for the carbonyl stretching region for complexes 7 are presented in Table VI and analytical and other characterizing data in Table VII. The observed order of frequencies ( $\text{L} = \text{P}(\text{OPh})_3 > \text{P}(\text{OMe})_3 > \text{P}(\text{OEt})_3 > \text{PPh}_3 > \text{PMe}_3 > \text{PMe}_2\text{Ph} > \text{P}(\text{C}_6\text{H}_{11})_3 > \text{AsPh}_3$ ) is much as expected, following the anticipated increase in electron density at the metal across the series. There is general agreement between the  $\eta^5$ -pentadienyl complexes and the corresponding cyclopentadienyl derivatives  $\eta^5\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{L}$ , except that the frequencies for the complex  $\eta^5\text{-C}_5\text{H}_7\text{Mn}(\text{CO})_2\text{AsPh}_3$  are somewhat lower than expected. Barbeau, however, reports that the electron density on the manganese atom decreases in the order  $\text{L} = \text{SbPh}_3 > \text{AsPh}_3 > \text{PPh}_3$  for the complexes  $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{L}$ .<sup>42</sup>

During the reactions between 5 and L bands of the intermediate 6 grow and then disappear in the infrared spectrum. These bands are clearly discernible for  $\text{L} = \text{PMe}_3$  or  $\text{PMe}_2\text{Ph}$  but less apparent for the other phosphines or phosphites. Independent of the molar ratio of reactants used in the syntheses of the phosphite derivatives ( $\text{L} = \text{P}(\text{OMe})_3$ ,  $\text{P}(\text{OEt})_3$ ), the infrared spectra of the reaction mixtures exhibit four, not two, carbonyl stretching bands corresponding to products. The pure complexes  $(\eta^5\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_2\text{L}$ , ( $\text{L} = \text{P}(\text{OMe})_3$  or  $\text{P}(\text{OEt})_3$ ), isolated by chromatography followed by recrystallization from reaction mixtures with a starting material:ligand ratio of 1:1, showed only two sharp bands (Table VI). A product isolated from a reaction mixture using excess  $\text{P}(\text{OMe})_3$  by recrystallization but without chromatography afforded four sharp bands in the infrared—1964 (s), 1946 (s), 1902 (s), and  $1876\text{ cm}^{-1}$  (vs) (in hexane). There seem to be two possible explanations of these results: either a mixture of two products  $(\eta^5\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_2\text{P}(\text{OMe})_3$  and  $(\eta^3\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_2[\text{P}(\text{OMe})_3]_2$  or the presence of isomers<sup>43</sup> in  $(\eta^5\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_2\text{P}(\text{OMe})_3$ . We are not able to distinguish these possibilities on the available evidence, although the first explanation is favored.

**Photochemical Reactions.** Thermal reactions between 5 and  $\text{AsPh}_3$ , pyridine, and  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$  in refluxing cyclohexane showed after 46, 10, and 26 h, respectively, the infrared spectrum of starting material. Irradiation of a mixture of 5 with  $\text{AsPh}_3$ , however, using a medium-pressure mercury lamp (125 W) and a soda glass filter ( $\lambda > 325\text{ nm}$ ) effected complete reaction after 3 h. The yellow crystalline product  $(\eta^5\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_2\text{AsPh}_3$  was isolated in 39% yield. Irradiation of 5 with pyridine did not yield a substitution product even after 30 h. A low yield (~6%) of a complex, possibly  $(\eta^3\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_3(\eta^2\text{-C}_5\text{H}_5)$ , was isolated. The complexes 7 ( $\text{L} = \text{PMe}_3$  and  $\text{PMe}_2\text{Ph}$ ) were also prepared photochemically, but the yields were lower

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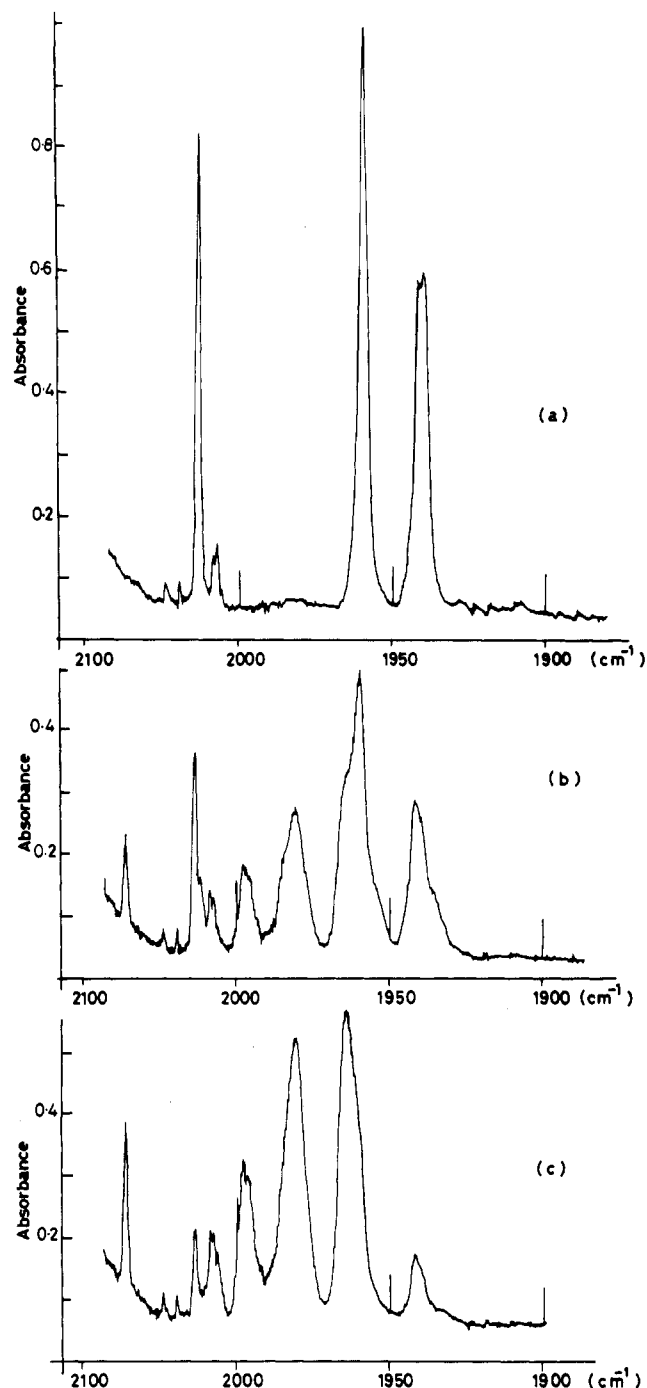
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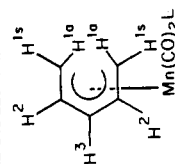
**Figure 2.** Infrared spectra from an experiment with  $(\eta^5\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_3$  isolated at high dilution in a CO matrix at 20 K (112-min deposition with sample at 247–254 K cocondensed with 6.4 mmol of CO): (a) after deposition, (b) after 10-min photolysis with  $220 < \lambda < 340$  nm (aqueous  $\text{CoSO}_4/\text{NiSO}_4$  filter), and (c) after 60-min photolysis ( $\lambda > 325$  nm) (soda glass filter).

than those in thermal reactions.

When  $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$  is irradiated in tetrahydrofuran, a red solution containing the labile complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{THF}$  is produced, from which THF can be displaced by a variety of ligands.<sup>7</sup> On irradiation of 5 in THF at 0 °C, however, either with or without soda glass filters, there was no evidence of reaction even after 10 h.

**NMR Spectra of  $(\eta^5\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_2\text{L}$ .**  $^1\text{H}$  NMR spectra of the substituted  $\eta^5$ -pentadienyl complexes are listed in Table VIII and  $^{13}\text{C}$  spectra in Table IX. The spectra are consistent with the presence of a symmetrical  $\eta^5$ -pentadienyl ligand. This pattern is similar to that shown by the tricarbonyl complex 5,<sup>2</sup> but all the resonances

**Table VIII.**  $^1\text{H}$  NMR Data for Complexes 7



L	chem shifts <sup>a</sup>					coupling const, Hz			
	H <sup>1a</sup>	H <sup>1s</sup>	H <sup>2</sup>	H <sup>3</sup>	L	H <sup>1a</sup> H <sup>2</sup>	H <sup>1s</sup> H <sup>2</sup>	H <sup>2</sup> H <sup>3</sup>	other
PPh <sub>3</sub>	0.24 (d)	2.08 (d)	4.70 (m)	5.38 (t)	7.35 and 7.52 (m, 15 H)	11.3	10	6.15	$J(\text{PH}^{1a}) = 2.5, J(\text{PH}^2) = 2$
$\text{P}(\text{C}_6\text{H}_{11})_3$ <sup>b</sup>	0.18 (d)	2.28 (d)	4.94 (m)	5.52	1.24 and 1.86 (br m, 38 H)	11.2	9.7	6.2	$J(\text{PH}^2) = 3$
$\text{PMe}_3$	-0.12	2.05 (d)	4.69	4.92 (t)	1.05 (d, 9 H)			6.7	$J(\text{PH}^2) \approx 1$
$\text{PMe}_2\text{Ph}$ <sup>b</sup>	0.29	2.02	4.56	4.85	1.37 (6 H)				
$\text{P}(\text{OMe})_3$	0.26	2.45 (d)	4.75 (m)	5.04 (t)	7.12 (5 H)	11.5	9.8	6.25	$J(\text{PH}^{1a}) = 2.2, J(\text{PH}^2), J(\text{PH}^3) \approx 1$
$\text{P}(\text{OEt})_3$ <sup>c</sup>	0.31 (dd)	2.52 (dd)	4.79 (td)	5.10 (t)	3.32 (d, 9 H)	11.3	9.75	6.25	$J(\text{H}^{1a}\text{H}^2) \approx 0.9, J(\text{PH}^{1a}) = 3,$ $J(\text{PH}^{1s}) \approx 1, J(\text{H}^{1a}\text{H}^{1s}) = 2,$ $J(\text{PH}^2) = 2.4, J(\text{PH}^3) = 1.25$
$\text{P}(\text{OPh})_3$	0.18 (d)	2.31 (d)	4.63 (t)	4.42 (m)	3.85 (m, 6 H)	11.2	9.8	6.5	$J(\text{PH}^{1a}) = 2.6, J(\text{PH}^2) = 3$
$\text{AsPh}_3$	0.05 (d)	2.13 (d)	4.64	5.31 (m)	1.06 (m, 9 H)	~11.5	~10	~6	

<sup>a</sup> In  $\text{C}_6\text{D}_6$  relative to  $\text{Me}_4\text{Si}$  ( $\delta$  0), 250 MHz. <sup>b</sup> In  $\text{CDCl}_3$  relative to  $\text{Me}_4\text{Si}$  ( $\delta$  0), 250 MHz. <sup>c</sup> Assignment based on  $^{31}\text{P}$  decoupling.

Table IX.  $^{13}\text{C}$  NMR Data for the Complexes  $(\eta^5\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_2\text{L}$ , 7

L	chem shifts <sup>a</sup>			
	C <sup>1</sup>	C <sup>2</sup>	C <sup>3</sup>	L
CO <sup>b</sup>	57.52	100.14	83.34	221.90 (br)
PMe <sub>3</sub>	55.08	99.37	87.77	20.2 226.4 (br CO)
PMe <sub>2</sub> Ph	56.11	99.32	87.98	19.39, 129.20 <sup>c</sup>
P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub>	55.32	96.80	87.02	26.8, 28.3, 30.3, 38.0
P(OMe) <sub>3</sub> <sup>d</sup>	56.13	98.60	88.30	51.59
P(OPh) <sub>3</sub> <sup>d</sup>	56.41	97.99	88.70	120.94, 124.35, 129.59, 151.66
AsPh <sub>3</sub>	54.90	97.71	88.86	128.84, 129.58, 133.12, 138.11

<sup>a</sup> In C<sub>6</sub>D<sub>6</sub> relative to Me<sub>4</sub>Si ( $\delta$  0), 22.63 MHz. <sup>b</sup> Reference 2 (CDCl<sub>3</sub>). <sup>c</sup> Ph overlapped with C<sub>6</sub>D<sub>6</sub>. <sup>d</sup> In CDCl<sub>3</sub> relative to Me<sub>4</sub>Si ( $\delta$  0), 22.63 MHz.

lie to higher field in the substituted compounds. Some difficulties were encountered in obtaining good spectra, peaks frequently being broad with the expected splittings obscured. However, the presence of paramagnetic impurities from oxidation would also give rise to line broadening,<sup>26</sup> and samples were always freshly purified before running the spectra.

The protons of the  $\eta^5$ -pentadienyl ligand couple to  $^{31}\text{P}$  to different extents. The anti protons (H<sup>1a</sup>) and protons H<sup>2</sup> show couplings of the order of 2–3 Hz. Smaller couplings (~1 Hz) are observed to the syn protons (H<sup>1b</sup>) and to the central proton (H<sup>3</sup>). As for other  $\eta^5$ -pentadienyl complexes the anti protons (H<sup>1a</sup>) resonate to highest field.<sup>22,44–46</sup>

Substitution of CO in 5 by a tertiary phosphine, phosphite, or arsine is accompanied by high-field shifts of the terminal (C<sup>1</sup>) and adjacent (C<sup>2</sup>) carbon nuclei and a low-field shift of the central carbon (C<sup>3</sup>). Very similar shifts are observed for the carbon nuclei in the spectra of a variety of  $\eta^5$ -pentadienyl and  $\eta^5$ -cyclohexadienyl complexes such as  $(\eta^5\text{-C}_5\text{H}_7)\text{Fe}(\text{CO})_3^+$ ,<sup>47</sup>  $(\eta^5\text{-C}_6\text{H}_7)\text{Fe}(\text{CO})_3^+$ ,<sup>48</sup> and  $\text{Fe}(\eta^5\text{-2,4-Me}_2\text{C}_5\text{H}_5)_2$ .<sup>22</sup> Only in the rhodium and iridium complexes e.g.,  $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-MeC}_5\text{H}_5)]^+$  are the C<sup>2</sup> and C<sup>3</sup> resonances reversed, the latter now being at lower field.<sup>45,49</sup>

### Conclusion

The reactions of phosphines and phosphites with the open-chain pentadienyl complex  $(\eta^5\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_3$  proceed via an adduct,  $(\eta^3\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_3\text{L}$ . The work, moreover, shows the expected propensity of the pentadienyl ligand to undergo ready  $\eta^5$  to  $\eta^3$  conversion to a much greater degree than the corresponding cyclopentadienyl group.

### Experimental Section

All preparative work was carried out in an atmosphere of dry oxygen free nitrogen, using conventional Schlenk techniques. Solvents were carefully dried; tetrahydrofuran was freshly distilled

from potassium and cyclohexane from calcium hydride. Liquid phosphines and phosphites were dried over sodium and distilled under vacuum before use, except for PMe<sub>3</sub> (Strem Chemicals) which was used as received.

Infrared spectra were determined on Perkin-Elmer 177 and 257 spectrophotometers, calibrated with polystyrene film. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker 250- and 90-MHz-instruments, respectively, at King's College, University of London. Mass spectra were measured by using a VG ZAB-IF spectrometer with an ionizing energy of 70 eV (EI) at The School of Pharmacy, London. Elemental analyses were by Butterworth Laboratories, Teddington, Middlesex, U.K.

Photochemical reactions were performed in a reaction vessel (Applied Photophysics) fitted with a quartz water-cooled immersion well, a reflux condenser, and a cannula for admission of nitrogen. The irradiation source was a 125-W medium-pressure mercury arc lamp.

**General Method of the Preparation of the Complexes  $(\eta^3\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_3\text{L}$ , 6.** A mixture of 5 (0.5 g, 2.43 mmol) and the phosphine (2.43 mmol) was stirred in cyclohexane (40 cm<sup>3</sup>) at room temperature until the infrared spectrum remained unchanged—PMe<sub>3</sub>, 2 h; PMe<sub>2</sub>Ph and P-*n*-Bu<sub>3</sub>, 3 h. Removal of solvent under reduced pressure left a solid or oily solid that was further purified as follows.

**L = PMe<sub>3</sub>.** The crystalline yellow residue was dissolved in hexane and the solution filtered. The solvent was reduced in volume and kept at 0 °C to yield pale yellow crystals that were filtered and dried in vacuo. The solid was crystallized from dichloromethane/hexane. A further purification by sublimation at 35 °C and 0.03 mm was finally performed. Single crystals were obtained for the X-ray determination by sealing a long ampule (20 cm × 1 cm) containing the sample (100 mg) under vacuum at 0.01 mm pressure. A temperature gradient between 35 °C and ambient temperature was maintained for several weeks to achieve slow sublimation.

**L = PMe<sub>2</sub>Ph.** The orange-red residue was dissolved in petroleum ether (bp 40–60 °C)–diethyl ether (12:1) and the solution filtered. The product crystallized at –60 °C from the filtrate and purified by recrystallization from the same solvent mixture.

**L = P-*n*-Bu<sub>3</sub>.** The residue was dissolved in petroleum ether and the solution filtered. The filtrate was reduced in volume and kept at –78 °C. The solid product was filtered and recrystallized from hexane at –78 °C.

**General Method for the Preparation of the Complexes  $(\eta^5\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_2\text{L}$  by Thermal Reactions.** A procedure similar to that of Brisdon<sup>26</sup> was followed. A mixture of 5 (2.43 mmol) and the respective phosphine or phosphite (2.43 mmol) was heated in refluxing cyclohexane (30 cm<sup>3</sup>) until infrared monitoring of the reaction mixture showed complete consumption of the starting material and no further change in the spectrum. The reaction times (h) were as follows: PMe<sub>3</sub>, 4; PMe<sub>2</sub>Ph, 4; P(OPh)<sub>3</sub>, 8; PPh<sub>3</sub>, 11; P(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>, 13; P(OEt)<sub>3</sub>, 19; P(OMe)<sub>3</sub>, 20. The solvent was evaporated under reduced pressure to yield a yellow solid or oil. Further purification was carried out as follows.

**L = PPh<sub>3</sub>.** The yellow residue was dissolved in petroleum ether–diethyl ether (12:1) and the solution filtered. Slow evaporation afforded golden yellow crystals that were filtered and recrystallized from petroleum ether–diethyl ether (6:1).

**L = P(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>.** The pale yellow solid was dissolved in dichloromethane and the solution filtered. Hexane was added and the solution slowly evaporated, giving a lemon yellow precipitate that was collected and dried in vacuo.

**L = P(OPh)<sub>3</sub>.** The yellow oil was dissolved in the minimum volume of petroleum ether–diethyl ether (12:1). Chromatography on Florisil using the same mixed solvent followed by removal of the solvent gave pale yellow crystals.

**L = PMe<sub>2</sub>Ph.** A similar procedure to that given above for L = P(OPh)<sub>3</sub> gave a yellow oil from the first pale yellow band collected from chromatography. A very low yield of pale lemon crystals (at –20 °C) was obtained after three recrystallizations at –78 °C.

**L = PMe<sub>3</sub>.** The yellow oil was dissolved in hexane and crystallized at –50 °C. The solid was twice recrystallized at –20 °C, first from dichloromethane–hexane and then from hexane alone. Further purification was effected by sublimation at 25 °C (0.05 mm).

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$L = P(OMe)_3$ . (a) The yellow oil was dissolved in petroleum ether–diethyl ether (12:1), filtered, and reduced to a small volume. The solution was cooled in ice, giving a pale yellow precipitate that was filtered, washed with hexane, and dried. A wide melting range (71–81 °C) and the infrared spectrum indicated a mixture of products (see text).

(b) The yellow oil was chromatographed by using petroleum ether–diethyl ether (12:1). Removal of the solvent, filtration of solid, and finally sublimation at 40 °C (0.05 mm) afforded the very pale yellow product, mp 81–83 °C.

$L = P(OEt)_3$ : A similar procedure to that above in b gave an oil after double chromatography. Four recrystallizations at –78 °C from hexane gave a pale yellow product that melted at 18 °C.

**Method of Preparation of the Complexes ( $\eta^5-C_5H_7$ )Mn(CO)<sub>2</sub>L by Photochemical Reactions.**  $L = AsPh_3$ . A mixture of **5** (0.5 g, 2.43 mmol) and  $AsPh_3$  (1.49 g, 4.86 mmol) dissolved in cyclohexane (75 cm<sup>3</sup>) was photolyzed at room temperature for 3 h. The infrared spectrum indicated complete consumption of **5**, showing only two strong CO bands from the dicarbonyl product. The solution was filtered and evaporated, giving an orange oil which was dissolved in petroleum ether–diethyl ether (1:2). This solution was filtered and reduced in volume, giving a yellow precipitate that was recrystallized from benzene–petroleum ether to yield golden yellow crystals.

$L = PMe_3$ ,  $PMe_2Ph$ , and  $P(OEt)_3$ . A similar procedure led to a mixture of products including ( $\eta^5-C_5H_7$ )Mn(CO)<sub>2</sub>L and ( $\eta^3-C_5H_7$ )Mn(CO)<sub>3</sub>L in each case.

**Reaction of **5** with Carbon Monoxide.** Complex **5** (0.47 g, 2.28 mmol) in hexane (75 cm<sup>3</sup>) was irradiated with a 125-W medium-pressure UV lamp using a soda glass filter ( $\lambda > 325$  nm) for 4 h while carbon monoxide was passed through the solution at –78 °C. Some products crystallized in the gas inlet tube at this temperature so the reaction mixture was allowed to warm up to –10 °C (15 h) and finally to room temperature (12 h) under continued photolysis. The progress of the reaction was monitored by infrared spectroscopy. No pure products could be isolated from the reaction mixture.

**Matrix Photochemistry.** Complex and carbon monoxide (BOC research grade) were cocondensed at 20 K onto a CsBr window cooled by an Air Products CS202 refrigerator and mounted in a Perkin-Elmer 580 spectrophotometer. The sample was evaporated from a side arm cooled to 250 K. The matrix was irradiated by using a medium-pressure mercury lamp (Philips HPK 125W) using appropriate filters.

**X-ray Crystal Structure Determination of ( $\eta^3-C_5H_7$ )Mn(CO)<sub>3</sub>PMe<sub>3</sub>.** Crystal data (I):  $C_{11}H_{16}MnO_3P$ ;  $M_r = 282.16$ ; monoclinic;  $a = 7.170$  (7) Å,  $b = 13.757$  (8) Å,  $c = 7.660$  (9) Å,  $\beta = 113.2$  (1)°,  $U = 694.4$  Å<sup>3</sup>,  $Z = 2$ ,  $d_{calcd} = 1.35$  cm<sup>-3</sup>,  $F(000) = 292$ ; (Mo  $K\alpha$ ) radiation,  $\lambda = 0.71069$  Å;  $\mu = 11.0$  cm<sup>-1</sup>;  $T = 298$  K; space group  $P2_1$ , from systematic absences  $0k0$ ,  $k = 2n + 1$ , and the successful structure determination.

Crystals were obtained as described above and one of approximate size 0.2 × 0.5 × 0.5 mm was set up to rotate around the  $a$  axis on a Stoe STADI2 diffractometer, and data were collected via variable width  $\omega$  scan. Background counts were 20 s and the scan rate of 0.033°/s was applied to a width of  $((1.5 + \sin \mu)/\tan \theta)$ . A total of 1327 ( $hkl$ ,  $\bar{h}kl$ ) independent reflections with  $2\theta < 50^\circ$  were measured of which 1041 with  $I > 3\sigma(I)$  were

used in subsequent refinement. The structure was solved by the Patterson method.

The positions of the remaining non-hydrogen atoms were obtained from Fourier syntheses. Methyl hydrogen atoms were included as rigid groups each with a common thermal parameter that successfully refined. Hydrogen atoms on the pentadienyl group were first positioned in trigonal positions, but their parameters were allowed to refine but with the constraint that the C–H bond length was 0.95 (5) Å. All hydrogen atoms refined successfully.

The structure was refined by full-matrix least-squares SHELX76.<sup>50</sup> The weighting scheme used was chosen to give equivalent values of  $w(F_o - F_c)^2$  over ranges of  $F_o$  and  $(\sin \theta)/\lambda$ . This was  $w = 1/(\sigma^2(F) + 0.003F^2)$  where  $\sigma(F)$  was taken from counting statistics. All atoms bar hydrogen were refined anisotropically. Scattering factors were taken from ref 51. The final R value was 0.061 ( $R_w = 0.062$ ). The absolute configuration was established by refining the ( $-x$ ,  $-y$ ,  $-z$ ) set of coordinates. These gave  $R = 0.065$ , and that configuration was therefore rejected.

Calculations were made by using SHELX76 on the CDC 7600 computer at the University of Manchester Computer Centre. Atomic coordinates are listed in Table IV. Details of the important interatomic distances and angles are listed in Table V. The anisotropic thermal parameters, remaining distances, observed and calculated structure factors, and hydrogen atom positions are given in the supplementary material.

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**Registry No.** **5**, 78805-93-3; **6** ( $L = PMe_3$ ), 89922-46-3; **6** ( $L = PMe_2Ph$ ), 89922-47-4; **6** ( $L = P(OEt)_3$ ), 89922-48-5; **6** ( $L = P-n-Bu_3$ ), 89922-49-6; **7** ( $L = PPh_3$ ), 89922-50-9; **7** ( $L = P(C_6H_{11})_3$ ), 89922-51-0; **7** ( $L = P(OPh)_3$ ), 89936-21-0; **7** ( $L = PMe_2Ph$ ), 89922-52-1; **7** ( $L = PMe_3$ ), 89922-53-2; **7** ( $L = P(OMe)_3$ ), 89922-54-3; **7** ( $L = P(OEt)_3$ ), 89922-55-4; **7** ( $L = AsPh_3$ ), 89936-22-1; ( $\eta^3-C_5H_7$ )Mn(CO)<sub>4</sub>, 90024-41-2; ( $\eta^3-C_5H_7$ )Mn(CO)<sub>3</sub>N<sub>2</sub>, 89936-23-2; ( $\eta^1-C_5H_7$ )Mn(CO)<sub>5</sub>, 89922-56-5; ( $\eta^5-C_5H_5$ )Mn(CO)<sub>2</sub>THF, 12093-26-4.

**Supplementary Material Available:** Tables of anisotropic thermal parameters, other angles and bond lengths, and structure factors (8 pages). Ordering information is given on any current masthead page.

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