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A STUDY OF STERIC EFFECTS IN THE REACTIONS OF SOME CHELATING DITERTIARY PHOSPHINE AND ARSINE LIGANDS WITH METHYLMANGANESE PENTACARBONYL

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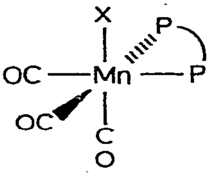
Summary

The reactions of the bidentate ligands, (L—L), $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ (n = 1, 2 or 3), $CH_3C[CH_2P(C_6H_5)_2]_3$, $(C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2$, o-$C_6H_4[As(CH_3)_2$, $(C_6H_5)_2PCH(CH_3)P(C_6H_5)_2$ and $(C_6H_5)_2PC(CH_3)_2P(C_6H_5)_2$ with methylmaganese pentacarbonyl proceed stepwise. The first-formed mono-substituted complexes, $CH_3COMn(CO)_4$(L—L), react at different rates to generate $CH_3COMn(CO)_3$(L—L). The thermodynamically favored isomer of each $CH_3COMn(CO)_3$(L—L) examined has a facial configuration except where L—L is $(C_6H_5)_2PC(CH_3)_2P(C_6H_5)_2$, for which the unique meridional structure is favored. Decarbonylation of all acetyl complexes yielded only *fac*-$CH_3Mn(CO)_3$(L—L). Interligand repulsion between an acetyl group and each of the chelating ligands is greater than for a methyl group and is responsible for the variations in the structures of the acetyl complexes. Structural assignments are based on ^1H NMR and IR observations.

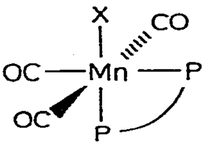
Introduction

The importance of interligand steric effects in the chemistry of transition metal complexes with phosphorus donor ligands is becoming well recognized. Some of the observations which have been accounted for by invoking steric effects include the following: The preferred configurations of phosphine substituted halo- [1], acetyl- [2] and benzoyl-manganese [3] carbonyls and of halomolybdenum and halotungsten carbonyls [4]; the extent of substitution and rates of ligand dissociation in phosphine-substituted cobalt carbonyls [5]; the relative rates of isomerization of $(\pi\text{-}C_5H_5)M(CO)_2LH$, where M = Mo or W and L is a phosphorus donor ligand [6]; the variations in oxidative-addition reactions of *trans*-$IrX(CO)L_2$, where X is a halogen and L is a phosphorus donor ligand [7]; the degree of dissociation in various NiL_4, where L is a phosphorus donor ligand [8]; the trends in enthalpies for the reactions of Lewis bases with [CH_3-$Pt\{P(C_6H_5)_2CH_3\}_2(THF)](PF_6)$ [9]; the rates of carbon monoxide absorption by mono- and di-substituted methylmanganese carbonyls [10]; the control of the mode of bonding of SCN^- to palladium [11]; and the spectral properties of cobaloxime complexes [12].

In a six-coordinate metal complex such as $Mn(CO)_3X(L—L)$, where L is an α,ω-bis(diphenylphosphino)alkane, the relative steric interactions of the X and CO ligands with the chelating ligand should determine the structure of the complex. Thus, with small X, such as methyl [13], acetyl [13], halogen [14,15,16], or hydrogen [14,17], the facial structure I should be preferred. In contrast, with larger X, such as p-FC_6H_4CO, m-FC_6H_4CO or m-$FC_6H_4CH_2$ a meridional structure II is found [18]. In this paper the reactions of a number of chelating ligands with $CH_3Mn(CO)_5$ are considered and further evidence is given for the steric control of the structures of $CH_3COMn(CO)_3(L—L)$ complexes as a function of the chelating ligand.



(I) *fac*



(II) *mer*

Experimental

Ligands. The method of Van Hecke and Horrocks was employed in the preparation of 1,3-bis(diphenylphosphino)propane [19]. Ligands not prepared were purchased from Strem Chemicals, Inc. and used without further purification.

1,1-Bis(diphenylphosphino)ethane. A solution of 26.3 g (0.15 mol) of 1,1-dibromoethane (Eastman) in 10 ml of ether was added dropwise to a solution of diphenylphosphide which had been prepared in the usual manner from 73.4 g (0.30 mol) of triphenylphosphine and 12.9 g (0.60 g-atom) of sodium in 500 ml of liquid ammonia. Ammonium bromide was used to remove phenylsodium prior to addition of the halocarbon. After the liquid ammonia had evaporated, the residual white solid was extracted with three 100 ml portions of methylene chloride. The extracts were combined, filtered and evaporated to approximately one-half of the original volume under aspirator vacuum. Addition of 200 ml of methanol to the solution precipitated the product as a white crystalline solid. Recrystallization of the solid from absolute ethanol gave 26 g (44%) of pure material, m.p. 111—113°C. (Found: C, 78.23; H, 6.03. $C_{26}H_{24}P_2$ calcd.: C, 78.38; H, 6.07%.

2,2-Bis(diphenylphosphino)propane. This compound was prepared from sodium diphenylphosphide and 2,2-dibromopropane (Columbia Organic Chemicals, Inc.) in 36% yield according to a procedure analogous to that employed for preparing 1,1-bis(diphenylphosphino)ethane. The white solid melts at 113—115°C. (Found: C, 78.38; H, 6.23. $C_{27}H_{26}P_2$ calcd.: C, 78.63; H, 6.35%).

Preparation of complexes

$CH_3COMn(CO)_3(L—L)$. Equimolar amounts of the chelating ligand and methylmanganese pentacarbonyl in tetrahydrofuran or benzene were allowed to react for 24—48 h at room temperature under a nitrogen atmosphere. The yellow acetyl complexes were precipitated from the reaction mixture by addition of n-hexane, collected by filtration and recrystallized from a dichloromethane/benzene mixture. Yields of the various products ranged from 40—70%.

$CH_3Mn(CO)_3(L—L)$. Decarbonylation of the various $CH_3COMn(CO)_3(L—L)$ complexes was effected by heating the acetyl complexes in refluxing benzene for 3—6 days. The sole exception is $CH_3COMn(CO)_3$ (*o*-$C_6H_4[As(CH_3)_2]_2$) which was heated in refluxing toluene for 4 days. Solutions were concentrated to approximately one-third of the original volume, after which sufficient n-hexane was added to complete precipitation of the products. Solids were collected by pressure filtration under nitrogen and recrystallized from a mixture of either benzene or dichloromethane with n-hexane. Yields of analytically pure products with the phosphine ligands were 50—90% and for the arsine ligands 30—45%.

Analytical and m.p. data on all complexes are given in Table 1.

General information

Infrared spectra were obtained with Perkin—Elmer 621 (Table 2) and Perkin—Elmer 257 (Table 5) instruments. ^1H NMR data were obtained with Varian A-60 and Hitachi Perkin—Elmer R20A instruments. Melting points are reported for samples sealed in capillary tubes under nitrogen. Elemental analyses were performed by Galbraith Laboratories, Inc. and Baron Consulting.

Reactions of the various ligands with $CH_3Mn(CO)_5$ at 34°C were monitored by ^1H NMR, normally with solutions of 0.2 mmol of each reagent in 0.5 ml of solvent. Different molar ratios of reagents were sometimes used to study intermediates. The capped tubes were vented periodically under nitrogen to release carbon monoxide generated in the reactions.

TABLE 1

ANALYSES (FOUND (CALCD.) %) AND MELTING POINTS OF ISOLATED COMPLEXES

L—L	$CH_3COMn(CO)_3L—L$			$CH_3Mn(CO)_3(L—L)$		
	C	H	M.p. (°C)	C	H	M.p. (°C)
$(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2$	64.79 (64.66)	5.06 (4.92)	204—207	65.43 (65.73)	5.16 (5.16)	202—204
$(C_6H_5)_2PCH(CH_3)P(C_6H_5)_2$	64.36 (64.14)	4.67 (4.69)	220—226	65.17 (65.28)	4.76 (4.93)	212—215
$(C_6H_5)_2PC(CH_3)_2P(C_6H_5)_2$	64.29 (64.66)	4.84 (4.92)	191—193	65.71 (65.73)	5.01 (5.16)	201—203
$[(C_6H_5)_2PCH_2]_3CCH_3$	obtained as an oil			69.17 (69.41)	5.58 (5.44)	200—202
$(C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2$	56.21 (55.71)	4.06 (4.07)	160—161	55.92 (55.27)	4.21 (4.25)	154—156
$C_6H_4[As(CH_3)_2]_2$	38.48 (38.49)	4.37 (4.09)	160—162	38.65 (38.21)	4.34 (4.35)	144—146

TABLE 2

SELECTED INFRARED BANDS OF ISOLATED COMPLEXES, $RMn(CO)_3(L—L)$ [a]

L—L	R	$\nu(C\equiv O)$ (cm^{-1})	$\nu(C=O)$ (cm^{-1})
$(C_6H_5)_2PCH_2P(C_6H_5)_2$	CH_3CO [b]	1999s, 1919s(br)	1585
	CH_3	1997s, 1918m, 1893m	
$(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$	CH_3CO	1999s, 1916s(br)	1588
	CH_3	1994s, 1917m, 1890m	
$(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2$	CH_3CO	1999s, 1919s(br)	1582
	CH_3	1998s, 1923m, 1887m	
$(C_6H_5)_2PCH(CH_3)P(C_6H_5)_2$	CH_3CO [b]	1999s, 1917s(br)	1586
	CH_3	1996s, 1920m, 1885m	
$(C_6H_5)_2PC(CH_3)_2P(C_6H_5)_2$	CH_3CO	2002w, 1922s, 1907m	1603
	CH_3	1995s, 1921m, 1884m	
$[(C_6H_5)_2PCH_2]_3CCH_3$	CH_3CO [c,d]	2000s, 1916s(br)	1583
	CH_3 [d]	1998s, 1926m, 1881m	
$(C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2$	CH_3CO	2001s, 1917s(br)	1582
	CH_3	1995s, 1916m, 1890m	
o-$C_6H_4(As(CH_3)_2)_2$	CH_3CO	1998s, 1912s(br)	1578
	CH_3	1993s, 1912m, 1885m	

[a] Obtained on solutions in CH_2Cl_2 except for $(C_6H_5)_2PC(CH_3)_2P(C_6H_5)_2$ complexes for which spectra were obtained of solutions in tetrachloroethylene. [b] Mixture of isomers as discussed in the text. [c] Isolated as an oil. [d] Only two phosphorus donor sites employed in chelation.

Results

The reactions of ditertiary phosphine and arsine ligands, L—L, with $CH_3Mn(CO)_5$ at 34° C proceed in a stepwise fashion. Initially, monosubstituted complexes, $CH_3COMn(CO)_4(L—L)$, are formed and these in a second step undergo an intramolecular substitution reaction with elimination of carbon monoxide to yield the chelate complexes, $CH_3COMn(CO)_3(L—L)$. Decarbonylation of the various $CH_3COMn(CO)_3(L—L)$ complexes required heating at 80° C or higher for several days for conversion to the corresponding $CH_3Mn(CO)_3(L—L)$.

$CH_3Mn(CO)_3(L—L)$ complexes. The previously reported assignment of a facial configuration to each of the two complexes $CH_3Mn(CO)_3[(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2]$, $n = 1$ or 2, followed from an analysis of their infrared and ^1H NMR spectral properties [13]. In Tables 2 and 3, selected enfrared and ^1H NMR spectral results for the new $CH_3Mn(CO)_3(L—L)$ prepared in this study are presented. Several facts indicate that each of these complexes, which we believe to be isomerically pure, has a facial configuration. First, three medium to strong infrared carbonyl stretching bands occur in the 2000—1800 cm^{-1} region for each complex as is shown for *fac*-$CH_3Mn(CO)_3[(C_6H_5)_2PC(CH_3)_2P(C_6H_5)_2]$ in Fig. 1. Although three bands are expected for either configuration I or II, the symmetric CO stretching mode for the two *trans*-oriented carbonyl groups in the meridional complex II is expected to yield a high energy band of relatively low intensity.

The ^1H NMR spectra (Table 3) also indicate that these complexes have a facial configuration. The 1/2/1 triplet observed between τ 10—11 ppm for the Mn—CH_3 results from coupling to the two equivalent phosphorus nuclei in I. Further, the aliphatic protons of $(C_6H_5)_2PCH_2P(C_6H_5)_2$ and $(C_6H_5)_2PC(CH_3)_2P$-

TABLE 3

^{1}H NMR DATA FOR $RMn(CO)_3$(L—L) COMPLEXES [a]

L—L	Group	R = CH_3CO		R = CH_3	
		Solvent C_6H_6	Solvent CH_2Cl_2	Solvent C_6H_6	Other solvent
$(C_6H_5)_2PCH_2P(C_6H_5)_2$	R	7.29 [b]; 7.12	7.57 [b]; 7.41	10.00 ($\lvert ^2J(HP)\rvert$ 10.2 Hz; T)	
	CH_2	5.40 (QT) [c]	*d*	6.73 (QT) [e]	
$(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$	R	7.68	7.99	10.85 (J(HP) 10.0 Hz; T)	11.40 (J(HP) 10.0 Hz; T), CH_2Cl_2
	$(CH_2)_2$	*d*	*d*	7.77 (br)	7.37 (br), CH_2Cl_2
$(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2$	R	7.40			
$(C_6H_5)_2PCH(CH_3)P(C_6H_5)_2$	R	7.50 [b]; 7.09	7.78 [b]; 7.35	10.13 (J(HP) 9.8 Hz; T)	10.63 (J(HP) 9.8 Hz; T), $CDCl_3$
	$C\underline{H_3}CH$	8.85 (DT) [b,f]; 9.05 (DT) [g]	8.50 (DT) [b,h]; 8.90 (DT) [i]	9.11 (DT) [j]	8.92 (DT) [k], $CDCl_3$
	$CH_3C\underline{H}$	*d*	*d*	*d*	5.22 [l], $CDCl_3$
$(C_6H_5)_2PC(CH_3)_2P(C_6H_5)_2$	R	7.00	7.34	9.98 (J(HP) 8.25 Hz; T)	10.61 (J(HP) 8.25 Hz; T), CH_2Cl_2
	CH_3C	8.81 (J(HP) 13.7 Hz; T)	8.66 (J(HP) 13.8 Hz; T)	8.84 (J(HP) 15.9 Hz; T) 8.30 (J(HP) 12.1 Hz; T)	8.79 (J(HP) 15.8 Hz; T), CH_2Cl_2 8.06 (J(HP) 12.5 Hz; T), CH_2Cl_2
o-$C_6H_4[As(CH_3)_2]_2$	R	7.20		10.88	
	CH_3As	8.90, 8.74		8.83, 8.79	
$(C_6H_5)_2As(CH_2)_2As(C_6H_5)_2$	R	7.42		10.78	
	$(CH_2)_2$	7.63, 7.37		7.93 (Unres. mult.)	
$[(C_6H_5)_2PCH_2]_3CCH_3$	R	7.74			10.39 (J(HP) 8.6 Hz; T), $CDCl_3$
	CH_3C	9.15 (br)			*d*
	CH_2	7.64 (unres.), 6.4 (br)			*d*

[a] τ values in ppm with TMS as internal standard at τ 10 ppm. Signals are singlets unless indicated; D = doublet; T = triplet; Q = quartet. [b] Major isomer (*facial* as described in text). [c] Center of AB portion of ABX_2 spectrum: $\Delta_A - \Delta_B = 1.20$ ppm; $J(AB)$ 15.1 ± 0.1 Hz; $\lvert J(HP)\rvert$ 12.3 ± 0.2 Hz; $\lvert J(BP)\rvert$ 9.7 ± 0.1 Hz. [d] Not observable or not readily apparent. [e] ABX_2 system: $\Delta_A - \Delta_B = 0.25$ ppm; $J(AB)$ 15.1 ± 0.1 Hz; $\lvert J(AP)\rvert$ 10.1 ± 0.3 Hz; $\lvert J(BP)\rvert$ 9.5 ± 0.2 Hz. [f] $^3J(HH)$ 7.6 Hz; $\lvert ^2J(HP)\rvert$ 13.5 Hz. [g] $^3J(HH)$ 7.9 Hz; $\lvert ^2J(HP)\rvert$ 14.1 Hz. [h] $^3J(HH)$ 7.9 Hz; $\lvert ^2J(HP)\rvert$ 13.9 Hz. [i] $^3J(HH)$ 7.9 Hz; $\lvert ^2J(HP)\rvert$ 14.4 Hz. [j] $^3J(HH)$ 7.2 Hz; $\lvert ^2J(HP)\rvert$ 13.0 Hz. [k] $^3J(HH)$ 7.1 Hz; $\lvert ^2J(HP)\rvert$ 13.0 Hz. [l] Unresolved multiplet; double irradiation at τ 8.92 ppm yielded a symmetrical triplet at τ 5.22 ppm with $^2J(HP)$ 11.5 ± 0.5 Hz.

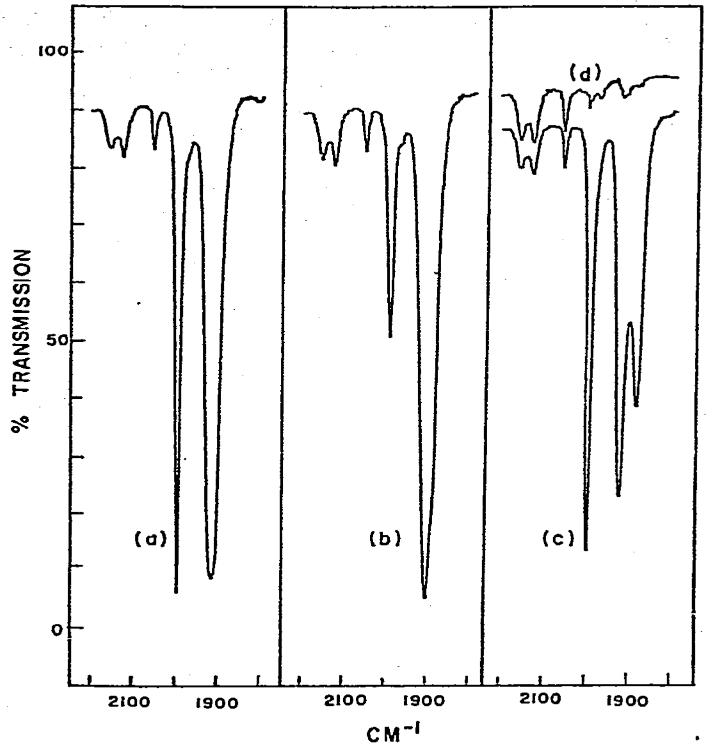
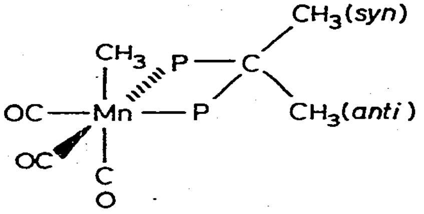


Fig. 1. Infrared spectra (CH_2Cl_2) between 2200 and 1800 cm^{-1}: (a) Predominately *fac*-$CH_3COMn(CO)_3(C_6H_5)_2PCH_2P(C_6H_5)_2$; (b) *mer*-$CH_3COMn(CO)_3(C_6H_5)_2PC(CH_3)_2P(C_6H_5)_2$; (c) *fac*-$CH_3Mn(CO)_3(C_6H_5)_2PC(CH_3)_2P(C_6H_5)_2$; (d) solvent and background absorption.

$(C_6H_5)_2$ show non-equivalent chemical shifts consistent with a facial configuration. This was noted earlier for *fac*-$CH_3Mn(CO)_3[(C_6H_5)_2PCH_2P(C_6H_5)_2]$ [14] and is clear in *fac*-$CH_3Mn(CO)_3[(C_6H_5)_2PC(CH_3)_2P(C_6H_5)_2]$. The C—$CH_3$ groups of the latter compound produce two distinct triplets with different ^3J(HP) values. The As—CH_3 groups in *fac*-$CH_3Mn(CO)_3[o\text{-}(CH_3)_2AsC_6HAs(CH_3)_2]$ also show chemical shift inequivalency.

Although the $CH_3Mn(CO)_3$(L—L) complexes can be assigned facial configurations with certainty, there do remain unanswered questions relating to (i) the exact assignments of ^1H NMR signals to specific protons, for example to the *syn*- and *anti*-C—CH_3 groups in III, and (ii) the geometry of the ligands where geometric isomerism is possible. A nuclear Overhauser effect experiment to answer the first question was suggested because of the possible close spatial prox-



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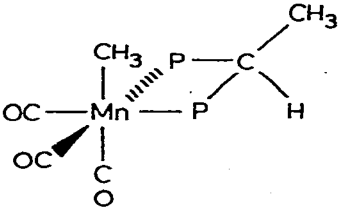

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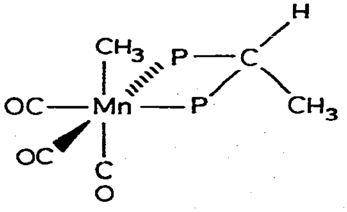


(V)

imity of the Mn—CH_3 and *syn*-C—CH_3 groups in III. The results were inconclusive as neither the high nor low field triplet C—CH_3 resonances exhibited any signal intensity enhancement upon double irradiation at the frequency of the Mn—CH_3 resonance.

^{1}H NMR spectra of *fac*-$XMn(CO)_3[(C_6H_5)_2PC(CH_3)_2(C_6H_5)_2]$, where X = H, Cl, Br and I show much more sensitivity of the chemical shift of the high field triplet [14]. We thus tentatively assign the high field triplet to the *syn*-C—CH_3 group.

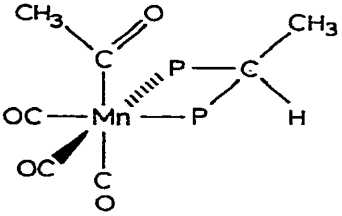
With $(C_6H_5)_2PCH(CH_3)P(C_6H_5)_2$, the possibility of the facial geometrical isomers IV and V arises. A mixture of IV and V is expected to show a 1/2/1 triplet for the Mn—CH_3 of each isomer in the τ 10—11 ppm region. However, only a single sharp triplet was observed. Thus, this product appears to be isomerically pure and based upon interligand and steric effects the geometry in V is preferred. The triphosphine $[(C_6H_5)_2PCH_2]_3CCH_3$ serves only as a bidentate ligand in the isolated facial complex as is shown by its elemental analysis and pattern of its carbonyl stretching bands. The configuration with the uncoordinated $CH_2P(C_6H_5)_2$ moiety *anti* to the Mn—CH_3 is suggested as being more likely.

$CH_3COMn(CO)_3$(L—L) complexes. The chelating ligands employed in this study can be classified according to the types of acetylmanganese complexes they form. The largest group gives exclusively facial complexes and includes $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ (where n = 2 or 3), *o*-$C_6H_4[As(CH_3)_2]_2$, $(C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2$ and $[(C_6H_5)_2PCH_2]_3CCH_3$. Two ligands, $(C_6H_5)_2PCH_2P(C_6H_5)_2$ and $(C_6H_5)_2PCH(CH_3)P(C_6H_5)_2$, produce a mixture of facial and meridional configurations. $(C_6H_5)_2PC(CH_3)_2P(C_6H_5)_2$ forms only a meridional complex.

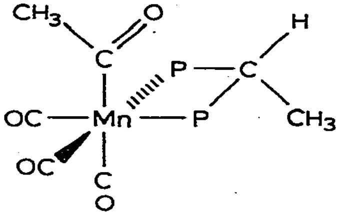
The $CH_3COMn(CO)_3$(L—L) complexes derived from the first group of ligands all exhibit a strong narrow infrared active band at 1999 ± 2 cm^{-1} and a broad strong band centered at 1917 ± 5 cm^{-1} (which may result from the overlapping of two strong bands), as expected for facial complexes. Their spectra in the 2200—1800 cm^{-1} region are essentially identical to that shown in Fig. 1a. The ^{1}H NMR spectra, either of isolated complexes or of reaction solutions monitored by ^{1}H NMR, contain only a single detectable acetyl group resonance signal. Thus, within the limits of detectability these complexes appear to be isomerically pure.

A meridional structure is assigned to $CH_3COMn(CO)_3[(C_6H_5)_2PC(CH_3)_2P(C_6H_5)_2]$. As can be seen in Fig. 1, the carbonyl stretching bands of this compound include a high energy, low intensity band as well as two overlapping lower energy bands of considerably higher intensity. Partial resolution of the two lower energy bands can be seen in tetrachloroethylene. The ^{1}H NMR spectrum of the substance is characterized by a single sharp acetyl resonance signal near τ 7 ppm and a single well-defined apparent triplet near τ 8.8 ppm for the methyl groups of the diphosphine. A pair of triplets would be expected for a facial complex as was seen for *fac*-$CH_3Mn(CO)_3(C_6H_5)_2PC(CH_3)_2P(C_6H_5)_2$ and as we have seen for other complexes with this same ligand. In the meridional configuration, the two methyl groups are chemical shift equivalent and if coupled unequally to the phosphorus nuclei should give rise to a doublet of doublets. Apparently, the two ^3J(HP) values are very close in magnitude inasmuch as a triplet signal is seen for the methyl protons. The peak separations in this apparent triplet do not change with solvent.

The one ligand employed in this study which clearly gives at least two isomeric $CH_3COMn(CO)_3(L{-}L)$ complexes is $(C_6H_5)_2PCH(CH_3)P(C_6H_5)_2$. The ^1H NMR spectrum of the mixture of $CH_3COMn(CO)_3(C_6H_5)_2PCH(CH_3)P(C_6H_5)_2$ isomers contains an acetyl group signal and a doublet of triplets for the methyl group signal and a doublet of triplets for the methyl group of the diphosphine for each isomer. An isomer ratio of approximately 3/1 was obtained from the integrated area of the two sets of peaks. Because of the inherent geometry of this diphosphine, two facial isomers, VI and VII, and one meridional isomer (*d,l*-mixture) VIII are possible.



(VI)



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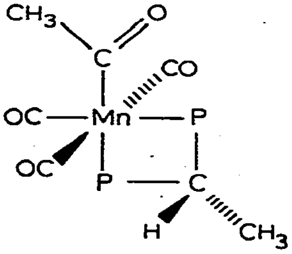

(VIII)

The isomer in greater proportion is assumed to have a facial configuration, preferably VII, based upon the gross features of the infrared spectrum of the mixture in the carbonyl stretching region. The second isomer could be VI or VIII. An argument to be presented below leads us to suggest that the second isomer is VIII. Efforts to separate these isomers have not been successful.

In an earlier paper [13], the ^1H NMR spectrum of *fac*-$CH_3COMn(CO)_3(C_6H_5)_2PCH_2P(C_6H_5)_2$ in benzene was discussed and played an instrumental role in the structural assignment proposed. Further examination of the ^1H NMR spectrum of this complex in benzene has led us to believe that a second signal near τ 7 ppm with an intensity of approximately 5—6% of the acetyl signal of the facial complex actually corresponds to the acetyl resonance signal of *mer*-$CH_3COMn(CO)_3(C_6H_5)_2PCH_2P(C_6H_5)_2$. The ratio of these two signals is solvent dependent. In methylene chloride it is approximately 85/15 in favor of the facial isomer. Owing to this low concentration of this minor isomer, neither the ^1H NMR signals for the methylene protons nor a separate set of carbonyl stretching bands were discernible. However, if this other substance is a simple geometric isomer of the previously characterized material, its structure must be meridional.

Assuming that the second $CH_3COMn(CO)_3(C_6H_5)_2PCH_2P(C_6H_5)_2$ isomer is meridional and knowing that $CH_3COMn(CO)_3(C_6H_5)_2PC(CH_3)_2P(C_6H_5)_2$ is exclusively meridional, one would predict that the percent of *mer*-$CH_3COMn(CO)_3(C_6H_5)_2PCH(CH_3)P(C_6H_5)_2$ in a facial—meridional mixture ought to be intermediate between the two previously mentioned percentages. Thus, a mixture of complexes obtained with $(C_6H_5)_2PCH(CH_3)P(C_6H_5)_2$ may be reasonably assumed to contain 75% of VII and 25% of VIII. The apparent doublet of triplets for the methyl group of the diphosphine in *mer*-$CH_3COMn(CO)_3(C_6H_5)_2PCH(CH_3)P(C_6H_5)_2$ can be accounted for if the two $^3J(HP)$ values are very nearly equal, as in *mer*-$CH_3COMn(CO)_3(C_6H_5)_2PC(CH_3)_2P(C_6H_5)_2$.

Observations on intermediate complexes. Ditertiary phosphines or arsines may coordinate to a metal through only one of the two donor atoms, as shown by a number of complexes [20]. Subsequently, the free end of the ligand could either form a chelate or bridged complex and one example of the stepwise coordination of $(C_6H_5)_2PCH_2CH_2P(C_6H_4)_2$ to a metal has been observed [21]. The reactions of chelating ligands with $CH_3Mn(CO)_5$ were carefully monitored in this work. Monosubstituted complexes were observed to be formed in each case. These $CH_3COMn(CO)_4(L—L)$ complexes were seen to undergo chelation in all instances and with $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ bridge formation was observed. The major source of information on these intermediate complexes was the readily observed changes in the ^1H NMR spectra of reaction mixtures. Although signals for each acetyl group can be observed easily, signals for the aliphatic protons of the singly attached ditertiary ligands are more difficult to decipher. Data in which we have confidence has been summarized in Table 4. For example, the intermediate $CH_3COMn(CO)_4(C_6H_5)_2PCH_2P(C_6H_5)_2$ exhibited a well-defined doublet of doublet of doublets for the methylene protons. The larger coupling constant $|^2J(HP)|$ 10.8 Hz was assigned to coupling of the methylene protons with the coordinated phosphorus atom, in line with other observations of increases in $J(HP)$ upon coördination [22]. Also, the $|^2J(HP)|$ value of 2.6 Hz for coupling to the uncoordinated phosphorus atom is very close to the 2.0 Hz value observed for the methylene protons in the free ligand. Qualitatively, the rate of formation of the various $CH_3COMn(CO)_4(L—L)$ complexes is effectively independent of the ditertiary ligands as shown by the rate of disappearance of the resonance signal of $CH_3Mn(CO)_5$. This general observation agrees with our earlier results [2].

Efforts to prove that the initially formed monosubstituted complex has a *cis* configuration were focused upon the ligands $(C_6H_5)_2PCH_2P(C_6H_5)_2$ and $(C_6H_5)_2PCH(CH_3)P(C_6H_5)_2$. As was noted from the ^1H NMR monitored reactions, each of these ligands formed primarily one $CH_3COMn(CO)_4(L—L)$ complex in high concentration before conversion to $CH_3COMn(CO)_3(L—L)$ was significant. Solutions of these intermediates were evaporated in a stream of dry nitrogen to remove solvent and unreacted $CH_3Mn(CO)_5$. The residue of $CH_3COMn(CO)_4(L—L)$ and unreacted ligand in hexane showed the infrared carbonyl stretching bands listed in Table 5. The positions and intensities of the observed bands agree well with previously noted values for complexes such as *cis*-$CH_3COMn(CO)_4(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ [23].

The course of the reaction of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ with $CH_3Mn(CO)_5$ was noted to be somewhat unique. When an equimolar mixture of the reagents was monitored by ^1H NMR, the rate of reaction of the manganese carbonyl was greater than the rate of consumption of the free ligand. In addition, a plethora o of lines in the τ 7.0—7.6 ppm region was seen. With a 2 : 1 ratio of $CH_3Mn(CO)_5$ to ligand, the major reaction was formation of the bridged complex $[CH_3COMn(CO)_4(C_6H_5)_2PCH_2]_2$. The spectral features which identified the complex are a very sharp singlet at τ 7.45 ppm (benzene) of intensity six corresponding to two identical acetyl groups and a broadened signal at τ 7.82 ppm (benzene) of intensity four due to the methylene protons of the diphosphine. Although the presence of weak signals in the acetyl region suggest that other acetylmanganese complexes are also formed under these reaction conditions, the single strong peak suggests that the two acetyl groups in the bridged complex are in identical environments. Presumably, the bridged complex has a *cis* configuration at each terminus of the diphosphine. In solution, the bridged complex was seen to de-

TABLE 4

^{1}H NMR DATA FOR $CH_3COMn(CO)_4(L—L)$ COMPLEXES AND FREE LIGANDS[a]

Ligand	Group	Intermediate complex		Uncomplexed ligand	
		C_6H_6	CH_2Cl_2	C_6H_6	CH_2Cl_2
$(C_6H_5)_2PCH_2P(C_6H_5)_2$	CH_3CO	7.37	7.50		
	$—CH_2—$	6.49 (DD)[b]	6.60 (DD)[c]	7.20 (|J(HP)| 2.0 Hz; T)	7.19 (|J(HP)| 1.8 Hz; T)
$(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$	CH_3CO	7.55	7.59		
	$—CH_2CH_2—$	[d]	[d]	7.81 (App.T)[e]	7.89 (App.T)[e]
$(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2$	CH_3CO	7.58	[f]		
	$—(CH_2)_3—$	[f]	[f]	[f]	[f]
$(C_6H_5)_2PCH(CH_3)P(C_6H_5)_2$	CH_3CO	7.45	7.52		
	$C\underline{H_3}CH$	[f]	8.78 (DDD)[g]	8.91 (DT)[h]	8.95 (DT)[h]
	$CH_3C\underline{H}$	[f]	[f]	6.74 (Q)[i]	6.75 (Q)[i]
$(C_6H_5)_2PC(CH_3)_2P(C_6H_5)_2$	CH_3CO	7.29			
	$(CH_3)_2C$	[f]		8.63 (J(HP) 10.2 Hz; T)	
o-$C_6H_4[As(CH_3)_2]_2$	CH_3CO	7.22, 7.29[j]			
	CH_3As (coord)	8.40, 8.60[j]		8.93	
	CH_3As (free)	9.04, 8.90[j]			

[a] Solvents as indicated; τ units in ppm from TMS as internal standard at τ 10 ppm; signals are singlets unless indicated; D = doublet; T = triplet; Q = quartet; τ values are believed to be accurate to ±0.02 ppm and J values to ±0.2 Hz. [b] ^3J(HP) (coord.)) 10.8 Hz; ^3J(HP (free)) 2.6 Hz. [c] $|^2J$(HP (coord))$|$ 9.7 Hz; $|^2J$(HP (free))$|$ 2.4 Hz. [d] Broad and unresolvable. [e] Apparent triplets with separation of lines equal to 4.7 Hz in C_6H_6 and 4.4 Hz in CH_2Cl_2. [f] Not readily resolved. [g] ^3J(HH) 15.0 Hz; $|^2J$(HP (coord))$|$ 7.7 Hz; $|^2J$(HP (free))$|$ 4.4 Hz. [h] ^3J(HP) 10.4 Hz; ^3J(HH) 7.1 Hz. [i] ^3J(HH) 7.1 Hz; ^2J(HP) $\simeq$ 0 Hz. [j] The second value on each line corresponds to an apparent second isomer or possibly a bridged complex of uncertain structure.

TABLE 5

SELECTED INFRARED BANDS OF SOME $CH_3COMn(CO)_4(L—L)$ COMPLEXES

Complex	ν(C=O) (cm^{-1})			
$CH_3COMn(CO)_4(C_6H_5)_2PCH_2P(C_6H_5)_2$ [a]	2066w	1990m	1969s	1950s
$CH_3COMn(CO)_4(C_6H_5)_2PCH(CH_3)P(C_6H_5)_2$ [a]	2064w	1989m	1966s	1950s
$CH_3COMn(CO)_4P(C_6H_5)_3$ [b]	2067w	1994m	1964s	1957s
$CH_3COMn(CO)_4(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ [c]	2065	1990	1955	

[a] Hexane solvent. [b] Ref. 26. [c] Ref. 24.

carbonylate to a small degree, as evidenced by the appearance of a doublet at τ 10.68 ppm with ^3J(HP) 8.1 Hz, presumably to *cis*-$CH_3Mn(CO)_4(C_6H_5)_2PCH_2$-$CH_2P(C_6H_5)_2$-*cis*-$CH_3COMn(CO)_4$. The observation of the formation of this latter complex is quite important inasmuch as this suggests that the energy required to break a P—Mn bond to allow chelation to take place is somewhat greater than that needed to break a Mn—CO bond. The bridged diacetyl complex was observed to convert ultimately to the acetyl chelate complex.

In contrast to the ease of bridged complex formation with $(C_6H_5)_2PCH_2CH_2$-$P(C_6H_5)_2$, the three bidentate ligands $(C_6H_5)_2PCH_n(CH_3)_{2-n}P(C_6H_5)_2$ (n = 0, 1 or 2) did not form detectable amounts of bridged complexes in either benzene or dichloromethane, even when the initial concnetration of $CH_3Mn(CO)_5$ was twice that of the diphosphine.

A final observation which should be noted is the relative rates of conversion of the monosubstituted complexes to the chelate complexes. In general, we have found that the smallest chelate ring systems are formed the fastest. The same conclusion has been drawn regarding ring closure in the formation of the chelate complexes $M(CO)_4(L—L)$, where M is a Group VI metal [20]. Further, we have observed that for the three ligands which form four-membered rings, the rate of chelation is fastest for $(C_6H_5)_2PC(CH_3)_2P(C_6H_5)_2$ and slowest for $(C_6H_5)_2PCH_2P$-$(C_6H_5)_2$.

Discussion

Previous studies [22,24] have shown that $CH_3COMn(CO)_4L$ complexes prefer a *cis* configuration unless L is large enough to interfere significantly with the acetyl ligand, in which case a *cis/trans* equilibrium mixture may result. The decarbonylated products $CH_3Mn(CO)_4L$ all have the *cis* structure. Thus the acetyl group exhibits a larger steric effect than the methyl ligand. The results of the present study with chelating ligands support this argument.

Each of the $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ ligands, where n = 1, 2, 3 forms a CH_3-$COMn(CO)_3(L—L)$ complex with the facial configuration. For n = 2 or 3, the facial complex is the exclusive product insofar as we have been able to detect. However, the complex of the ligand with the smallest bite, i.e. n = 1, seems to form a small amount of a second complex which presumably is meridional. The percentage of meridional isomer increases to ca. 25% with $(C_6H_5)_2PCH(CH_3)P$-$(C_6H_5)_2$, and only a *mer* complex is formed with $(C_6H_5)_2PC(CH_3)_2P(C_6H_4)_2$.

From our results we conclude that the magnitude of the steric interaction decreases with increasing chain length between the donor atoms and increases with substitution of the methylene protons in $(C_6H_5)_2PCH_2P(C_6H_5)_2$ with methyl groups. To argue that the trend noted with the chelating ligands which form four-membered rings results from a cross-ring interaction between the acetyl group and the hydrogen or methyl groups on the carbon atom in the ring is very attractive. However, with these small ring systems, the methyl groups and phenyl groups also interact strongly. Thus, the methyl groups may in fact increase phenyl—acetyl interaction rather than being directly involved in steric interaction with the acetyl group.

At this time we cannot prove the exact nature of the steric effect which has produced the results reported here. However, the effect is very real and the importance of these secondary steric effects on the geometry and chemistry of metal complexes of chelating ligands is under further study.

Some closing comments regarding the structures assigned to the complexes prepared in this work are in order. Based upon the available IR and ^1H NMR evidence, the $CH_3Mn(CO)_3(L—L)$ complexes would appear to be isomerically pure. However, Mawby and Pringle have reported that in the solid state $CH_3Mn(CO)_4P(C_6H_5)_3$ exists as a mixture of the *cis* and *trans* isomers [25]. A suggestion has been made that the ^1H NMR doublet observed for the methyl ligand in this complex might result from H—P coupling in rapidly interconverting isomers [26]. While this may possibly be the case for $CH_3Mn(CO)_4L$ complexes, our results dictate against rapid *mer—fac* isomerization of the $CH_3Mn(CO)_3(L—L)$ at ambient temperatures. In particular, the observed chemical shift inequivalence of the aliphatic protons on the chelating ligands $(C_6H_5)_2PCH_2P(C_6H_5)_2$ and $(C_6H_5)_2PC(CH_3)_2P(C_6H_5)$ can be best explained only if a static geometry at the manganese atom is assumed.

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