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THE STEREOCHEMICAL COURSE OF REACTIONS LEADING TO FORMATION OF MONO-LIGATED (PHENYLACETYL)MANGANESE TETRACARBONYL COMPOUNDS

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Summary

The stereochemistry of $LMn(CO)_4COCH_2Ph$ (L = phosphines, phosphites) is dependent on the mode of preparation. Thus preparation and stereochemistry of the title compound according to reactions of phenylacetylmanganese pentacarbonyl with L, of benzylmanganese pentacarbonyl with L, of $Na[LMn(CO)_4]$ with phenylacetyl chloride, and of $[Mn(CO)_5L][PF_6]$ with benzylmagnesium chloride are reported.

Introduction

During the course of our continuing investigation of reactions of Grignard reagents with mono-substituted octahedral metal carbonyl complexes such as $LM(CO)_5$ (M = Cr, Mo, W; L = phosphines and phosphites) [1-3] a convenient synthesis of the isoelectric $[LMn(CO)_5]^+$ series became available [4]. Benzylmagnesium chloride for example is expected to add to a carbonyl carbon of $[LMn(CO)_5]^+$ yielding the neutral phenylacetyl complex, $LMn(CO)_4COCH_2Ph$. In order to lend confidence to assignment of the stereochemistry of such addition reaction products or product mixtures, other routes to preparation of the acetyl complexes were investigated. Four modes of preparation as shown in Scheme 1 were studied; in most cases analysis of initial reaction products was complicated by the facile thermal decarbonylation reaction 5.

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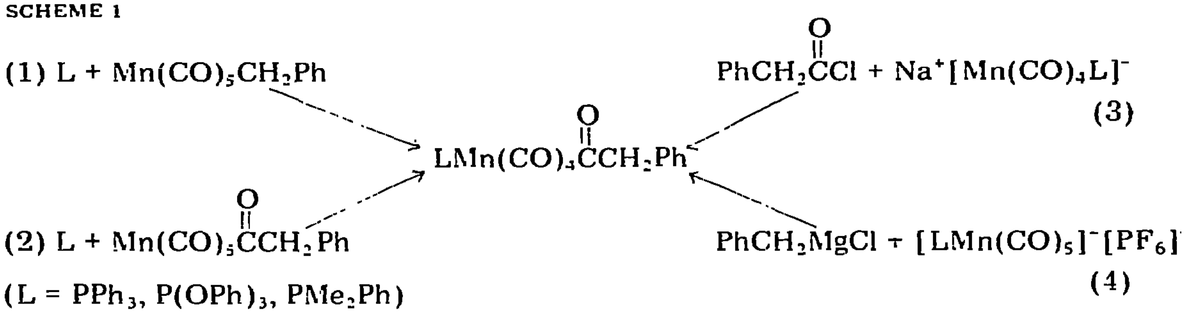
SCHEME 1



$$cis \text{ or } trans\text{-LMn(CO)}_4\text{C(O)CH}_2\text{Ph} \xrightarrow{-\text{CO}} cis\text{-LMn(CO)}_4\text{CH}_2\text{Ph} \qquad (5)$$

Experimental

Materials and equipment

Tetrahydrofuran was purified by distillation from sodium benzophenone dianion under N_2. All other solvents and reagents were reagent grade and used without further treatment. Methylcyclopentadienylmanganese tricarbonyl, used in the preparation of $Mn_2(CO)_{10}$ [5], was generously donated by the Ethyl Corporation. The phosphine and phosphite ligands were purchased from Strem Chemical Co.

Melting points were taken in open capillary tubes on a Thomas—Hoover apparatus and are uncorrected. Infrared spectra were taken on a Perkin—Elmer 521 grating spectrophotometer; the NMR spectra were obtained on a JEOLCO MH-100; and the ESR measurements were made on a Varian E-3.

Preparations

Phenylacetylmanganese pentacarbonyl and benzylmanganese pentacarbonyl. The procedure of Closson, Coffield and Kozikowski used in the preparation of acetyl- and methyl-manganese pentacarbonyl was followed [6]. A 1.60 g sample of $Mn_2(CO)_{10}$ (4.1 mmol) dissolved in 40 ml THF was reduced under N_2 with excess Na/Hg amalgam. The excess amalgam was removed through a stopcock near the bottom of the reaction flask. 2.0 ml of phenylacetylchloride was added to the green solution and stirring continued for 2 h. The color changed to yellow and the product, $PhCH_2COMn(CO)_5$, precipitated along with NaCl. The precipitate was isolated and repeatedly washed with water and finally with acetone. The air-dried white microcrystals were obtained in 87% yield, 2.24 g, m.p. 106-107° (dec.).

Benzylmanganese pentacarbonyl was obtained similarly. 2.0 ml of $PhCH_2Cl$ was stirred for 3 h with $NaMn(CO)_5$ prepared from a 3.0 g sample of $Mn_2(CO)_{10}$ and excess Na/Hg amalgam. THF was removed under vacuum and the orange residue extracted with petroleum ether. The hydrocarbon extract was reduced to dryness and the product purified by sublimation (70°/1 mm) giving 3.11 g (72%) of light yellow crystals, m.p. 38-39°.

cis-Phenylacetyl(triphenyl phosphite)manganese tetracarbonyl and cis-phenylacetyl(dimethylphenylphosphine)manganese tetracarbonyl. A solution of 0.50 g $PhCH_2Mn(CO)_5$ (1.74 mmol) and 0.47 ml $(PhO)_3P$ (1.7 mmol) in 20 ml THF was stirred under N_2 for 19 h at which time approximately 75% conversion had taken place. The solvent was removed under vacuum giving a non-volatile oil which was chromatographed on a 1 × 10″ SiO_2 column. Eluting with CH_2Cl_2 produced an initial yellow fraction shown by infrared to be a mixture of $PhCH_2Mn(CO)_5$ and $PhCH_2Mn(CO)_4P(OPh)_3$. The next, almost colorless, fraction of 100 ml was stripped of CH_2Cl_2 yielding a light yellow oil identified by IR and NMR to be *cis*-$PhCH_2COMn(CO)_4P(OPh)_3$.

Likewise a solution containing 0.60 g $PhCH_2Mn(CO)_5$ (2.0 mmol) and 0.3 ml Me_2PhP (2 mmol) in 15 ml THF was stirred under N_2 for 6 h. Removal of solvent gave 0.65 g (77%) of yellow oil identified by IR and NMR as *cis*-$PhCH_2COMn(CO)_4PMe_2Ph$.

cis-Benzyl(triphenyl phosphite)manganese tetracarbonyl and cis-benzyl-(dimethylphenylphosphine)manganese tetracarbonyl. A 0.2 g sample of $PhCH_2COMn(CO)_4L$ (L = $P(OPh)_3$ and PMe_2Ph) in 10 ml hexane was refluxed under N_2 for 4 h. Removal of the solvent under vacuum gave non-volatile yellow oils identified by IR and NMR as $PhCH_2Mn(CO)_4P(OPh)_3$ and $PhCH_2Mn(CO)_4$-PMe_2Ph, respectively.

cis-Benzyl(triphenylphosphine)manganese tetracarbonyl. A solution containing 2.2 mmol each of $PhCH_2Mn(CO)_5$ and Ph_3P dissolved in 15 ml THF was stirred under N_2 for 15 h. The volume of solution was reduced to 5 ml and the product precipitate was washed repeatedly with pentane and air-dried giving 0.55 g (48%) white microcrystals, m.p. 155° (dec.). Only the decarbonylated product, *cis*-$PhCH_2Mn(CO)_4PPh_3$, was obtained.

Preparation of Na[LMn(CO)$_4$] and reaction with phenylacetyl chloride. $[LMn(CO)_4]_2$ compounds used in the preparation of $Na[LMn(CO)_4]$ (L = PPh_3, $P(OPh)_3$ and PMe_2Ph) were obtained by a published method, using 1-butanol as solvent [7]. The reduction of the substituted dimeric products was readily effected in THF by Na/Hg amalgam. Stoichiometric amounts of phenylacetyl chloride were syringed into the THF solution of $Na[LMn(CO)_4]$, previously separated from the excess amalgam. At all times air was rigorously excluded. Product identification was accomplished by IR and NMR of the THF solutions.

Preparation of [LMn(CO)$_5$][PF$_6$] and reaction with a Grignard reagent. The preparation of a series of the mono-ligated manganese pentacarbonyl cations has been developed [4]. THF solutions of benzylmagnesium chloride (1 *M*) were syringed into samples of $[LMn(CO)_5][PF_6]$ (L = CO, PMe_2Ph) made up in THF.

Reagents for reactions to be monitored with time by IR were placed in degassed flasks and samples withdrawn via syringe. Solutions used to determine the course of reaction by NMR were prepared directly in NMR tubes sealed with a tight plastic or rubber septum cap. Small amounts of these solutions could be withdrawn for complementary IR spectra.

Results

Product identification of the mono-ligated phenylacetylmanganese tetracarbonyl derivatives was accomplished by combining IR and NMR techniques. Table 1 summarizes spectroscopic properties of compounds appropriate to this study.

TABLE 1

SPECTROSCOPIC AND PHYSICAL PROPERTIES OF MANGANESE CARBONYL DERIVATIVES

Complex	Properties	ν(CO) (hexane)				δ (ppm) of $-CH_2-$ ($CDCl_3$ soln.)
$PhCH_2Mn(CO)_5$	white m.p. 38°	2105.5 w	2013.5 vs	2006.5 vs	1991.0 s	2.38
$PhCH_2(O)CMn(CO)_5$	white m.p. 106°	2110.5 w	2048.5 w	2010.5 s	1998.3 m	4.09
cis-$PhCH_2Mn(CO)_4P(OPh)_3$	yellow oil	2066.3 m	2005.8 m	1982.5 s	1961.8 m	2.44 [$J(^{31}P-H)$ = 8.0 Hz]
cis-$PhCH_2(O)CMn(CO)_4P(OPh)_3$	yellow oil	[2079.5 m 2073.5 (sh)]	2009.3 m	1983.0 vs	1974.0 s	4.14
trans-$PhCH_2(O)CMn(CO)_4P(OPh)_3$ [a]	yellow oil	2074.0 m		1978.8 vs		4.05
cis-$PhCH_2Mn(CO)_4PPh_3$	dec. 155°	2050.0 m	1987.3 m	1963.3 s	1936.0 m	1.74 [$J(^{31}P-H)$ = 5.8 Hz]
cis-$PhCH_2(O)CMn(CO)_4PPh_3$	not isolated	2060.5 m	1984.3 m	1969.8 vs	1957.8 s	4.16 [b]
trans-$PhCH_2(O)CMn(CO)_4PPh_3$ [a]	not isolated	2056.5 m		1954.0 vs		4.36 [b]
cis-$PhCH_2Mn(CO)_4PMe_2Ph$	orange oil	2053.5 m	1988.3 m	1960.8 s	1934.0 m	[c]
cis-$PhCH_2(O)CMn(CO)_4PMe_2Ph$	yellow oil	[2062.5 (sh) 2056.0 m]	1984.3 m	1959.5 vs	1950.3 s	4.03

[a] IR spectrum measured in THF. [b] NMR measured in benzene-d_6. [c] Hidden under CH_3 resonance.

NMR assignments are consistent with IR results as well as the published assignments based on the monoligated acetylmanganese tetracarbonyl system [8, 9]. *Trans* derivatives of $LMn(CO)_4COCH_2Ph$ exhibit a two-line spectrum in the carbonyl stretching region of the infrared spectrum, a weak absorbance at 2060-2070 cm^{-1} (the formally forbidden A_1 vibration) and a strong one at 1950-1980 cm^{-1} (E mode) as illustrated in Fig. 1. Pure compounds of *cis* configuration exhibit a 4-line $\nu(CO)$ spectrum typical of unsymmetrically disubstituted octahedral complexes of C_s symmetry [intensities = medium weak ($A_1^{(2)}$), medium ($A_1^{(1)}$), strong (B_1) and medium (B_2); high to low frequencies, (Fig. 1.)]. There are two bands in the $A_1^{(2)}$ CO absorbance region for the *cis*-acyl complexes of $PhMe_2P$ and $(PhO)_3P$, (Fig. 2). (In addition the $A_1^{(1)}$ band of the $PhMe_2P$ derivative exhibits considerable flattening.) Since the *trans* isomer A_1 mode would be expected in this region, attention was directed toward the source of this doublet character. NMR data suggested these samples to be the all *cis* isomer and repeated purifications did not change the IR spectrum. Furthermore the two bands in the $A_1^{(2)}$ region are of equal intensity. Assuming one of these to be due to the presence of the *trans* isomer, the accompanying *trans* E mode should be of considerable intensity, certainly modifying the typical *cis* profile of the lower frequency bands. Although the source of the doublet character of the $A_1^{(2)}$ vibration is as yet undetermined it was concluded that the spectra represent the purely *cis* isomers.

The ligand substitution accompanied by benzyl migration (or CO insertion) reaction (eqn. 1) occurred slowly in THF at 25° requiring about 24 h for maximum

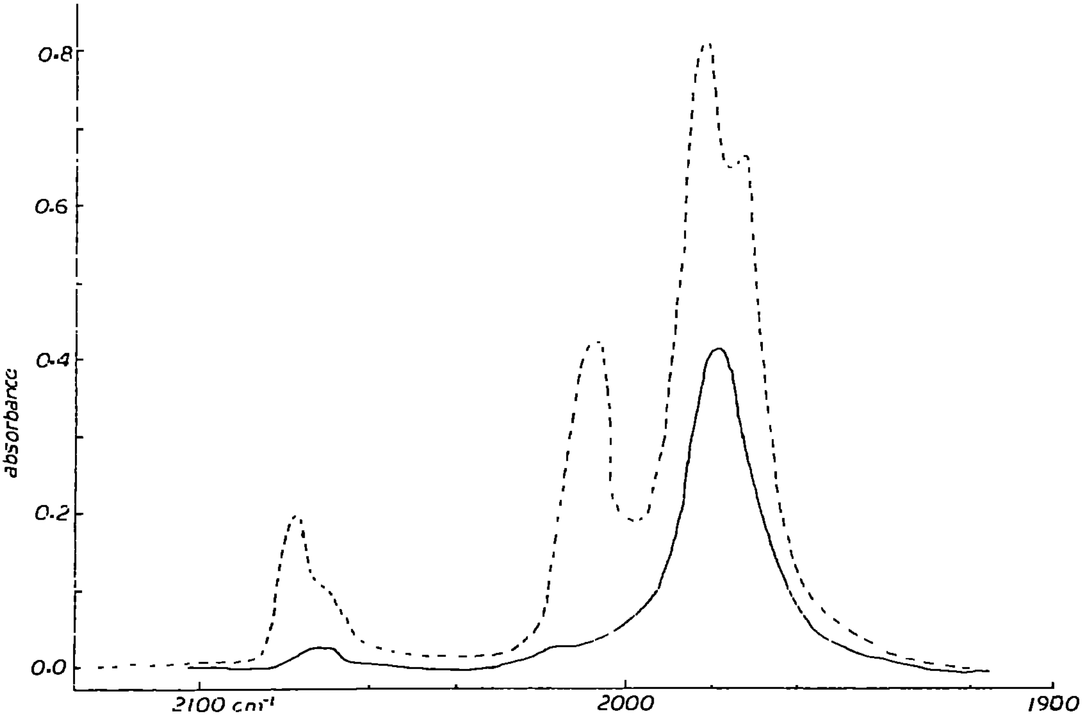


Fig. 1. Typical traces of *cis*- and *trans* $PhCH_2COMn(CO)_4L$ $\nu(CO)$ IR spectra. ———, *trans*-$PhCH_2COMn(CO)_4P(OPh)_3$; ------, *cis*-$PhCH_2COMn(CO)_4P(OPh)_3$.

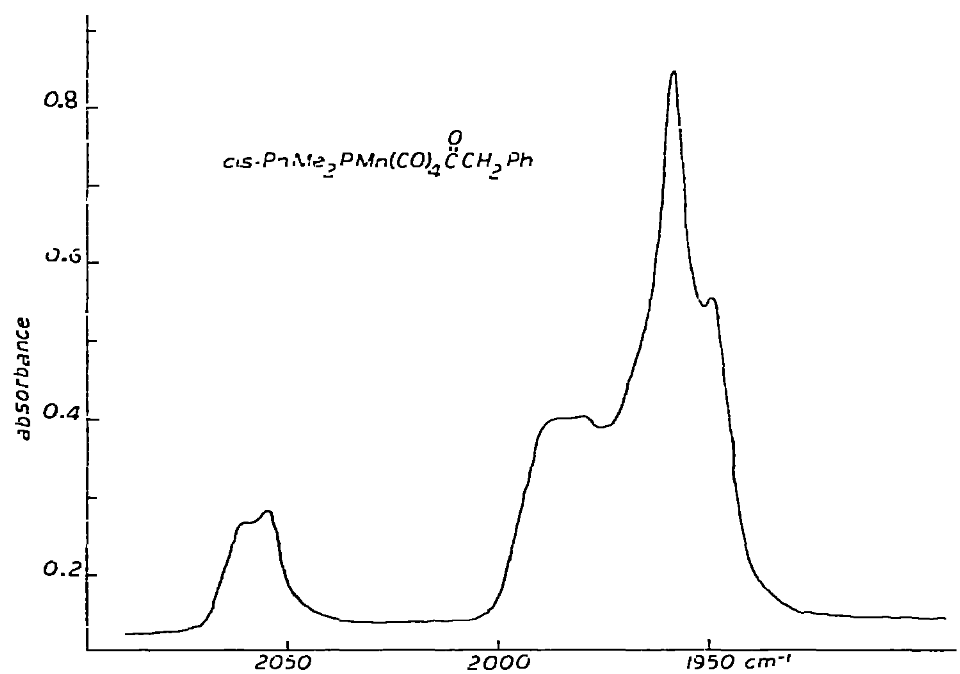


Fig. 2. IR spectrum in the CO stretching frequency region of *cis* $PhMe_2PMn(CO)_4COCH_2Ph$ in hexane.

product formation. Whereas with PMe_2Ph the phenylacetyl product was completely of *cis* geometry, $P(OPh)_3$ and PPh_3 derivatives produced in this manner contained some *trans* isomer, 15 and 25% respectively. Both *cis* and *trans*-$PhCH_2COMn(CO)_4(PPh_3)$ underwent extensive decarbonylation (eqn. 1) at 25° whereas the PMe_2Ph and $P(OPh)_3$ derivatives underwent decarbonylation only at higher temperatures.

The reaction of direct ligand replacement of a CO group in phenylacetylmanganese pentacarbonyl by PPh_3 (eqn. 2) was monitored by NMR in benzene-d_6 solution (Fig. 3). The resonance at 3.72 ppm is due to the methylene protons of $PhCH_2Mn(CO)_5$; at 4.18, to the methylene protons of *cis*-$PhCH_2COMn(CO)_4(PPh_3)$; and at 4.36, to the methylene protons of *trans*-$PhCH_2COMn(CO)_4(PPh_3)$. Over the course of 25 h maximum product formation is observed and the methylene proton resonance of the decarbonylated compound, *cis*-$PhCH_2Mn(CO)_4(PPh_3)$, begins to appear at 2.04 ppm with J(P—H) = 5.8 Hz. Again the phenylacetyl product distribution of 75% *cis*- and 25% *trans*-$PhCH_2COMn(CO)_4(PPh_3)$ is maintained throughout the displacement reaction (2) as well as during the disappearance of products due to decarbonylation (5). It was noted that the decarbonylate is quite stable and in refluxing THF, toluene, or heptane undergoes appreciable decomposition to unknown products only after 4-5 days. The expected product, $Ph_2P\text{-}\mu\text{-}C_6H_4Mn(CO)_4$, was never observed. This is contrary to the behavior of $CH_3Mn(CO)_4PPh_3$ which in refluxing toluene eliminates CH_4, producing the orthometallated $(CO)_4Mn(PPh_2\text{-}\mu\text{-}C_6H_4]$ [10].

Reaction of $P(OPh)_3$ and $Mn(CO)_5COCH_2Ph$ in benzene-d_6 at 25° led initially to production of *cis*-$(PhO)_3PMn(CO)_4COCH_2Ph$ with partial isomerization of *cis* to *trans* ensuing. After 125 h reaction a product distribution of 23% *trans*- to 77% *cis*-acetyl complex was obtained; no starting Mn complex remained and

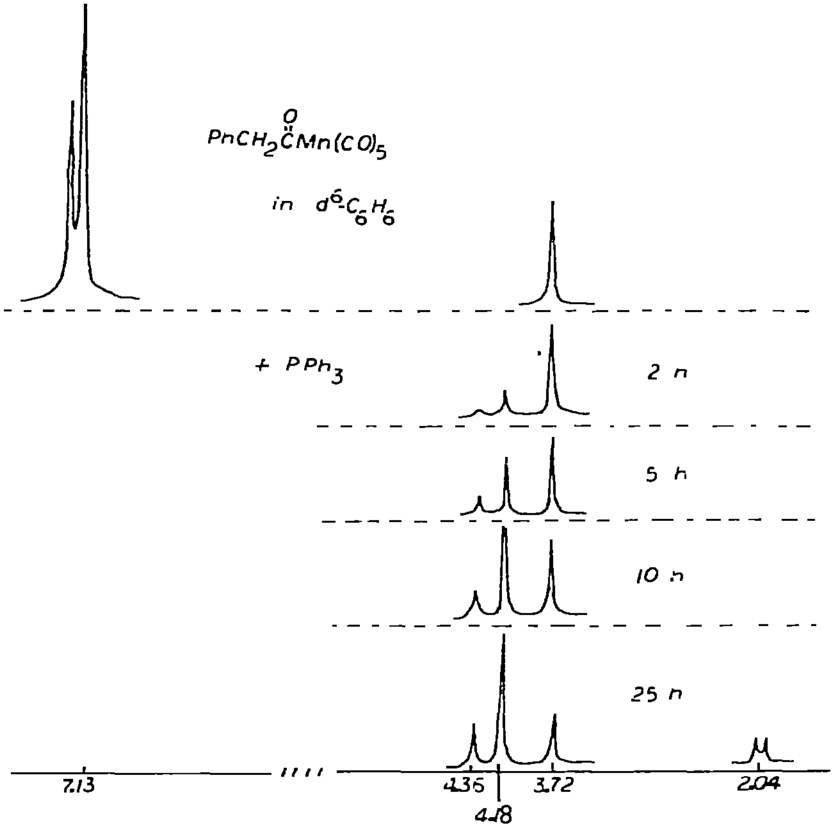


Fig. 3. NMR monitor of the reaction of PhCH$_2$COMn(CO)$_5$ and PPh$_3$ in C$_6$H$_6$-d_6 at 35°.

no decarbonylated product was observed. At higher temperatures (55° in hexane) decarbonylation was competitive with reaction 2 and hence the initial product observed was *cis*-(PhO)$_3$PMn(CO)$_4$CH$_2$Ph. Upon further reaction in the presence of excess ligand another molecule of P(OPh)$_3$ added to the decarbonylate and toluene was eliminated. The resulting white crystalline compound was determined to be the facial isomer of $\overline{\text{(PhO)}_3\text{PMn[P(OPh)}_2\text{-}\mu\text{-OC}_6\text{H}_4}$](CO)$_3$ [11].

The initial reaction of PMe$_2$Ph according to eqn. 2 also resulted in formation of *cis*-(Me$_2$Ph)PMn(CO)$_4$COCH$_2$Ph. No decarbonylation or isomerization was observed however due to the presence of excess L. Over a period of 10 days a considerable amount (~ 50% of reaction product) of the disubstituted product *fac*-(PhMe$_2$P)$_2$Mn(CO)$_3$COCH$_2$Ph built up. Identification of the stereochemistry of the latter product was facilitated by the preparation and isolation of (diphos)-Mn(CO)$_3$COCH$_2$Ph via the carbonyl replacement route (eqn. 2). Two ν(CO) bands at 1996 and 1915 cm^{-1} of relative area ratios 1/2 were consistent with its formulation as the facial isomer. A nearly identical spectrum was obtained for the disubstituted PMe$_2$Ph derivative with absorbances at 1996 and 1912 cm^{-1} also of 1/2 intensity ratio.

The ν(CO) IR spectrum of Na[PhMe$_2$PMn(CO)$_4$] in THF shows absorptions at 1940 m, 1847 m and 1817 s cm^{-1}, assigned to A_1, A_1 and E IR active modes of an axially substituted trigonal bipyramidal species (Similar frequencies and assignments are reported for Na[$Ph_3PMn(CO)_4$] [12].) Another small band seen at 1765 cm^{-1} is tentatively assigned to the presence of some disubstituted anion, [$(PhMe_2P)_2Mn(CO)_3$]$^-$. The sodium salt of [$(PhO)_3PMn(CO)_4$]$^-$ has a similar band pattern at somewhat higher frequencies, 1962 m, 1876 m, 1848 s and again the lower frequency band at 1802 cm^{-1} is seen*. The reaction of Na[$PhMe_2PMn(CO)_4$] with equimolar quantities of $PhCH_2COCl$ in THF produced *cis*-$PhCH_2COMn(CO)_4$-PMe_2Ph immediately and exclusively. To the contrary, the IR spectrum of the reaction mixture of $PhCH_2COCl$ and Na[$(PhO)_3PMn(CO)_4$] taken 5 min after mixing the reagents indicated *trans*-$PhCH_2COMn(CO)_4P(OPh)_3$ as the sole reaction product. The *trans* compound is stable for some hours and gradually (over the course of two days in THF solution) its IR spectrum changes to that of $(PhO)_3$-$PMn(CO)_4Cl$ plus some unknown carbonyl-containing product. Only a trace amount of the *cis* isomer is ever observed.

Equimolar quantities of $PhCH_2MgCl$ and [$Mn(CO)_6$][PF_6] in THF resulted in rapid formation of $PhCH_2COMn(CO)_5$. In the presence of a 30-fold molar excess of the Grignard reagent $Mn(CO)_6^+$ was immediately converted into an extremely air-sensitive species whose ν(CO) spectrum in THF consists of two bands, at 1962 and 1869 cm^{-1}, of intensity ratio 1/2. A broad ESR signal of g factor approximately 2 was obtained on this solution at 25° and was centered at 3250 Gauss. The 77 K frozen solution spectrum was resolved into a 6-line hyperfine structure ($A \simeq 78$ g) as expected for Mn d^7 radicals [13]. Since the air-sensitivity of this species precluded its isolation, magnetic susceptibility studies have not been done. Hence paramagnetism of the major product which gave rise to the IR spectrum has not been established. For example, paramagnetic Mn species such as those described by Wojcicki and Hallock [13] and by Pöe et al. [14] i.e., $Mn(CO)_5$ and $Mn(CO)_4L$, might well exist in such a reducing medium.

The same two-band ν(CO) spectrum is immediately produced on reacting $PhCH_2COMn(CO)_5$ with a 20-fold excess of $PhCH_2MgCl$. If however the Grignard is titrated into a solution of $PhCH_2COMn(CO)_5$ and the reaction monitored, a multi-band ν(CO) structure is observed to build up at 2046 and in the 1950 cm^{-1} region (Fig. 4). This intermediate spectrum may be clarified by introducing air into the reaction mixture thus destroying the species giving rise to the two-band structure. Thus a four-band ν(CO) spectrum remains, 2046 m, 1961 ms, 1950 s and 1930 m, and it has the typical profile of *cis* disubstituted octahedral metal carbonyls. Two weak absorptions are found in the acyl ν(CO) region, at 1600 and 1578 cm^{-1}. In the absence of air the intermediate spectrum may be totally converted into the final two-band structure on addition of more Grignard. On basis of frequency and intensity of the two CO bands this final product is believed to be the facial isomer of [$(PhCH_2CO)_3Mn(CO)_3$]$^{2-}$; although further definitive evidence has not been obtained, the four-band intermediate spectrum is believed to be due to the mono-anion, *cis*-[$(PhCH_2CO)_2Mn(CO)_4$]$^-$. The tendency for the

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* As reported, reactions of these [$Mn(CO)_4L$]$^-$ species with $PhCH_2COCl$ are clean, yielding $PhCH_2COMn$-$(CO)_4L$ as the only products in solution. If the low frequency band is indeed correctly assigned to [$L_2Mn(CO)_3$]$^-$, reaction with $PhCH_2COCl$ must produce either an insoluble or unstable product which is not seen by IR. No precipitates are observed. The source of this low frequency absorption is being further investigated.

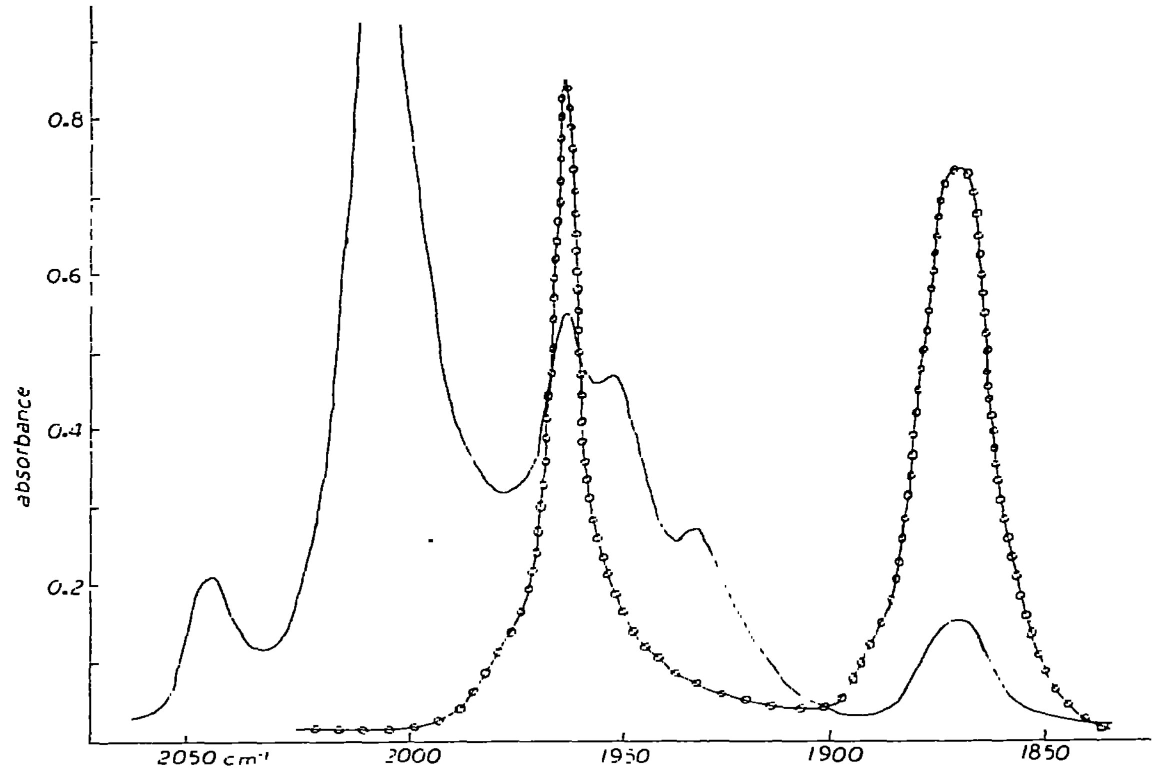

Fig. 4. IR monitor of the reaction of $PhCH_2COMn(CO)_5$ with added aliquots of $PhCH_2MgCl$ in THF ———, $[PhCH_2MgCl] < [PhCH_2COMn(CO)_5]$; θθθ, 2·1 excess of $PhCH_2MgCl$ and assigned to *fac*-$(PhCH_2CO)_3Mn(CO)_3{}^{2-}$.

mono-anion to react further with $PhCH_2MgCl$ is not understood; the vanadium hexacarbonyl anion for example is found to be completely unreactive with Grignard or organolithium reagents [15]. Multiple addition of RMgX or RLi to $M(CO)_6$ (M = Cr, Mo, W) has not been observed, but $[Ph_3PFe(CO)_3COR]^-$ tends to decompose in the presence of excess RLi of RMgX [15]. On the other hand, $Os(CO)_4Br_2$ has been observed to react with MeMgBr to yield $[(MeCO)_2Os(CO)_2Br_2]^{2-}$ which was isolated and characterized as the $[MgBr]_2[Os(COMe)_2(CO)_2Br_2] \cdot 5THF$ salt [16].

The results of addition of $PhCH_2MgCl$ to $[Me_2PhPMn(CO)_5][PF_6]$ as monitored by ν(CO) IR are shown in Fig. 5. Within a few minutes after mixing the reactants in 1/1 quantities the four-band spectrum typical of *cis* derivatives is obtained. It should be noted that since CO absorptions for the *trans*-$Me_2PhPMn(CO)_4COCH_2Ph$ isomer are expected to be in the same frequency region, 100% stereospecificity cannot be assumed. Analysis of NMR data on this system was difficult due to paramagnetic species believed to be present in small amounts as impurities. Certainly however the addition is predominantly in the *cis* position. In the presence of excess Grignard reagent further reaction occurs and a two-band ν(CO) spectrum, at 1980 and (1901, 1885) cm^{-1}, is observed. This spectrum is assumed to be due to *fac*-$[(PhMe_2P)Mn(CO)_3(COCH_2Ph)_2]^-$. The splitting of the low frequency band into two components is consistent with the asymmetry

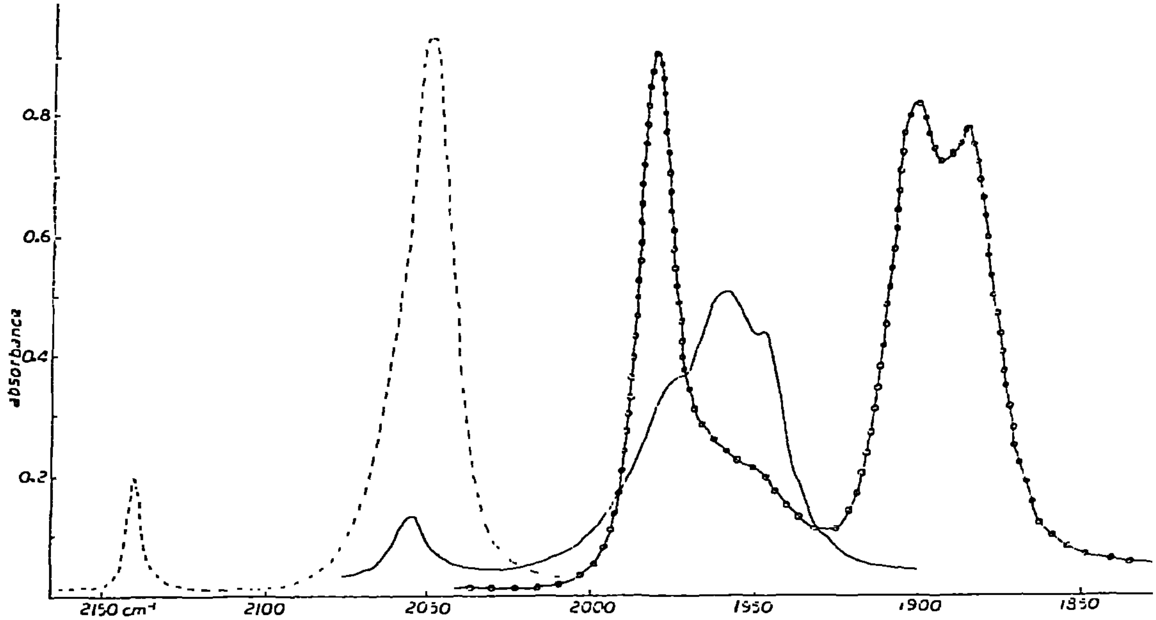

Fig. 5. IR spectra of THF solutions of $Me_2PhPMn(CO)_5{}^+PF_6{}^-$, ·········; *cis* $Me_2PhPMn(CO)_4COCH_2Ph$, ————; and *fac* $Me_2PhPMn(CO)_3(COCH_2Ph)_2{}^- MgCl^+$, o—o—o, as prepared by the reaction of $Me_2PhPMn(CO)_5{}^+PF_6{}^-$ with $PhCH_2MgCl$.

of the facial L_2L' grouping. No further addition to this proposed mono-anion occurs.

$[(PhO)_3PMn(CO)_5][PF_6]$ as well as $[Ph_3PMn(CO)_5][PF_6]$ also react with $PhCH_2MgCl$ instantaneously yielding *cis*-$PhCH_2COMn(CO)_4L$. Further reaction in the presence of excess Grignard led only to decomposition products in these cases.

Discussion

The results reported here on reaction 1 are entirely consistent with the studies of Kraihanzel and Maples on the reaction of $MeMn(CO)_5$ with a variety of ligands [8]. Evidently the phenylacetyl group does not significantly change the relative stability of the *cis* vs. *trans* isomers or their tendency to decarbonylate as compared to the acetyl derivatives. The primary difference observed here was the formation of some *trans*-$LMn(CO)_4COCH_2Ph$ in the case of $L = P(OPh)_3$ whereas in the acetyl derivative only *cis* product was observed. In view of the larger size of phenylacetyl relative to the acetyl group this observation corroborates Kraihanzel and Maples' suggestion that it is the steric interaction between ligand and acetyl groups that primarily determines the *cis*/*trans* equilibrium ratio.

Calderazzo et al. have studied the kinetics of the reaction of PPh_3 with $Me^{13}COMn(CO)_5$, concluding that a simple dissociative mechanism is involved in the ligand replacement to give $Me^{13}COMn(CO)_4PPh_3$ [9]. They were unable to ascertain the initially formed isomer. Similarly, an unfavorable kinetic situation in benzene-d_6 prevented observation of an initial isomeric ratio other than the equilibrium ratio in our studies of the reaction between PPh_3 and $PhCH_2COMn(CO)_5$ [2]. However, in the case of $P(OPh)_3$, the results are clear; *cis*-$PhCH_2COMn(CO)_4P(OPh)_3$ forms first and isomerization to the *trans* form follows in a slower step.

A most dramatic result of these studies is the extreme sensitivity of product stereochemistry towards ligand in reaction 3. Whether this is due to differences in stereochemistry or rigidity of stereochemistry as L changes in $[LMn(CO)_4]^-$ or to differences in reaction pathway dependent on L is unclear.

The Cotton—Kraihanzel CO stretching force constants of $[Mn(CO)_6]^+$ (k = 18.13 mdyn/Å), $[Mn(CO)_5PMe_2Ph]^+$ (k_{trans} = 17.36; k_{cis} = 17.44) and $[Mn(CO)_5P(OPh)_3]^+$ (k_{trans} = 17.74; k_{cis} = 17.65) are quite high compared with similar isoelectronic Cr complexes: $Cr(CO)_6$ (k = 16.44), $Cr(CO)_5PMe_3$ (k_{trans} = 15.54, k_{cis} = 15.75) and $Cr(CO)_5P(OEt)_3$ (k_{trans} = 15.74, k_{cis} = 15.88)*. The $V(CO)_6^-$ anion has of course a still lower force constant, k = 14.55 [17]. The fact that the manganese cations reacts instantaneously with $PhCH_2MgCl$; that the neutral chromium complexes have moderate rates which have been followed by conventional kinetic techniques [2]; and that the vanadium anion shows no reaction whatsoever, is consistent with the argument that higher force constants are indicative of higher positive charge on carbonyl C atoms [1]. Furthermore the exclusively *cis* geometry of addition products of $LM(CO)_5$ (M = Cr, Mo, W) with RLi of RMgX has been attributed to electronic stereochemical control since $k_{cis} > k_{trans}$ for these complexes. It will be noted that in the case of $[LMn(CO)_5]^+$ species the values of k_{cis} are much closer to that of k_{trans} and in the case of the $(PhO)_3P$ derivative their order is inverted compared to the similar $Cr(CO)_5P(OEt)_3$ complex. However in *all* cases *cis* addition products are obtained. It should also be pointed out that $[Mn(CO)_5PMe_2Ph][PF_6]$ was found to rapidly react with primary amines, e.g., $C_6H_{11}NH_2$, to form carbamoyl derivatives of *cis* geometry such as *cis*-$(PhMe_2P)Mn(CO)_4CONHC_6H_{11}$ [4].

It has been suggested that the apparent anomalies in the *cis* and *trans* CO force constants of the $LMn(CO)_5^+$ series as compared to the isoelectronic $LCr(CO)_5$ series to be due to "direct donation" of donor L (L = phosphine or phosphite) electron density into π^* CO orbitals [4]. In such cases it is entirely possible that the previous arguments regarding the relationship between force constant and charge must be altered.

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* More complete compilations may be found in ref. 2 and 4.

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