

CARBONYLATION AND HYDROGENATION OF *cis*-CH₃Mn(CO)₄L, SUBSTITUTIONAL REACTIVITY OF *cis*-HMn(CO)₄L, AND BINUCLEAR ELIMINATION BETWEEN *cis*-CH₃Mn(CO)₄P(OPh)₃ AND *cis*-HMn(CO)₄P(OPh)₃ (L = CO, PPh₃, P(OPh)₃, PBu₃ AND P(OMe)₃)

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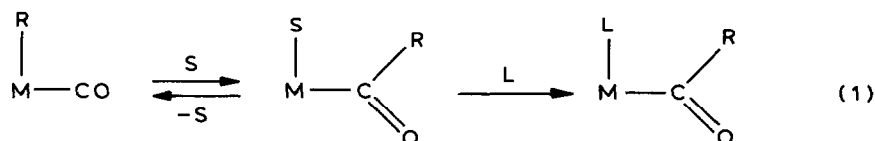
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Summary

Several reactions of *cis*-CH₃Mn(CO)₄L and *cis*-HMn(CO)₄L, have been investigated. The carbonylation of *cis*-CH₃Mn(CO)₄L (L = CO, P(OPh)₃, P(OMe)₃ and PBu₃) shows only a very small ligand effect, indicating a transition state that has little unsaturation. Reaction with H₂ has very similar observed rate constants and activation parameters to the carbonylation. The hydrides, *cis*-HMn(CO)₄L (L = P(OPh)₃, PPh₃ and PBu₃), are remarkably unreactive toward substitution, requiring temperatures of 100°C. A radical mechanism is most likely. Reactions of *cis*-HMn(CO)₄P(OPh)₃ with *cis*-CH₃Mn(CO)₄P(OPh)₃ and *cis*-HMn(CO)₄PBu₃ with CH₃C(O)Mn(CO)₅ occur at temperatures where methyl migration is readily established and the hydride complexes are unreactive. Thus methyl migration, followed by coordination to a bridging hydride, is indicated for these binuclear reductive elimination reactions.

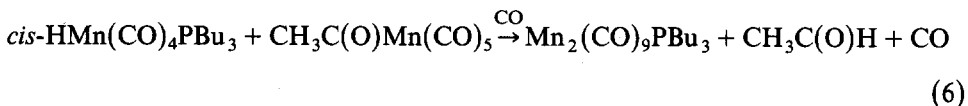
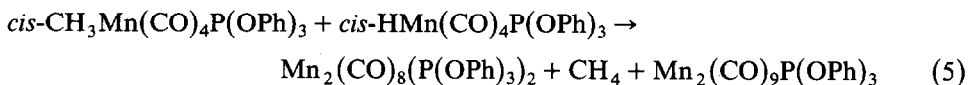
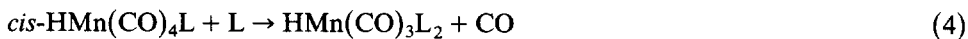
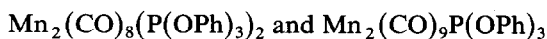
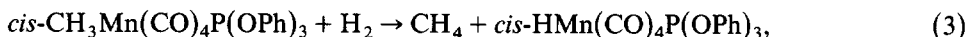
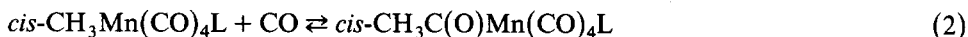
Knowledge of the reactivity of alkyl and hydride complexes is vital to an understanding of many important organometallic reactions. Carbonylation reactions, where an alkyl transition metal complex is converted to an acyl transition metal complex, are of fundamental importance to several catalytic processes, [1–6]. A number of studies have focused on the nature of the carbonylation reaction and the data have been interpreted in terms of an alkyl migration with the mechanism as shown in eq. 1 [7–16].



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The reaction rate depends on the solvent (S), the entering nucleophile (L) and the alkyl group (R) [7–22]. On the other hand, the reactions of transition metal hydride complexes, which are equally important in catalytic reactions [3,4] are not as readily summarized. Stoichiometric reactions of hydride complexes often occur through 17-electron intermediates in contrast to catalytic reactions which are suggested to occur through ligand dissociation [23–31].

Continuing our studies of the modification of organometallic reactivity by changes in the ligand environment at a transition metal center [32–36], we have investigated the following reactions:



where L = P(OMe)₃, P(OPh)₃, P^tBu₃, and CO

To minimize complications from solvent effects we have utilized decane as the solvent for these reactions.

Experimental

Preparations

Hexane, octane, and benzene were refluxed over calcium hydride until dry, then vacuum distilled. Toluene and THF were refluxed over sodium/benzophenone until dry, and vacuum distilled. These solvents were stored over molecular sieves until used. Decane was purified by stirring twice, 24 h each, with sulfuric acid. The sulfuric acid was removed and the decane washed with water, passed down an alumina column, and stored over sodium until used. Methanol, xylene, methyl iodide (Baker Chemicals) and diglyme (Aldrich Chemical Co.) were used as obtained. Triphenylphosphite, trimethylphosphite, tributylphosphine, triphenylphosphine, triphenylarsine and dimanganese decacarbonyl were purchased from Strem Chemicals. Literature procedures were followed for the synthesis of CH₃Mn(CO)₅ [37].

All reactions were carried out under nitrogen or argon atmospheres, using Schlenk techniques. Infrared spectra were recorded on a Beckman 4240 infrared spectrophotometer; NMR spectra were recorded on either a Varian EM390 or JEOL FX 90Q spectrometer.

Syntheses of *cis*-CH₃Mn(CO)₄L's [38]

Stoichiometric quantities of L and CH₃Mn(CO)₅ were refluxed in a solvent for a period of time, the solvent removed, and the oily residue crystallized from hexane: L = PPh₃, toluene, 24 h; L = AsPh₃, benzene, 8 h; L = P(OPh)₃, THF, 5 h;

TABLE 1

INFRARED SPECTRA FOR *cis*-RMn(CO)₄L (R = CH₃, CH₃C(O), or H; L = PPh₃, AsPh₃, P(OPh)₃, PBu₃, P(OMe)₃, CO) IN DECANE

R	L	$\nu(\text{CO}) (\text{cm}^{-1})$
CH ₃	PPh ₃	2059w, 1988m, 1972s, 1939m
CH ₃	AsPh ₃	2055s, 1979m, 1968s, 1934m
CH ₃	P(OPh) ₃	2072w, 2001m, 1985s, 1961m
CH ₃	PBu ₃	2055w, 1980m, 1963s, 1928m
CH ₃	P(OMe) ₃	2069w, 1999m, 1978s, 1945m
CH ₃	CO	2115w, 2015s, 1994s
CH ₃ C(O)	P(OPh) ₃	2085w, 2015s, 1990m, 1978w
CH ₃ C(O)	PBu ₃	2057w, 1987s, 1964m, 1949m
CH ₃ C(O)	P(OMe) ₃	2065w, 2012s, 1990m, 1967w
CH ₃ C(O)	CO	2115w, 2052m, 2011s, 2006sh
H	PPh ₃	2061w, 1983m, 1957s
H	P(OPh) ₃	2071w, 1998m, 1978s, 1953sh
H	PBu ₃	2054m, 1975m, 1956s, 1946s
H	P(OMe) ₃	2073m, 1977vs, 1965s, 1947sh

L = PBu₃, benzene, 5 h; L = P(OMe)₃, THF, 4 h. Further purification was effected by recrystallization from hexane or column chromatography. The infrared spectra are reported in Table 1; the NMR spectra (benzene-*d*₆) are: L = PBu₃, δ 0.95(m), 1.42(m) and -0.12 (d) ($J(\text{P-H})$ 7 Hz); L = P(OMe)₃, δ 2.95(d) ($J(\text{P-H})$ 10 Hz) and -0.24 (d) ($J(\text{P-H})$ 8 Hz).

Acetylmanganesepentacarbonyl was prepared by carbonylation of CH₃Mn(CO)₅ at room temperature for 5 d at 750 psi. Slowly cooling the autoclave to dry ice temperature resulted in colorless needles which were collected by filtration. Further purification was effected by sublimation at -5°C . The infrared spectrum is reported in Table 1; the ¹H NMR spectrum showed a singlet at δ 2.26 ppm.

Syntheses of *cis*-HMn(CO)₄L

The hydrides are all prepared by protonation of the anions Mn(CO)₄L[−] which are prepared from the dimers Mn₂(CO)₈L₂ [40,41]. The dimers were prepared by refluxing stoichiometric quantities of Mn₂(CO)₁₀ and L (IR's in hexane): L = PBu₃, toluene, 8 h, 91% (IR, 1972w, 1947vs, 1934vw); L = P(OPh)₃, 1-butanol, 6 h, 41% (IR, 2039w, 1977vs); L = PPh₃, 1-butanol, 2 h, 52% (IR, 1985sh, 1955vs; L = P(OMe)₃, toluene, 5 h, 22% (IR, 2066vw, 1995w, 1967vs, 1947vw, 1929vw.) The dimers were cleaved to the anions by reaction with Na/Hg in THF under an inert atmosphere. The solid products were isolated by decantation, filtration and THF removal and were then thoroughly washed with hydrocarbon solvents. Protonation was accomplished by addition of acetic acid in THF. The hydride product was purified on a Florisil column with mixtures of hexane/benzene. The infrared spectra are given in Table 1; the NMR spectra (benzene-*d*₆) are: L = PPh₃, τ 16.9, $J(\text{P-H})$ 33 Hz; L = P(OPh)₃, τ 17.8 ppm, $J(\text{P-H})$ 56 Hz; L = PBu₃, τ 17.7, $J(\text{P-H})$ 37 Hz; L = P(OMe)₃, τ 17.8 ppm $J(\text{P-H})$ 50 Hz.

Kinetic studies

Cis-methylmanganese tetracarbonyl tributylphosphine, *cis*-methylmanganese tetracarbonyl trimethylphosphite and *cis*-hydridomanganese tetracarbonyl tri-

butylphosphine were purified before use by chromatographing on an alumina column with hexane. Solutions of substituted methylmanganese carbonyls and hydrides were made up to be approximately 1 mM and 20 ml portions of these solutions were used for each kinetics experiment. The solutions were stored in the dark under nitrogen until used.

The reactions were accomplished in foil wrapped, 100 ml, 2 necked, jacketed vessels in darkened hoods and followed by infrared spectroscopy. Infrared spectra were measured on a Beckman 4240 Infrared Spectrophotometer in the absorbance mode using 1.0 mm NaCl solution cells. The reactions were followed until equilibrium or completion (~ 3 half-lives) was reached.

The reaction vessel was flushed with nitrogen before the kinetics solution was introduced. The solution was brought to reaction temperature, and maintained at that temperature by a Haake FS constant temperature circulator to within $\pm 0.1^\circ\text{C}$. For reactions under CO, excess nitrogen was evacuated from the vessel and carbon monoxide at one atmosphere pressure was introduced. The vessel was evacuated and filled with carbon monoxide three times. At appropriate time intervals, 0.5 ml of solution was removed via syringe through a septum and the infrared spectrum immediately recorded.

Carbonylation reactions produced an equilibrium (reaction 2) with the equilibrium constant,

$$K_{\text{eq}} = \frac{[\text{CH}_3\text{C}(\text{O})\text{Mn}(\text{CO})_4\text{L}]}{[\text{CH}_3\text{Mn}(\text{CO})_4\text{L}][\text{CO}]}$$

For experiments with one atmosphere of CO the $[\text{CO}]$ was assumed to be $1.0 \times 10^{-2} M$ from comparison to the solubility in heptane [42,43]. The $[\text{CO}]$ will decrease with increasing temperature but the change over a 20°C range should be no more than 20% [42,43]. Since the rate constants for carbonylation appear to be invariant to $[\text{CO}]$ only the equilibrium constants are affected.

Results and Discussion

The reactions under consideration are those shown in reactions 2–6. The rate and equilibrium constants for the carbonylation of *cis*- $\text{CH}_3\text{Mn}(\text{CO})_4\text{L}$ at 70°C are given in Table 2 and the activation parameters in Table 3. The complexes with more weakly bonding ligands, $\text{L} = \text{PPh}_3$ and AsPh_3 , underwent L loss at comparable rates to the migration precluding detailed investigation of the alkyl migration.

TABLE 2

COMPARATIVE DATA AT 70°C FOR THE CARBONYLATION OF *cis*- $\text{CH}_3\text{Mn}(\text{CO})_4\text{L}$

L	$k_f (\text{s}^{-1})$	$K_{\text{eq}} (M^{-1})$
CO	1.9×10^{-5}	120
$\text{P}(\text{OMe})_3$	2.3×10^{-5}	140
$\text{P}(\text{OPh})_3$	3.6×10^{-5}	170
$\text{P}(\text{OPh})_3^a$	3.5×10^{-5}	170
PBu_3	4.5×10^{-4}	180

^a $1/2$ atmosphere CO.

TABLE 3

 ACTIVATION PARAMETERS FOR CARBONYLATION AND HYDROGENATION REACTIONS OF *cis*-CH₃Mn(CO)₄L

L	ΔH_i^* (kcal mol ⁻¹)	ΔS_i^* (cal K ⁻¹ mol ⁻¹)
CO	10.5 ± 1.7	-50 ± 5
P(OPh) ₃	15.3 ± 1.3	-34 ± 4
P(OMe) ₃	15.1 ± 1.7	-36 ± 5
PBu ₃	23.2 ± 0.6	-7 ± 2
P(OPh) ₃ ^a	23.0 ± 5.0	-11 ± 13
P(OPh) ₃ ^b	20.6 ± 5.0	-22 ± 12

^a 1/2 atmosphere CO. ^b H₂.

The comparative equilibrium constants show small variation with the nature of the ligand. Equilibrium constants for L = CO (CH₃Mn(CO)₅) in various solvents have been previously evaluated [7]. Given that the previous study did not include decane as a solvent and that the temperature ranges are different, the agreement between our value for *K* and that previously reported is satisfactory [7]. The variation of equilibrium constant with the nature of the ligand at 70°C suggests a steric contribution to the equilibrium constant with the bulkier ligand favoring the acyl product. The cone angle of an acyl and an alkyl are approximately the same. However, as a planar species, the acyl may orient to minimize steric interactions. The equilibrium constants do not correlate directly with any electronic bonding parameter.

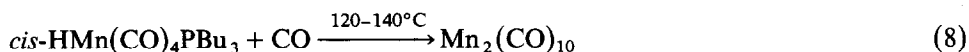
The rate constant variations with L are not very large as shown in Table 2, a factor of 20 for the ligands investigated, there is essentially no variation with the exclusion of L = PBu₃. This effect is considerably smaller than the effect of these ligands on dissociative reactions where the donor ability of the ligand is important for stabilization of the unsaturated transition state [32–36]. This small ligand effect for the alkyl migration indicates that the transition state is not coordinatively unsaturated or that the stabilization of the transition state is offset by a stabilization of the ground state. The stabilization of the ground state by donor ligands should be reflected in the equilibrium constants. Thus it is likely that in decane the transition state for methyl migration on *cis*-CH₃Mn(CO)₄L does not contain a coordinatively unsaturated metal center.

The very similar rates and activation parameters for reaction with 1/2 atmosphere CO, with 1 atmosphere CO and with 1 atmosphere H₂ indicate little contribution from the entering ligand. The difference in the rates and activation parameters for L = PBu₃ may indicate a shift in the transition state.

The reaction of *cis*-CH₃Mn(CO)₄P(OPh)₃ with H₂ occurs with very similar rates and activation parameters to the carbonylation reaction. This reaction, in contrast to the carbonylation, goes to completion with a mixture of products, CH₄, *cis*-HMn(CO)₄P(OPh)₃, Mn₂(CO)₈(P(OPh)₃)₂ and Mn₂(CO)₉P(OPh)₃. The similarity in rate to carbonylation suggests that the reaction proceeds initially by methyl migration; subsequent reactions are speculative, perhaps oxidation addition of H₂ (as suggested for catalytic hydrogenation of alkenes by *cis*-HMn(CO)₄PPh₃ in a photochemical reaction) [28], dissociation of CO and reductive-elimination of CH₄. The dimeric species could arise from binuclear reductive elimination as *cis*-

$\text{HMn}(\text{CO})_4\text{P}(\text{OPh})_3$ builds up in solution. Overlap of infrared absorptions makes it impossible to further define the mechanism for reaction of H_2 with *cis*- $\text{CH}_3\text{Mn}(\text{CO})_4\text{P}(\text{OPh})_3$.

The hydride complexes, *cis*- $\text{HMn}(\text{CO})_4\text{L}$ (L = phosphine or phosphite ligand) are amazingly unreactive. Carefully purified complexes are unreactive toward ligand substitution at temperatures less than $\sim 90^\circ\text{C}$ in the absence of light. At 90°C *cis*- $\text{HMn}(\text{CO})_4\text{PPh}_3$ undergoes PPh_3 replacement; *cis*- $\text{HMn}(\text{CO})_4\text{P}(\text{OPh})_3$ is unreactive under similar conditions. *cis*- $\text{HMn}(\text{CO})_4\text{PBu}_3$ undergoes substitution reactions between 120 – 140°C :



Several characteristics of these reactions of the hydrides indicate seventeen-electron intermediates: (1) The rates are inconsistent from one reaction to another and even within a given reaction. (2) Light strongly catalyzes the substitution reactions. (3) The product of the reaction with CO is $\text{Mn}_2(\text{CO})_{10}$. (4) The presence of CO does not significantly affect the rate of reaction of PBu_3 with *cis*- $\text{HMn}(\text{CO})_4\text{PBu}_3$.

The significant feature of the reactivity of the hydrides is the greatly lowered ligand substitutional reactivity of *cis*- $\text{HMn}(\text{CO})_4\text{L}$ (L = phosphine or phosphite) in comparison to $\text{HMn}(\text{CO})_5$. This represents a very large ligand effect and apparently a change in mechanism. The rate data for $\text{HMn}(\text{CO})_5$ indicated either direct nucleophilic attack or a hydride migration [25]. Both steric interactions and electronic factors would indicate a decrease in rate for nucleophilic attack on *cis*- $\text{HMn}(\text{CO})_4\text{L}$ in comparison to $\text{HMn}(\text{CO})_5$, consistent with the observations. For such a dramatic ligand effect a hydride migration would have to be very different than methyl migration. Thus the probable mechanism for $\text{HMn}(\text{CO})_5$ (nucleophilic attack) is sufficiently inhibited that homolysis of the H–Mn bond becomes rate-determining for *cis*- $\text{HMn}(\text{CO})_4\text{L}$ at considerably more severe conditions than required for substitution of $\text{HMn}(\text{CO})_5$.

We have also investigated the reactions of *cis*- $\text{CH}_3\text{Mn}(\text{CO})_4\text{P}(\text{OPh})_3$ with *cis*- $\text{HMn}(\text{CO})_4\text{P}(\text{OPh})_3$ and of $\text{CH}_3\text{C}(\text{O})\text{Mn}(\text{CO})_5$ with *cis*- $\text{HMn}(\text{CO})_4\text{PBu}_3$ [44]. Both of these reactions occur at moderate conditions (60°C) where no ligand substitution behavior is seen for *cis*- $\text{HMn}(\text{CO})_4\text{PBu}_3$ or *cis*- $\text{HMn}(\text{CO})_4\text{P}(\text{OPh})_3$. Thus, rate-determining rearrangement of the alkyl or acyl group is indicated. Quantitative studies of these reactions (reactions 5 and 6) were prohibited by severe overlap of infrared spectra. However, the reactions proceeded at conditions where methyl migration occurs. Thus a binuclear hydride transfer such as that suggested for reaction of $\text{CH}_3\text{MoCp}(\text{CO})_3$ with $\text{HMoCp}(\text{CO})_3$ or $\text{HCo}(\text{CO})_4$ with $\text{EtOOCCH}_2\text{Co}(\text{CO})_4$ is indicated [45,46].

A study of binuclear elimination from $\text{HMn}(\text{CO})_5$ and *p*- $\text{CH}_3\text{OC}_6\text{H}_4\text{-CH}_2\text{Mn}(\text{CO})_5$ indicated that the product observed may be sensitive to the solvent and to ligand effects, [47,48]. The mechanism of alkane formation involved either CO dissociation or cleavage of the R–Mn bond on *p*- $\text{CH}_3\text{O-C}_6\text{H}_4\text{CH}_2\text{Mn}(\text{CO})_5$. We cannot rule out these mechanisms for reaction 5, but believe the similarity in rates to the carbonylation reaction suggests an initial methyl migration for reaction 5.

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