X-Ray diffraction, proton resonance, and infrared evidence indicate that the hydrogen occupies a coordination site in its octahedral complexes.[4-6] Because of the small size of the hydride ligand, it may be possible for it to slip between two of the bulkier ligands without producing much steric strain. If the activation energy for this inversion process were small, then the reaction would be extremely rapid.

However, also plausible at this juncture is an exchange mechanism in which the hydrogen ionizes as a proton, leaving behind the five-coordinate $Mn(PF_3)_x$-$(CO)_{5-x}^-$ anion which undergoes an inversion by the re-formation of the hydride, or, alternately, it could be attributed to the random attack of the proton at various positions of the anion to give all possible hydride isomers. By this approach, one need not postulate that the hydride atom is small enough to allow the other groups to pass by it, only that it be able to ionize. The pK of the $HMn(CO)_x(PF_3)_{5-x}$ species can be estimated to be 7—the same as that of the parent carbonyl.[3]

The substitution of bulky preferentially σ-bonding organic phosphines into manganese pentacarbonyl hydride results in the formation of geometric isomers.[15] These ligands place a greater electron density on the central metal atom which results in an increase in the metal–hydrogen bond strength leading to a decrease in acidic properties. If the inversion takes place by a proton ionization path, then the isolability of geometric isomers is perhaps explicable.

However, it cannot necessarily be concluded that this is the only explanation for the occurrence of isomers in species such as $HMn(CO)_4(PR_3)$. In the first place, all acidic properties are probably not lost. We could not find any data for the pK of any organic-phosphine-

substituted manganese hydrides. However, the pK of $HCo(CO)_4$ changes from 1 to 7 on going to $HCo(CO)_3P(C_6H_5)_3$.[16] A similar change with $HMn(CO)_4P(C_6H_5)_3$ would yield a pK of 12–14 which might still allow for rapid exchange. The increase in size of the ligand and the effect of its steric hindrance would probably make inversion much slower and would be a far more important factor than pK decrease.

The relative behavior of manganese pentacarbonyl hydride toward fluoro and organic phosphines is paralleled by a similar relationship in iron carbonyls. In the iron carbonyls, no ionization is possible. The $Fe(PF_3)_x(CO)_{5-x}$ species show every sign of undergoing internal inversion, whereas compounds of the types $Fe(CO)_4(PR_3)$ and $Fe(CO)_3(PR_3)_2$ do not.[17] Experiments in progress[18] show clearly that very little change in the $Fe(PF_3)_x(CO)_{5-x}$ species needs to be made to change the isomer mixture. The change to which we refer is solvolysis of the P–F bond to P–OR groups.

The existence of a rapid inversion mechanism for manganese pentacarbonyl hydride is consistent with $C^{13}O$-exchange experiments performed by Kaesz, *et al.*[5] In a rigid octahedral structure, the hydride should exert a *trans* effect on the axial carbon monoxide so that $C^{13}O$ enrichment at this position would occur at a different rate than for the radial positions. Their results showed that enrichment occurs at the same rate for substitution at both positions. This equivalence of the carbonyls to exchange could be brought about by a rapid internal inversion.

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The Reactions of Lewis Bases with Methylmanganese Pentacarbonyl

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The reactions of a variety of Lewis bases with $CH_3Mn(CO)_5$ were examined as a function of time by H^1 nmr and infrared spectral methods. Triphenylphosphine, triphenylarsine, and trimethyl phosphite react with $CH_3Mn(CO)_5$ to yield a mixture of *cis*- and *trans*-$CH_3COMn(CO)_4L$ complexes. Other phosphorus donor ligands, triphenylstibine, and various amines yield exclusively *cis*-$CH_3COMn(CO)_4L$ derivatives. All acetylmanganese complexes, except those with L = amine, were shown to decarbonylate upon heating to yield exclusively *cis*-$CH_3Mn(CO)_4L$. The reaction equilibria are affected by variations in the nucleophilicities and steric requirements of the ligands. A modified methyl-migration mechanism is able to explain the stereochemistry of the products of the decarbonylation reaction.

Introduction

The reactions of methylmanganese pentacarbonyl, $CH_3Mn(CO)_5$, with amines[2] and a number of phos-

phine and arsine derivatives[3,4] to produce monoligated acetylmanganese tetracarbonyl complexes, CH_3CO-$Mn(CO)_4L$, have been known for some time. More

(1) NASA Fellow, Lehigh University, 1964–1967.
(2) K. A. Keblys and A. H. Fibley, *J. Am. Chem. Soc.*, **82**, 4204 (1960).

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recently, attention has been focused on the elucidation of the structures of these products and the implications that these structures lead to with respect to the mechanism of the carbonylation–decarbonylation equilibrium. The first evidence that both *cis-* and *trans*-CH$_3$COMn(CO)$_4$L (where L is triphenylphosphine,[5,6] iodide ion,[5] or triphenylarsine[6]) could be formed was the appearance of two H[1] nmr signals of unequal intensities between τ 7 and 8 for the acetyl groups of the two geometric isomers. A recent study[7] has shown unequivocally that the initial assignments[6] of the two signals for *cis-* and *trans*-CH$_3$COMn(CO)$_4$P-(C$_6$H$_5$)$_3$ were incorrect and should be reversed.

Our interest in the mechanism of the carbonylation–decarbonylation reaction led us to examine in close detail by nmr and infrared spectral techniques the reactions of a number of Lewis bases with CH$_3$Mn(CO)$_5$. The results of our studies on the formation of CH$_3$CO-Mn(CO)$_4$L complexes and their subsequent decarbonylation to CH$_3$Mn(CO)$_4$L derivatives are reported in this paper.

Experimental Section

Reagents.—Triphenylphosphine, triphenylarsine, triphenylstibine, and triphenylbismuthine (Eastman Organic Chemicals, Rochester, N. Y.) were used as received. No impurities in commercial samples of triethylphosphine (K & K Laboratories, Plainview, N. J.), dimethylphenylphosphine (Columbia Organic Chemicals, Columbia, S. C.), trimethyl phosphite, and triphenyl phosphite (Baker Chemical Co.) could be detected by nmr and these materials were used without purification. Diphenylphosphine had been prepared previously in these laboratories from diphenylchlorophosphine and lithium aluminum hydride and was pure (glpc and nmr). Diphenylmethylphosphine[8] and 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane[9] were prepared by literature methods. Reagent grade pyridine (Baker Chemical Co.), aniline (Fisher Scientific Co.), cyclohexylamine, dicyclohexylamine, and N-methylcyclohexylamine (Abbott Laboratories, North Chicago, Ill.) were fractionally distilled under nitrogen before use.

Manganese carbonyl was purchased from Pressure Chemical Co. (Pittsburgh, Pa.) and used as received. Methylmanganese pentacarbonyl was prepared by the method of King[10] and sublimed twice before use. Acetylmanganese pentacarbonyl, prepared according to the procedure of Closson,[11] was purified by sublimation at 25° at water aspirator vacuum. An nmr spectrum of a freshly prepared solution of the sublimed sample in carbon tetrachloride initially indicated an absence of methylmanganese pentacarbonyl. However, the decarbonylated product was formed slowly as a function of time in the solution.

Tetrahydrofuran was refluxed over and distilled from calcium hydride or lithium aluminum hydride. Benzene was dried with phosphorus pentoxide and subsequently distilled. Other solvents were used as received as drying to remove traces of water appeared to have no effect on the reactions studied.

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.

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(8) L. Maier, *Progr. Inorg. Chem.*, **5**, 85 (1963).

(9) C. W. Heitsch and J. G. Verkade, *Inorg. Chem.*, **1**, 392 (1962).

(10) R. B. King, "Organometallic Syntheses," Vol. I, Academic Press Inc., New York, N. Y., 1965, p 147.

(11) R. D. Closson, J. Kozikowski, and T. H. Coffield, *J. Org. Chem.*, **22**, 598 (1957).

Chemical shift values and coupling constants are considered accurate to ±0.05 τ unit and ±0.05 Hz, respectively.

Solutions used to determine the course of a reaction with time were prepared directly in the nmr tubes. Liquid ligands and the solvents were transferred to the tubes in precision syringes. All operations were performed in a nitrogen atmosphere. 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.). For the work reported in this paper, equimolar amounts of CH$_3$Mn(CO)$_5$ and the ligand were employed. The concentrations of reagents ranged from 0.1 to 0.5 *M*. Benzene, tetrahydrofuran, and carbon disulfide were found to be useful nmr solvents in which to study these reactions.

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 the product(s).

Infrared Spectra.—Routine spectral observations were carried out on a Perkin-Elmer Model 21 spectrophotometer. Data for analyzed solids and oils of high purity were obtained with a Perkin-Elmer Model 16 spectrophotometer equipped with a single-beam, double-pass grating monochromator. The instrument was calibrated with germane in the metallocarbonyl stretching region.

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.

CH$_3$COMn(CO)$_4$L Complexes.—Preparations for the acetylmanganese tetracarbonyl derivatives of triphenylphosphine,[3,4] triphenylarsine,[4] triphenylstibine,[4] cyclohexylamine,[2] aniline,[2] and N-methylcyclohexylamine[2] have been reported. Each of the compounds reported below, except for the first one, is being reported for the first time.

cis-**4-Methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octaneacetylmanganese Tetracarbonyl.**—A mixture of 0.39 g (1.80 mmol) of CH$_3$Mn(CO)$_5$ and 0.28 g (1.80 mmol) of 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane in 15 ml of deoxygenated THF was allowed to react under nitrogen for 3 hr at 25°. The solution was filtered and the filtrate volume was reduced to 5 ml under water aspirator vacuum. Addition of 10 ml of *n*-pentane to the pale yellow solution caused precipitation of a white crystalline solid. After cooling the solution to 0°, the solid was collected and washed with *n*-pentane. The white solid was dissolved in a minimum amount of benzene after which *n*-pentane was added until the cloud point was reached. Concentration of the solution under a stream of nitrogen produced 0.52 g (90%) of white crystals which decomposed from 140 to 210°. *Anal.* Calcd for C$_{11}$H$_{12}$O$_8$PMn: C, 36.89; H, 3.38. Found: C, 36.83; H, 3.48.

cis-**Diphenylmethylphosphineacetylmanganese Tetracarbonyl.**—A mixture of 0.30 g (1.40 mmol) of CH$_3$Mn(CO)$_5$ and 0.30 ml (1.40 mmol) of diphenylmethylphosphine in 10 ml of deoxygenated benzene was allowed to react at 25° under nitrogen for 48 hr. The benzene was evaporated in a stream of nitrogen until a solid began to precipitate. At this point 5 ml of *n*-pentane was added to the solution and the precipitated solid was collected by filtration. The yellow solid was recrystallized from *n*-pentane by slowly reducing the volume of a saturated solution under a nitrogen stream. This yielded 0.40 g (70%) of light yellow crystals, mp 68.0–69.0°. *Anal.* Calcd for C$_{19}$H$_{16}$O$_5$PMn: C, 55.63; H, 3.93. Found: C, 55.84; H, 3.98.

cis-**(Triphenyl phosphite)acetylmanganese Tetracarbonyl.**—A mixture of 0.20 g (0.93 mmol) of CH$_3$Mn(CO)$_5$ and 0.25 ml (0.93 mmol) of triphenyl phosphite in 10 ml of deoxygenated THF was allowed to react under nitrogen at 25° for 3 hr. The reaction time had to be limited to 3 hr in order to prevent conversion of the monosubstituted acetyl derivative to a second unidentified acetyl species (see text). The solution was filtered and the volume of the filtrate was reduced to 5 ml under water aspirator vacuum. Addition of 15 ml of *n*-pentane to the solution caused precipitation of a white crystalline solid which was collected by

filtration, washed with cold *n*-pentane, and dried under a stream of nitrogen. This procedure yielded 0.28 g (58%) of pure white crystals, mp 69.5–70.0°. *Anal.* Calcd for $C_{24}H_{18}O_8PMn$: C, 55.40; H, 3.49. Found: C, 55.55; H, 3.71.

Substances Isolated as Oils.—A mixture containing approximately 1.10 mmol of $CH_3Mn(CO)_5$ and 1.00 mmol of the phosphine ligand (dimethylphenylphosphine, triethylphosphine, trimethyl phosphite, or diphenylphosphine) in 10 ml of deoxygenated benzene was allowed to react for 5–10 hr at room temperature. The mixture was then filtered and concentrated under aspirator vacuum to leave a yellow oil. Addition of *n*-pentane (or *n*-hexane) did not induce crystallization even upon long standing at 0°. In each preparation, removal of the solvent under vacuum left a clear, yellow to orange-yellow oil. The slight excess of $CH_3Mn(CO)_5$ which had been added to ensure complete consumption of the phosphine was readily removed under vacuum. The substances prepared in this manner were not submitted for elemental analysis. However, the purity of each of these materials was as high as that for any one of the solid, recrystallizable complexes on which an analysis was obtained. Within the limits of detection by nmr, no excess $CH_3Mn(CO)_5$, free ligand, residual solvents, or $CH_3Mn(CO)_4L$ was present in any of the samples for which data are reported in the tables.

cis-**CH₃Mn(CO)₄L Complexes.**—The preparation of *cis*-$CH_3Mn(CO)_4P(C_6H_5)_3$ has been previously reported.[6,12]

cis-**Triphenylarsinemethylmanganese Tetracarbonyl.**—A mixture of 0.21 g (1.00 mmol) of $CH_3Mn(CO)_5$ and 0.31 g (1.00 mmol) of triphenylarsine in 20 ml of deoxygenated benzene was refluxed for 8 hr under nitrogen. The solution was filtered and concentrated to a volume of 5 ml. Orange crystals were obtained by adding *n*-pentane and blowing down the solution with a stream of nitrogen. Recrystallization was effected by redissolving the solid in *n*-hexane and blowing down under nitrogen until a large mass of crystals had formed. The solid was collected by filtration, washed with *n*-hexane, and dried in a stream of nitrogen. This yielded 0.30 g (61%) of orange crystals, mp 102.5–103.5°. *Anal.* Calcd for $C_{23}H_{15}O_4AsMn$: C, 56.58; H, 3.72. Found: C, 56.87; H, 4.05.

cis-**Triphenylstibinemethylmanganese Tetracarbonyl.**—This preparation was similar to the previous one except that a reflux time of 24 hr was required. A mixture of 0.21 g (1.00 mmol) of $CH_3Mn(CO)_5$ and 0.35 g (1.00 mmol) of triphenylstibine yielded 0.35 g (65%) of orange crystals, mp 114.5–116.0°. *Anal.* Calcd for $C_{23}H_{15}O_4SbMn$: C, 51.62; H, 3.39. Found: C, 51.80; H, 3.50.

cis-**(Triphenyl phosphite)methylmanganese Tetracarbonyl.**—A solution of 0.42 g (2.00 mmol) of $CH_3Mn(CO)_5$ and 0.53 ml (2.00 mmol) of triphenyl phosphite in 15 ml of deoxygenated THF was refluxed under nitrogen for 5 hr. The yellow solution was cooled and filtered under nitrogen. The filtrate was concentrated under water aspirator vacuum until light yellow crystals began to precipitate. After addition of 10 ml of *n*-pentane, the solution was cooled to 0°. The pale yellow crystals were collected by filtration under nitrogen and washed with cold *n*-pentane. Recrystallization was effected by slowly reducing the volume of an *n*-pentane solution of the solid in a stream of nitrogen until a sizable mass of crystals was obtained. The procedure yielded 0.38 g (39%) of light yellow crystals, mp 79.0–80.5° (lit.[13] mp 71–72°). *Anal.* Calcd for $C_{23}H_{18}O_7PMn$: C, 56.11; H, 3.69. Found: C, 56.27; H, 3.81.

cis-**4-Methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octanemethylmanganese Tetracarbonyl.**—A solution of 0.21 g (1.00 mmol) of $CH_3Mn(CO)_5$ and 0.15 g (1.00 mmol) of 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane in 10 ml of deoxygenated THF was refluxed under nitrogen for 8 hr. The work-up procedure was similar to the previous one except that a 1:5 mixture of THF and *n*-hexane was used in the recrystallization step. This procedure yielded 0.24 g (72%) of white crystals, mp 180–

(12) R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **86**, 5043 (1964).

(13) W. Kieber, G. Faulhaber, and F. Thenbert, *Z. Anorg. Allgem. Chem.*, **314**, 125 (1964).

200° dec. *Anal.* Calcd for $C_{10}H_{12}O_7PMn$: C, 36.38; H, 3.66. Found: C, 36.56; H, 3.65.

CH₃Mn(CO)₄L Complexes Isolated as Oils.—Each of the products obtained upon reaction of an excess of $CH_3Mn(CO)_5$ with diphenylmethylphosphine, dimethylphenylphosphine, diphenylphosphine, triethylphosphine, or trimethyl phosphite was an oil and could not be induced to crystallize. Filtration of solutions of these products removed suspended material. Exhaustive pumping on the oils which remained after removal of the solvent resulted in samples which upon careful nmr examination contained no detectable amounts of free ligand, solvent, residual $CH_3Mn(CO)_5$, or $CH_3COMn(CO)_4L$.

Unsuccessful Reactions.—A number of attempts were made to prepare $CH_3COMn(CO)_4L$ complexes where L would be triphenylbismuthine, phosphorus trichloride, dicyclohexylamine, diphenylamine, tris(*o*-tolyl)phosphine, or phenylphosphine. The first five ligands did not react at all under our reaction conditions. Phenylphosphine did produce an acetylmanganese compound, but this compound decomposed rapidly in solution.
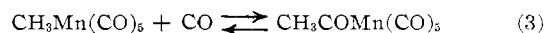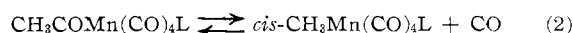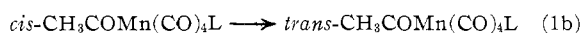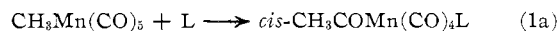
Several attempts were made to isolate *cis*-$CH_3COMn(CO)_4$-NC_5H_5 from solutions which had been monitored by infrared and nmr methods. However, these solutions were extremely oxygen sensitive and only red, oily materials were obtained which could not be purified.

Inasmuch as a number of methylmanganese complexes containing phosphine ligands had been prepared, it was of interest to try to obtain an amine-substituted methylmanganese tetracarbonyl. However, whenever mixtures of $CH_3Mn(CO)_5$ and amines (aniline, cyclohexylamine, pyridine, or N-methylcyclohexylamine) were refluxed in deoxygenated benzene, only red oils were obtained which contained manganese carbonyl but no $CH_3Mn(CO)_4L$ complexes.

Irradiation of a mixture of $CH_3Mn(CO)_5$ and cyclohexylamine in deoxygenated benzene for 30 hr with a PCZ9G-1 photochemical immersion lamp (Ultra-violet Products, Inc., San Gabriel, Calif.) yielded only *cis*-cyclohexylamineacetylmanganese tetracarbonyl.

Results

Although an explicit definition of the nature of the reaction between $CH_3Mn(CO)_5$ and a Lewis base is not obtainable by any one chemical or physical technique, such information is accessible though a complementary usage of H^1 nmr and infrared spectral methods. In general, the nmr results listed in Tables I and II were obtained by following the reaction between equimolar amounts (0.1–0.5 M) of $CH_3Mn(CO)_5$ and the ligand in a sealed nmr tube as a function of time. In this way, both the isomers generated according to reaction 1 and the materials involved in the auxiliary equilibria represented by reactions 2 and 3 could be detected from their separate, readily discernible signals. Each reac-

$$CH_3Mn(CO)_5 + L \longrightarrow \textit{cis-}CH_3COMn(CO)_4L \quad (1a)$$

$$\textit{cis-}CH_3COMn(CO)_4L \longrightarrow \textit{trans-}CH_3COMn(CO)_4L \quad (1b)$$

$$CH_3COMn(CO)_4L \rightleftarrows \textit{cis-}CH_3Mn(CO)_4L + CO \quad (2)$$

$$CH_3Mn(CO)_5 + CO \rightleftarrows CH_3COMn(CO)_5 \quad (3)$$

tion was studied in several solvents in order to eliminate the possibility of coincidental chemical shifts for *cis*- and *trans*-$CH_3COMn(CO)_4L$. However, the possibility always exists that a trace amount of a second isomer might not be detected under the experimental conditions.

The wave numbers for the metallocarbonyl stretching modes of the $CH_3COMn(CO)_4L$ and $CH_3Mn(CO)_4L$ complexes are given in Table III. The appear-

TABLE I

H¹ NMR DATA FOR $CH_3COMn(CO)_4L$ AND $CH_3Mn(CO)_4L$ COMPLEXES[a]

Ligand	Group	$CH_3COMn(CO)_4L$ C_6H_6	THF	CS_2	$CH_3Mn(CO)_4L$ C_6H_6	THF	CS_2	Free ligand C_6H_6	THF	CS_2
CO	CH_3	7.76	7.43	7.45	10.23	10.16	10.11			
cis-P(C₆H₅)₃	CH_3	7.58	7.72	7.78	10.14 (J = 7.6)	10.50 (J = 7.6)	10.59 (J = 7.6)			
	C_6H_5	b	2.57	2.67	b	2.53	2.67	b	2.70	2.82
trans-P(C₆H₅)₃	CH_3	7.32	7.43	7.51	c	c	c			
	C_6H_5	b	2.57	2.67				b	2.70	2.82
cis-As(C₆H₅)₃	CH_3	7.50	7.60	7.64	10.03	10.33	10.45			
	C_6H_5	b	2.55	2.67	b	2.52	2.63	b	2.70	2.80
trans-As(C₆H₅)₃	CH_3	7.38	7.41	7.50	c	c	c			
	C_6H_4	b	2.55	2.67	b			b	2.70	2.80
cis-Sb(C₆H₅)₃	CH_3	7.53	7.50	7.55	10.08	10.33	10.36			
	C_6H_5	b	2.55	2.65	b	2.52	2.63	b	2.70	2.73
cis-P(C₆H₅)₂CH₃	CH_3	7.60	7.72	7.75	10.25 (J = 8.6)	10.50 (J = 8.4)	10.56 (J = 8.6)			
	CH_3P	8.22 (J = 8.4)	7.87 (J = 8.8)	7.98 (J = 8.6)	8.54 (J = 7.9)	8.04 (J = 8.0)	8.14 (J = 7.9)	8.65 (J = 4.1)	b	8.47 (J = 4.2)
	C_6H_5	b	2.53	2.65	b	2.53	2.62	b	2.72	2.77
cis-P(C₆H₅)(CH₃)₂	CH_3	7.53	7.60	7.60	10.31 (J = 8.9)	10.53 (J = 8.7)	d			
	CH_2P	8.62 (J = 9.0)	b	d	8.84 (J = 8.4)	b	d	8.92 (J = 3.4)	8.75 (J = 3.4)	d
	C_6H_5	b	2.55	d	b	2.55		b	2.77	d
cis-P(OCH₃)₃	CH_3	7.43	7.55	7.55	10.03 (J = 8.4)	10.33 (J = 8.4)	10.38 (J = 8.4)			
	CH_3O	6.76 (J = 11.2)	b	6.30 (J = 11.2)	6.82 (J = 11.2)	b	6.34 (J = 11.2)	6.67 (J = 10.8)	b	6.60 (J = 10.6)
trans-P(OCH₃)₃	CH_3	7.38	c	7.53	c	c	c			
	CH_3O	6.90 (J = 11.8)	e	6.40 (J = 11.8)		e		6.67 (J = 10.8)	b	6.60 (J = 10.6)
cis-P(OCH₂)₃CCH₃	CH_3	7.30	7.57		9.85 (J = 8.6)	10.38 (J = 8.1)	10.38 (J = 8.6)			
	CH_2O	6.43 (J = 4.6)	5.75 (J = 4.6)		6.70 (J = 4.5)	5.75 (J = 4.5)	5.75 (J = 4.5)	6.49 (J = 1.9)	6.10 (J = 2.0)	
	CH_3C	10.08	9.10		10.45	2.34	2.83	10.03	9.32	2.90
cis-P(OC₆H₅)₃	CH_3	7.42	7.53	7.63	9.78 (J = 8.8)	10.19 (J = 8.8)	10.17 (J = 8.8)			
	C_6H_5	b	2.77	2.90	b	2.75	2.88	b	2.78	
cis-P(C₂H₅)₃	CH_3	7.37	7.50		10.25 (J = 7.6)	10.47 (J = 7.6)	d			
	CH_2P	8.52 (complex)	b	d	8.6 (complex)	b	d	9.0 (complex)	b	d
	CH_3C	9.30 (complex)	b	d	b	b			b	d
cis-P(C₆H₅)₂H	CH_3	7.45	e	7.55	10.05 (J = 12.0)	10.32 (J = 12.0)	e			
	HP	3.65 (J = 385)	e	3.67 (J = 385)	4.15 (J = 364)	4.12 (J = 364)	e	4.82 (J = 215)	e	4.87 (J = 215)
	C_6H_5	b	2.58	2.58	b	2.50		b	e	2.73
cis-NH₂(C₆H₁₁)	CH_3	7.30	7.38		c	c				
cis-NH(CH₃)(C₆H₁₁)	CH_3	7.33	7.37		c	c				
cis-NH₂C₆H₅	CH_3	7.30	7.45		c	c				
cis-Pyridine	CH_3	7.27[f]	7.35[f]		c	c				

[a] Relative to TMS at τ 10; J values in Hz. [b] Unable to observe owing to coincidence of ligand and solvent signals. [c] Formation of complex not observed. [d] Not obtained; ligands react with CS_2. [e] Not examined. [f] Observed in solution only.

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TABLE II

EQUILIBRIUM DISTRIBUTION OF REACTANTS AND PRODUCTS FROM
THE REACTIONS OF EQUIMOLAR AMOUNTS OF $CH_3Mn(CO)_5$ AND
LIGAND AT 25° IN BENZENE[a]

	CH₃COMn-(CO)₄L		cis-CH₃Mn-(CO)₄L	CH₃Mn-(CO)₅	CH₃CO-Mn(CO)₅
	cis	trans			
P(C₆H₅)₃	64	27	9	<2	...
As(C₆H₅)₃	36	4	13	40	12
Sb(C₆H₅)₃	77	...	<2	23	...
P(C₆H₅)(CH₃)₂	100	...	...	...	...
P(C₆H₅)₂CH₃	100	...	...	...	...
P(OCH₃)₃	90	10	...	...	...
P(OC₆H₅)₃[b]	100	...	...	...	...
P(OCH₂)₃CCH₃	100	...	...	...	...
P(C₂H₅)₃	100	...	...	...	...
P(C₆H₅)₂H	100	...	...	...	...
NH₂C₆H₁₁	94	...	...	6	...
NH(CH₃)(C₆H₁₁)	55	...	...	45	...
NH₂C₆H₅	26	...	...	74	...
NC₅H₅[c]	37	...	...	63	...

[a] Initial concentrations approximately 0.1 *M*. [b] Prior to conversion to unidentified compound. [c] Prior to onset of decomposition.

is faster than the rearrangement step when tetrahydrofuran is the solvent. By comparison, when benzene is the solvent, the relative concentrations of the two acetyl isomers remain essentially constant throughout the reaction as had been originally reported.[6] Since the over-all reaction is observably slower in benzene or carbon disulfide than in tetrahydrofuran, this means that in benzene the rate of reaction 1a is slower than or comparable to the rate of reaction 1b. In these solvents all of the $CH_3Mn(CO)_5$ is initially converted to the two $CH_3COMn(CO)_4P(C_6H_5)_3$ isomers after which these two species diminish slightly in concentration and a small amount (see Table II) of cis-$CH_3Mn(CO)_4L$ is formed according to reaction 2. The carbon monoxide released in the reaction becomes distributed between the solution phase and the void above the solution.

The reaction of triphenylarsine with $CH_3Mn(CO)_5$ was also examined in various solvents and the course of the reaction in benzene at room temperature has been

TABLE III

METALLOCARBONYL STRETCHING BANDS (CM⁻¹)[a]

Ligand	cis-CH₃COMn(CO)₄L				cis-CH₃Mn(CO)₄L			
P(C₆H₅)₃	2067 w	1994 m	1964 s	1957 s[b]	2055 w	1983 m	1969 s	1939 m
As(C₆H₅)₃	2064 w	1993 m	1967 s	1955 m[c]	2059 w	1982 m	1967 s	1939 m
Sb(C₆H₅)₃	2056 w	1984 m	1968 s	1957 m	2054 w	1982 m	1970 s	1941 m
P(C₆H₅)₂CH₃	2071 w	1995 m	1963 s	1956 m	2062 w	1986 m	1967 s	1941 m
P(C₆H₅)(CH₃)₂	2062 w	1989 m	1962 s	1952 m	2059 w	1975 m	1965 s	1935 m
P(C₆H₅)₂H	2062 w	1985 m	1974 s	1958 m	2064 w	1991 m	1978 s	1942 m
P(C₂H₅)₃	2058 w	1984 m	1963 s	1949 s	2057 w	1981 m	1962 s	1933 m
P(OC₆H₅)₃	2083 w	2013 m	1984 m	1973 m	2074 w	2003 m	1985 s	1961 m
P(OCH₃)₃	2071 w	2009 m	1988 s	1975 s[c]	2069 w	1997 m	1078 s	1945 m
P(OCH₂)₃CCH₃	2087 w	2013 m	1991 s	1981 s[a]	2060 w	1999 m	1989 s	1967 m
NH₂(C₆H₁₁)	2064 w	1978 m	1969 s	1941 m				
NH(CH₃)(C₆H₁₁)	2063 w	1978 m	1967 s	1940 m				
NH₂C₆H₅	2070 w	1987 m	1975 s	1945 m				
NC₅H₅	2062 w	1973 sh	1969 s	1943 m				

[a] Of hexane solutions except for cis-$CH_3COMn(CO)_4P(OCH_2)_3CCH_3$ for which dichloroethane was the solvent. [b] Reference %. [c] Contains approximately 10% of *trans* isomer.

ance of four metallocarbonyl stretching bands for each of the complexes studied suggests that each complex has a *cis* configuration with C_1 symmetry. The original incorrect assignment of a *trans* configuration for the major triphenylphosphine product was based on a three-band spectrum in which there was severe overlapping of bands.[6] Fortunately, in the two instances discussed below in which *cis-* and *trans-*$CH_3COMn(CO)_4L$ products are obtained, the percentage of *trans* isomer is so low (*ca.* 10%) that the bands corresponding to the *trans* isomer do not disrupt the band pattern of the predominant *cis* isomer.

$CH_3COMn(CO)_4L$ **Complexes with L = $(C_6H_5)_3P$, -As, -Sb, -Bi.**—Recently Noack, Ruch, and Calderazzo[7] have shown that the reaction of triphenylphosphine with methylmanganese pentacarbonyl in acetone produces cis-$CH_3COMn(CO)_4P(C_6H_5)_3$ as the initial product (reaction 1a), which then diminishes in concentration as it rearranges to the *trans* isomer (reaction 1b). We have also noted that the initial step in this reaction

diagrammed in Figure 1. Within a few hours the formation of *cis-* and *trans-*$CH_3COMn(CO)_4As(C_6H_5)_3$, τ 7.50 and 7.34, respectively, is readily apparent. However, before 50% of the $CH_3Mn(CO)_5$ is consumed according to reaction 1, two new proton signals (Figure 1C) corresponding to $CH_3COMn(CO)_5$ at τ 7.76 and to cis-$CH_3Mn(CO)_4As(C_6H_5)_3$ at τ 10.33 are seen. After 60 hr this complex system has reached the equilibrium distribution shown in Figure 1D. This same equilibrium mixture may be approached from the other direction as shown in Figure 2. When isolated samples of *cis-* and *trans-*$CH_3COMn(CO)_4As(C_6H_5)_3$ are dissolved in benzene, deacetylation takes place by two paths—by the reverse of reaction 1 and by reaction 2. The line diagrams in Figure 2 illustrate clearly that the first reaction is faster than the second. As the concentration of CO builds up in the reaction mixture, carbonylation of $CH_3Mn(CO)_5$ occurs to form $CH_3COMn(CO)_5$. At equilibrium, the concentration of $CH_3COMn(CO)_5$ is less than the concentration of
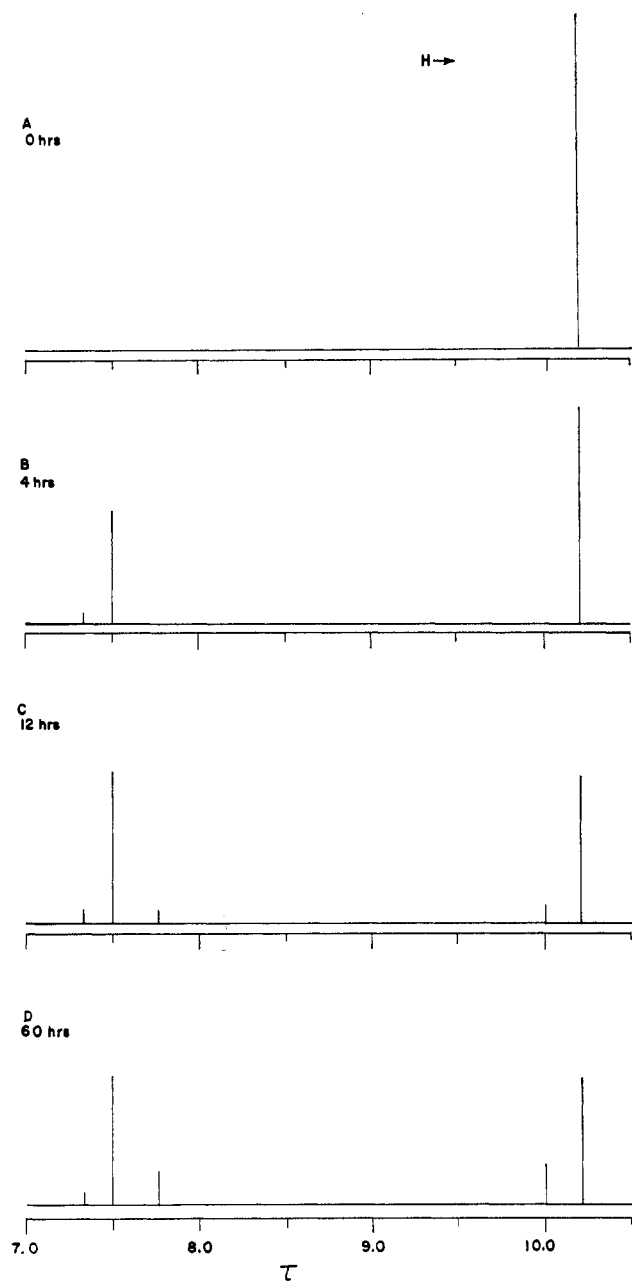
Figure 1.—Schematic representation of the time-dependent pmr spectra of a 1:1 mixture of triphenylarsine and CH₃Mn(CO)₅ at 25° in benzene.

Figure 2.—Schematic representation of the time-dependent spectra of a mixture of *cis*- and *trans*-CH₃COMn(CO)₄As(C₆H₅)₃ at 25° in benzene.

CH₃Mn(CO)₄As(C₆H₅)₃, a fact which is undoubtedly an artifact of the distribution of CO between the solution and free volume in the nmr tube used in the study.

When the reaction between CH₃Mn(CO)₅ and triphenylarsine was carried out in tetrahydrofuran, the rate of formation of the *cis* isomer was found to exceed the rate of formation of the *trans* isomer. This observation, although not as striking in this case as with triphenylphosphine, does lend further support to the earlier conclusions that *cis*-CH₃COMn(CO)₄L is formed first and that the *trans* isomer is obtained upon subsequent rearrangement.[7]

The reaction of triphenylstibine with CH₃Mn(CO)₅ is different from those previously described as *cis*-CH₃COMn(CO)₄Sb(C₆H₅)₃ is the only detectable acetyl

product. Although complete conversion of CH₃Mn(CO)₅ to this acetyl product does not occur, a relatively small amount of *cis*-CH₃Mn(CO)₄Sb(C₆H₅)₃ is formed while no CH₃COMn(CO)₅ can be detected.

Reactions with Phosphorus Donors.—Except for trimethyl phosphite and triphenyl phosphite, each of the other phosphorus-donating ligands reacts completely with CH₃Mn(CO)₅ to generate exclusively a *cis*-CH₃COMn(CO)₄L complex. The reaction between CH₃Mn(CO)₅ and trimethyl phosphite has been followed carefully by both infrared and nmr spectra. As was found for the reactions with triphenylphosphine and triphenylarsine, the first product to be formed is *cis*-CH₃COMn(CO)₄P(OCH₃)₃. After 24 hr, an
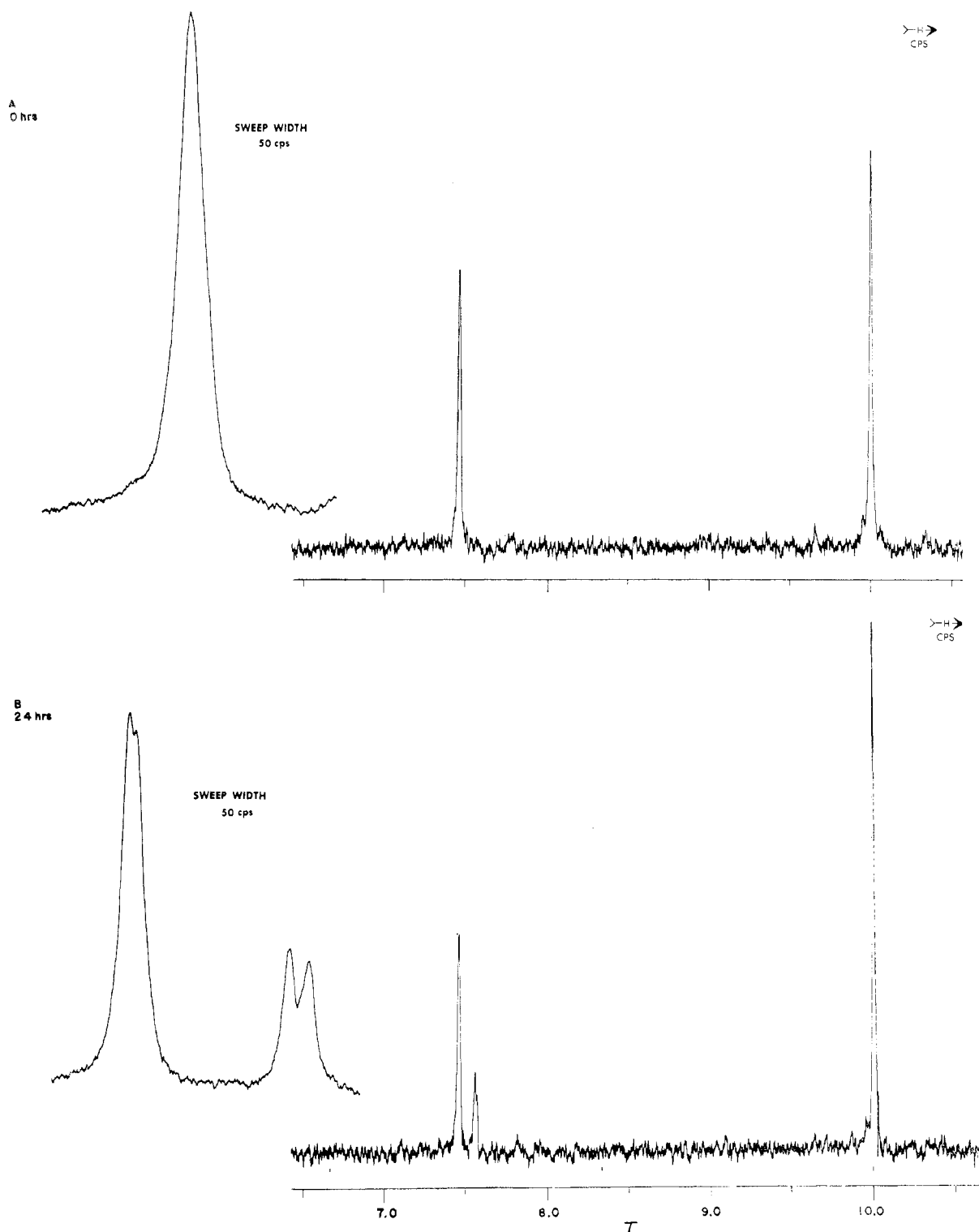
Figure 3.—Time-dependent pmr spectra of cis-CH$_3$COMn(CO)$_4$P(OC$_6$H$_5$)$_3$ at 25° in benzene; TMS at τ 10.

equilibrium consisting of 10% *trans* and 90% *cis* is reached as determined from the resonance signals of both (Table I) the acetyl groups and the hydrogens of the bonded ligand.

The nmr spectrum (Figure 3A) of isolated and analyzed cis-CH$_3$COMn(CO)$_4$P(OC$_6$H$_5$)$_3$ consists initially of a single sharp acetyl peak at τ 7.42. However, the nmr spectrum of this sample changes with time to that shown in Figure 3B. The expanded-scale insert

clearly shows that the new higher field signal at τ 7.4 is essentially a symmetrical doublet with $J = 0.7$ cps. A simultaneous change in the τ 7.5 region also takes place as a signal which may be either a new singlet or part of a doublet which overlaps the original signal appears 0.4–0.5 cps on the high-field side of the original signal of cis-CH$_3$COMn(CO)$_4$P(OC$_6$H$_5$)$_3$. When CH$_3$Mn(CO)$_5$ and triphenyl phosphite are allowed to react in tetrahydrofuran at room tempera-

ture, complete conversion of the reactants to *cis*-CH₃-COMn(CO)₄P(OC₆H₅)₃ occurs before the additional signals appear, although they appear with time. In other solvents such as benzene, dichloromethane, and carbon disulfide the initial reaction is much slower than in tetrahydrofuran and the unassigned proton signals appear before all of the CH₃Mn(CO)₅ is consumed. In benzene, this forward reaction reached an apparent equilibrium position which is identical with that shown in Figure 3B. No simple explanation for the position and relative intensities for these additional signals can be given at this time.

Reactions with Amines.—The reactions of alkylamines and aniline with CH₃Mn(CO)₅ do not go to completion as indicated by the equilibrium distribution of reactants and products given in Table III. For each nitrogen-donor ligand studied, only a single *cis*-acetyl isomer was detected. The instability of these complexes has not been recognized before and it is important to mention that spurious infrared bands in the metallocarbonyl region appear with time when solutions of these complexes are allowed to stand.

In the present study, as well as in earlier work,[2] no acetylmanganese carbonyl derivative of pyridine could be isolated. However, it is apparent from the nmr spectrum of a reaction mixture containing pyridine and CH₃Mn(CO)₅ that *cis*-CH₃COMn(CO)₄NC₅H₅ is formed. Unfortunately, even in solution this complex deteriorates rapidly to undefined products. The equilibrium values given in Table II correspond to the percentages of materials present prior to the occurrence of decomposition. When the concentration of *cis*-CH₃COMn(CO)₄NC₅H₅ had reached a maximum, an aliquot of the solution was diluted in hexane and then used to obtain the infrared bands listed in Table III.

cis-**CH₃Mn(CO)₄L Products.**—Although the monoligated acetylmanganese tetracarbonyl derivatives of triphenylphosphine, -arsine, and -stibine each decarbonylate partially to *cis*-CH₃Mn(CO)₄L product on standing in solution, complete decarbonylation is best accomplished by refluxing mixtures of the ligand and CH₃Mn(CO)₅ in benzene or tetrahydrofuran. With the other phosphorus-donor ligands the heating process is absolutely necessary to effect reaction 2. The spectral properties of these compounds are listed in Tables I and II.

All efforts to effect decarbonylation of the *cis*-CH₃COMn(CO)₄(amine) complexes to a monoligated methylmanganese tetracarbonyl derivative were unsuccessful.

Discussion

The results presented in the previous section constitute a considerable body of information which supports the methyl migration mechanism proposed by Noack, Ruch, and Calderazzo[7] for the carbonylation reaction on CH₃Mn(CO)₅ as induced by CO[14] and triphenylphosphine.[7] For each system studied here the first formed or exclusive CH₃COMn(CO)₄L complex

apparently has a *cis* configuration. The *cis* configuration had been noted previously for the monoligated acetylmanganese tetracarbonyl complexes when L was an amine[6] or 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane.[15] In addition, the present results provide an insight into some of the factors that control the extent to which reactions 1a, 1b, and 2 proceed for the individual ligands. These factors include: (1) the nucleophilicity of the ligand as determined by the inherent σ- and π-bonding characteristics of the donor atom; (2) the inductive effects of the groups appended to the donor atom of the ligand; (3) the steric requirements of the ligand as determined by the sizes of both the donor atom and the appended groups.

Both inductive and steric effects of the groups bonded to nitrogen are influential in determining the position of equilibrium for reaction 1a with an amine ligand. The data in Table II show that the acetylmanganese complex obtained with cyclohexylamine is thermodynamically more stable than the complexes of N-methylcyclohexylamine or aniline. The first observation is explained readily since N-methylcyclohexylamine, even though it should be a stronger base than cyclohexylamine, has the greater steric requirement of the two amines. The second result is attributable to the fact that aniline is a poorer base than cyclohexylamine. The steric effect is even more apparent from the observations that neither dicyclohexylamine nor diphenylamine react at all with CH₃Mn(CO)₅ under the conditions employed here.

The larger size of the phosphorus atom, compared to nitrogen, can account in part for the ability of sterically demanding ligands such as triphenylphosphine to yield CH₃COMn(CO)₄L complexes. The completeness (Table II) with which the phosphorus-donor ligands react with CH₃Mn(CO)₅ is a function of the inherent nucleophilicity of phosphorus and this is probably determined primarily by metal–ligand dπ–dπ orbital overlap. Extra axial bonding is usually considered to be nonexistent with amine ligands. However, the size of the phosphorus atom does not eliminate the possibility of steric interaction between the acetyl group on the metal atom and the organic groups appended to phosphorus. In fact, the formation of both *cis*- and *trans*-CH₃COMn(CO)₄L, where L is triphenylphosphine or trimethyl phosphite, is probably a result of just such steric interaction. Apparently, the degree of interaction in these cases is not large as the *cis* isomer always predominates. However, the inability of tris(*o*-tolylphosphine) to form a complex according to reaction 1 does indicate that even with phosphorus steric hindrance can become severe. One further point regarding the *cis–trans* isomerization may be made. Carbon monoxide groups *trans* to poor π-acceptor ligands, especially an alkyl or acetyl group, are considered to engage in π bonding with the metal d levels to a much greater extent than *cis* CO groups. Thus, any ligand which replaces the CO group *trans* to acetyl must be capable of performing this same charge-

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

(15) M. Green and D. C. Wood, *J. Am. Chem. Soc.,* **88,** 4106 (1966).

withdrawal function. For example, triethylphosphine and trimethyl phosphite have essentially equal spatial requirements, yet only the second ligand, which has the greater π-bonding capability, is observed to yield a *trans* isomer. In agreement with the trends noted previously for $LM(CO)_5$ complexes,[16] where M is Cr, Mo, or W, the CO stretching bands for *cis*-$CH_3COMn(CO)_4P(OCH_3)_3$ are of higher energy than those of *cis*-$CH_3COMn(CO)_4P(C_2H_5)_3$. Presumably, the steric problems with the other phosphorus ligands are minimal and there is no driving force for isomerization.

The steric argument used in the previous paragraph also leads to the prediction that the ratio of *cis* to *trans* isomers of $CH_3COMn(CO)_4E(C_6H_5)_3$ ought to be directly proportional to the size of E. This appears to be so as this ratio increases rapidly from 7:3 to 9:1 to 10:0 for E = P, As, and Sb, respectively.

Another important point to note concerning the $CH_3COMn(CO)_4E(C_6H_5)_3$ complexes is that the amount of $CH_3Mn(CO)_5$ which remains at equilibrium decreases in the order E = As > Sb $\gg$ P. The fact that the inherent nucleophilicity of triphenylstibine is slightly less than that of triphenylarsine[17] leads to the expectation of more $CH_3Mn(CO)_5$ at equilibrium in reaction with the former ligand. However, the steric interaction between the acetyl group and the former ligand in a *cis*-$CH_3COMn(CO)_4L$ complex must be considerably less than with the latter ligand in order to explain the observed order. The completeness with which phosphorus-donor ligands react must be a result of their relatively great nucleophilicity which completely overpowers any steric demands of the products. Finally, triphenylbismuthine appears to be ineffective as a nucleophile in this reaction.

This above-mentioned combination of unfavorable bonding properties of triphenylarsine is also manifested in an initial rapid reversion of an isolated mixture of *cis*- and *trans*-$CH_3COMn(CO)_4As(C_6H_5)_3$ to $CH_3Mn(CO)_5$ and free ligand. *cis*-$CH_3Mn(CO)_4As(C_6H_5)_3$ is generated slowly until equilibrium is attained. By comparison, upon redissolution in benzene, pure *cis*-$CH_3COMn(CO)_4P(C_6H_5)_3$ reverts primarily to *cis*-$CH_3Mn(CO)_4P(C_6H_5)_3$. Pure *cis*-$CH_3COMn(CO)_4$-$Sb(C_6H_5)_3$ yields only $CH_3Mn(CO)_5$, but the per cent of reversion is less for the antimony derivative than for the arsenic compound.

Nmr Chemical Shifts.—The differences in the chemical shifts of the methyl protons for the various CH_3-$Mn(CO)_4L$ or $CH_3COMn(CO)_4L$ complexes ought to be a function of the electron density at manganese, a factor which should be determined by the σ-donor and π-acceptor characteristics of L. Inasmuch as all of the L groups examined here are normally considered to be better Lewis bases and poorer π acceptors than CO, a deshielding of the CH_3 protons in the substituted complexes relative to the corresponding signals for CH_3Mn-

$(CO)_5$ and $CH_3COMn(CO)_5$ would be anticipated. The results obtained with tetrahydrofuran and carbon disulfide as solvents agree reasonably well with this prediction. However, there is the obvious exception of the $CH_3COMn(CO)_4$(amine) complexes, while the observations on all of the complexes with benzene as the solvent are even less straightforward. All attempts to correlate the chemical shifts in any of the solvents with the infrared spectra of the complexes which presumably also reflect the electronic characteristics of the ligands were completely unsuccessful.

There does appear to be one valid correlation, however. For the $CH_3COMn(CO)_4L$ complexes with the ligands triphenylphosphine, trimethyl phosphite, and triphenylarsine, the signal for the acetyl group in the *trans* isomer was always seen at lower field than that of the acetyl group of the *cis* isomer.

Mechanistic Considerations.—The conversion of the mixture of *cis*- and *trans*-$CH_3COMn(CO)_4P(C_6H_5)_3$ to exclusively *cis*-$CH_3Mn(CO)_4P(C_6H_5)_3$ was noted some time ago.[6] However, the results of the present study indicate that all acetylmanganese complexes with ligands other than amines, including many for which only *cis*-$CH_3COMn(CO)_4L$ is observed, can be converted to *cis*-$CH_3Mn(CO)_4L$ complexes. This general observation suggests that even with those ligands for which two acetyl isomers are obtained, only the *cis* isomer need be considered to undergo decarbonylation as shown in reaction 1a. In those cases in which two isomers are seen, the *trans* isomer can readily convert to the *cis* isomer which may then decarbonylate. Theoretically, if this decarbonylation step occurs by a methyl-migration mechanism, the product should consist of a 2:1 mixture of *cis*- and *trans*-$CH_3Mn(CO)_4L$, respectively. Experimentally, there is no indication in any of the reactions studied that a *trans*-CH_3Mn-$(CO)L$ complex is formed. However, the decarbonylation process may still be rationalized on the basis of a modified methyl-migration mechanism which takes into account the fact that multiple bonding between low-valent metal d orbitals and the π-antibonding levels of a metallocarbonyl group is considered to be greater for a CO group *trans* to a substituent ligand with poor π bonding capabilities than for mutually *trans* CO groups. As such then, if the L–M bond is sufficiently robust, and such appears not to be the case for amine complexes, either one of the CO groups *cis* to L would be lost more easily than the CO group *trans* to L. Thus *cis*-CH_3-$Mn(CO)_4L$ would be the more likely product. The greater reluctance for exchange of CO groups *trans* to the halogen in the halomanganese pentacarbonyls has been known for some time.[18] Although there is a competition between loss of CO and ligand in the decarbonylation step, that is between reaction 2 and the reverse of reaction 1a, the driving force for the over-all conversion to *cis*-$CH_3Mn(CO)_4L$ is the removal of carbon monoxide from solution.

Our observations on a number of $CH_3COMn(CO)_3L_2$

(16) For example, see summary by F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

(17) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1967, p 399.

(18) A. Wojicki and F. Basolo, *J. Am. Chem. Soc.*, **83**, 525 (1961).

complexes, which substantiate and extend the ideas discussed here, will be communicated shortly.[19]

Conclusions

Lewis bases will react with $CH_3Mn(CO)_5$, most likely by a methyl-migration mechanism, to yield *cis*-

(19) P. K. Maples and C. S. Kraihanzel, *J. Am. Chem. Soc.*, in press.

$CH_3COMn(CO)_4L$ as the preferred product. Whether or not partial conversion of a *cis*-acetylmanganese complex to the *trans* isomer will occur is apparently a function of particular steric, nucleophilic, and π-acceptor properties of that ligand. The decarbonylation of *cis*-$CH_3COMn(CO)_4L$ complexes to *cis*-$CH_3Mn(CO)_4L$ can be rationalized on the basis of a modified methyl-migration mechanism.

Contribution from the Centro Nazionale di Chimica dei Composti di Coordinazione ed Elemento Organici del CNR, Laboratorio di Pisa, and Istituto di Chimica Organica Industriale, Università di Pisa, Pisa, Italy
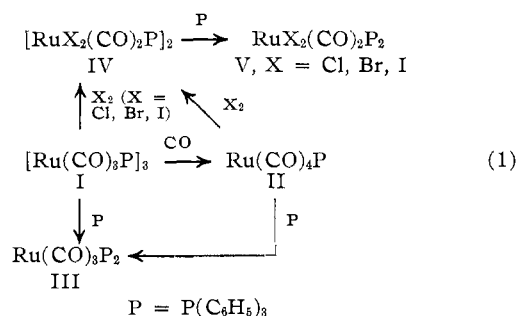
On the Reactivity of Tris(triphenylphosphine)triruthenium Enneacarbonyl

By F. PIACENTI, M. BIANCHI, E. BENEDETTI, and G. BRACA

By reaction of $[Ru(CO)_3P(C_6H_5)_3]_3$ with CO, $Ru(CO)_4P(C_6H_5)_3$ has been prepared from which, with halogens (X = Cl, Br, I) or $CHCl_3$, $[RuX_2(CO)_2P(C_6H_5)_3]_2$ complexes were obtained. These last compounds could also be formed from $[Ru(CO)_3P-(C_6H_5)_3]_3$ and halogens. From the ir spectral data a structure with bridging halogens is suggested for the dimeric compounds $[RuX_2(CO)_2P(C_6H_5)_3]_2$. $[Os(CO)_3P(C_6H_5)_3]_3$ reacts with CO with displacement of $P(C_6H_5)_3$ and formation of $[Os(CO)_4]_3$.

Investigating the chemical behavior of cluster ruthenium carbonyls,[1,2] the reactivity of $[Ru(CO)_3-P(C_6H_5)_3]_3$ (I) with CO and halogens has been studied. At 150°, in benzene solution, I reacts with CO (150 atm) to give, in quantitative yield, a pale yellow crystalline compound which analyzes as $Ru(CO)_4P(C_6H_5)_3$ (II), the first example of a monosubstituted derivative of $Ru(CO)_5$ (eq 1).

$$[RuX_2(CO)_2P]_2 \xrightarrow{P} RuX_2(CO)_2P_2$$
$$\text{IV} \qquad\qquad \text{V, X = Cl, Br, I}$$

$$[Ru(CO)_3P]_3 \xrightarrow{CO} Ru(CO)_4P \qquad (1)$$
$$\text{I} \qquad\qquad\qquad \text{II}$$

$$Ru(CO)_3P_2$$
$$\text{III}$$

$$P = P(C_6H_5)_3$$

The cleavage of the metal–metal bonds in I by CO is analogous to the one performed by $P(C_6H_5)_3$ on I and $P(C_4H_9)_3$ on $[Ru(CO)_3P(C_4H_9)_3]_3$ to obtain $Ru(CO)_3-[P(C_6H_5)_3]_2$ and $Ru(CO)_3[P(C_4H_9)_3]_2$ previously reported.[1] These reactions, like the formation of $RuI_2-(CO)_3P(C_6H_5)_3$ from $[Ru(CO)_3P(C_6H_5)_3]_3$ and I_2,[2,3] support a symmetrical structure for I, with a phosphine molecule attached to each Ru atom.

By heating II with an excess $P(C_6H_5)_3$, in benzene

(1) (a) F. Piacenti, M. Bianchi, E. Benedetti, and G. Sbrana, *Chim. Ind* (Milan), **48**, 762 (1966); (b) F. Piacenti, M. Bianchi, E. Benedetti, and G. Sbrana, *J. Inorg. Nucl. Chem.*, **29**, 1389 (1967).
(2) J. P. Candlin, K. K. Joshi, and D. T. Thompson, *Chem. Ind.* (London), 1960 (1966).
(3) D. Seyferth and R. B. King, "Annual Surveys of Organometallic Chemistry," Elsevier Publishing Co., Amsterdam, 1967, p 370.

solution at 100°, $Ru(CO)_3[P(C_6H_5)_3]_2$ (III) is formed in quantitative yield.

By reaction of II with an equimolecular amount of I_2 in refluxing acetone $[Ru(CO)_2P(C_6H_5)_3I_2]_2$ (IVc) is obtained. The same compound (identical ir spectrum) is obtained by treating I with I_2 (1:3 mol) under the same conditions.

$[Ru(CO)_2P(C_6H_5)_3Br_2]_2$(IVb) and $[Ru(CO)_2P(C_6H_5)_3-Cl_2]_2$ (IVa), analogous to IVc, are obtained by treating I with a stoichiometric amount of the corresponding halogen.

The formation of IVa is obtained also by reaction of II with CCl_4 or $CHCl_3$ at room temperature and from I in refluxing CCl_4 with a behavior analogous to the one observed when CCl_4 or $CHCl_3$ reacts with $[Ru(CO)_4]_3$.[4] The fate of the residue of the CCl_4 and $CHCl_3$ molecules after chlorine abstraction is not clear: in the case of $CHCl_3$ small amounts of CH_2Cl_2 have been detected by vpc.

The binuclear ruthenium carbonyls IVa, IVb, and IVc react at 30–50° with an excess of $P(C_6H_5)_3$ to give the corresponding $Ru(CO)_2[P(C_6H_5)_3]_2X_2$ (V) derivatives described by Collman and Roper.[5]

The ir spectrum of II (Table I) in the C=O stretching region is analogous to that of $Fe(CO)_4P(C_6H_5)_3$[6] and suggests also for II a trigonal-bipyramidal structure. The weak band at 1906 cm^{-1} might be related to the ^{13}C isotopic shift associated with the strong band appearing at 1940 cm^{-1}.

The ir spectra of the binuclear ruthenium carbonyls

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