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Protonolysis reactions in the series $RMn(CO)_5$ and $RC(O)Mn(CO)_5$

Philip L. Motz, Daniel J. Sheeran *, and Milton Orchin

Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221 (U.S.A.)

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Abstract

Proton cleavage (protonolysis) of the R–Mn bond in $RMn(CO)_5$ complexes occurs readily and cleanly with CF_3SO_3H to give the corresponding RH compounds. The relative order of reactivity in the series of $RMn(CO)_5$ compounds we have prepared is R = H, CH_3, Ph, *p*-$CH_3C_6H_4$, *p*-BrC_6H_4, *p*-$CF_3C_6H_4$ > $PhCH_2$ > *p*-$ClC_6H_4CH_2$ ≅ *p*-$CH_3OC_6H_4CH_2$ ≫ $PhCH_2CH_2$. Protonolysis with HBF_4 is much slower than with triflic acid in every case. The reaction with both acids very likely proceeds by attack of the proton on Mn followed by reductive elimination.

Surprisingly, the corresponding $RC(O)Mn(CO)_5$ compounds on treatment with triflic acid do not undergo protonolysis to aldehydes. Instead, hydroxycarbenes are formed reversibly and the acyls are slowly decarbonylated to $RMn(CO)_5$ which then undergo protonolysis and reductive elimination to give quantitative yields of RH.

Introduction

Acylcobalt tetracarbonyls, $RC(O)Co(CO)_4$, and acylmanganese pentacarbonyls, $RC(O)Mn(CO)_5$, are precursors to aldehydes, acids, and esters in many catalytic reactions involving synthesis gas (H_2/CO). The cleavage agent in these reactions is either dihydrogen, a metal hydride, or a protic solvent. Cleavage of these acyls with the hydridometal carbonyls, $HCo(CO)_4$ and $HMn(CO)_5$, in a stoichiometric reaction to give aldehydes has been rather thoroughly studied [1]. $HCo(CO)_4$ is known to be a rather strong acid (estimates of its pKa range from -1.3 to -5) [2] but its reaction with both cobalt and manganese acyls almost certainly proceeds by a binuclear elimination mechanism involving the undissociated hydride rather than by cleavage with the proton (protonolysis). The few reports dealing with the reaction of protons with acylmetal carbonyl complexes indicate that attack occurs at the ketocarbonyl oxygen [3] rather than at the metal, yielding cationic hydroxycarbenes,

* Present address: Department of Chemistry, Wagner College, Staten Island, N.Y. 10301.

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but such compounds have not been isolated. A study was therefore undertaken to determine whether the acyls could be cleaved by the very strong acids CF_3SO_3H (triflic acid) and HBF_4.

In the studies reported here manganese carbonyls were used rather than the corresponding more commercially important cobalt complexes because the latter are very unstable even in solution at room conditions whereas both acyl- and alkylmanganese pentacarbonyls are almost always stable solids. Furthermore, the triflate and terafluoroborate salts of the cationic manganese pentacarbonyl which are products of the cleavage reaction are exceedingly stable, unreactive solids.

Results of reaction of triflic acid with $RMn(CO)_5$

Although our initial interest concerned the cleavage reaction with acylmanganese carbonyls it soon became apparent that such compounds readily undergo decarbonylation (eq. 1) prior to cleavage:

$$RC(O)Mn(CO)_5 \rightleftharpoons RMn(CO)_5 + CO \quad (1)$$

In fact most of our $RMn(CO)_5$ compounds were prepared by thermal decarbonylation of the corresponding acyl complexes. Fortunately methylene chloride solutions of alkylmanganese carbonyls are stable at room temperature in an inert atmosphere and hence their reactions with triflic acid are not complicated by the presence of an equilibrium concentration of the corresponding acyl complex.

A series of ten $RMn(CO)_5$ compounds was prepared where R = H, CH_3, Ph, p-$CF_3C_6H_4$, p-$CH_3C_6H_4$, p-BrC_6H_4, $PhCH_2$, p-$ClC_6H_4CH_2$, p-$CH_3OC_6H_4CH_2$, and $PhCH_2CH_2$. These compounds are characterized in the experimental section and their IR spectra are summarized in Table 1.

Approximately 1 mmol of each $RMn(CO)_5$ was dissolved in CH_2Cl_2 in a serum-capped flask under an inert atmosphere and then a stoichiometric quantity of triflic acid (or tetrafluoroboric acid) was added through the serum stopper. In cases where gases were evolved (R = H, CH_3) the reaction was monitored by attachment of the reaction flask to a gas buret. In other cases, samples were removed periodically and subjected to TLC and IR examination in order to track the disappearance

Table 1 [a]

Carbonyl Stretching Frequencies of Acylmanganese Pentacarbonyls, $RC(O)Mn(CO)_5$ [b]

R	ν(CO) (cm^{-1}) [d]				ν(keto) (cm^{-1})
	A_1	B_1	E	A_1	
CH_3 [c]	2108 (w)	2045 (w)	2000 (s)	1975 (m, sh)	1658 (m)
C_6H_5	2117 (m)	2058 (w)	2016 (s)	2010 (s)	1634 (w)
p-$CH_3C_6H_4$	2117 (m)	2056 (w)	2021 (s)	2014 (s)	1634 (w)
p-$CH_3OC_6H_4$	2117 (m)	2055 (w)	2014 (s)	1999 (s)	1606 (m)
p-BrC_6H_4	2119 (m)	2059 (m)	2017 (s, br)		1601 (m, br)
p-$CF_3C_6H_4$	2121 (m)	2060 (m)	2016 (s, br)		1618 (w)
$C_6H_5CH_2CH_2$	2113 (m)	2055 (w)	2014 (s)	1982 (sh)	1635 (m)
$C_6H_5CH_2$	2117 (m)	2055 (w)	2018 (s)	2010 (s)	1631 (w, br)
$p-ClC_6H_4CH_2$	2117 (m)	2057 (w)	2017 (s, br)		1641 (w, br)

[a] For references to previous literature, see experimental. [b] Chloroform solutions. [c] Pentane solution. [d] Assignments based on C_{4v} symmetry for the terminal carbonyls.

of $RMn(CO)_5$. During the course of the reaction no $RC(O)Mn(CO)_5$ or RCHO was ever observed. After the disappearance of all the $RMn(CO)_5$ (TLC) the solvent and other volatile compounds were removed by vacuum distillation and condensed in a cold receiver. The infrared spectra and the GLC of the condensate were examined. Compounds corresponding to RH were obtained in all cases and in essentially quantitative yield. The residue remaining after the removal of volatiles was pure crystalline $[Mn(CO)_5]OSO_2CF_3$ (or $[Mn(CO)_5]BF_4$ when HBF_4 was used).

The relative rates of reaction of the ten $RMn(CO)_5$ compounds with triflic acid were: R = H, CH_3, Ph, p-$CH_3C_6H_4$, p-BrC_6H_4, p-$CF_3C_6H_4$, > $PhCH_2$ > p-$ClC_6H_4CH_2$ ≅ p-$CH_3OC_6H_4CH_2$ ≫ $PhCH_2CH_2$. The six very fast reaction were complete as soon as all the triflic acid could be syringed into the solution. In the case of $HMn(CO)_5$ a stoichiometric quantity of dihydrogen was evolved and a 95% yield of $[Mn(CO)_5]OSO_2CF_3$ was recovered from the solution. This reaction has been used previously to demonstrate the hydridic character of $HMn(CO)_5$ [4].

Cleavage of some of the $RMn(CO)_5$ compounds with HBF_4 was also studied. In general the same relative order of protonolysis with this acid as with CF_3SO_3H was observed and as with triflic acid the only products formed were the expected corresponding RH compounds and the bright yellow $[Mn(CO)_5]BF_4$. The rate of reaction of the four phenyl derivatives p-$XC_6H_4Mn(CO)_5$ with HBF_4 was found to be dependent on X: H > CH_3 > Br ≫ CF_3. For example the fastest reacting of these, $PhMn(CO)_5$, was completely cleaved in 8–10 minutes (compared to less than 20 seconds with CF_3SO_3H) and benzene was identified as the only cleavage product. After removal of volatiles, $[Mn(CO)_5]BF_4$ was isolated in quantitative yield. Protonolysis was very slow when p-$BrC_6H_4Mn(CO)_5$ was treated with one equivalent of HBF_4 and was complete only after 24 h at room temperature. Comparable reaction with CF_3SO_3H took less than 2 min. It has been shown [5] that the kinetic isotope effect k_H/k_D for the protonolysis of a related complex p-$BrC_6H_4CH_2Fe(CO)_2Cp$ is extraordinarily high (15 to 30 depending on conditions). We have also observed a very high (~ 20) isotope effect for the protonolysis of p-$BrC_6H_4Mn(CO)_5$ with DBF_4. Such an unusually high isotope effect is purported to be consistent with protonation at the metal site preceding reductive elimination.

Because p-$ClC_6H_4CH_2Mn(CO)_5$ reacted with CF_3SO_3H at a convenient rate it was used for further study. A qualitative rate study showed that when the relative concentration of either Mn complex or triflic acid was increased the rate of protonolysis increased consistent with a second order rate expression. When the reaction was carried out in the presence of triflate anion, provided by CH_2Cl_2-soluble $[N(CH_2CH_3)_4]OTf$ [6], the rate of reaction was decreased compared to that under similar conditions but without the common ion. The reaction with CF_3SO_3D showed D exchange with the phenyl protons but no exchange with the benzyl hydrogens. The reductive elimination product, p-chlorotoluene, also showed D exchange with phenyl protons but not with the methyl protons. The exchange results are in agreement with those reported earlier on somewhat related compounds [5].

Discussion of the protonolysis of $RMn(CO)_5$

There have been quite a few reports on the cleavage of alkylmetal complexes initiated by electrophiles [7]. There is general agreement that these reactions proceed

by electrophilic attack at the metal center, followed by reductive elimination:

$$RML_x + E^+ \longrightarrow \underset{\displaystyle \underset{E}{|}}{[RML_x]^+} \longrightarrow RE + ML_x^+ \qquad (2)$$

In fact in at least one case the cationic intermediate has been isolated [8]. However there have been only a few reports dealing with the protonolysis of $RMn(CO)_5$ compounds. In an early study, the cleavage of $CH_3Mn(CO)_5$ with HCl in methanol was investigated [9]. This reaction proceeded smoothly to generate methane. However, the addition of KCl to the solution gave a common ion effect that resulted in an enhancement of the rate of protonolysis. This was interpreted as evidence for the reaction proceeding by oxidative addition of undissociated HCl to the Mn, increasing its coordination from six to eight, followed by reductive elimination of methane. In our studies of the cleavage of $RMn(CO)_5$ ($R = p\text{-}ClC_6H_4CH_2$) by triflic acid in CH_2Cl_2 we found that addition of the common ion in the form of $[N(CH_2CH_3)_4]OTf$ retarded the rate of cleavage. It is possible to reconcile these apparently contradictory facts by recognizing that triflate is a much poorer coordinating ligand than chloride hence the intermediate with triflic acid is seven coordinate and ionic as shown in eq. 2 rather than eight coordinate and covalent as in the HCl case.

Although we have not performed detailed kinetic work, such studies have been performed by others on a somewhat related example in which a series of cyclopentadienyl iron complexes $\eta^5\text{-}CpFe(CO)_2R$ was treated with CF_3CO_2H to give the corresponding RH compounds [5,10]. The data were shown to be consistent with protonation of the iron to give a cationic intermediate which then proceeded by reductive elimination to give the observed RH compounds. In view of the work in the literature and our own work we propose the sequence shown in eq. 3–5 for our protonolysis with triflic acid.

$$CF_3SO_3H \overset{K}{\rightleftharpoons} CF_3SO_3^- + H^+ \qquad (3)$$

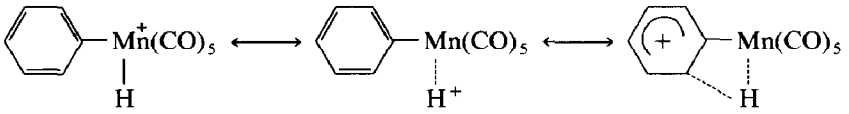
$$H^+ + RMn(CO)_5 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \left[\underset{\displaystyle \underset{H}{|}}{RMn(CO)_5} \right]^+ \qquad (4)$$

$$\left[\underset{\displaystyle \underset{H}{|}}{RMn(CO)_5} \right]^+ \xrightarrow{k_3} RH + Mn(CO)_5^+ \qquad (5)$$

Our experiments suggest that k_2, eq. 4, is rate controlling. It has recently been shown that treatment of a series of rhenium complexes $\eta^5\text{-}CpRe(NO)(PPh_3)(L)$ with HBF_4 results in proton addition to give analogous cationic intermediates $[\eta^5\text{-}CpRe(NO)(PPh_3)(L)(H)]^+BF_4$ ($L = H$, CH_3, $CH_2C_6H_5$) [11].

We now address the observed relative order of the rate of protonolysis as a function of the R in $RMn(CO)_5$. The cleavage is fastest with $R = H$, CH_3, and all the phenyl derivatives. There is now considerable evidence that the H in $HMn(CO)_5$ possesses a relatively large negative charge [12]. Steric factors as well as the high exothermicity associated with the formation of dihydrogen and of methane also may

contribute to the rapid rate of protonolysis of $HMn(CO)_5$ and $CH_3Mn(CO)_5$. The rapid rate of $PhMn(CO)_5$ protonolysis and of all the other phenyl complexes requires comment. The relative dissociation energies (kcal mol^{-1}) of the R–Mn bond in $RMn(CO)_5$ complexes is: H, 59; Ph, 49; CH_3, 44; $PhCH_2$, 29 [13]. Clearly these values do not correspond to our relative rate data. The relatively fast rates with all phenyl derivatives may be due to the possibility that the phenyl group stabilizes the intermediate protonated species by delocalization of positive charge over the ring:



If such delocalization were important one might expect that substitution at the *para* positions by substituents of differing electronic character would affect the degree of charge delocalization. That appears to be the case with HBF_4 cleavage but we see no such effect with triflic acid possibly because the rate is so fast with this acid that distinctions are not obvious under our conditions. A considerable break in rates does occur with the slower reacting benzyl derivatives. In studies of D-H exchange of $PhCH_2Mn(CO)_5$ with CF_3CO_2D it has been shown that when the substituent $CH_2Mn(CO)_5$ is attached to a phenyl group it behaves as a strong electron-releasing group, with a σ_p^+ of about -1.0, i.e., somewhere between OCH_3 and NH_2 [5]. On treatment of our benzylmanganese carbonyls, there may therefore be substantial competition for the proton to attack the ring rather than the manganese thus making fewer protons available for the intermediate required for reductive elimination and slowing the rate of protonolysis. It will be noted that the rates for all our benzyl compounds are indeed slower than phenyl and $PhCH_2CH_2Mn(CO)_5$ is cleaved even much more slowly than the benzyl complexes which perhaps might be expected if $CH_2CH_2Mn(CO)_5$ were more strongly electron releasing than $CH_2Mn(CO)_5$. Steric factors may also play a role and clearly additional investigation is required.

Results and discussion of reactions of triflic acid with $RC(O)Mn(CO)_5$

Most $RC(O)Mn(CO)_5$ compounds are readily prepared from the reactions of the acyl chlorides RC(O)Cl with $[Mn(CO)_5]^-$ in ether solution. The following acyls were prepared: R = CH_3, Ph, $p-CH_3C_6H_4$, p-BrC_6H_4, $p-CF_3C_6H_4$, p-$CH_3OC_6H_4$, $PhCH_2$, p-$ClC_6H_4CH_2$, $PhCH_2CH_2$. These acyls can all be thermally decarbonylated to the corresponding alkylmanganese pentacarbonyls and such decarbonylations are usually the preferred route to the alkyls. The acyl complexes used in our studies are characterized in the experimental section and their IR spectra are summarized in Table 2.

All of the acylmanganese pentacarbonyls listed above were treated with triflic acid and several were also treated with HBF_4. In no case was any aldehydic product formed. Instead the acyls slowly lose a mole of CO and the resulting alkyls then undergo protonolysis to give the corresponding RH compounds. As with the alkylmanganese compounds, the reaction with HBF_4 was slower than with triflic acid.

Table 2 [a]

Carbonyl stretching frequencies of alkylmanganese pentacarbonyls, $RMn(CO)_5$ [b]

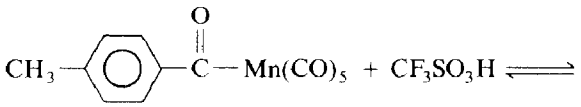
R	$\nu(CO)$ (cm^{-1}) [c]			
	A_1	B_1	E	A_1
H [d]			2015 (s)	2007 (m)
CH_3	2110 (w)		2013 (s)	1991 (s)
C_6H_5	2114 (m)	2045 (w)	2021 (s)	1999 (s)
p-$CH_3C_6H_4$	2113 (m)	2042 (w)	2016 (s)	1996 (s)
p-BrC_6H_4	2116 (m)	2047 (w)	2025 (s)	2002 (s)
			2020 (s)	
p-$CF_3C_6H_4$	2118 (m)		2022 (s)	2005 (s)
$C_6H_5CH_2$	2107 (m)	2043 (w)	2015 (s)	1992 (s)
			2010 (s)	
$C_6H_5CH_2CH_2$	2106 (w)	2041 (w)	2009 (s)	1992 (s)
p-$ClC_6H_4CH_2$	2108 (m)	2044 (w)	2018 (s)	1995 (s)
			2011 (s)	1994 (s)
p-$CH_3OC_6H_4CH_2$	2109 (m)	2044 (w)	2014 (s)	
			2090 (s)	

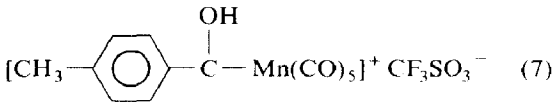
[a] For references to previous literature, see experimental. [b] Hexane solution. [c] Assignments based on C_{4v}-symmetry. [d] Cyclohexane solution.

It is generally assumed that in the absence of free ligand in solution (e.g. PR_3, NH_2R, etc.) the decarbonylation–carbonylation equilibrium with manganese proceeds as shown in eq. 6, with k_1 being rate determining [14]. There is now

$$RC(O)Mn(CO)_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RC(O)Mn(CO)_4 + CO \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} RMn(CO)_5 \qquad (6)$$

substantial evidence that the unsaturated tetracarbonyl is partially stabilized owing to the dihapto character of the keto group [15]. The decarbonylation reactions employed to prepare our alkylmanganese compounds were conducted in non-polar solvents under 1 atm of nitrogen. When this reaction was carried out with p-$CH_3C_6H_4C(O)Mn(CO)_5$ under one atm of carbon monoxide, there was relatively little difference in the rate of CO evolution as compared to the rate under nitrogen. However when the reaction was carried out in the presence of one mole of triflic acid (under nitrogen) the rate of CO evolution was dramatically retarded, Fig. 1. The nature of the acid-retarded decarbonylation may be quite complex. The proton can conceivably attack the substrate at any or all of four different sites: at the metal; at the carbonyl oxygen; at a coordinated CO; or at the phenyl ring. We believe preferential attack occurs at the carbonyl oxygen to form a hydroxycarbene in agreement with previous reports on related complexes [16] (eq. 7).





(7)

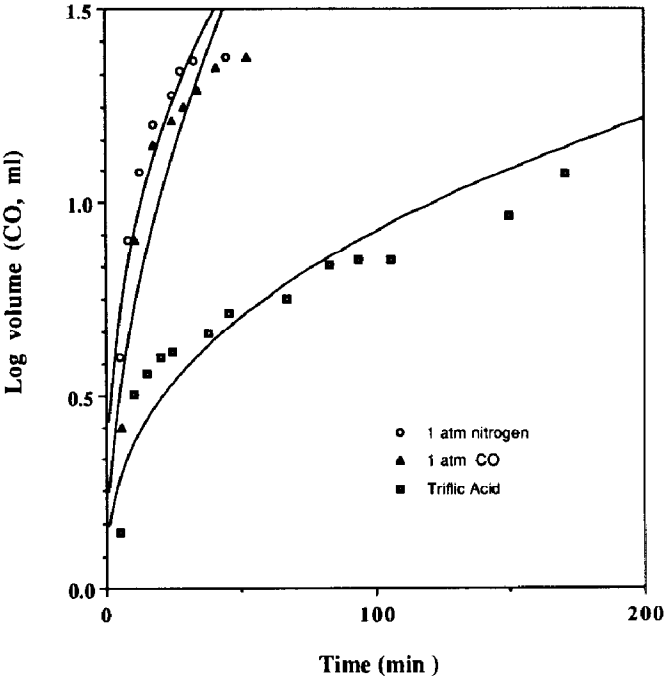


Fig. 1. Effect of triflic acid on rate of CO evolution from p-$CH_3C_6H_4C(O)Mn(CO)_5$ in refluxing CH_2Cl_2.

We have been unable to isolate the cationic hydroxycarbene shown in eq. 7. Prolonged standing in vacuum or exposure to air results in loss of triflic acid and formation of the acyl complex. However we have isolated the air-stable crystalline cationic hydroxycarbene shown in eq. 8 (DPPP = $Ph_2PCH_2CH_2CH_2PPh_2$) and will shortly publish its crystal structure.

$$CH_3-\overset{\overset{O}{\|}}{C}-Mn(CO)_3(DPPP) \xrightarrow{HOTf} \left[CH_3-\overset{\overset{OH}{|}}{C}-Mn(CO)_3(DPPP)\right]^+ CF_3SO_3^- \quad (8)$$

The reverse of our decarbonylation reaction, namely the methyl migration leading to the formation of an acyl, eq. 9, has been extensively investigated. It has

$$CH_3Mn(CO)_5 + CO \rightleftharpoons CH_3C(O)Mn(CO)_5 \quad (9)$$

been convincingly demonstrated that not only is the carbonyl group in the acyl derived from one of the coordinated CO's rather than the incoming CO, but also that in the reverse reaction, one of the terminal CO's first dissociates while the acyl-carbonyl group remains coordinated and after methyl migration becomes one of the equivalent terminal CO's. The rate of the reaction in eq. 9 is known to be dramatically accelerated by both Lewis acids and strong protic acids [17] because of coordination at one of the 5 equiv. CO's. In the decarbonylation reaction carried out in the presence of strong acid the putative terminal CO, namely the keto carbonyl, is tied up by the proton in the form of a cationic hydroxycarbene, eq. 7. One might

speculate that because of the positive charge on the carbon in the hydroxycarbene (which can be delocalized on the metal), back-bonding between the Mn and the terminal CO's would be weakened and thus facilitate CO departure. On the other hand the argument has also been made that as a consequence of removal of electron density at the metal center, the loss of additional electrons involved in the departure of a coordinated CO would be retarded [18]. Support for this latter suggestion also comes from the work on the decarbonylation of manganese carbonyls referenced earlier [14a].

Experimental

General

All reactions were carried out in oven-dried glassware under an inert atmosphere. The infrared solution spectra were all recorded with a Perkin–Elmer 1600 series (FT) spectrophotometer using potassium bromide (0.1 mm) cells. In recording spectral intensities in Tables 1 and 2 the abbreviations w, m, s, br, and sh refer to weak, medium, strong, broad, and shoulder, respectively. Proton nuclear magnetic resonance spectra were obtained on an IBM NR-80 instrument. Mass spectral data were obtained using a HP5995A quadrupole GC/MS system. Reaction mixtures were generally analysed by GC/MS (OV-101, 12 m capillary column) and pure solids were analysed by direct inlet. Reaction mixtures were also examined by GLC (HP-5890, 3% OV-17, $1/8'' \times 6'$, temperature programming). Analytical thin-layer chromatography was conducted using E. Merck silica gel 60-PF254 precoated plates. The positions of the compounds were made visible by UV light (254 nm) and by I_2 vapor. Preparative chromatographic separations were conducted by column chromatography using E. Merck silica gel, finer than 220 mesh. Melting points were determined using open end capillaries with a Mel-Temp apparatus and are uncorrected.

Tetrahydrofuran (THF) was freshly distilled under nitrogen from sodium benzophenone ketyl. Dimanganese decacarbonyl was purchased from either Pressure Chemical or Strem and was used as received. Triflic anhydride [19], $[N(CH_2CH_3)_4][SO_3CF_3]$ [6], and CF_3SO_3D [20] were prepared by standard literature methods. Benzyl- [21], *p*-methoxybenzyl-, and *p*-chlorobenzyl-manganese pentacarbonyl were prepared from the corresponding benzyl chloride and $NaMn(CO)_5$. Methylmanganese pentacarbonyl [21] and *p*-toluoylmanganese pentacarbonyl [15] were prepared according to previously described procedures. All other laboratory chemicals and solvents were reagent grade and used without further purification.

Synthesis of the acylmanganese pentacarbonyls

All of the acyl complexes were prepared from $[Mn(CO)_5]^-$ and the appropriate acyl halide [22]. The anion, $[Mn(CO)_5]^-$ was generated from $Mn_2(CO)_{10}$ by either Na/Hg or K/Hg reduction in anhydrous diethyl ether using a modified literature procedure [23]. A typical example is the preparation of *p*-bromobenzoylmanganese pentacarbonyl which was conducted as follows: Sodium metal (1.0 g, 43 mmol) was cut into small pieces, which after rinsing with hexane were added slowly to 15 ml Hg with vigorous stirring. After the sodium had reacted with the Hg, the amalgam was allowed to cool to room temperature. $Mn_2(CO)_{10}$ (2.50 g, 6.41 mmol) was

added with 100 ml of diethyl ether. The mixture was stirred for 2 h. The anion solution was transferred to a second flask, via a transfer needle. The amalgam was washed with 20 ml fresh ether and this was transferred to the second flask as well. The anion solution was cooled to −23°C and *p*-bromobenzoyl chloride (2.81 g, 12.80 mmol), dissolved in 10 ml of diethyl ether was added dropwise via syringe. Immediate precipitation of both NaCl and acyl complex occurred. The mixture was kept for 0.5 h at −23°C and then allowed to warm to room temperature. The solids were collected by filtration and washed with CH_2Cl_2 until the washings remained colorless. The CH_2Cl_2 solution was combined with the ether filtrate and diluted with 50 ml of hexane. The volume was reduced by rotary evaporation until the first appearance of a solid and the flask and contents then cooled to −35°C. The product was collected as fine yellow needles by filtration, washed with two 5 ml portions of cold hexane and air dried. Obtained: 2.17 g (6.18 mmol) 44.7% yield. M.p. 96–97°C (lit. [24] 100–102°C). Mass spectrum: 380($M = 1^+$, 1), 378($M - 1^+$, 1), 352(8), 350(8), 324(8), 322(8), 296(5), 294(6), 268(11), 266(11), 240(15), 238(16), 212(14), 210(14), 185(42), 183(40), 157(9), 155(8), 83(15), 55(100).

Acetylmanganese pentacarbonyl was prepared in 42% yield from $[Mn(CO)_5]^-$ and acetyl chloride as colorless crystals. M.p. 52–54°C (lit. [21] 54–55°C). Mass spectrum: 238 (M^+, 2), 223(2), 210(10), 182(4), 154(1), 126(4), 98(23), 55(100).

Benzoylmanganese pentacarbonyl was prepared from $[Mn(CO)_5]^-$ and benzoyl chloride in 45% yield as a light yellow powder. M.p. 88–89°C (lit. [21] 95–96°C) Mass spectrum: 300(M^+, 1), 272(7), 244(9), 216(6), 188(4), 160(17), 132(15), 105(74), 77(25), 55(100).

p-Anisoylmanganese pentacarbonyl was prepared from $[Mn(CO)_5]^-$ and *p*-anisoyl chloride in 61% yield as fine yellow needles. M.p. 88–89°C (lit. [25] 94–95°C). Mass spectrum: 330(M^+, 1), 302(1), 274(3), 246(6), 218(6), 190(15), 135(100), 107(4), 77(24), 55(99).

3-Phenylpropionylmanganese pentacarbonyl was prepared from $[Mn(CO)_5]^-$ and 3-phenylpropionyl chloride in 66% yield as pale yellow crystals. M.p. 66–67°C. Mass spectrum: 328(M^+, 1), 300(1), 272(1), 244(2), 225(1), 216(1), 188(9), 132(15), 91(4), 77(13), 55(100).

Phenylacetylmanganese pentacarbonyl was prepared from $[Mn(CO)_5]^-$ and phenylacetyl chloride in 53% yield as colorless crystals. M.p. 103–104°C (lit. [21] 111–113°C). Mass spectrum: 314 (M^+, not observed), 258(1), 230(1), 223(34), 202(1), 195(20), 167(6), 146(26), 111(10), 91(44), 202(1), 195(20), 167(6), 146(26), 111(10), 91(44), 55(100).

(*p*-Trifluoromethyl)benzoylmanganese pentacarbonyl was prepared from $[Mn(CO)_5]^-$ and (*p*-trifluoromethyl)benzoyl chloride in 55% yield as fine yellow needles. M.p. 88–89°C. Mass spectrum: 368(M^+, not observed), 340(11), 312(9), 284(9), 256(3), 228(15), 200(13), 173(52), 126(28), 107(32), 55(100). After isolation of the acyl, the filtrate was taken to dryness. The resulting pale yellow residue was taken up in a minimum of hexane and the solution poured onto a silica gel column. Elution with hexane removed unreacted $Mn_2(CO)_{10}$ and further elution gave (*p*-trifluoromethyl)phenylmanganese pentacarbonyl. Recrystallization (−35°C, pentane) afforded the alkyl in 20% yield (based on starting $Mn_2(CO)_{10}$) as colorless rectangular prisms. M.p. 76–77°C. Mass spectrum: 340(M^+, 6), 312(20), 284(41), 256(12), 228(29), 200(100), 125(20), 107(95), 81(21), 55(94).

Synthesis of alkylmanganese pentacarbonyls

Several of the alkyl complexes were prepared from thermal decarbonylation of the corresponding acyl complex in non-polar solvents. A typical example is the preparation of *p*-bromophenylmanganese pentacarbonyl which was conducted as follows: *p*-bromobenzoylmanganese pentacarbonyl (1.67 g, 4.40 mmol) was placed in a 2-necked 100 ml round bottom flask equipped with a micro-reflux condenser. After the flask was evacuated and filled with argon three times, 40 ml of dichloromethane was syringed into the flask. The flask was lowered into a sand-filled heating mantle and the external temperature raised to 70 °C. As the reaction progressed the yellow color slowly faded. After refluxing for 90 min, analysis by TLC (1/1 $CHCl_3$/hexane) revealed no acyl. The reaction mixture was cooled to room temperature and the solvent removed at reduced pressure. Recrystallization (−35 °C, hexane) afforded the product as colorless prisms. Obtained 1.33 g (3.77 mmol), 86%. M.p. 66.5–67 °C (lit. [24] 65–66 °C). Mass spectrum: 352(M^+, 24), 350($M-1$, 24), 324(31), 322(33), 296(41), 294(45), 268(49), 266(49), 240(35), 238(35), 212(99), 210(99), 136(100), 134(99), 76(23), 55(100).

(2-Phenyl)ethylmanganese pentacarbonyl was prepared by refluxing a hexane solution of 3-phenylpropionylmanganese pentacarbonyl [22] for 1 h. Recrystallization (−78 °C, hexane) afforded the product as colorless crystal in 56% yield. M.p. 78–79 °C. Mass spectrum: 300(M^+, 1) 272(1), 244(5), 216(4), 188(4), 160(36), 105(60), 55(100).

p-Tolylmanganese pentacarbonyl was prepared by refluxing a dichloromethane solution of *p*-toluoylmanganese pentacarbonyl for 60 min. Recrystallization (−35 °C, pentane) afforded the product colorless crystals in 78% yield. M.p. 44–45 °C (lit. [26] 43 °C). Mass spectrum: 286(M^+, 5), 258(9), 230(11), 202(4), 174(8), 146(63), 91(13), 55(100).

$HMn(CO)_5$ was prepared in 60% yield using a modified literature procedure [23]. After the anion $[Mn(CO)_5]^-$ was prepared in diethyl ether as described above, the anion solution was transferred to a 250 ml three-necked round-bottom flask equipped with two two-way stopcocks and a dropping funnel. One stopcock was connected to a vacuum source and carbon monoxide inlet. The second stopcock was connected by 12″ of butyl tubing to the inlet of a −78 °C cooled trap. The butyl tubing was separated in half by a polyethylene drying tube (3″ in length; 5/8″ wide) loosely filled with dry P_2O_5 and plugged at both ends with glass wool. All joints of this drying tube were sealed externally with Teflon tape. The diethyl ether was removed in vacuo with the aid of a warm water bath, leaving a pale gray residue. After admitting CO into the evacuated flask, the dropping funnel was charged with 85% phosphoric acid. The flask was cooled to 0 °C and the phosphoric acid added at roughly 0.5 ml per minute. After the addition of 5 ml, the stopcock leading to the −78 °C cooled trap was opened. As the reaction proceeded, $HMn(CO)_5$ was swept by a vigorous stream of CO into the −78 °C cooled trap where it solidified as a pale yellow solid.

General reaction procedures

The reactions of $RMn(CO)_5$ and $RC(O)Mn(CO)_5$ with either CF_3SO_3H or HBF_4 were carried out in a 2-necked round-bottom flask equipped with a side-arm for gas inlet and outlet. Solid manganese compounds (0.25–1.00 mmol) were placed in the flask and sealed with a serum cap. After the flask was evacuated and filled with

argon (three times), dichloromethane (10–30 ml) was injected into the flask. Following the addition of acid, the solutions were kept at ambient temperature while stirring.

Rates of reaction were determined by following the disappearance of the high-energy A_1 CO stretching absorption or the appearance of the high energy CO absorption of $[Mn(CO)_5]SO_3CF_3$ (2072 cm^{-1} in CH_2Cl_2 [27]) or $[Mn(CO)_5]BF_4$ (2052 cm^{-1} in CH_2Cl_2). Absorbance readings were made by withdrawing samples (0.050–0.070 ml) with a gas tight syringe at various time intervals. It should be noted that the assumption of C_{4v} symmetry for our $RMn(CO)_5$ and $RC(O)Mn(CO)_5$ compounds is not strictly correct owing to distortions from such symmetry caused by some R groups. Such distortion should lead to splitting of the doubly degenerate E mode. We could not observe such splitting with our $RC(O)Mn(CO)_5$ compounds but did see it with four of our $RMn(CO)_5$ compounds, Table 2. In a very careful infrared studies reported elsewhere [25] with similar compounds the lack of E splitting was also noted.

After the reaction was complete, CH_2Cl_2 and other volatiles were removed in vacuo and condensed in a $-78°C$ trap. Examination of most of the distillates by IR and GLC revealed only CH_2Cl_2 and the cleavage products RH. In reactions between p-$CH_3OC_6H_4CH_2Mn(CO)_5$ or $C_6H_5CH_2CH_2Mn(CO)_5$ with CF_3SO_3H, several other minor unidentifiable products were detected by GLC.

Manometric measurements were used to determine the rate of formation of CH_4 and H_2 in the cleavage of $CH_3Mn(CO)_5$ and $HMn(CO)_5$, respectively. The apparatus consisted of a three-neck round-bottom flask one neck of which was attached by a two-way stopcock to a mercury filled manometer and another neck was fitted with a three-way stopcock connected to a vacuum and argon inlet. For $MeMn(CO)_5$, the addition of reagents was as described above. For $HMn(CO)_5$, the flask was evacuated, filled with argon and dichloromethane syringed in prior to the addition of $HMn(CO)_5$.

Manometric measurements were also used to determine the rate of decarbonylation of p-$CH_3C_6H_4C(O)Mn(CO)_5$. For these studies 1.0 mmol of solid acyl was added to a 10 ml dropping funnel and the funnel sealed with a serum cap. After the system was evacuated and flushed with argon, 30 ml of dichloromethane was syringed into the flask. The flask was lowered into a sand filled heating mantle and slowly heated to, and maintained at, 48–50°C (external thermometer), in order to achieve gentle reflux. The acyl was dissolved in 1 ml of dichloromethane and added at once to the refluxing dichloromethane. In reactions involving triflic acid, the acid was syringed into the dropping funnel to assure that the acyl oxygen was protonated prior to heating.

The deuterium content in p-$ClC_6H_4CH_2Mn(CO)_5$, in the reaction with CF_3SO_3D, was determined by mass spectrophotometry using a previously published method [5]. The proportion of molecules containing deuterium was determined from a comparison of the appropriate mass peaks (m/e 320, 321, and 322; 292, 293, and 294; 125, 126, and 127) corresponding to the M, $M - CO$, and p-chlorobenzyl ions.

A similar procedure was used to determine the amount of deuterium in the cleavage product, p-chlorotoluene. The complex p-$ClC_6H_4CH_2Mn(CO)_5$ (ca. 0.160 g) was dissolved in 5 ml of dichloromethane and then allowed to react with CF_3SO_3D (0.090 ml). After the reaction was complete (IR), the volatiles were removed in vacuo and examined by mass spectrometry. The amount of deuterium

was determined from the dominant peaks in the spectrum (m/e 91, 92, and 93) corresponding to the $M - Cl$ ion and its mono- and di-deuterated products.

Deuterium exchange in p-$ClC_6H_4CH_2Mn(CO)_5$ was also examined by NMR. In a typical experiment the alkyl complex (0.080 g) in an NMR tube was dissolved in 1 ml of $CDCl_3$ and the spectrum recorded. CF_3SO_3D (0.025 ml) was added, the tube sealed and shaken for five minutes. The reaction was followed by observation of the changes in the resonances of the benzyl methylene protons (2.34 ppm) and the methyl group of product p-chlorotoluene (2.30 ppm). The integrated area of the total aromatic region (7.3–7.0 ppm) decreased as the reaction proceeded. The final integration ratio of phenyl protons to methyl protons in product p-chlorotoluene was found to be 2 to 3, respectively.

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