the complexes in methanol are at the high-energy end of the ligand series, *i.e.*, close to those of the fluoride complexes. The value of R (V/VI) is also consistent with this position.

The exact nature of the porphyrin–metal d-orbital π interaction is difficult to describe since the structure of the complexes is unknown. One possibility is a tetragonal geometry with the metal atom in the plane of the four porphyrin nitrogen donors and the axial anion and solvent molecules at a somewhat larger distance from the metal. If a water molecule is not bound to the metal, then the geometry would be square pyramidal. For either of these arrangements the d_{xz}, d_{yz} orbitals would be of proper symmetry for overlap with the porphyrin-filled π orbitals. The d_{xz}, d_{yz} pair can also interact with the filled π orbitals on the axial anion. Competition for this orbital then could give rise to the observed anion dependence of the porphyrin $\pi \rightarrow \pi^*$ transition. It must be admitted, however, that the porphyrin interaction must be the more important of the two. The anion dependence is, after all, only a small perturbation on the manganese(III) porphyrin spectrum.

Another likely choice for the geometry of the manganese(III) porphyrin complex would be one in which the metal atom was out of the plane of the porphyrin and closer to the axial anion. The solvent molecule would then be weakly bound (if at all) to the metal in the axial position on the opposite side of the metal. This situation is in fact observed for the iron(III) porphyrin complexes.[22] In this case the separation of the d orbitals into σ and π bonding sets is not straightforward. For example, the d_{z^2} orbital can now mix into the filled $a_{2u}(\pi)$ orbital of the porphyrin.[20] Since the metal orbital is involved in bonding to the axial anion, some anion character can be entered into the $a_{2u}(\pi)$ porphyrin orbital.

The unusual porphyrin–manganese interaction suggested here is manifest in several other properties of the complexes. The materials are photochemically active, being reduced by visible light in the absence of air.[5,6] The presence of visible charge-transfer bands in the near-infrared provides a convenient route for the photoreduction of the complexes. Many simple manganese(III) complexes are photoactive, presumably for the same reason.[23] The absorption spectra indicate that the electronic structure of the metalloporphyrin is dependent on the anion (ligand) bound to the metal in the axial coordination positions. It seems reasonable to assume that the photochemical properties and redox potentials will also be dependent on these ligands.

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Hydrogen-1 Nuclear Magnetic Resonance Studies of the Formation and Decarbonylation of Diphosphine-Substituted Acetylmanganese Tricarbonyl Complexes

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Abstract: The reactions of a number of phosphorus donor ligands, L, with *cis*-$CH_3Mn(CO)_4L$ or *cis*-$CH_3COMn(CO)_4L$ were observed to fall into three categories: (1) when L is $P(OCH_2)_3CCH_3$ or $P(C_6H_5)_2H$, the exclusive product is 2,3-L_2-1-$CH_3COMn(CO)_3$ (facial); (2) for L equal to $P(C_6H_5)_2CH_3$, $P(OC_6H_5)_3$, or $P(C_2H_5)_3$, the only product observed is 2,4-L_2-1-$CH_3COMn(CO_3)$ (meridional *trans*-L_2); (3) the ligands $P(C_6H_5)(CH_3)_2$ and $P(OCH_3)_3$ were seen to yield facial complexes which rearranged rapidly to the meridional structure. These variations in products are explained in terms of L–L and L–acetyl steric interaction as the facial isomer is thermodynamically favored when L is relatively small and the meridional isomer is preferred when L has more stringent spacial requirements. Each meridional acetylmanganese complex, but not the facial complexes, was decarbonylated to 2,4-L_2-1-$CH_3Mn(CO)_3$. Structural assignments are based on infrared and ^1H nmr spectral observations and on dipole moments in selected cases.

Most of the investigations on the reactions of methylmanganese pentacarbonyl with Lewis bases have dealt with the formation of *cis*- and *trans*-$CH_3COMn(CO)_4L$ complexes and their subsequent decarbonylation to *cis*-$CH_3Mn(CO)_4L$ complexes.[2] However, there are two literature reports on the direct formation of $CH_3COMn(CO)_3L_2$ complexes from $CH_3Mn(CO)_5$ and L, where L is $(C_6H_5O)_3P_3$, $(C_6H_5O)_2PCH_3$,[3] or the chelating ligand $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$.[3,4]

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[1] NASA Fellow, Lehigh University, 1964–1967.

[2] C. S. Kraihanzel and P. K. Maples, *Inorg. Chem.*, 7, 1806 (1968).

[3] W. D. Bannister, M. Green, and R. N. Haszeldine, *Chem. Commun.*, 55 (1965).

[4] R. J. Mawby, D. Morris, E. M. Thorsteinson, and F. Basolo, *Inorg. Chem.*, 5, 27 (1966).

The results of a detailed examination of the formation of $CH_3COMn(CO)_3L_2$ complexes are presented in this paper in an effort to add to the present understanding of the mechanism of the carbonylation–decarbonylation process.

Experimental Section

Reagents. The sources of reagents and preparations for the $CH_3Mn(CO)_4L$ complexes have been previously reported.[2]

Experimental Techniques. Proton Magnetic Resonance. Nmr spectra were obtained with a Varian Associates A-60 spectrometer. Peak positions are relative to internal TMS at τ 10. Chemical shift values and coupling constants are considered accurate to ± 0.05 τ unit and ± 0.05 Hz, respectively.

In order to ascertain the course of formation of each $CH_3COMn(CO)_3L_2$ complex as unequivocally as possible, the reaction mixtures were prepared under nitrogen directly in nmr tubes and monitored with time. Liquid ligands and solvents were transferred to the tubes in precision syringes. Solvents were saturated with nitrogen prior to addition. Each tube was closed with an air-tight plastic cap (Protective Closures Co., Inc., Buffalo, N. Y.). The concentrations of reagents ranged from 0.1 to 0.5 *M*. Benzene, tetrahydrofuran, methylene chloride, and carbon disulfide were found to be useful nmr solvents in which to study these reactions, although for some of the ligands not all of these solvents could be employed.

In some instances aliquots of the reaction mixture were withdrawn under nitrogen from the nmr tube with a syringe and diluted 1:10 with *n*-hexane. Infrared spectra of these solutions were used only as a rough means of determining the stereochemical configuration of products.

Infrared Spectra. Routine spectral observations were made with a Perkin-Elmer Model 21 spectrophotometer. The data listed in Table III were obtained with a Perkin-Elmer Model 16 spectrophotometer equipped with a single-beam, double-pass grating monochromator which was calibrated with germane in the metallocarbonyl stretching region.

Dipole Moments. The method of Guggenheim[5] was used to calculate dipole moments from the relationship between the rate of change of dielectric constant with weight fraction for benzene solutions of the compounds. A Wissenshaftich Technische Werkstatten Type DM-01 dipolemeter was employed in the determination. Both the dipolemeter and the Abbe refractometer used for refractive index measurements were thermostated at 25.0 ± 0.1°. Benzene, used as the solvent, was distilled twice from lithium aluminum hydride to ensure the absence of water. The results are given in Table I.

Table I. Dipole Moments of Manganese Carbonyl Derivatives

	μ, D[a]
$CH_3Mn(CO)_5$	0.81[b]
cis-$CH_3Mn(CO)_4P(C_6H_5)_3$	5.18
2,4-$((CH_3)_2PC_6H_5)_2$-1-$CH_3COMn(CO)_3$	2.62
2,4-$((CH_3)_2PC_6H_5)_2$-1-$CH_3Mn(CO)_3$	2.57
2,4-$(CH_3P(C_6H_5)_2)_2$-1-$CH_3Mn(CO)_3$	2.28
2,4-$((C_6H_5O)_3P)_2$-1-$CH_3COMn(CO)_3$	3.01
2,4-$((C_6H_5O)_3P)_2$-1-$CH_3Mn(CO)_3$	2.60

[a] In benzene, 25°. [b] W. Beck, W. Hieber, and H. Tengler, *Chem. Ber.*, **94**, 862 (1961), report $\mu = 0.79 \pm 0.07$ D for $CH_3Mn(CO)_5$ and $\mu = 2.27$ D for $CH_3COMn(CO)_5$.

General. All melting points were obtained on samples sealed in nitrogen-filled capillary tubes. Analyses were performed by Professor V. B. Fish, Lehigh University, and Galbraith Laboratories, Knoxville, Tenn.

Disubstituted Acetylmanganese Tricarbonyl Complexes.[6] 2,4-Bis(diphenylmethylphosphine)-1-acetylmanganese Tricarbonyl. A mixture of methylmanganese pentacarbonyl, 0.40 g (1.90 mmoles), and 0.80 ml (4.30 mmoles) of diphenylmethylphosphine in 10 ml of THF, which had been previously saturated with carbon monoxide, was heated at 40° for 16 hr under a positive pressure of carbon monoxide. The yellow solution was filtered under nitrogen and the volume of the filtrate was reduced to approximately 3 ml with a stream of nitrogen. Addition of 5 ml of *n*-pentane to the concentrated solution caused the precipitation of a light yellow solid, which was collected by filtration, washed with cold *n*-pentane, and dried under a stream of nitrogen. The yield was 0.51 g (46%) of light yellow crystals, mp 104.0–105.5°.

Anal. Calcd for $C_{31}H_{29}O_4P_2Mn$: C, 63.93; H, 5.02. Found: C, 63.84; H, 5.25.

2,4-Bis(dimethylphenylphosphine-1-acetylmanganese Tricarbonyl. A mixture of 1.26 g (6.00 mmoles) of $CH_3Mn(CO)_5$ and 1.70 ml (12.00 mmoles) of dimethylphenylphosphine in 15 ml of benzene, which had been previously saturated with carbon monoxide, was heated for 48 hr at 40° under a positive pressure of carbon monoxide. The crude product, obtained by the method described in the previous synthesis, was recrystallized from a 1:5 methylene chloride-*n*-pentane mixture and yielded 1.16 g (42%) of pale yellow crystals, mp 131.0–132.0°.

Anal. Calcd for $C_{21}H_{25}O_4P_2Mn$: C, 55.03; H, 5.50. Found: C, 55.64; H, 5.87.

2,4-Bis(triphenyl phosphite)-1-acetylmanganese Tricarbonyl. A mixture of 0.56 g (2.70 mmoles) of $CH_3Mn(CO)_5$ and 1.50 ml (5.70 mmoles) of triphenyl phosphite in 20 ml of carbon monoxide saturated THF was allowed to react for 64 hr at 40° under a slight positive pressure of carbon monoxide. The light yellow solution was filtered under nitrogen and the solvent volume reduced under water aspirator vacuum until a white crystalline solid began to precipitate. A 5-ml portion of *n*-pentane was added to the solution to complete the precipitation. The resultant white solid was filtered under nitrogen, washed with *n*-pentane, and then recrystallized from a 1:4 THF-*n*-hexane mixture. The yield was 0.81 g (38%) of snow white crystals, mp 147.0–148.0° (lit.[3] 146.5–147.5°).

Anal. Calcd for $C_{39}H_{33}O_8P_2Mn$: C, 61.35; H, 4.14. Found: C, 61.67; H, 4.52.

2,3-Bis(4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)-1-acetylmanganese Tricarbonyl. A mixture of 0.21 g (1.00 mmole) of $CH_3Mn(CO)_5$ and 0.30 g (2.00 mmoles) of 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane in 30 ml of carbon monoxide saturated THF was heated for 48 hr at 45° under a slight positive pressure of carbon monoxide. A colorless solid, obtained in the manner employed in the previous synthesis, was recrystallized from dichloromethane by slowly reducing the volume of a saturated solution under a stream of nitrogen. This procedure yielded 0.30 g (67%) of white crystals, mp 290–320° dec.

Anal. Calcd for $C_{15}H_{21}O_{10}P_2Mn$: C, 37.73; H, 4.43. Found: C, 37.42; H, 4.58.

Complexes Obtained as Oils. As was also observed in the formation of certain *cis*-$CH_3COMn(CO)_4L$ complexes,[2] some disubstituted acetylmanganese tricarbonyls were obtained only as oils. Carbon and hydrogen analyses were not obtained for these compounds. However, spectral data (pmr and infrared) indicated that the purity of each complex was comparable to that of the analyzed crystalline $CH_3COMn(CO)_3L_2$ complexes as no excess solvent, excess ligand, $CH_3COMn(CO)_4L$, $CH_3Mn(CO)_4L$, or $CH_3Mn(CO)_3L_2$ could be detected.

The compounds 2,4-bis(triethylphosphine)-1-acetylmanganese tricarbonyl and 2,4-bis(trimethyl phosphite)-1-acetylmanganese tricarbonyl were obtained as an orange oil and pale yellow oil,

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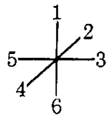
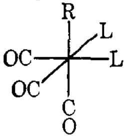
(5) E. A. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949).

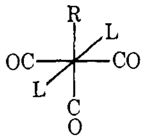
(6) The naming of these compounds, as well as the disubstituted methylmanganese tricarbonyl complexes, is based upon a method proposed by R. F. Pasternak and P. M. McDonnell, *Inorg. Chem.*, 4, 600 (1965). The six coordination sites of an octahedron are numbered as shown below. The methyl or acetyl group has been assigned the 1 position.



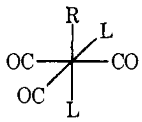
An alternative nomenclature which is more convenient when discussing these compounds is



facial



meridional *trans*-L



meridional *cis*-L

respectively, by heating a benzene or THF solution of a 1:2 mole ratio mixture of $CH_3Mn(CO)_5$ and the ligand at 40–50° for 48 hr under a positive pressure of carbon monoxide. The preparation of 2,3-bis(diphenylphosphine)-1-acetylmanganese tricarbonyl had to be carried out at room temperature to prevent decomposition of the product. Each of the above reactions was monitored by withdrawing aliquots from the reaction as a function of time and observing the various changes that took place in the nmr spectrum of the mixture.

Disubstituted Methylmanganese Tricarbonyl Complexes. 2,4-Bis(diphenylmethylphosphine)-1-methylmanganese Tricarbonyl. A mixture of 1.00 g (4.70 mmoles) of $CH_3Mn(CO)_5$ and 2.00 ml (10.80 mmoles) of diphenylmethylphosphine in 20 ml of deoxygenated benzene was refluxed under nitrogen for 16 hr. The yellow-orange solution was filtered under nitrogen. After the filtrate had been concentrated to 3 ml under water aspirator vacuum, 10 ml of *n*-pentane was added. The volume of the mixture was reduced by evaporation under vacuum until a sizable mass of orange crystals had precipitated. The solid was collected by filtration and recrystallized by slowly concentrating a *n*-pentane solution under a stream of nitrogen. The yield was 1.49 g (56%) of orange crystals, mp 145.0–146.5°.

Anal. Calcd for $C_{30}H_{29}O_3P_2Mn$: C, 64.98; H, 5.27. Found: C, 64.86; H, 5.35.

2,4-Bis(dimethylphenylphosphine)-1-methylmanganese Tricarbonyl. A synthetic procedure identical with that presented for 2,4-bis(diphenylmethylphosphine)-1-methylmanganese tricarbonyl was followed in preparing the dimethylphenylphosphine analog. A mixture of 1.00 g of (4.70 mmoles) of $CH_3Mn(CO)_5$ and 1.50 ml (10.60 mmoles) of dimethylphenylphosphine in 20 ml of benzene yielded 0.90 g (44%) of orange crystalline solid, mp 112.0–113.5°.

Anal. Calcd for $C_{20}H_{25}O_3P_2Mn$: C, 55.82; H, 5.86. Found: C, 56.01; H, 6.06.

2,4-Bis(triethylphosphine)-1-methylmanganese Tricarbonyl. A mixture of 0.21 g (1.00 mmole) of $CH_3Mn(CO)_5$ and 0.30 ml (2.00 mmoles) of triethylphosphine was refluxed under nitrogen in 10 ml of deoxygenated benzene for 18 hr. The deep orange solution was filtered under nitrogen and evaporated to dryness under vacuum. A solution of the residue in 15 ml of *n*-pentane was concentrated by evaporation under a stream of nitrogen until a sizable mass of orange crystals had precipitated. The solid was collected by filtration and recrystallized twice from *n*-pentane to yield 0.094 g (24%) of orange crystals, mp 44.0–46.0°.

Anal. Calcd for $C_{16}H_{33}O_3P_2Mn$: C, 49.73; H, 8.52. Found: C, 49.67; H, 8.51.

2,4-Bis(trimethyl phosphite)-1-methylmanganese Tricarbonyl. A mixture of 0.40 g (1.90 mmoles) of $CH_3Mn(CO)_5$ and 0.50 ml (4.30 mmoles) of trimethyl phosphite was refluxed under nitrogen in 15 ml of deoxygenated benzene for 24 hr. The work-up of the reaction was similar to that for 2,4-bis(diphenylmethylphosphine)-1-acetylmanganese tricarbonyl. Recrystallization of the crude colorless product from *n*-hexane produced 0.51 g (67%) of white crystals, mp 60.0–61.5°.

Anal. Calcd for $C_{10}H_{21}O_9P_2Mn$: C, 29.87; H, 5.22. Found: C, 29.73; H, 5.53.

2,4-Bis(triphenyl phosphite)-1-methylmanganese Tricarbonyl. A mixture of 1.00 g (4.70 mmoles) of $CH_3Mn(CO)_5$ and 2.63 ml (10.00 mmoles) of triphenyl phosphite was refluxed under nitrogen in 20 ml of deoxygenated THF for 12 hr. The crude product, obtained in a manner similar to that used in the previous synthesis, was recrystallized from a 1:4 mixture of THF and *n*-hexane by slowly reducing the solvent volume under a stream of nitrogen. This procedure yielded 2.30 g (63%) of white crystals, mp 148–150°.

Anal. Calcd for $C_{40}H_{33}O_9P_2Mn$: C, 62.02; H, 4.29. Found: C, 62.02; H, 4.65.

Unsuccessful Attempts to Prepare Certain Disubstituted Methylmanganese Tricarbonyl Complexes. Bis(triphenylphosphine)-methylmanganese Tricarbonyl. A mixture of 0.21 g (1.00 mmole) of $CH_3Mn(CO)_5$ and 0.54 g (2.00 mmoles) of triphenylphosphine in 10 ml of deoxygenated THF was refluxed for 48 hr. The amount of carbon monoxide evolved during reaction was approximately equal to that expected for formation of a monosubstituted methylmanganese tetracarbonyl product. The physical properties of the isolated solid (pmr, infrared, and melting point) indicated that the exclusive product of the reaction was *cis*-triphenylphosphinemethylmanganese tricarbonyl. Triphenylarsine and triphenylstibine derivatives likewise resulted in formation of the corresponding monosubstituted methyl products. Extended heating of these samples in THF with excess ligand yielded no further reaction.

Bis(diphenylphosphine)methylmanganese Tricarbonyl. A mixture of 0.21 g (1.00 mmole) of $CH_3Mn(CO)_5$ and 0.26 ml (2.00 mmoles) of diphenylphosphine in 10 ml of deoxygenated benzene was refluxed under nitrogen for 4 hr. The red solution was cooled and filtered under nitrogen, and the solvent was evaporated completely under water aspirator vacuum. Attempts to crystallize the resultant red oil from a variety of solvents were unsuccessful. The infrared spectrum of the oil indicated that it contained considerable manganese carbonyl. The nmr spectrum of the oil contained no observable methyl or acetyl proton resonances.

Bis(4-methyl-2,6,7-trioxa-1-phosphobicyclo[2.2.2]octane)methylmanganese Tricarbonyl. Numerous attempts were made to obtain this as yet unknown compound by extensive heating of mixtures of $CH_3Mn(CO)_5$ and $P(OCH_2)_3$ in THF or benzene. The final product obtained in each reaction was $2,3\text{-}(P(OCH_3)_2)_2\text{-}1\text{-}CH_3COMn(CO)_3$. Likewise, as expected, heating of solutions of the preformed complex for days resulted in essentially a quantitative recovery of the disubstituted acetylmanganese product.

Spectral Results and Structural Assignments

The formation of a disubstituted acetylmanganese complex according to reaction 1, or by the sequential

$$\textit{cis}\text{-}CH_3Mn(CO)_4L + L \xrightarrow{\text{room temp}} CH_3COMn(CO)_3L_2 \quad (1)$$

$$CH_3Mn(CO)_5 + L \xrightarrow{\text{room temp}} CH_3COMn(CO)_4L \quad (2)$$

$$CH_3COMn(CO)_4L + L \xrightarrow[\text{under CO}]{50\text{–}70°} CH_3COMn(CO)_3L_2 + CO \quad (3)$$

reactions 2 and 3, was monitored by nmr. Reaction 1 was found to proceed readily in a number of solvents at room temperature for the phosphorus donor ligands examined. Although reaction 2 is also known to proceed readily at room temperature,[2] the conversion of $CH_3COMn(CO)_4L$ to the disubstituted product according to reaction 3 is considerably more difficult and slower than is the formation of the product by reaction 1. *However, reactions 1 and 3, insofar as is possible to detect, proceed by identical paths to identical products for a particular L in spite of this considerable difference in relative rates.* There is no unique over-all reaction that can be written for the formation of the $CH_3COMn(CO)_3L_2$ complexes. However, the reactions do fall very nicely into three categories: (a) those in which only $2,3\text{-}L_2\text{-}1\text{-}CH_3COMn(CO)_3$, also to be called *fac*-$CH_3COMn(CO)_3L_2$, is formed; (b) those in which only $2,4\text{-}L_2\text{-}1\text{-}CH_3COMn(CO)_3$, also denoted as *mer*-(*trans*-L_2)$CH_3COMn(CO)_3$, is observed; and (c) those in which the facial isomer is generated initially but then subsequently isomerizes completely to $2,4\text{-}L_2\text{-}1\text{-}CH_3COMn(CO)_3$. As will become readily apparent from the ensuing description of the time-dependent nmr observations of these systems, such a categorization could not have been made just on the basis of the products isolated by the bench procedures as given in the Experimental Section of this paper.

Category a Reactions. $P(OCH_2)_3CCH_3$. A mixture of equimolar amounts of $P(OCH_2)_3CCH_3$ and *cis*-$CH_3COMn(CO)_4P(OCH_2)_3CCH_3$ in dichloromethane was prepared in an nmr tube and heated at 55° for 24 hr. During this time the proton signals of the reactants decreased steadily and resonance signals for a single $CH_3COMn(CO)_3(P(OCH_2)_3CCH_3)_2$ compound appeared. Unfortunately, this reaction could not be monitored in benzene, carbon disulfide, or tetrahydrofuran owing to the low solubility of the product in these solvents. At completion of the reaction, the nmr spectrum (Table II) was identical with that of the product isolated

Table II. ^{1}H Nmr Data for $CH_3COMn(CO)_3L_2$ and $CH_3Mn(CO)_3L_2$ Complexes[a]

Ligand = L	Group	$CH_3COMn(CO)_3L_2$				$CH_3Mn(CO)_3L_2$			
		C_6H_6	THF	CS_2	CH_2Cl_2	C_6H_6	THF	CS_2	CH_2Cl_2
CO	CH_3	7.76	7.43	7.45	7.43	10.23	10.16	10.11	10.12
2,4-$P(C_6H_5)_2CH_3$	CH_3	7.95	*b*	8.48	8.23	10.47 (7.4; T)	10.93 (7.4; T)	11.04 (7.4; T)	10.63 (7.5; T)
	CH_3-P	8.08 (7.9; D)	*b*	8.05 (8.0; D)	7.96 (7.8; D)	8.18 (6.8; D)	*b*	8.13 (7.4; D)	8.08 (7.0; D)
	C_6H_5	*b*	2.58	2.65	2.58	*b*	2.60	2.69	2.53
2,4-$P(C_6H_5)(CH_3)_2$	CH_3	7.90	*b*		7.24	10.72 (7.8; T)	10.92 (7.8; T)	11.04 (7.8; T)	10.65 (7.8; T)
	CH_3-P	8.53 (7.9; D)	*b*		8.27 (7.9; D)	8.63 (7.4; D)	*b*	8.38 (7.2; D)	8.31 (7.3; D)
	C_6H_5	*b*	2.56		2.60	*b*	2.65	2.57	2.57
2,3-$P(C_6H_5)(CH_3)_2$	CH_3	7.31	*b*	*c*					
	CH_3-P	8.75 (Figure 3)	*b*		8.58 (Figure 3)	*d*			
	C_6H_5	*b*	2.54						
2,4-$P(OC_6H_5)_3$	CH_3	6.98	7.45	7.65	*e*	9.52 (8.0; T)	10.13 (8.0; T)	10.60 (8.0; T)	*e*
	C_6H_5	*b*	2.83	2.95		*b*	2.80	2.96	
2,4-$P(C_2H_5)_3$	CH_3	7.48	7.68			10.50 (7.0; T)	10.80 (7.0; T)		
	CH_2-P	8.45 (comp)	*b*	*c*	*e*	8.47 (comp)	*b*	*c*	*e*
	CH_3-C	9.05 (comp)	*b*			8.98 (comp)	*b*		
2,4-$P(OCH_3)_3$	CH_3	7.18	7.65	7.70		10.05 (7.5; T)	10.50 (7.6; T)	10.60 (7.6; T)	
	CH_3O	6.53 (11.0; VCT)	*b*	6.37 (10.9; VCT)	*e*	6.55 (10.8; VCT)	*b*	6.42 (10.9; VCT)	*e*
2,3-$P(OCH_3)_3$	CH_3	7.22	7.62	7.65		*d*			
	CH_3O	*f*							
2,3-$P(OCH_2)_3CCH_3$	CH_3				7.58				
	CH_2O	*g*	*g*	*g*	5.73 (4.7; VCT)	*d*			
	CH_3C				2.16				
2,3-$P(C_6H_5)_2H$	CH_3	7.48		7.68					
	H-P	3.86 (380; D)	*e*	4.15 (380; D)	*e*	*d*			
	C_6H_5	*b*		2.76					

[a] Chemical shift (*J* in Hz; multiplicity). Chemical shift in τ units relative to TMS at τ 10. Multiplicity: D, doublet; T, triplet; comp, complex; VCT, virtual coupling triplet, see text. The observed areas of the signals agreed with suggested formulas in all instances. [b] Unable to observe owing to coincidence of solvent and ligand signals. [c] Ligand and solvent react. [d] No evidence seen for formation of complex. [e] Not examined. [f] Signal obscured by signal of OCH_3 protons of 2,4-$P(OCH_3)_3)_2$-1-$CH_3COMn(CO)_3$. [g] Not obtainable owing to insolubility of complex in the solvent.

Table III. Infrared Bands for $CH_3COMn(CO_3)L_2$ and $CH_3Mn(CO)_3L_2$ Compounds[a]

Compound	ν_{CO}, cm^{-1}			>C=O
2,3-$CH_3COMn(CO)_3[P(OCH_2)_3CCH_3]_2$[b]	2032 (s)	1963 (s)	1944 (s)	1604
2,3-$CH_3COMn(CO)_3[P(C_6H_5)_2H]_2$[c]	2005 (s)	1935 (s)	1918 (s)	1578
2,4-$CH_3COMn(CO)_3[P(OC_6H_5)_3]_2$[b]	2051 (vw)	1970 (s)	1956 (s)	1596
2,4-$CH_3COMn(CO)_3[P(OCH_3)_3]_2$[c,d]	2046 (vw)	1960 (s)	1941 (s)	1592
2,4-$CH_3COMn(CO)_3[P(C_6H_5)_2CH_3]_2$	2019 (vw)	1930 (s)	1907 (s)	1578
2,4-$CH_3COMn(CO)_3[PC_6H_5(CH_3)_2]_2$	2013 (vw)	1924 (s)	1903 (s)	1573
2,4-$CH_3COMn(CO)_3[P(C_2H_5)_3]_2$[c]	2010 (vw)	1919 (s)	1896 (s)	1581
2,4-$CH_3Mn(CO)_3[P(OC_6H_5)_3]_2$[b]	2031 (vw)	1957 (s)	1926 (s)	. . .
2,4-$CH_3Mn(CO)_3[P(OCH_3)_3]_2$	2024 (vw)	1943 (s)	1905 (s)	. . .
2,4-$CH_3Mn(CO)_3[P(C_6H_5)_2CH_3]_2$[b]	1996 (vw)	1910 (s)	1880 (s)	. . .
2,4-$CH_3Mn(CO)_3[PC_6H_5(CH_3)_2]_2$	1997 (vw)	1915 (s)	1881 (s)	. . .
2,4-$CH_3Mn(CO)_3[P(C_2H_5)_3]_2$	1991 (vw)	1903 (s)	1887 (s)	. . .

[a] In hexane solution unless otherwise noted. [b] In dichloroethylene. [c] Oils, see text. [d] In tetrachloroethylene.

in the preparatory scale reaction. This complex is assigned the structure 2,3-L_2-1-$CH_3COMn(CO)_3$, as its infrared spectrum contains three strong metallocarbonyl stretching bands (Table III). If this complex had either of the two possible meridional structures, then the highest frequency CO band would be relatively weak and would correspond to a symmetrical stretching of *trans*-CO groups. The other two CO bands should be strong.[7,8] The equivalence of the phosphite groups, as required by this structure, is apparent from the sharp singlet at τ 9.22 for the ligand methyl protons. There is one further important feature in this nmr spectrum, namely the apparent 1:2:1 triplet at τ 5.73 for the ligand methylene protons. This phenomenon arises from strong ^{31}P–^{31}P coupling and until very recently had been noted only in the ^1H nmr spectra of metal complexes in which phosphorus donor ligands are found *trans* to each other.[9] Grim[10] has obtained ^{31}P nmr spectra of phosphine complexes and shown that ^{31}P–^{31}P coupling between *cis* positioned ligands is strongest for ligands which are considered to have the greatest π-acceptor capacity. Inasmuch as $P(OCH_2)_3CCH_3$ is known to have a relatively large π-acceptor ability, it is not unreasonable to expect a manifestation of ^{31}P–^{31}P virtual coupling in the ^1H nmr spectrum of 2,3-$(P(OCH_2)_3CCH_3)_2$-1-$CH_3COMn(CO)_3$. The separation of the outer lines of this triplet corresponds closely to $J_{CH_2\text{-}P}$ and is 4.70 Hz, a value which is somewhat less than the ~11-Hz separation between the outer lines in similar virtual coupling triplets observed for 2,4-$(P(OCH_3)_3)_2$-1-$CH_3COMn(CO)_3$ and 2,4-$(P(OCH_3)_3)_2$-1-$CH_3Mn(CO)_3$ to be considered below. Thus, the apparent *cis* coupling observed here is less strong than *trans* coupling of phosphorus nuclei in agreement with Grim's[10] observations.

$P(C_6H_5)_2H$. The reaction of *cis*-$CH_3COMn(CO)_4$-$P(C_6H_5)_2H$ with a second mole of $P(C_6H_5)_2H$ in carbon disulfide at 40° was complete within 8 hr. Only a single disubstituted acetylmanganese tricarbonyl complex appeared to be formed in solution. The nmr spectrum of this product was identical with the spectrum of the oil obtained in the bench preparation. Longer heating of this product led to decomposition which presumably arises from rupture of the P–H bond. The nmr spectrum of the product prior to onset of this decomposition indicated that two $P(C_6H_5)_2H$ were bonded to manganese, and a single sharp doublet for the phosphine hydride proton (Table II) suggested equivalence of the ligands. The structure of the complex is 2,3-$(P(C_6H_5)_2H)_2$-1-$CH_3COMn(CO)_3$ as three strong metallocarbonyl stretching bands (Table III) are seen in the infrared spectrum of the complex.

Category b Reactions. The reactions of each of the three ligands $P(C_6H_5)_2CH_3$, $P(OC_6H_5)_3$, and $P(C_2H_5)_3$ with either a corresponding *cis*-$CH_3COMn(CO)_4L$ or *cis*-$CH_3Mn(CO)_4L$ complex were found to be similar. In each case the formation of only a single new acetyl group resonance signal for a $CH_3COMn(CO)_3L_2$ complex was observed. The infrared and nmr spectral properties of the complexes prepared in solution and the corresponding products of the bench preparations were identical.

Each disubstituted complex has a meridional structure which is evidenced by the relative intensities of the metallocarbonyl stretching bands given in Table III. However, other evidence must be employed to differentiate between the two meridional structural possibilities. The nmr spectrum of the $P(C_6H_5)_2CH_3$ complex contains only a simple doublet for the bonded ligand methyl groups (Table II) in several different solvents and thus indicates that the ligands are equivalent and the complex must be 2,4-$(P(C_6H_5)_2CH_3)_2$-1-$CH_3COMn(CO)_3$. Although a similar argument cannot be employed for the complex with $P(OC_6H_5)_3$ as the ligand, the dipole moment of this complex is very close to that of $CH_3COMn(CO)_5$. This would be expected only if the $P(OC_6H_5)_3$ groups are mutually *trans* and this complex must be 2,4-$(P(OC_6H_5)_3)_2$-1-$CH_3COMn(CO)_3$. The $P(C_2H_5)_3$ complex is also considered to be of the *mer-trans*-L_2 type, but the evidence is primarily circumstantial. First, the wave numbers of the metallocarbonyl stretching bands are quite reasonable when compared to the wave numbers of the other 2,4-L_2-1-$CH_3COMn(CO)_3$ complexes. Secondly, the nmr spectrum of the ethyl groups, although not indicating clearly that all ethyl groups are equivalent, is essentially identical with the spectrum of 2,4-$(P(C_2H_5)_3)_2$-1-$CH_3Mn(CO)_3$, whose structure has been assigned unequivocally (see below), and very different from the proton resonance pattern of the free ligand. Unfortunately, a dipole moment was not readily obtainable as this substance could only be isolated as an oil.

Category c Reactions. $P(C_6H_5)(CH_3)_2$. Several selected nmr spectra from a time study of the reaction

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(7) F. A. Cotton, *Inorg. Chem.*, 3, 702 (1964).

(8) L. W. Houk and G. R. Dobson, *ibid.*, 5, 2119 (1966).

(9) W. E. Stanclift and D. G. Hendricker, *ibid.*, 7, 1242 (1968), and references cited therein.

(10) S. O. Grim, D. A. Wheatland, and P. R. McAllister, *ibid.*, 7, 161 (1968).

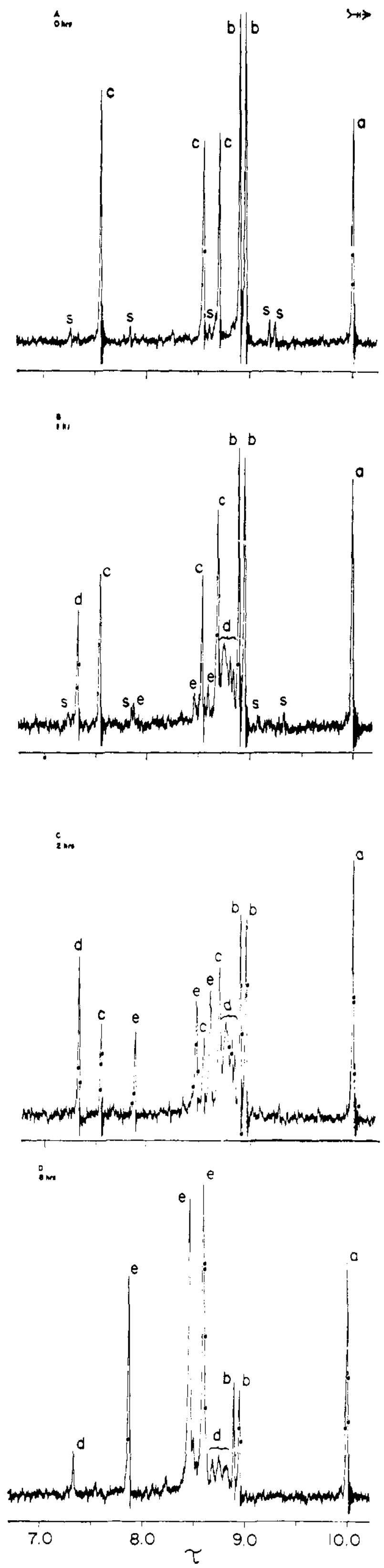

Figure 1. Selected time-dependent nmr spectra from the reaction of *cis*-$CH_3COMn(CO)_4P(C_6H_5)(CH_3)_2$ with a second mole of $P(C_6H_5)(CH_3)_2$ in benzene at 64°: a, TMS; b, L; c, $CH_3COMn(CO)_4L$; d, 2,3-L_2-1-$CH_3COMn(CO)_3$; e, 2,4-L_2-1-$CH_3COMn(CO)_3$.

between approximately equimolar amounts of *cis*-$CH_3COMn(CO)_4P(C_6H_5)(CH_3)_2$ and $P(C_6H_5)(CH_3)_2$ in benzene at 64° are presented in Figure 1. Initially, three resonance signals are observed: (i) a sharp singlet at τ 7.53 for the acetyl methyl protons of the starting material; (ii) a doublet at τ 8.62 for the methyl protons of bonded $P(C_6H_5)(CH_3)_2$; (iii) a doublet at τ 8.93 for the methyl protons of the free $P(C_6H_5)(CH_3)_2$. Within 1 hr under the specified conditions, resonance signals corresponding to two $CH_3COMn(CO)_3(P(C_6H_5)(CH_3)_2)_2$ complexes may be seen. The more rapidly formed acetylmanganese complex, whose signals are indicated by d in Figure 1, exhibits a complex pattern centered at τ 8.75 for the methyl groups of the bonded ligands. By comparison, the signal for the ligand methyl groups of the more slowly formed isomer, indicated by e in Figure 1, is a simple doublet with J_{P-CH_3} = 7.9 Hz. Owing to the rapid conversion of the first isomer to the second, no attempt was made to isolate the first isomer. However, a low-resolution infrared spectrum of the first isomer was obtained. An aliquot from a reaction mixture at about the stage represented by Figure 1B was diluted with *n*-hexane, and an infrared spectrum was taken with a solution of *cis*-$CH_3COMn(CO)_4P(C_6H_5)(CH_3)_2$ in benzene–hexane as reference. This procedure showed quite clearly that the infrared spectrum of the first formed complex contained a strong metallocarbonyl stretching band at 2000 cm^{-1} and a strong, asymmetric band centered near 1914 cm^{-1} which appeared to consist of two close-lying bands. An acetylcarbonyl stretching band at 1591 cm^{-1} was also seen. This band pattern is like that seen for the facial complexes of category a and indicates that this complex is most likely 2,3-$(P(C_6H_5)(CH_3)_2)_2$-1-$CH_3COMn(CO)_3$.

The signals of the second formed complex, indicated by e in Figure 1, increase continuously with time until after 12 hr all of the first formed isomer has disappeared. The nmr and infrared spectra of this second and apparently thermodynamically stable complex are identical with the spectra of the pure complex isolated in the bench scale preparation reported in the Experimental Section. The structure 2,4-$(P(C_6H_5)(CH_3)_2)_2$-1-$CH_3COMn(CO)_3$ can be readily assigned to this second product as the ligands are obviously nmr equivalent and the pattern of the metallocarbonyl stretching bands is that expected for a meridional complex. Furthermore, this structural assignment is supported by the low dipole moment of 2.62 D obtained on the isolated complex. It is interesting to note that no virtual coupling is observed for the ligand methyl groups in this compound even though this is the ligand which almost invariably exhibits virtual coupling in *trans*-substituted complexes.[9]

The complex splitting pattern for the ligand methyl resonances of 2,3-$(P(C_6H_5)(CH_3)_2)_2$-1-$CH_3COMn(CO)_3$ in benzene and dichloromethane is shown in Figure 2. Although these signals may be rationalized on the basis of virtual coupling, two facts appear to dictate against this possibility. Firstly, since no virtual coupling is observed for the meridional isomer with this ligand, and inasmuch as *trans* coupling is normally greater than *cis* coupling, then no observable coupling of *cis*-oriented ligands might be expected. Secondly, the pattern of this signal is solvent dependent. Although this fact does not preclude virtual coupling, it is more likely that this is a manifestation of the dependency of chemical shifts upon solvents. The line separations which have been indicated in Figure 2 are very close to the J_{P-CH_3} coupling constants noted for *cis*-$CH_3COMn(CO)_4P(C_6H_5)(CH_3)_2$, *cis*-$CH_3Mn(CO)_4P(C_6H_5)(CH_3)_2$,[2] and 2,4-$(P(C_6H_5)(CH_3)_2)_2$-1-$CH_3COMn(CO)_3$. The existence of these two pairs of lines is indicative of environmentally nonequivalent methyl groups on phosphorus, a situation which can arise only if the plane of symmetry of the molecule does not include the Mn–P bonds.[9] This concept provides support for our assignments based on the infrared observations since only the facial isomer, and not the meridional structure, satisfies this symmetry requirement. Although, an unequivocal explanation of the origin of the broad "central" band observed in the partial spectra given in Figure 2 is not easily provided, the band most likely is the result of relatively rapid relaxation of the ligand methyl protons through an exchange process resulting from conformational changes of the ligands. Owing to the transient nature of this complex, no temperature-dependence study of the nature and relative areas of the various parts of the total signal was undertaken.

$P(OCH_3)_3$. The nmr spectral results for the reaction between *cis*-$CH_3COMn(CO)_4P(OCH_3)_3$ and a second mole of the phosphite ester in benzene at 50° were observed to parallel the observations with the previously discussed ligand, $P(C_6H_5)(CH_3)_2$. In particular, two new substituted acetylmanganese tricarbonyl complexes are generated. The acetyl signal of the first formed $P(OCH_3)_3$ complex, τ 7.22, reached a maximum after a few hours and then decreased as the thermodynamically favored isomer, acetyl signal at τ 7.18, was formed. Unfortunately, the spectral characteristics of the first formed isomer in the τ 6.0–7.0 region were not observable since the rate of formation of the second isomer with $P(OCH_3)_3$ as the ligand is sufficiently fast that at no time can a spectrum characteristic of primarily the first formed isomer be seen. For the same reason, no unambiguous infrared spectrum of the first isomer was obtained.

The thermodynamically stable isomer appears to be 2,4-$(POCH_3)_3)_2$-1-$CH_3COMn(CO)$ as the relative intensities of the metallocarbonyl stretching bands are those expected of a meridional complex, and the two phosphite ester ligands appear to be nmr equivalent. A 1:2:1 triplet with a broad central peak is centered at τ 6.53 and apparently is the result of virtual coupling. An identical but much more rapid reaction sequence was observed when a 1:1 mixture of *cis*-$CH_3Mn(CO)_4$-$P(OCH_3)_3$ and trimethyl phosphite was observed as a function of time at room temperature.

In retrospect, the first formed isomer must then be either 2,3-$(P(OCH_3)_3)_2$-1-$CH_3COMn(CO)_3$ or 2,6-$(P(OCH_3)_3)_2$-1-$CH_3COMn(CO)_3$. The previous observations with $P(C_6H_5)(CH_3)_2$ and the nature of the reactions described under categories a and b lead us to suggest that the more likely structure of the first formed isomer is the facial one.

Decarbonylation Reactions. Decarbonylation of each of the 2,4-L_2-1-$CH_3COMn(CO)_3$ complexes to a 2,4-L_2-$CH_3Mn(CO)_3$ compound was effected most readily by heating solutions of the acetyl complexes at reflux in various solvents. When these reactions were monitored by infrared and nmr methods, no evidence for any other disubstituted methylmanganese tricarbonyl complex was observed. The structures of the products are readily assigned, as the relative intensities of the metallocarbonyl bands, which are listed in Table III, are as expected only for a meridional complex. That the phosphorus donor ligands are *trans* and not *cis* is apparent from (i) the equivalence of the ligand proton signals and (ii) the highly symmetrical and sharp triplets observed for the methyl group on manganese which can result only from splitting by two equivalent phosphorus nuclei. Further support for these structures is provided by the relatively low dipole moments (Table I) observed for the complexes where L is $P(C_6H_5)(CH_3)_2$, $P(C_6H_5)_2(CH_3)$, or $P(OC_6H_5)_3$.

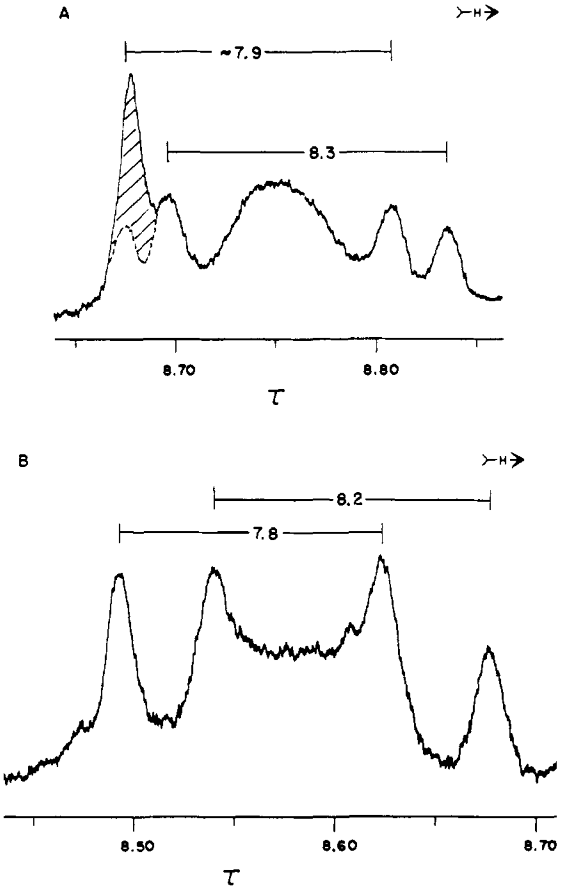

Figure 2. Ligand methyl resonances for 2,3-$(P(C_6H_5)(CH_3)_2)_2$-1-$CH_3COMn(CO)_3$: A, in benzene with an overlapping signal indicated; B, in dichloroethylene.

No disubstituted methylmanganese tricarbonyl complexes could be obtained from the two acetylmanganese compounds with the 2,3-L_2-1-$CH_3COMn(CO)_3$ structures. The compound where L is the constrained phospite ester was heated in refluxing benzene for several days without any observable change. By comparison, the complex with $P(C_6H_5)_2H$ decomposed upon heating at reflux in benzene but did not form the sought-after product.

Discussion

Mechanistic Considerations. Although the carbonylation of $CH_3Mn(CO)_5$ to form $CH_3COMn(CO)_5$ is known to proceed by way of a methyl migration step,[11] it cannot be stated with certainty that such a mechanism is involved in the formation of *cis*-$CH_3COMn(CO)_4L$

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(11) K. Noack and F. Calderazzo, *J. Organometal. Chem.*, 10, 101 (1967).

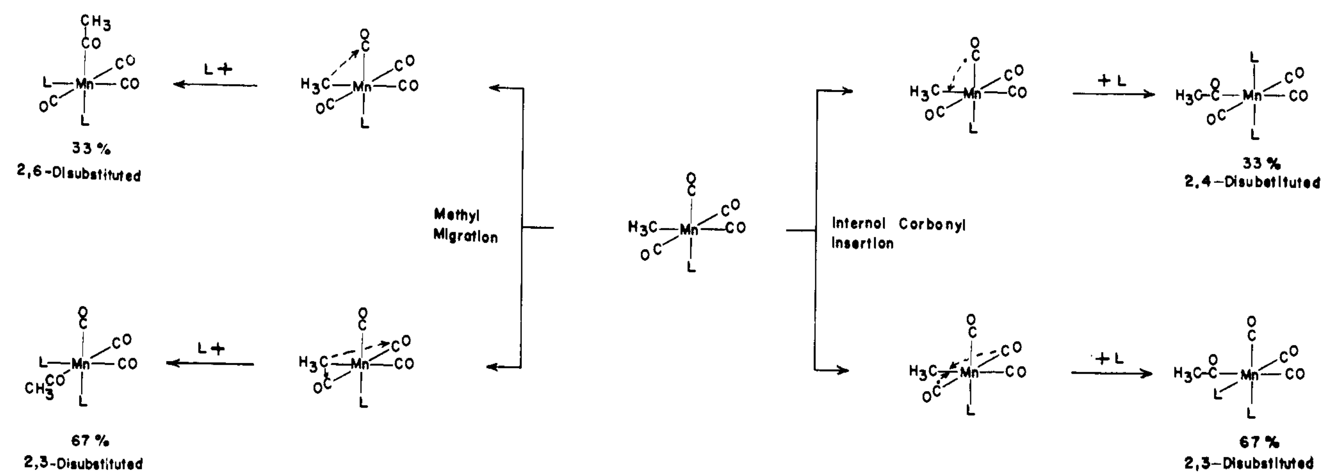

Figure 3. Theoretical distribution of products expected from the reaction of a second mole of L with *cis*-$CH_3Mn(CO)_4L$ according to the methyl migration and internal carbonyl insertion mechanisms.

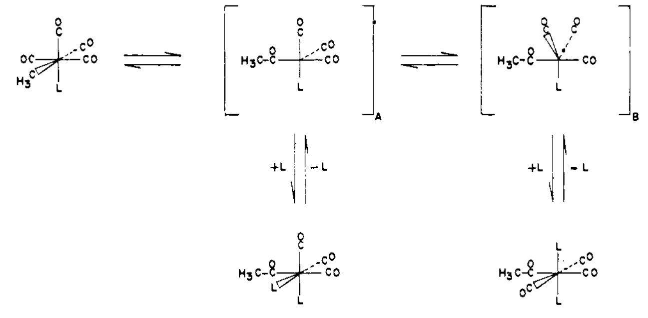

Figure 4. A proposed mechanism to account for the nature of products obtained in the reaction of L with *cis*-$CH_3Mn(CO)_4L$.

complexes from $CH_3Mn(CO)_5$ and Lewis bases.[2] In particular, the possibility of an internal CO insertion reaction cannot be eliminated from consideration at this time. The strict application of these two basic processes to the reaction of a second mole of L with *cis*-$CH_3Mn(CO)_4L$, that is reaction 1, has been diagrammed in Figure 3. The only assumption made in preparing this diagram is that the incoming L group occupies the site vacated by either the methyl group (methyl migration) or a CO group (internal insertion). The obvious observation to make is that the distribution of products obtained experimentally with the various ligands employed in this study does not agree at all with the prediction of either mechanistic process.

Therefore, a possible mechanism, which is based on the recent proposal by Noack, Ruch, and Calderazzo,[11,12] is offered in Figure 4 as an explanation of the stereochemical results observed in this study. The formation of the square-pyramidal, formally unsaturated intermediate [A], which may arise by either methyl migration or internal CO insertion, is suggested on the basis of earlier kinetic work in this area in which the rate-determining step in the carbonylation reaction is independent of the concentration of the incoming ligand. Once [A] is formed, combination with L ought to yield 2,3-L_2-1-$CH_3COMn(CO)_3$. Inasmuch as steric interaction, between L and the CH_3CO group were shown to be important in the cases of those $CH_3COMn(CO)_4L$ complexes in which *cis* ⇄ *trans* isomerism can occur, such steric interaction ought to be compounded in a *fac*-$CH_3COMn(CO)_3L_2$ complex. Thus, only with those ligands for which steric interaction is minimized either because of compactness of the ligand, such as with $P(OCH_2)_3CCH_3$, or because the ligand may attain a "comfortable" position, such as $P(C_6H_5)_2H$, will a 2,3-L_2-1-$CH_3COMn(CO)_3$ complex result. In terms of current bonding concepts and exclusive of the effects of steric interaction, this structure would allow for maximum π bonding between the metal and CO and thus would be the most favored configuration.

However, should the energy of steric repulsion in 2,3-L_2-1-$CH_3COMn(CO)_3$ approximate or exceed the energy gained in maximum π bonding between CO and the metal, then conversion of this isomer to the structurally less-hindered complex 2,4-L_2-1-$CH_3COMn(CO)_3$ might occur. This appears to be the case with $P(C_6H_5)(CH_3)_2$ and $P(OCH_3)_3$ as the initially formed facial isomer does revert to the *mer-trans*-L_2 configuration completely in time. Although none of the ligands studied yielded an equilibrium mixture of these two isomers, surely, some ligand with a steric requirement intermediate between those of ligands in classes a and c will be found. The suggestion is made here that intermediate [A] may slowly convert to a trigonal-bipyramidal intermediate [B], or some other possible configuration, which may readily add a second molecule of L in the equatorial plane *trans* to the L group to yield the final thermodynamically stable product.

Category b ligands, $P(C_6H_5)_2CH_3$ and $P(OC_6H_5)_3$, apparently have such stringent steric requirements that either (i) no facial product can be formed at all and [A] converts directly to [B] or (ii) the amount of facial product is very small and eludes detection by nmr. As to why $P(C_2H_5)_3$ is not in class c with $P(OCH_3)_3$ is not clear, but possibly steric repulsion with $P(C_2H_5)_3$ is just enough greater than that of $P(OCH_3)_3$ to prohibit formation of a detectable amount of the facial isomer.

To carry this steric argument one step further, a second molecule of triphenylphosphine, which demonstrates significant steric demands by forming both *cis*- and *trans*-$CH_3COMn(CO)_4L$,[2,12] cannot be added to manganese to form a $CH_3COMn(CO)_3L_2$ complex.

Isomerizations of a similar nature with substituted halomanganese carbonyl derivatives have been reported, and the distribution of products was found to depend

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[12] W. Noack, M. Ruch, and F. Calderazzo, *Inorg. Chem.*, 7, 345 (1968).

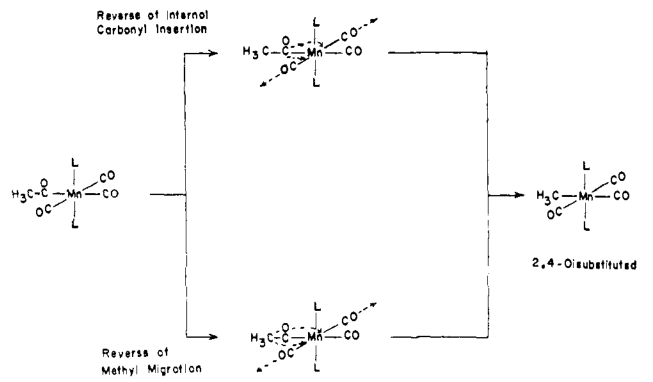

Figure 5. The decarbonylation of a 2,4-L_2-1-$CH_3COMn(CO)_3$ complex to 2,4-L_2-1-$CH_3Mn(CO)_3$.

on L and the halogen in several cases.[13] These workers were able to detect some of these isomerizations *in situ* only by infrared studies.

The decarbonylation of 2,4-L_2-1-$CH_3COMn(CO)_3$ is illustrated in Figure 5. Either a methyl migration or an internal carbonyl desertion mechanism can account for the observation. The inability of 2,3-$(P(OCH_2)_3CCH_3)_2$-1-$CH_3COMn(CO)_3$ to be decarbonylated after long heating suggests that CO groups *trans* to L are more difficult to remove than CO *trans* to CO as has been mentioned earlier.[2] Although, the possibility exists of a slow rearrangement of this facial product to 2,4-$(P(OCH_2)_3CCH_3)_2$-1-$CH_3COMn(CO)_3$ which in turn might decarbonylate to 2,4-$(P(OCH_2)_3CCH_3)_2$-1-$CH_3Mn(CO)_3$, no evidence of any type was observed to suggest that such does occur even to a small extent. Presumably, the P–Mn bond in this complex is so robust that ligand dissociation, which might allow [B] in Figure 3 to form, is prohibited. However, it is premature to state that only 2,4-L_2-1-$CH_3COMn(CO)_3$ compounds are capable of decarbonylation.

Nmr Spectra. A comparison of the chemical shifts for the methylmanganese protons of the diligated complexes with the earlier data[2] on the *cis*-$CH_3Mn(CO)_4L$ complexes reveals that the addition of a second molecule of the phosphorus donor ligands leads to a further increase in the shielding of the methylmanganese protons as well as the ligand protons. This effect is less striking for the CH_3COMn complexes, and in fact there appear to be some inconsistencies. In general, ligands which reveal the greatest shielding of the CH_3Mn protons are those which have the poorest ability to remove charge from the metal by way of π-acceptor bonding.

An interesting feature in the nmr spectra of these complexes is the variation in J_{P-CH_3} for $P(C_6H_5)(CH_3)_2$ and $P(C_6H_5)_2CH_3$ with the chemical shifts of the ligand methyl protons as shown in Figure 6. Doubling of J_{P-CH_3} upon complexation is a result of increased s character in the P–CH_3 bond as the hybridization at phosphorus becomes more nearly sp^3 in nature upon sharing of the unbonded pair, which has considerable s character in the free ligand, with the metal. Furthermore, Bent[14] has suggested that the magnitude of the coupling constants ought to be linearly related to the proton chemical shifts for series of compounds where variations in hybridization occur. Furthermore, a correlation of these factors with the charge on phosphorus in a series of saturated organophosphorus compounds has been demonstrated.[15] The Mn–P bond in any one of the complexes studied here or earlier[2] must be partially polarized with the positive charge on phosphorus and the negative charge on manganese. The relative magnitude of the positive charge on phosphorus, as well as the amount of s character in the P–CH_3 bond, will be determined by the electron-withdrawing capacities of the other groups bonded to manganese. This order is CO > PR_3 > CH_3CO > CH_3. Thus, the chemical shifts (τ) of the ligand methyl groups ought to increase linearly with decreasing coupling in the order: free ligand > $CH_3Mn(CO)_4L$ > $CH_3COMn(CO)_4L$ > $CH_3Mn(CO)_3L_2$ > $CH_3COMn(CO)_3L_2$. The plots in Figure 6 show excellent agreement with this idea. Others have noted a similar relationship.[16,17] In exception to this relationship, 2,3-$(P(C_6H_5)(CH_3)_2)_2$-1-$CH_3COMn(CO)_3$ falls very badly out of line, possibly because of the peculiar, but as yet defined, circumstance which gives rise to the somewhat unusual signal shown in Figure 2.

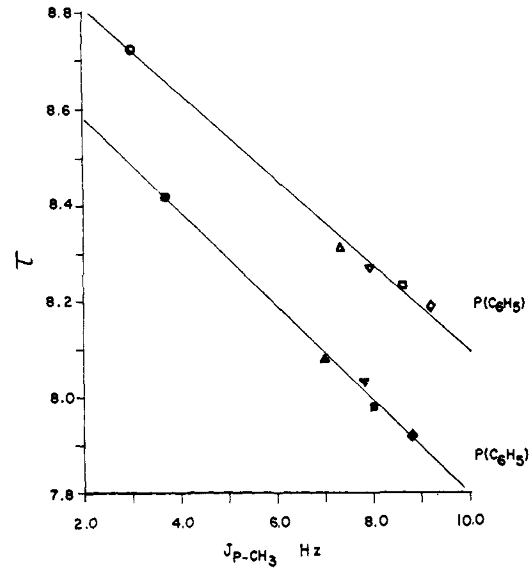

Figure 6. Variation of the chemical shifts of the ligand methyl protons with J_{P-CH_3} for ○, L; □, $CH_3Mn(CO)_4L$; ◇, $CH_3COMn(CO)_4L_2$; △, $CH_3Mn(CO)_3L_2$; ▽, $CH_3COMn(CO)_3L_2$ (in dichloromethane).

Complexes of the other ligands also seem to fit the trend shown in Figure 6, but variations in $J_{P-L(H)}$ between $CH_3Mn(CO)_4L$ and $CH_3COMn(CO)_4L$ and between $CH_3Mn(CO)_3L_2$ and $CH_3COMn(CO)_3L_2$ are very small. This suggests that the electron-withdrawing capacity of the ligands, particularly the phospite esters, must be sufficiently great to overshadow the difference between the electron effects of the CH_3–Mn and CH_3CO–Mn groups.

The same factors which are responsible for the linear relationship shown in Figure 6 also manifest themselves in the chemical shifts of the CH_3Mn protons and in the

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

(14) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

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coupling of these protons with the phosphorus nuclei given in Table II. For example, J_{P-MnCH_3} is greater in cis-$CH_3Mn(CO)_4L$[2] than in 2,4-L_2-1-$CH_3Mn(CO)_3$ for the same L as the positive charge on phosphorus in the monoligated complex is greater than in the diligated complex. Also, those complexes with the greater positive charge on phosphorus should have the greater negative charge on manganese. The chemical shift (τ) of the CH_3Mn protons (Table II) reflect this fact as these protons are usually more shielded in the disubstituted complexes than in cis-$CH_3Mn(CO)_4L$.[2]

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Competition Studies and the Stereochemistry for the Base Hydrolysis and Induced Aquation of Some Acidoamminebis(ethylenediamine)cobalt(III) Ions

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Abstract: The stereochemistry of the *cis*- and *trans*-hydroxo products from the base hydrolysis of $(+)_{589}$-$[Co(en)_2NH_3X]^{2+}$ (X = Cl, Br, NO_3) and *trans*-$[Co(en)_2NH_3X]^{2+}$ (X = Cl, NO_3) is independent of the nature of the leaving groups. In the presence of anions (Y^-) such as N_3^-, NCS^-, and NO_2^-, base hydrolysis leads to incorporation of the anion, and the competition ratio $[Co(en)_2NH_3Y]^{2+}/[Co(en)_2NH_3OH]^{2+}$ also is independent of the leaving group. Also, the stereochemistry of the $[Co(en)_2NH_3Y]^{2+}$ products is constant for each competing anion within each series of reactants. These results suggest the formation of a common intermediate or intermediates from a series of reactants.

In some recent studies[1-3] on the mechanism of base hydrolysis of acidopentaamminecobalt(III) complexes, results are reported which appear to support an SN1CB mechanism. The studies embrace competition experiments[1,2] and the stereochemistry of the products,[3] and the conclusion concerning the mechanism was drawn from the fact that all the results were independent of the nature of the leaving group. This suggested the formation of a common intermediate by the following path[4]

$$[Co(NH_3)_5X]^{2+} + OH^- \overset{\text{fast}}{\rightleftarrows} [Co(NH_3)_4NH_2X]^+ + H_2O$$

$$[Co(NH_3)_4NH_2X]^+ \xrightarrow{\text{slow}} [Co(NH_3)_4NH_2]^{2+} + X^-$$

$$[Co(NH_3)_4NH_2]^{2+} + H_2O \xrightarrow{\text{fast}} [Co(NH_3)_5OH]^{2+}$$

Bimolecular attack of OH^- at the cobalt atom (SN2)[5]

$$[Co(NH_3)_5X]^{2+} OH^- \xrightarrow{k} [Co(NH_3)_5OH]^{2+} + X^-$$

does not permit the competition products observed and would be unlikely to give the same stereochemistry for the products with different substrates. The SN2CB mechanism[6]

$$[Co(NH_3)_5X]^{2+} + OH^- \overset{\text{fast}}{\rightleftarrows} [Co(NH_3)_4NH_2X]^+ + H_2O$$

$$[Co(NH_3)_4NH_2X]^+ + H_2O \xrightarrow{k} [Co(NH_3)_5OH]^{2+} + X^-$$

or

$$[Co(NH_3)_4NH_2X]^+ + Y^- + H^+ \longrightarrow [Co(NH_3)_5Y]^{2+} + X^-$$

still contains X in the intermediate and would also be expected to give different competition values and stereochemistry of the products for different substrates. All of these mechanistic proposals conform to the observed rate law $R = k[\text{complex}][OH^-]$.

In one of these previous studies the stereochemistry of the products of base hydrolysis of *trans*-$[Co(NH_3)_4(^{15}NH_3)X]^{2+}$ ions (X = Cl, Br, NO_3) was examined using pmr spectroscopy.[3] Also the stereochemistry of the competition product $[Co(NH_3)_4(^{15}NH_3)N_3]^{2+}$, obtained by base hydrolysis in the presence of N_3^-, was examined by the same technique. Close to 50% *cis*- and 50% *trans*-aquo product was observed for all the substrates, whereas the azido product was described as totally *trans*. This aspect of the original study[3a] was in error and the correct result is 70% *cis* and 30% *trans* for the azido product.[3b] The results were rationalized tentatively in favor of a trigonal-bipyramidal intermediate. However, no firm conclusions were reached concerning the intermediate's structure and the possibility of the intermediate competing for the species in solution and rearranging before the competition was not excluded.

The ^{15}N isotope experiments were expensive and the isolation of the competition products for the pmr measurements was difficult. To look at the problems more

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