Table VIII. Crystallization Conditions

material	solvent	concn, mg/mL	method	add concn % w/w
(*E*)-cinnamide	ethyl acetate	35	slow cooling	10
benzamide	ethanol	240	slow evap	10, 5, 3
p-toluamide	ethanol	100	slow evap	10
p-clorobenzamide	ethanol	120	slow evap	10
p-aminobenzamide	water	20	slow evap	10
(*E*)-cinnamic acid	ethanol	160	slow evap	10
benzoic acid	petroleum ether/acetone	10	slow evap	10
androsterone	ethyl acetate	25	slow evap	25
epiandrosterone	ethyl acetate/petroleum (6:1)	28	slow evap	20

handedness. Direct evidence for this hypothesis has been provided by the enantiomeric segregation of occluded α-amino acid additives into the crystals of α-glycine[6] and (*R*,*S*)-serine.[5]

A consequence of this analysis is that systems of solid solutions which are chemically and thermodynamically very similar may in fact display different extents of solid miscibilities, depending upon the symmetry of the growing crystal face. Thus, the structure and the extent of solid solubility may be a kinetically controlled surface phenomenon, as well as a thermodynamical bulk phenomenon.

Experimental Section

Materials were prepared by conventional methods. They were purified by liquid chromatography followed by multiple recrystallizations from doubly distilled solvents, and their purity was checked by HPLC. The analyses of the amounts of additive occluded inside the substrate crystals were performed by HPLC (column 250 × 4 mm, Nucleosil 10 C18, 10 μm), using as eluent 0.05 M acetate buffer, pH 4, 40% in methanol, on a liquid chromatograph, Waters Assoc., equipped with UV detection (254 nm).

Crystallization Conditions. Appropriate conditions for crystallization of the various pure compounds were first determined such that the crystals formed are homogeneous and reproducible with respect to their morphology. This means that at least 90% of the crystals have the same habit. The affected crystals were grown in parallel under exactly the same conditions. Inhibitors were dissolved into the supersaturated solution of the substrate before the onset of crystallization. The definition of typical habit of the affected crystal follows the same criteria as for the pure compound. The habit and morphology of typical pure and affected crystals were determined on a Siemens X-ray diffractometer[37] and compared. The new faces which develop in the affected crystals, or those which substantially increase in their surface area, relative to the other faces, are referred to as affected faces. Crystallizations were performed in the conditions specified in Table VIII from 10 to 25 mL batches of solution in 25–50 mL Erlenmeyers, at room temperature. (*E*)-Cinnamide was crystallized in a thermostat over a temperature gradient 60–30 °C, lowering the temperature 2 °C/day. All data are the result of many multiple sets of experiments.

Acknowledgment. We thank the Israel Academy of Science and Humanities, the US–Israel Binational Foundation, Jerusalem, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work. One of us (L.A.) is the recipient of the Helena Rubinstein Career Development Chair. We thank Rachel Yerushalmi for assisting in the growth of some of the crystals.

Registry No. (*E*)-Cinnamide, 22031-64-7; (*E*)-cinnamic acid, 140-10-3; (*E*)-*o*-chlorocinnamide, 95422-22-3; (*E*)-*p*-chlorocinnamide, 36650-34-7; (*Z*)-β-chlorocinnamide, 95422-23-4; (*Z*)-α-chlorocinnamide, 74305-85-4; benzamide, 55-21-0; *o*-toluamide, 527-85-5; *p*-toluamide, 619-55-6; benzoic acid, 65-85-0.

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Kinetics and Mechanism of Substitution Reactions of Some (η^3-Allyl)manganese Tetracarbonyl Compounds

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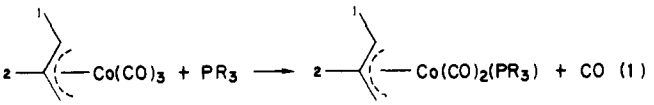
Abstract: Kinetic data are reported for CO substitution of (η^3-C_3H_4X)$Mn(CO)_4$, where X is a substituent in the 1- or the 2-position of the allyl ligand and where X[1] = H, Me, Ph, *t*-Bu, and Cl. Also the *anti*- and the *syn*-(η^3-C_3H_3(1,2-Ph_2))$Mn(CO)_4$ isomers were prepared for the first time and their rates of substitution determined. In all cases the rates of reaction are first order in substrate concentration and zero order in entering nucleophile concentrations. Studies on decarbonylation reactions of (η^1-C_3H_5)$Mn(CO)_4L$ rule out an $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ mechanism. It appears that CO substitution takes place by a dissociation (S_N1) process, and the kinetic parameters for (η^3-C_3H_5)$Mn(CO)_4$ are k(45 °C) = 2.8 × 10^{-4} s^{-1}, $\Delta H^{\ddagger}$ = 26.8 kcal/mol, and $\Delta S^{\ddagger}$ = 9.6 eu. Substituents on the 1-position of the allyl group have a small retardation effect on the rates of CO substitution. Substituents on the 2-position enhance the rates of reaction; furthermore, this rate enhancement increases with increasing bulkiness of the substituent. Still, the maximum rate observed was only 500 times greater than that for the parent compound, and this is for the 2-*tert*-butylallyl compound. Unfortunately, all attempts to prepare the desired compounds with strong electron-donating and -withdrawing substituents on the allyl ligand failed.

There has been much interest in η^3-allyl organometallic complexes,[2] since it was first demonstrated[3] in the late 1950's that (C_4H_7)$Co(CO)_3$ has an η^3-bonding configuration. Kinetic studies[4] on carbonyl-substitution reactions of (η^3-C_3H_5)$Co(CO)_3$ (eq 1)



(1)

(1) Abbreviations: A = absorbance, *n*-Bu = *n*-butyl, *t*-Bu = *tert*-butyl, Cy = cyclohexyl, Et = ethyl, k_{obsd} = observed rate constant, Me = methyl, NBS = *N*-bromosuccinimide, Ph = phenyl, $\Delta H^{\ddagger}$ = enthalpy of activation, $\Delta S^{\ddagger}$ = entropy of activation.

0002-7863/85/1507-3122$01.50/0

indicated that the rate-determining step is CO dissociation. It was also reported that substituents in the 1-position decrease the substitution rate, whereas substituents in the 2-position increase the substitution rate. No clear explanation was given for the substituent effects on the reaction rates.

In contrast, studies[5] on CO substitution reactions of $(\eta^3\text{-}C_3H_4X)Fe(CO)_2(NO)$, where X = H, 1-Me, 2-Me, 1-Ph, 1-CN, 1-Cl, 2-Cl, or 2-Br, showed it to be associative, and to proceed through an η^1-allyl intermediate (eq 2). In some cases the η^1-allyl

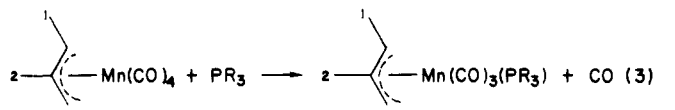
$$(\eta^3\text{-}C_3H_4X)Fe(CO)_2(NO) + PR_3 \xrightarrow{\text{slow}} (\eta^1\text{-}C_3H_4X)Fe(CO)_2(NO)(PR_3) \xrightarrow{\text{fast}} (\eta^3\text{-}C_3H_4X)Fe(CO)(NO)(PR_3) + CO \quad (2)$$

intermediate was identified by IR spectroscopy. The general pattern of substituent effects on the reaction rate is that electron-donating groups in either the 1- or 2-position decrease the rates of CO substitution, and electron-withdrawing groups in either position increase the rates. It was concluded[5,6] that electron-donating substituents increase the electron density on the metal thereby hindering nucleophilic attack, whereas electron-withdrawing substituents have the opposite effect. Similarly, $(\eta^3\text{-}C_3H_5)Fe(CO)_3X$, where X = Cl, Br, I, has been shown[7] to react with phosphines by an associative process.

Investigations by Muetterties and co-workers[8] show that $(\eta^3\text{-}C_3H_5)Co(PR_3)_3$ and $(\eta^3\text{-}C_3H_5)Mn(CO)_2(PR_3)_2$ act as catalysts for hydrogenation of alkenes and arenes. Originally, it was proposed[8] that catalysis involved a $\eta^3 \rightarrow \eta^1$-allyl conversion in order to open up a coordination site on the metal. However, subsequent work[8e] on $(\eta^3\text{-}C_8H_{13})Co(P(OCH_3)_3)_3$ suggested that η^1-allyl complexes are not involved in catalysis. In fact the allyl group is hydrogenated to give the corresponding alkane which comes off the metal resulting in formation of coordinatively unsaturated $Co(P(OCH_3)_3)_3$, which is believed to be the active catalyst.

Although several methods are known[9] for the syntheses of $(\eta^3\text{-}C_3H_5)Mn(CO)_4$ and its derivatives, there appears to be no report on the kinetics and mechanism of CO substitution for these manganese allyl complexes.[10] Either CO dissociation or an associative process involving or not involving an η^1-allyl intermediate, or other paths, is possible for the substitution reaction. Although the rigidity of the η^3-allyl ligand in $(\eta^3\text{-}C_3H_5)Mn(CO)_4$, as shown by an NMR study,[11] suggests that spontaneous $\eta^3 \rightarrow \eta^1$ conversion is not important for temperatures at or below 180 °C, this does not rule out such conversion induced by a nucleophile.

We have examined reactions of the type shown in eq 3 for various allyl complexes and report here that manganese allyl complexes appear to react by a simple S_N1 CO dissociative process.



Further, the rate of CO dissociation is dependent upon the steric bulk and the isomeric configuration of the substituted allyl ligands.

Experimental Section

Compounds and Solvents. All manipulations involving manganese allyl compounds were performed under an atmosphere of N_2 by using standard Schlenk techniques or a N_2-filled glovebox. Ether, hexane, and THF were distilled over Na under a N_2 atmosphere. The hexane was stored over H_2SO_4 and washed with a $NaHCO_3$ solution before distillation. Methylene chloride was distilled over P_2O_5 under a N_2 atmosphere. Reagent grade pentane was used without distillation after degassing under a dynamic vacuum. Celite was obtained from Johns-Manville.

The manganese starting materials $Mn(CO)_5Br$,[12] $Mn_2(CO)_8(PMe_2Ph)_2$,[13] $Mn_2(CO)_8(PPh_3)_2$,[13] $KMn(CO)_5$,[14] $KMn(CO)_4(PMe_2Ph)$,[14] and $KMn(CO)_4(PPh_3)$[14] were prepared by the literature methods. The reagents $Mn_2(CO)_{10}$ and PPh_3 were obtained from Aldrich Chemical Co.; $Mn_2(CO)_{10}$ was used without further purification, and PPh_3 was recrystallized from ethanol. The phosphines $P(n\text{-}Bu)_3$, PMe_2Ph, PCy_3, and $P(OEt)_3$ were obtained from Strem Chemicals Inc. and distilled over Na before use. Allyl chloride, 1-chloro-2-butene, 3-chloro-2-methyl-1-propene, 1,3-dichloropropene, and 2,3-dichloro-1-propene were obtained from Aldrich Chemical Co. and used without further purification. Cinnamyl chloride was obtained from Pfaltz and Bauer, Inc. and used without further purification. Starting materials used for the synthesis of other allyl halides, α-methylstyrene, α-phenylcinnamic acid, 2-methyl-3-buten-2-ol, and *N*-bromosuccinimide (NBS) were obtained from Aldrich Chemical Co., and *cis*-4,4-dimethyl-2-pentene, 2,3,3-trimethyl-1-butene, and crotononitrile were obtained from Pfaltz and Bauer, Inc. The allyl halides 3-bromo-2-phenyl-1-propene,[15] 1-bromo-4,4-dimethyl-2-pentene,[15] 3-bromo-2-*tert*-butyl-1-propene,[15] 3-chloro-1,2-diphenyl-1-propene,[16] 1-chloro-3-methyl-2-butene,[16] and 4-bromo-2-butenonitrile[15,17] were prepared according to the literature methods.

Instrumentation. Infrared spectra were obtained on either a Nicolet 7199 FT-IR or a Perkin-Elmer 283 spectrophotometer with 0.2-mm KBr-windowed cells. Nuclear magnetic resonance spectra were obtained on either a JEOL FX-90Q or a VARIAN 390 spectrometer. Kinetic reactions were performed in a Polyscience Model 90 temperature bath, with temperature regulated to ±0.2 °C. Microanalysis was performed by Galbraith Laboratories, Inc., Knoxville, TN. The mass spectra were obtained by Dr. D. Hung of Northwestern University Analytical Services Laboratory on a HP5985A spectrometer using 70-eV ionization.

Kinetic Measurements. For CO substitution reactions, approximately 2×10^{-2} M solutions of compound in cyclohexane were used with at least a tenfold excess of nucleophile. For decarbonylation reactions, approximately 1×10^{-1} M solutions of compound in decalin were used. Prepared samples of 2.0 mL were placed in a constant-temperature bath. The reactions were monitored with IR spectroscopy by abstracting 6–10 0.2-mL aliquots periodically over 3–4 half-lives and injecting these samples into an IR cell which had been purged with N_2.

Rate constants were determined by measuring the decrease of one of the carbonyl bands of the starting carbonyl compound (typically the highest frequency band for the η^1-allyl compounds and the second highest frequency band for the η^3-allyl compounds). Plots of ln *A* vs. time were linear for at least 3 half-lives, and k_{obsd} was the slope of this line as determined by the least-squares method. Correlations of these least-squares lines were very good ($r^2 > 0.997$). Activation parameters ΔH^* and ΔS^* were the slope and intercept, respectively, calculated by the least-squares method for the plot of ln (k_{obsd}/T) vs. $1/T$, where T = temperature. Correlations of the activation parameter least-squares lines were also very good ($r^2 > 0.998$).

Syntheses of Compounds. $(\eta^1\text{-Allyls})(\eta^1\text{-}C_3H_4X)Mn(CO)_5$ **(X = 1-Me, 1-Cl, 2-Cl, 1-CN, 1-*t*-Bu, 2-*t*-Bu):** $(\eta^1\text{-}C_3H_3(1,1\text{-}Me_2))Mn(CO)_5$ **and** $(\eta^1\text{-}C_3H_3(1,2\text{-}Ph_2))Mn(CO)_5$**.** These compounds were prepared by a variation of the literature method.[9a,b] A 0.04 M solution of $KMn(CO)_5$ in THF was added dropwise to a stirred 0.16 M solution of the appropriate allyl halide in THF, over a 1-h period. Equal quantities of both

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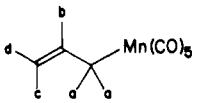
Table I. Infrared Spectra in the Carbonyl Region of (η^1-Allyl)manganese Carbonyls[a]

compound	carbonyl stretches, cm^{-1}
(η^1-C_3H_5)$Mn(CO)_5$[b]	2110 w, 2013 s, 1995 s
(η^1-C_3H_4(1-Me))$Mn(CO)_5$[c]	2105 w, 2007 s, 1992 s
(η^1-C_3H_4(1-Cl))$Mn(CO)_5$	2109 w, 2019 s, 1992 s
(η^1-C_6H_4(2-Cl))$Mn(CO)_5$	2113 w, 2019 s, 1997 m
(η^1-C_3H_4(1-CN))$Mn(CO)_5$	2114 w, 2022 s, 2001 m
(η^1-C_3H_4(1-t-Bu))$Mn(CO)_5$	2104 w, 2009 s, 1988 m
(η^1-C_3H_4(2-t-Bu))$Mn(CO)_5$	2106 w, 2014 s, 2008 s,[d] 1989 m
(η^1-C_3H_3(1,1-Me_2))$Mn(CO)_5$	2103 w, 2005 s, 1988 m
(η^1-C_3H_3(1,2-Ph_2))$Mn(CO)_5$	2105 w, 2010 s, 1989 m

[a] In cyclohexane. [b] Previously reported, ref 9a,b. [c] Previously reported, ref 9b. [d] Peaks at 2014 and 2008 cm^{-1} appear as a doublet.

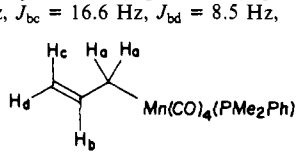
solutions were used, usually 30 mL, so that there was a 3-fold excess of the allyl halide over the manganese anion. Using an excess of the allyl halide minimized the amount of $Mn_2(CO)_{10}$ in the product. Completion of the reaction was monitored by IR spectroscopy. After completion of the reaction, the THF was removed under vacuum and 20 mL of pentane were added. The resulting yellow solution was filtered through Celite. For the 1-Me, 1-Cl, 2-Cl, 1-CN, 1,1-Me_2, and 1,2-Ph_2 substituted allyl compounds, the filtered pentane solutions were approximately 95% pure with small amounts of $Mn_2(CO)_{10}$, as determined from the carbonyl region of the IR spectra. The syntheses of 1-*t*-Bu and 2-*t*-Bu allyl compounds produced $Mn(CO)_5Br$ as a byproduct. Therefore, the filtered pentane solutions were cooled to −78 °C and then syringed off the orange crystals of $Mn(CO)_5Br$ which formed. For both, lemon yellow solutions were obtained which were approximately 90% pure with small amounts of $Mn_2(CO)_{10}$ and $Mn(CO)_5Br$ as determined from the carbonyl region of the IR spectra.

The IR ν_{CO} bands of these η^1-allyl compounds are listed in Table I. For the 1,1-Me_2, 1-*t*-Bu, 2-*t*-Bu, and 2-Cl η^1-allyl compounds and the cis and trans isomers of the 1,2-Ph_2 and 1-CN η^1-allyl compounds, ^1H NMR spectra were recorded:



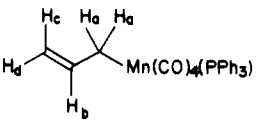
(η^1-C_3H_3(1,1-Me_2))$Mn(CO)_5$ (benzene-d_6) δ 1.60 s (Me_c), 1.66 s (Me_d), 1.77 d (H_a), 5.63 t (H_b), J_{ab} = 9 Hz; (η^1-C_3H_4(1-*t*-Bu))$Mn(CO)_5$ (benzene-d_6) δ 1.00 s (*t*-Bu_d), 1.75 d (H_a), 5.41 d (H_c), 5.71 m (H_b), J_{ab} = 7 Hz, J_{bc} = 16 Hz; (η^1-C_3H_4(2-*t*-Bu))$Mn(CO)_5$(benzene-d_6) δ 1.04 s (*t*-Bu_b), 1.80 s (H_a), 5.00 s (H_d), 5.11 s (H_c); (η^1-C_3H_4(2-Cl))$Mn(CO)_5$ (acetone-d_6) δ 2.06 s (H_a), 4.68 s (H_c), 5.05 s (H_d); (*cis*-η^1-C_3H_3(1,2-Ph_2))$Mn(CO)_5$ (acetone-d_6) δ 2.49 s (H_a), 6.33 s (H_c); (*trans*-η^1-C_3H_3-(1,2-Ph_2))$Mn(CO)_5$ (acetone-d_6) δ 2.31 s (H_a), 6.66 s (H_d); (*cis*-η^1-C_3H_4(1-CN))$Mn(CO)_5$ (benzene-d_6) δ 3.54 d (H_a), 4.45 d (H_d), 5.60 m (H_b), J_{ab} = 8 Hz, J_{bc} = 10 Hz; (*trans*-η^1-C_3H_4(1-CN))$Mn(CO)_5$ (benzene-d_6) δ 2.98 d (H_a), 4.63 d (H_c), 5.81 m (H_b), J_{ab} = 7 Hz, J_{bc} = 16 Hz. For the 1-*t*-Bu, 2-*t*-Bu, and 1-CN compounds, mass spectral data were also recorded: *m/e* (relative intensity) (η^1-C_3H_4(1-*t*-Bu))-$Mn(CO)_5$, M^+ 292 (5.9%), $(M - CO)^+$ 264 (33.7%), $(M - 2CO)^+$ 236 (1.8%), $(M - 3CO)^+$ 208 (35.0%), $(M - C_7H_{13})^+$ 195 (4.4%), $(M - 4CO)^+$ 180 (33.9%), $(M - C_7H_{13}, CO)^+$ 167 (7.2%), $(M - 5CO)^+$ 152 (100.0%), $(M - C_7H_{13}, 2CO)^+$ 139 (6.6%); (η^1-C_3H_4(2-*t*-Bu)$Mn(CO)_5$, M^+ 292 (1.4%), $(M - C_7H_{13})^+$ 195 (100.0%), $(M - 4CO)^+$ 180 (44.4%), $(M - C_7H_{13}, CO)^+$ 167 (55.6%), $(M - C_7H_{13}, 2CO)^+$ 139 (35.3%); (η^1-C_3H_4(1-CN))$Mn(CO)_5$, M^+ 261 (1.2%), $(M - CO)^+$ 233 (6.6%), $(M - 2CO)^+$ 205 (6.7%), $(M - C_4H_4N)^+$ 195 (1.5%), $(M - 3CO)^+$ 177 (13.8%), $(M - C_4H_4N, CO)^+$ 167 (100.0%), $(M - 4CO)^+$ 149 (18.5%).

(η^1-C_3H_5)$Mn(CO)_4$(PMe_2Ph). To a stirred solution of 0.60 g (1.7×10^{-3} mol) of $KMn(CO)_4(PMe_2Ph)$ in 20 mL of THF were added 0.18 mL (2.2×10^{-3} mol) of allyl chloride. The mixture was stirred for 1 h, then the THF was removed under vacuum and 20 mL of pentane were added to the residue. The pentane solution was filtered through a medium frit and the volume then reduced to 5 mL. Upon cooling the solution to −78 °C, light yellow needles were obtained: IR see Table I; NMR ^1H (acetone-d_6) δ 1.29 d (H_a), 4.35 d (H_d), 4.57 d (H_c), 6.08 m (H_b), J_{ab} = 8.3 Hz, J_{bc} = 16.6 Hz, J_{bd} = 8.5 Hz,



^{13}C (acetone-d_6 decoupled, ppm relative to Me_4Si) 13.38 (CH_2CHC-H_2Mn), 16.12 ($P(CH_3)_2$), 103.36 (CH_2CHCH_2Mn), 130 (PC_6H_5), 149.21 (CH_2CHCH_2Mn); mass spectrum, *m/e* (relative intensity) M^+ 346 (1%), $(M - CO)^+$ 318 (2%), $(M - C_3H_5)^+$ 305 (73%), $(M - C_3H_5, CO)^+$ 277 (80%), $(M - C_3H_5, 2CO)^+$ 249 (41%), $(M - 4CO)^+$ 234 (47%), $(M - C_3H_5, 3CO)^+$ 221 (25%), $(M - C_3H_5, 4CO)^+$ 193 (100%). Anal. Calcd for $C_{15}H_{16}MnO_4P$: C, 52.04; H, 4.66; P, 8.95. Found: C, 51.73; H, 4.48; P, 8.88.

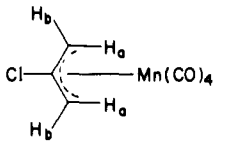
(η^1-C_3H_5)$Mn(CO)_4(PPh_3)$. A solution of $KMn(CO)_4(PPh_3)$ and allyl chloride were reacted and worked up in the same manner outlined in the synthesis of (η^1-C_3H_5)$Mn(CO)_4(PMe_2Ph)$. Upon filtering, a light yellow pentane solution was obtained which gave the IR ν_{CO} bands which are listed in Table I. After removing the pentane and adding acetone-d_6 to the resulting yellow oil, a ^1H NMR spectrum was obtained (acetone-d_6): 1.30 d (H_a), 4.43 d (H_d), 4.57 (H_c), 6.04 m (H_b), J_{ab} = 8.4 Hz, J_{bc} = 16.6 Hz, J_{bd} = 8.6 Hz,



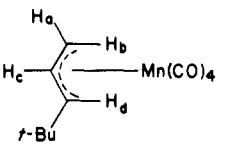
Solutions of the product were kept cool (0 °C) when not being used since the product decomposes through phosphine loss at room temperature.

(η^3-Allyls)(η^3-C_3H_4(1-Cl))$Mn(CO)_4$. This allyl was prepared by a variation of the literature method.[9a,b] A 2×10^{-2} M solution of (η^1-C_3H_4(1-Cl))$Mn(CO)_5$ in decalin was heated to 90 °C until none of the starting material was evident on IR spectra (approximately 3 h). The resulting solution was light yellow with approximately 95% purity as determined from the carbonyl region of IR spectra. The IR ν_{CO} bands are listed in Table II.

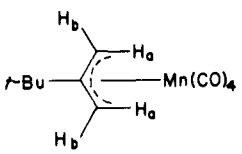
(η^3-C_3H_4X)$Mn(CO)_4$ (X = 2-Cl, 1-*t*-Bu). A 2×10^{-2} M solution of (η^1-C_3H_4X)$Mn(CO)_5$ in cyclohexane was irradiated for 45 min in a 20 mm o.d. Pyrex tube at a distance of 15 cm from a 550 W Hanovia Ultraviolet Lamp. After filtration through a Celite-covered frit, a light yellow solution was obtained. For X = 2-Cl the filtered solution was approximately 99% pure as determined from the carbonyl region of the IR spectra; IR ν_{CO} bands are listed in Table II; ^1H NMR (acetone-d_6) δ 2.59 d (H_a), 3.38 d (H_b), J_{ab} = 4.6 Hz,



For X = 1-*t*-Bu the filtered solution was approximately 95% pure as determined from the carbonyl region of the IR spectra. The IR ν_{CO} bands are listed in Table II; ^1H NMR (benzene-d_6) δ 0.87 s (*t*-Bu), 0.92 d (H_b), 1.92 d (H_a), 2.51 d (H_d), 4.00 m (H_c), J_{ab} = 2 Hz, J_{ac} = 8 Hz, J_{bc} = J_{dc} = 12 Hz,



(η^3-C_3H_4(2-*t*-Bu))$Mn(CO)_4$. A 1×10^{-2} M solution of (η^1-C_3H_4(2-*t*-Bu))$Mn(CO)_5$ in pentane was irradiated 25 min and filtered in the same manner as for (η^3-C_3H_4(2-Cl))$Mn(CO)_4$. The light yellow solution was approximately 90% pure with a small amount of $Mn(CO)_5Br$ as determined from the carbonyl region of the IR spectra; IR ν_{CO} bands are listed in Table II; ^1H NMR (benzene-d_6) δ 0.93 s (*t*-Bu), 1.63 s (H_a), 2.54 s (H_b),



(η^3-C_3H_3(1,1-Me_2))$Mn(CO)_4$. A 1×10^{-2} M solution of (η^1-C_3H_3-(1,1-Me_2))$Mn(CO)_5$ in pentane was irradiated 20 min and filtered in the same manner as for (η^3-C_3H_4(2-Cl))$Mn(CO)_4$. The light yellow solution was approximately 99% pure as determined from the carbonyl region of the IR spectra; IR ν_{CO} bands are listed in Table II. After removal of the pentane and addition of benzene-d_6, ^1H NMR spectra were obtained:[18]

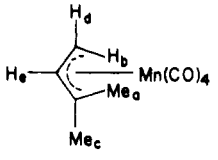
(18) Kormer, V. A.; Lobach, M. I.; Druz, N. N.; Klepikova, V. I.; Kiseleva, N. V. *Dokl. Akad. Nauk SSSR* **1979**, *246*, 1372–1376.

Table II. Infrared Spectra in the Carbonyl Region of (η^3-Allyl)manganese Carbonyls[a]

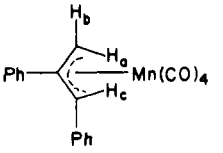
compound	carbonyl stretches, cm^{-1}
$(\eta^1\text{-}C_3H_5)Mn(CO)_4$[b]	2072 m, 1995 m, 1978 s, 1963 s
$(\eta^3\text{-}C_3H_4(1\text{-Me}))Mn(CO)_4$[c]	2067 m, 1990 m, 1973 s, 1958 s
$(\eta^3\text{-}C_3H_4(2\text{-Me}))Mn(CO)_4$	2069 m, 1992 m, 1973 s, 1960 s
$(\eta^3\text{-}C_3H_4(1\text{-Ph}))Mn(CO)_4$	2067 m, 1994 m, 1974 s, 1964 s
$(\eta^3\text{-}C_3H_4(2\text{-Ph}))Mn(CO)_4$	2069 m, 1992 m, 1981 s, 1960 s
$(\eta^3\text{-}C_3H_4(1\text{-Cl}))Mn(CO)_4$	2077 m, 2002 m, 1987 s, 1973 s
$(\eta^3\text{-}C_3H_4(2\text{-Cl}))Mn(CO)_4$	2078 m, 2000 m, 1992 s, 1970 s
$(\eta^3\text{-}C_3H_4(1\text{-}t\text{-Bu}))Mn(CO)_4$	2066 m, 1989 m, 1973 s, 1955 s
$(\eta^3\text{-}C_3H_4(2\text{-}t\text{-Bu}))Mn(CO)_4$	2066 m, 1993 m, 1978 w, 1961 vs
$(\eta^3\text{-}C_3H_3(1,1\text{-}Me_2))Mn(CO)_4$	2064 m, 1987 m, 1970 s, 1956 s
anti-$(\eta^3\text{-}C_3H_3(1,2\text{-}Ph_2))Mn(CO)_4$	2069 m, 1997 s, 1980 s, 1958 s
syn-$(\eta^3\text{-}C_3H_3(1,2\text{-}Ph_2))Mn(CO)_4$	2065 m, 1997 m, 1973 s, 1966 s
$(\eta^3\text{-}C_3H_5)Mn(CO)_3(PPh_3)$[d]	2010 s, 1938 s, 1913 s
$(\eta^3\text{-}C_3H_5)Mn(CO)_3(PMe_2Ph)$	2005 s, 1935 s, 1906 s
$(\eta^3\text{-}C_3H_5)Mn(CO)_3(P(n\text{-Bu})_3)$[e]	2007 s, 1932 s, 1923 sh, 1906 s
$(\eta^3\text{-}C_3H_5)Mn(CO)_3(PCy_3)$[e]	2004 m, 1928 m, 1919 s, 1905 s
$(\eta^3\text{-}C_3H_5)Mn(CO)_3(P(OEt)_3)$	2012 s, 1944 s, 1912 s
$(\eta^3\text{-}C_3H_4(1\text{-Me}))Mn(CO)_3(PPh_3)$	2002 s, 1930 s, 1925 sh, 1910 s, 1905 sh
$(\eta^3\text{-}C_3H_4(2\text{-Me}))Mn(CO)_3(PPh_3)$	2005 m, 1927 s, 1910 s
$(\eta^3\text{-}C_3H_4(1\text{-Ph}))Mn(CO)_3(PPh_3)$	2004 s, 1932 s, 1914 s
$(\eta^3\text{-}C_3H_4(2\text{-Ph}))Mn(CO)_3(PPh_3)$	2008 m, 1935 s, 1915 s
$(\eta^3\text{-}C_3H_4(1\text{-Cl}))Mn(CO)_3(PPh_3)$	2021 m, 1942 s, 1920 s
$(\eta^3\text{-}C_3H_4(1\text{-Cl}))Mn(CO)_3(P(n\text{-Bu})_3)$	2016 m, 1938 s, 1916 s
$(\eta^3\text{-}C_3H_4(1\text{-}t\text{-Bu}))Mn(CO)_3(PPh_3)$	2000 m, 1929 s, 1907 s
$(\eta^3\text{-}C_3H_4(2\text{-}t\text{-Bu}))Mn(CO)_3(PPh_3)$	1999 s, 1921 s, 1907 s
$(\eta^3\text{-}C_3H_4(2\text{-}t\text{-Bu}))Mn(CO)_3(P(n\text{-Bu})_3)$	1996 s, 1922 s, 1910 s
$(\eta^3\text{-}C_3H_3(1,1\text{-}Me_2))Mn(CO)_3(PPh_3)$	1994 m, 1925 s, 1906 m
$(\eta^3\text{-}C_3H_3(1,2\text{-}Ph_2))Mn(CO)_3(PPh_3)$	2020 w, 1940 s, 1914 m
$(\eta^3\text{-}C_3H_3(1,2\text{-}Ph_2))Mn(CO)_3(PMe_2Ph)$	2012 w, 1935 s, 1912 m
$(\eta^3\text{-}C_3H_3(1,2\text{-}Ph_2))Mn(CO)_3(PCy_3)$	2006 w, 1923 s, 1902 m
$(\eta^3\text{-}C_3H_5)Mn(CO)_2(PMe_2Ph)_2$	1916 s, 1847 s
$(\eta^3\text{-}C_3H_5)Mn(CO)_2(P(OEt)_3)_2$[e]	1947 m, 1869 s

[a] In cyclohexane. [b] Previously reported, ref 9a,b. [c] Previously reported, ref 9b. [d] Previously reported: Bruce, M. I.; Iqbal, M. Z.; Stone, F. G. A. *J. Organomet. Chem.* **1969**, *20*, 161–168. [e] Previously reported, ref 19.

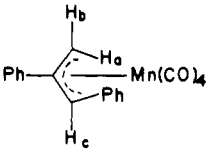
(benzene-d_6) δ 1.05 s (H_a), 1.35 d of d (H_b), 1.48 s (H_c), 2.31 d of d (H_d), 4.00 d of d (H_e), J_{bd} = 2 Hz, J_{be} = 12 Hz, J_{de} = 7 Hz,



$(\eta^3\text{-}C_3H_3(1,2\text{-Ph}_2))Mn(CO)_4$. The compound (*cis*-$\eta^1\text{-}C_3H_3(1,2\text{-}Ph_2))Mn(CO)_5$ was irradiated in the same way as for $(\eta^3\text{-}C_3H_3(1,1\text{-}Me_2))Mn(CO)_4$. Infrared spectra of the filtered solution indicated the presence of both the syn and anti isomers. The solution was concentrated to 1 mL and then eluted with hexane through a 25 cm × 12 mm column packed with neutral "Aluminum oxide 90 active" obtained from EM Laboratories Inc. The first band off was a mixture of the syn and anti isomers free of any allyl halide. The ratio of syn to anti in the band was the same as that in the starting solution. Further elution of the column gave only 3-chloro-1,2-diphenyl-1-propene. After removing the solvent under vacuum from the solution of the first band, the yellow oil was dissolved in acetone-d_6 to give ^1H NMR spectra. After remaining at room temperature for 1 week, a pentane solution of the isomer mixture had converted to approximately 95% anti isomer as determined by the carbonyl region of IR spectra and by ^1H NMR spectra. Characterization—(*syn*-$\eta^3\text{-}C_3H_3(1,2\text{-}Ph_2))Mn(CO)_4$): IR see Table II; NMR ^1H (acetone-d_6) δ 2.31 d (H_a), 2.93 d (H_b), 3.80 s (H_c);

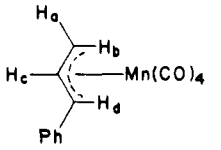


(*anti*-$\eta^3\text{-}C_3H_3(1,2\text{-}Ph_2))Mn(CO)_4$—IR see Table II; NMR ^1H (acetone-d_6) δ 3.43 d (H_a), 4.10 d (H_b), 5.87 s (H_c), 7.4–7.2 m (H_{Ph}), J_{ab} = 2.93 Hz,



mass spectrum, *m/e* (relative intensity) M^+ 360 (0.3%), $(M - CO)^+$ 332 (3.5%), $(M - 2CO)^+$ 304 (16.2%), $(M - 3CO)^+$ 276 (15.8%), $(M - 4CO)^+$ 248 (100%).

$(\eta^3\text{-}C_3H_4X)Mn(CO)_4$ (X = H, 1-Me, 2-Me, 1-Ph, 2-Ph). These η^3-allyl compounds were prepared by the literature method.[9d] Purification of the products was achieved by dissolving the residue from the CH_2Cl_2 solution in 20 mL of pentane and filtering through a Celite-covered frit. The resulting solutions were light yellow and were approximately 99% pure as determined from the carbonyl region of the IR spectra. The IR ν_{CO} bands are listed in Table II. For X = 1-Ph, a ^1H NMR spectrum was obtained: (benzene-d_6) δ 1.56 d,d (H_b), 2.42 d,d (H_a), 3.28 d (H_d), 5.21 m (H_c), 7.28 s (Ph), J_{ab} = 2 Hz, J_{ac} = 7 Hz, J_{bc} = J_{cd} = 12 Hz,



$(\eta^3\text{-}C_3H_5)Mn(CO)_3L$ (L = PPh_3, PMe_2Ph, $P(n\text{-Bu})_3$, PCy_3, $P(OEt)_3$), $(\eta^3\text{-}C_3H_4X)Mn(CO)_3(PPh_3)$ (X = 1-Me, 2-Me, 1-Ph, 2-Ph, 1-Cl, 1-*t*-Bu, 2-*t*-Bu), $(\eta^3\text{-}C_3H_4X)Mn(CO)_3(P(n\text{-Bu})_3)$ (X = 1-Cl, 2-*t*-Bu), $(\eta^3\text{-}C_3H_3(1,1\text{-}Me_2))Mn(CO)_3PPh_3$, $(\eta^3\text{-}C_3H_3(1,2\text{-}Ph_2))Mn(CO)_3L$ (L = PPh_3, PMe_2Ph, PCy_3), and $(\eta^3\text{-}C_3H_5)Mn(CO)_2L_2$ (L = PMe_2Ph, $P(OEt)_3$). These compounds were prepared only during kinetic reactions, which are analogous conditions to those of the thermal literature method.[19] The IR ν_{CO} bands are listed in Table II.

Results

Syntheses of the (η^1-allyl)manganese carbonyls were accomplished by modification of the literature methods.[9a,b] The (η^3-allyl)manganese carbonyls were synthesized by either decarbonylation of the η^1-allyl compounds[9a,b] or directly by the phase transfer method of Gibson and co-workers.[9d] The phase-transfer method has the advantage of yielding a product which is not contaminated with $Mn_2(CO)_{10}$, a byproduct which is very difficult to separate from the allyl compound. However, this method failed to produce $(\eta^3\text{-}C_3H_4(2\text{-Cl}))Mn(CO)_4$ which required UV irradiation of $(\eta^1\text{-}C_3H_4(2\text{-Cl}))Mn(CO)_5$ to afford the (η^3-allyl)-manganese carbonyl.

Similarly, neither $(\eta^3\text{-}C_3H_4(1\text{-CN}))Mn(CO)_4$ nor $(\eta^3\text{-}C_3H_4\text{-}(1\text{-}p\text{-}NO_2Ph))Mn(CO)_4$ could be produced by the phase-transfer method. Attempts to form the η^1-allyl compounds by reacting $KMn(CO)_5$ with the allyl halides failed for *p*-nitrocinnamyl chloride, yielding only a red polymerized solid, but succeeded for 4-bromo-2-butenonitrile. Decarbonylation of $(\eta^1\text{-}C_3H_4(1\text{-CN}))Mn(CO)_5$ to produce the η^3-allyl compound was not possible by the methods attempted, those methods being thermal, photochemical, and treatment with Me_3NO.[20] The reagent Me_3NO is commonly used to abstract a carbonyl ligand, by converting it into CO_2 and forming Me_3N.

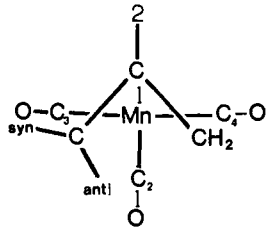
The compounds $(\eta^3\text{-}C_3H_4(2\text{-}t\text{-Bu}))Mn(CO)_4$ and $(\eta^3\text{-}C_3H_3\text{-}(1,2\text{-}Ph_2))Mn(CO)_4$ were synthesized by UV irradiation of a solution of the corresponding η^1-allyl compounds. For the 1,2-

Table III. Kinetic Parameters for Substitution Reactions (eq 3) of (η^3-Allyl)manganese Carbonyls in Cyclohexane

compound	$\Delta H^{\ddagger}$ (kcal/mole)	$\Delta S^{\ddagger}$ (eu)	k (s^{-1}) at 45 °C	k_{rel}[a] at 45 °C	k_{rel} (Co)[b] at 0 °C
(η^3-C_3H_5)$Mn(CO)_4$[c]	26.8 ± 0.3	9.6 ± 0.8	2.80×10^{-4} [d,e]	1.0	1.0
(η^3-C_3H_4(1-Me))$Mn(CO)_4$[f]	23.4 ± 1.2	−2.0 ± 4.0	1.98×10^{-4}	0.71	0.6
(η^3-C_3H_4(2-Me))$Mn(CO)_4$[f]	23.0 ± 1.5	2.7 ± 5.0	4.07×10^{-3} [g]	15	8.6
(η^3-C_3H_4(1-Ph))$Mn(CO)_4$[f]	26.6 ± 0.6	7.9 ± 1.8	2.05×10^{-4}	0.73	
(η^3-C_3H_4(2-Ph))$Mn(CO)_4$[f]	20.8 ± 1.2	−3.4 ± 3.6	5.68×10^{-3} [g]	20	3.4
(η^3-C_3H_4(1-Cl))$Mn(CO)_4$[f]	25.8 ± 0.5	2.1 ± 1.6	3.70×10^{-5}	0.13	0.3
(η^3-C_3H_4(1-*t*-Bu))$Mn(CO)_4$[f]			4.04×10^{-4}	1.4	
(η^3-C_3H_4(2-*t*-Bu))$Mn(CO)_4$[h]			1.87×10^{-2} [i]	490[j]	
(η^3-C_3H_3(1,1-Me_2))$Mn(CO)_4$[f]			7.58×10^{-4}	2.7	
anti-(η^3-C_3H_3(1,2-Ph_2))$Mn(CO)_4$[k]	20.3 ± 1.7	0.7 ± 5.0	9.77×10^{-2} [g]	349	
syn-(η^3-C_3H_3(1,2-Ph_2))$Mn(CO)_4$[h]			7.50×10^{-3} [l]	200[j]	
(η^3-C_3H_5)$Mn(CO)_3(PMe_2Ph)$[k]	32.0 ± 0.9	15.1 ± 2.6	1.45×10^{-6} [g]	0.005	
(η^3-C_3H_5)$Mn(CO)_3(P(OEt)_3)$[l]	30.0 ± 0.7	12.8 ± 2.0	9.51×10^{-6} [g]	0.03	

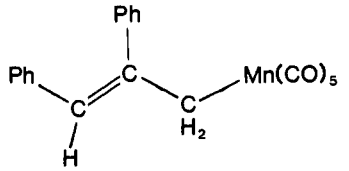
[a] ±5%. [b] Relative rates for CO substitution reactions of (η^3-C_3H_4X)$Co(CO)_3$ with PPh_3, for (η^3-C_3H_5)$Co(CO)_3$, $k = 3.28 \times 10^{-4}$ s at 0 °C, ref 4. [c] Reaction with PPh_3, PMe_2PH, and PCy_3. [d] Rate for 0.21 M PPh_3 under 1 atm of CO at 45 °C, $k = 2.20 \times 10^{-4}$ s^{-1}; rate for 0.21 M PMe_2Ph under 1 atm of CO at 45 °C, $k = 2.84 \times 10^{-4}$ s^{-1}. [e] Rates for P(*n*-Bu)$_3$, $k_1 = 2.61 \times 10^{-4}$ s^{-1}, $k_2 = 9.03 \times 10^{-5}$ M^{-1} s^{-1} at 45 °C; rates for $P(OEt)_3$, $k_1 = 2.81 \times 10^{-4}$ s^{-1}, $k_2 = 5.30 \times 10^{-5}$ M^{-1} s^{-1} at 45 °C. [f] Reaction with PPh_3. [g] Estimated for 45 °C from activation parameters. [h] Reaction with PCy_3. [i] Rate at 27.0 °C. [j] By comparison with the reaction rate of *anti*-(η^3-C_3H_3(1,2-Ph_2))$Mn(CO)_4$ which is at 27.0 °C, $k = 1.34 \times 10^{-2}$ s as calculated from the activation parameters. [k] Reaction with PMe_2Ph. [l] Reaction with $P(OEt)_3$.

diphenylallyl compound, a mixture of the syn and anti isomers (I) was obtained. When the cis isomer of (η^1-C_3H_3(1,2-Ph_2))-

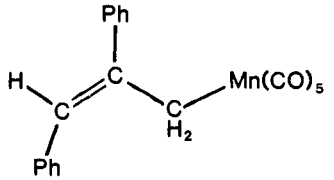


1

$Mn(CO)_5$ (II) was irradiated or treated with Me_3NO, a 1:1 ratio of the syn:anti isomers was obtained. When a mixture of cis and trans (III) isomers (ratio 2:3) of the η^1-allyl compound was irradiated, an approximately 1:5 ratio of the syn:anti isomers was obtained. Characterization of the (allyl)manganese carbonyls was accomplished by IR, NMR, and mass spectroscopy.



II, cis



III, trans

The syntheses of allyl halide derivatives containing either strong electron-withdrawing or electron-donating substituents in either the 1- or 2-position were attempted. However, as described in the discussion section these attempts failed. Syntheses of allyl halide derivatives containing bulky groups were successfully performed. The reaction of NBS[15] with α-methylstyrene, *cis*-4,4-dimethyl-2-pentane, and 2,3,3-trimethyl-1-butene gave the corresponding allyl halides. The compounds 3-chloro-1,2-diphenyl-1-propene and 1-chloro-3-methyl-2-butene were prepared by the addition of thionyl chloride[16] to the corresponding allyl alcohols. All of these allyl halides react with either $KMn(CO)_5$ or $Mn(CO)_5Br$ to give the desired corresponding (allyl)manganese compounds.

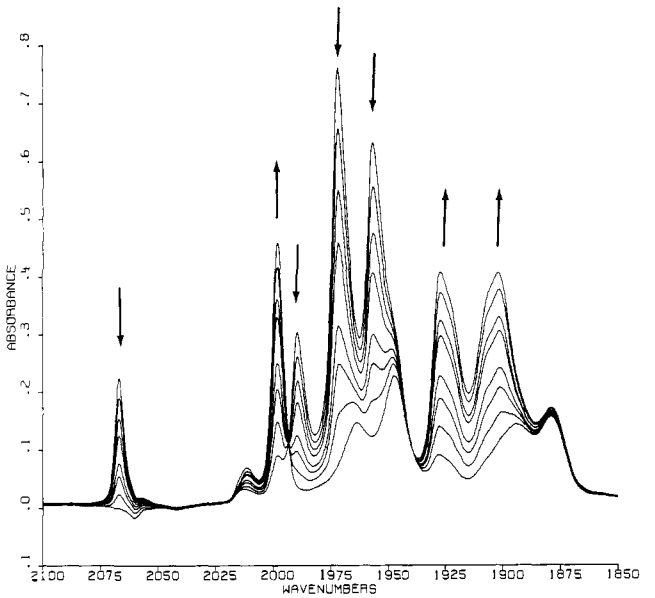


Figure 1. Infrared spectral changes vs. time for the reaction (η^3-C_3H_4-(1-Me))$Mn(CO)_4$ + PPh_3 → (η^3-C_3H_4(1-Me))$Mn(CO)_3PPh_3$ + CO in cyclohexane.

Data from the kinetic reactions of the (η^3-allyl)manganese carbonyls with phosphines in cyclohexane (eq 2) are summarized in Table III. A representative example of IR spectra recorded during kinetic reactions is shown in Figure 1. The rates are first order in manganese complex concentration and zero order in phosphine concentration for PPh_3, PMe_2Ph, and PCy_3. Reacting P(*n*-Bu)$_3$ and $(POEt)_3$ with (η^3-C_3H_5)$Mn(CO)_4$ a second, slower pathway was also observed which is first order in both manganese complex and nucleophile concentrations. The reaction of (η^3-C_3H_4(2-Cl))$Mn(CO)_4$ with PPh_3 produced $Mn(CO)_4(PPh_3)Cl$, instead of the expected (η^3-C_3H_4(2-Cl))$Mn(CO)_3(PPh_3)$.

Reactions of (η^3-C_3H_5)$Mn(CO)_4$ with PPh_3 and PMe_2Ph were also performed under 1 atm of CO. During the first half-life, a 20% rate reduction was seen for the reaction with PPh_3, but no rate decrease was observed for the reaction with PMe_2Ph. Upon standing, these reactions come to equilibria (eq 4). For PPh_3 the equilibrium constant (K_{eq}) is approximately 4 and for PMe_2Ph it is approximately 100.

$$(\eta^3\text{-}C_3H_5)Mn(CO)_4 + L \underset{}{\overset{K_{eq}}{\rightleftharpoons}} (\eta^3\text{-}C_3H_5)Mn(CO)_3L + CO \quad (4)$$

Table IV. Kinetic Parameters for Thermal Decarbonylations (eq 5) of (η^1-Allyl)manganese Carbonyls in Decalin

compound	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (eu)	k (s^{-1})[a] at 80 °C	k_{rel} at 80 °C
$(\eta^1\text{-}C_3H_5)Mn(CO)_5$	25.6 ± 1.4	−3.1 ± 0.4	1.64×10^{-4}	1.0
$(\eta^1\text{-}C_3H_4(1\text{-Me}))Mn(CO)_5$	27.0 ± 0.9	2.2 ± 2.6	4.44×10^{-4}	2.71
$(\eta^1\text{-}C_3H_4(1\text{-Cl}))Mn(CO)_5$	24.5 ± 2.0	−6.5 ± 4.0	2.05×10^{-4}	1.25
$(\eta^1\text{-}C_3H_4(1\text{-}t\text{-Bu}))Mn(CO)_5$			1.54×10^{-4}	0.94
$(\eta^1\text{-}C_3H_5)Mn(CO)_4(PMe_2Ph)$	27.6 ± 0.4	−1.1 ± 1.1	3.59×10^{-5}	0.22
$(\eta^1\text{-}C_3H_5)Mn(CO)_4(PPh_3)$[b]	24.5 ± 1.6	1.2 ± 2.6	9.19×10^{-3}	

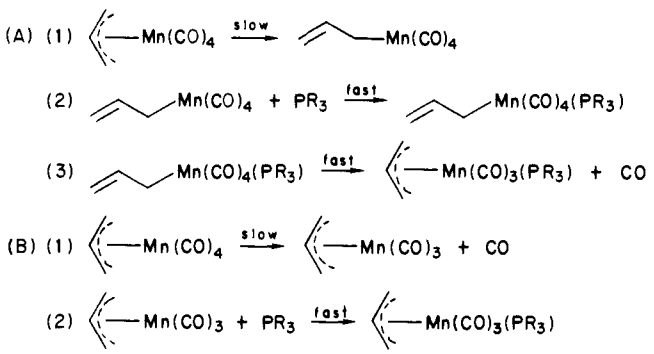
[a] ±5%. [b] Compound loses PPh_3 instead of CO, eq 7.

Activation parameters and relative rates for the thermal decarbonylation of the η^1-allyl complexes in cyclohexane or decalin (eq 5) are listed in Table IV.

$$(\eta^1\text{-}C_3H_5)Mn(CO)_5 \xrightarrow{\Delta} (\eta^3\text{-}C_3H_5)Mn(CO)_4 + CO \quad (5)$$

Discussion

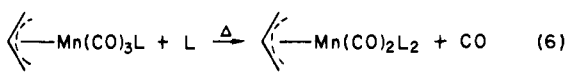
Substitution Mechanism. Rate data showing that the reactions of η^3-$C_3H_5Mn(CO)_4$ with phosphines (eq 3) are independent of the nature and the concentrations of the phosphines indicate two possible mechanism. These two mechanisms are represented by



with either A1 or B1 as the rate-determining steps. Activation parameters (Table III) are similar to those of other reactions[4,21] where CO dissociation is the rate-determining step. However, this only suggests mechanism B but does not rule out mechanism A. Reactions carried out in 1 atm of CO were inconclusive, since the reaction rate with PPh_3 decreased but the reaction rate with PMe_2Ph was unaffected. The lack of $\eta^3 \leftrightarrow \eta^1$ fluxionality of $(\eta^3\text{-}C_3H_5)Mn(CO)_4$ up to 180 °C[11] indicates mechanism A is probably not the correct mechanism.

It was though that if the intermediate to mechanism A, $(\eta^1\text{-}C_3H_5)Mn(CO)_4(PR_3)$, could be made and found to decarbonylate at a rate slower than the substitution reaction, mechanism A could be positively ruled out. The rate of decarbonylation for $(\eta^1\text{-}C_3H_5)Mn(CO)_5$ suggested this would be the case, for it reacts about 100 times slower than does the CO substitution reaction of $(\eta^3\text{-}C_3H_5)Mn(CO)_4$ (eq 3). The corresponding monophosphine adduct, $(\eta^1\text{-}C_3H_5)Mn(CO)_4(PR_3)$, was expected to decarbonylate even more slowly, owing to the increased electron density on the metal which results in a stronger Mn–CO bond. What was observed for $(\eta^1\text{-}C_3H_5)Mn(CO)_4(PPh_3)$ was most unexpected, in that PPh_3 was lost instead of CO to form $(\eta^3\text{-}C_3H_5)Mn(CO)_4$. This rules out an η^1-allyl intermediate for the PPh_3 substitution reaction (eq 3). When $(\eta^1\text{-}C_3H_5)Mn(CO)_4(PMe_2Ph)$ was heated, the expected result was observed with the loss of CO instead of PMe_2Ph. The rate of CO loss is almost 1000 times slower than the substitution reaction rate of $(\eta^3\text{-}C_3H_5)Mn(CO)_4$ at the same temperature, ruling out mechanism A. Since mechanism A was found to be incorrect, this leaves mechanism B as a plausible mechanism which is in accord with the experimental facts.

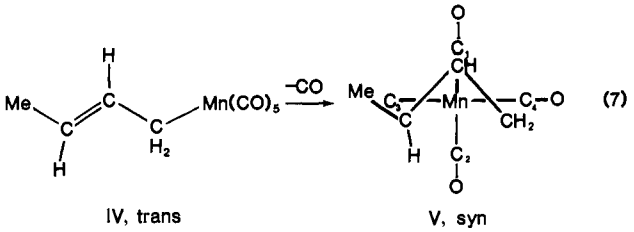
For the reaction of $(\eta^3\text{-}C_3H_5)Mn(CO)_3L$ with L, where L = PMe_2Ph or $P(OEt)_3$, (eq 6), a CO dissociation mechanism is again



(6)

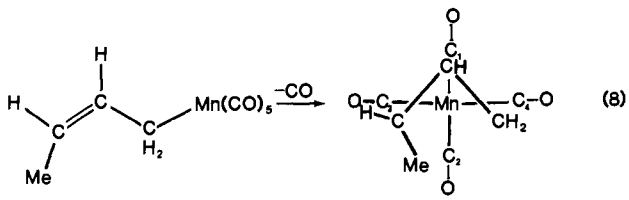
suggested. The reaction is independent of phosphine concentration, thereby ruling out an associative mechanism. In addition, the value of $\Delta H^{\ddagger}$ is increased over that for $(\eta^3\text{-}C_3H_5)Mn(CO)_4$ as is expected owing to the increased electron density on the metal that strengthens the metal–CO bonds.

Isomers of $(\eta^3\text{-}C_3H_3(1,2\text{-}Ph_2))Mn(CO)_4$. For the 1-Me substituted allyl compound, the nonthermal conversion $\eta^1 \rightarrow \eta^3$ is stereospecific,[18,22] i.e., the *trans*-η^1 (IV) → *syn*-η^3 (V) (eq 7) and the *cis*-η^1 (VI) → *anti*-η^3 (VII) (eq 8). The 1,2-Ph_2 substituted



(7)

IV, trans V, syn



(8)

VI, cis VII, anti

allyl isomers follow a similar structural pattern. The *cis*-diphenyl allyl isomer (II) yields a mixture of the syn and anti isomers, and the *trans*-diphenyl allyl isomer (III) yields the anti isomer. This mixture of syn and anti isomers that results from $(cis\text{-}\eta^1\text{-}C_3H_3(1,2\text{-}Ph_2))Mn(CO)_5$ is obtained for both the irradiation and the Me_3NO methods of $\eta^1 \rightarrow \eta^3$ conversion. Rearrangement of the *cis*-η^1-1,2-Ph_2-allyl isomer to yield some anti product during decarbonylation is probably due to the large steric interaction of the two adjacent phenyl groups. Upon conversion of the allyl from $\eta^1 \rightarrow \eta^3$, the C–C–C bond angle increases from 120° to 125°[23] thereby bringing the two phenyl groups into even closer proximity. Relief of the Ph–Ph crowding is probably the driving force for conversion of syn to anti isomer, both during formation of the η^3-allyl complex and after it is formed. The mechanism for syn → anti conversion is uncertain, since $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ conversion probably cannot be invoked in view of the rigidity of the parent allyl compound[11] and the mechanism for CO substitution proposed in this work.

The ^1H NMR spectra for the isomers of $(\eta^3\text{-}C_3H_3(1,2\text{-}Ph_2))Mn(CO)_4$ are in general agreement with that reported[18,22] for the isomers of $(\eta^3\text{-}C_3H_4(1\text{-Me}))Mn(CO)_4$. For both compounds there is a downfield shift of the 1-position protons for the anti isomer with respect to the syn isomer. There appears to be no reported IR data with which to compare the changes in the IR spectra for the syn and anti isomers.

Substituent Effects. The substituent effects for (η^3-allyl)manganese carbonyls on the rates of CO substitution (eq 3) are larger than, yet parallel to, those found for (η^3-allyl)cobalt carbonyls (Table III).[4] The general pattern is that a substituent in the 2-position increases the reaction rate, whereas a substituent

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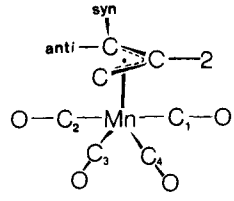
in the 1-position decreases the reaction rate. On the basis of the evidence available, neither steric nor electronic effects adequately explain this pattern for cobalt compounds. However, for the manganese compounds, steric effects do appear to be responsible in part for the observed pattern.

The crystal structure of $(\eta^3\text{-}C_3H_5)Mn(CO)_3(CNMe)$[23a] shows that the 2-position of the allyl ligand is eclipsed by one of the carbonyl ligands (VIII). A similar configuration was reported



VIII

for $(\eta^3\text{-}C_3H_5)Mn(CO)_4$ from analyses of IR and Raman spectra[24] (I). This configuration brings a substituent in the 2-position of the allyl ligand into close proximity with the eclipsed carbonyl (CO(1)—I, VIII). The resulting steric crowding is expected to cause a steric acceleration of the loss of this eclipsed CO, in accord with experimental fact. In agreement with this reasoning is the structure of $(\eta^3\text{-}C_3H_5)Mn(CO)_3(PMe_3)$ which shows[25] that the PMe_3 ligand occupies the position eclipsed with the 2-position of the allyl group. Thus the rate of CO loss increases with increasing size of the 2-substituent, H < Me < Ph ≪ *t*-Bu.

With the *syn*-1,2-Ph_2 substituted allyl compound, the effective bulk of the 2-Ph group is increased by the presence of the adjacent 1-Ph group. The 1-Ph group, particularly in view of the large C–C–C angle of an η^3-allyl ligand, hinders rotation of the 2-Ph group forcing it to assume a more perpendicular position with respect to the allyl ligand. This configuration means that the phenyl ring is in closer proximity to CO(1) (VIII), resulting in greater steric interaction than the 2-Ph allyl compound. Since inductive effects of substituents are small, it appears this greater steric interaction is responsible for enhancing the CO substitution rate of the *syn*-1,2-Ph_2 allyl complex over that of the 2-Ph (allyl)manganese carbonyl.

For the *anti*-1,2-Ph_2 substituted allyl compound, a steric argument can again be made to explain its CO substitution rate enhancement with respect to the mono-substituted 2-Ph allyl compound. On the anti isomer of $(\eta^3\text{-}C_3H_3(1,2\text{-}Ph_2))Mn(CO)_4$ both Ph groups are in eclipsed positions with respect to the two *cis*-carbonyls, the 1-Ph group being located over CO(2) (I).[26] This causes steric crowding of both the *cis*-carbonyls thereby enhancing the CO dissociation rate for the 1,2-Ph_2 allyl compound tenfold over that of $(\eta^3\text{-}C_3H_4(2\text{-}Ph))Mn(CO)_4$.

Similarly, the 1,1-Me_2 substituted allyl compound shows a CO substitution rate enhancement as compared with the 1-Me substituted allyl compound. For $(\eta^3\text{-}C_3H_3(1,1\text{-}Me_2))Mn(CO)_4$, with two Me groups on the terminal carbon of the allyl ligand, one Me group must be in the anti position which then forces it to occupy a position eclipsed with a carbonyl group (CO(2)—VII). The presence of the second Me group increases the electron donation of the 1,1-Me_2 allyl group over that of the 1-Me allyl group, as evidenced by the IR spectra (Table II) thereby increasing the strength of the Mn–CO bonding. However, the steric interaction of the eclipsed Me group causes an effect larger than the inductive effect of the Me groups, resulting in a fourfold enhancement of the CO substitution rate for $(\eta^3\text{-}C_3H_3(1,1\text{-}Me_2))Mn(CO)_4$ compared with that of *syn*-$(\eta^3\text{-}C_3H_4(1\text{-}Me))Mn(CO)_4$.

The compound $(\eta^3\text{-}C_3H_4(1\text{-}Me))Mn(CO)_4$ has been shown to be primarily the syn isomer if it is formed by thermal decarbonylation of the η^1-allyl compound.[18,22] Similarly, the 1-Ph and 1-*t*-Bu substituted allyl complexes synthesized in this study were syn isomers. By analogy, $(\eta^3\text{-}C_3H_4(1\text{-}Cl))Mn(CO)_4$ has been assumed to be the syn isomer, which is consistent with observing only one set of IR bands and obtaining linear, first-order kinetic plots for the substitution reaction of this compound. Similar reasoning had been applied to the 1-substituted allyl cobalt compounds.[4] For the syn isomers, the substituents in the 1-position are pointed away from the carbonyls cis to the allyl ligand and cause little steric crowding. In fact, almost no steric influence is observed even for the bulky 1-*t*-Bu allyl compound which reacts only 1.4 times faster than does the unsubstituted allyl compound (Table III). The substituent effects of the 1-substituted allyl compounds appear to be primarily the result of inductive effects.

The IR carbonyl stretching frequencies of the allyl manganese compounds decrease with the addition of an alkyl or aryl substituent (Table II). This indicates that more electron density is being back donated from the manganese atom to the carbonyl ligand which strengthens the Mn–CO bond. Strengthening of the Mn–CO bond is expected to decrease the rate of CO substitution, which is in fact the observed effect. Both the 1-Me and 1-Ph substituted allyl compounds showed a decrease in the CO substitution rate as compared with the parent $(\eta^3\text{-}C_3H_5)Mn(CO)_4$.

However, $(\eta^3\text{-}C_3H_4(1\text{-}Cl))Mn(CO)_4$ does not fit this explanation. For this compound an increase in the IR carbonyl stretching frequencies is observed, whereas a weakening of the Mn–CO bond with an accompanying increase in the CO substitution rate is expected. Just the opposite is found, with an almost tenfold decrease in rate compared to $(\eta^3\text{-}C_3H_5)Mn(CO)_4$. No ground-state effect for the 1-Cl substituted allyl compound can be readily invoked to explain the observed effect. One may suggest this is a transition-state effect, where the proposed $(\eta^3\text{-}C_3H_4(1\text{-}Cl))Mn(CO)_3$ species is stabilized by the electron-withdrawing ability of the chloro substituent.

Allyl Halide Syntheses. Attempts to produce $(\eta^3\text{-}C_3H_4X)Mn(CO)_4$ with X being a strong electron-withdrawing group were unsuccessful. The most direct method seemed to be bromination of the substituted allyl compound with NBS.[27] For crotononitrile this synthetic method worked well because of the resonance stabilization provided by the cyano group.[17] However, under similar conditions methacrylonitrile, 2-*p*-chlorophenylpropene, 2-*p*-nitrophenylpropene, and 2-nitropropene do not react with NBS. Presumably this is due to the strong electron-withdrawing effect of the substituent group. The deactivating effects of electron-withdrawing groups α to the substituting position have been reported[28] for NBS reactions, with destabilization of the intermediate in the radical formation step being given as the explanation.[28a] Attempts to reduce 2-*p*-nitrophenylpropene and 1-*p*-nitrophenyl-3-chloro-1-propene to the strongly electron-donating paraamine derivatives by the classical Fe method[29] were also unsuccessful.

Allyl–Metal Bonding. The only (allyl)manganese carbonyl prepared with a strong electron-withdrawing substituent was $(\eta^1\text{-}C_3H_4(1\text{-}CN))Mn(CO)_5$. Unfortunately this compound could not be decarbonylated to form the η^3-allyl compound. Since the cyano group is not large, steric effects cannot be what prevents the $\eta^1 \rightarrow \eta^3$ conversion. It could be that the cyano group withdraws too much electron density from the double bond for it to effectively π-bond to the manganese. The compound $(HC{\equiv}CCH_2)Mn(CO)_5$, in which the triple bond of the acetylide group is more electron deficient than the double bond of the allyl group, will not form an η^3-compound upon heating.[30] However, a 1-CN group does

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not prevent η^3-bonding which is reported for $(\eta^3\text{-}C_3H_4(1\text{-}CN))Fe(CO)_2NO$. This difference between the iron and manganese systems may be explained in terms of the electron density around each metal. Orbital population studies[31] of the allyl ligand indicate that it bonds to a metal atom mainly through electron donation. The manganese atom bound to four carbonyls would be more electron deficient than is the iron atom bound to two carbonyls and a nitrosyl. Orbital population studies[32] on CO and NO indicate that the neutral NO ligand withdraws slightly less π electron density from a metal than does CO. This greater electron deficiency of the $Mn(CO)_4$ moiety over the $Fe(CO)_2(NO)$ moiety must therefore require more electron donation from the allyl ligand to achieve η^3-bonding. Thus electron-withdrawing substituents on allyl may retard $\eta^1 \rightarrow \eta^3$ conversion more in the Mn than the Fe system.

Conclusion. Substitution of CO in (η^3-allyl)manganese tetracarbonyls takes place by a dissociation (S_N1) mechanism. This is the same mechanism involved in the CO substitution reactions of (η^3-allyl)cobalt tricarbonyls, with $(\eta^3\text{-}C_3H_5)Co(CO)_3$ reacting 200 times faster at 45 °C than does $(\eta^3\text{-}C_3H_5)Mn(CO)_4$. Decarbonylation reactions of (η^1-allyl)manganese compounds rule out the possibility of an $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ process. Nonbulky hydrocarbon groups in the 1-position of allyl with a syn structure have generally a small retardation effect on the rate of substitution. Substituents in the anti-1-position have an enhancing effect on the CO substitution rate. It seems reasonable that this should happen, because in the syn structure the substituent group points away from the metal and offers no steric destabilization to the coordinated CO groups. In contrast, the anti structure has the group in toward the metal which does sterically promote the loss of CO.

Substituents in the 2-position of the allyl enhance the rate of CO substitution. This seems to be a steric effect because the rate enhancement correlates to the size of the substituent and because of the structure of the compound which places the group in the 2-position near one of the COs. The importance of steric effects is to be expected, for it has long been known[33] that steric acceleration occurs for dissociation (S_N1) reactions. One disappointment of our study is we were unable to prepare the desired compounds with strong electron-donating or -withdrawing substituents on the allyl ligand in order to test these electronic effects on the rates of CO substitution.

Acknowledgment. We thank the donors of the Petroleum Research Foundation, administered by the American Chemical Society, and the National Science Foundation for support of this research. We greatly appreciate the helpful suggestions and advice on the syntheses of allyl derivatives given us by our colleague Dr. Robert C. Gadwood.

Registry No. $(\eta^1\text{-}C_3H_5)Mn(CO)_5$, 14057-83-1; $(\eta^1\text{-}C_3H_4(1\text{-}Me))Mn(CO)_5$, 18131-46-9; $(\eta^1\text{-}C_3H_4(1\text{-}Cl))Mn(CO)_5$, 92820-72-9; $(\eta^1\text{-}C_3H_4(2\text{-}Cl))Mn(CO)_5$, 23108-59-0; $(cis\text{-}\eta^1\text{-}C_3H_4(1\text{-}CN))Mn(CO)_5$, 96021-30-6; $(trans\text{-}\eta^1\text{-}C_3H_4(1\text{-}CN))Mn(CO)_5$, 96093-37-7; $(\eta^1\text{-}C_3H_4(1\text{-}t\text{-}Bu))Mn(CO)_5$, 96021-31-7; $(\eta^1\text{-}C_3H_4(2\text{-}t\text{-}Bu))Mn(CO)_5$, 96021-32-8; $(\eta^1\text{-}C_3H_3(1,1\text{-}Me_2))Mn(CO)_5$, 18131-47-0; $(cis\text{-}\eta^1\text{-}C_3H_3(1,2\text{-}Ph_2))Mn(CO)_5$, 96021-33-9; $(trans\text{-}\eta^1\text{-}C_3H_3(1,2\text{-}Ph_2))Mn(CO)_5$, 96093-38-8; $(\eta^1\text{-}C_3H_5)Mn(CO)_4(PMe_2Ph)$, 96021-34-0; $(\eta^1\text{-}C_3H_5)Mn(CO)_4(PPh_3)$, 96021-35-1; $(\eta^3\text{-}C_3H_5)Mn(CO)_4$, 33307-30-1; $(\eta^3\text{-}C_3H_4(2\text{-}Me))Mn(CO)_4$, 33307-32-3; $(\eta^3\text{-}C_3H_4(1\text{-}Ph))Mn(CO)_4$, 96021-36-2; $(\eta^3\text{-}C_3H_4(2\text{-}Ph))Mn(CO)_4$, 96021-37-3; $(\eta^3\text{-}C_3H_4(1\text{-}Cl))Mn(CO)_4$, 96021-38-4; $(\eta^3\text{-}C_3H_4(2\text{-}Cl))Mn(CO)_4$, 96021-39-5; $(\eta^3\text{-}C_3H_4(1\text{-}t\text{-}Bu))Mn(CO)_4$, 96021-40-8; $(\eta^3\text{-}C_3H_4(2\text{-}t\text{-}Bu))Mn(CO)_4$, 96021-41-9; $(\eta^3\text{-}C_3H_3(1,1\text{-}Me_2))Mn(CO)_4$, 71713-51-4; $anti\text{-}(\eta^3\text{-}C_3H_3(1,2\text{-}Ph_2))Mn(CO)_4$, 96021-42-0; $syn\text{-}(\eta^3\text{-}C_3H_3(1,2\text{-}Ph_2))Mn(CO)_4$, 96093-39-9; $(\eta^3\text{-}C_3H_5)Mn(CO)_3(PPh_3)$, 33011-91-5; $(\eta^3\text{-}C_3H_5)Mn(CO)_3(PMe_2Ph)$, 96021-43-1; $(\eta^3\text{-}C_3H_5)Mn(CO)_3(P(n\text{-}Bu)_3)$, 76294-42-3; $(\eta^3\text{-}C_3H_5)Mn(CO)_3(PCy_3)$, 76294-41-2; $(\eta^3\text{-}C_3H_5)Mn(CO)_3(P(OEt)_3)$, 96021-44-2; $(\eta^3\text{-}C_3H_4(1\text{-}Me))Mn(CO)_3(PPh_3)$, 96021-45-3; $(\eta^3\text{-}C_3H_4(2\text{-}Me))Mn(CO)_3(PPh_3)$, 96021-46-4; $(\eta^3\text{-}C_3H_4(1\text{-}Ph))Mn(CO)_3(PPh_3)$, 96021-47-5; $(\eta^3\text{-}C_3H_4(2\text{-}Ph))Mn(CO)_3(PPh_3)$, 96021-48-6; $(\eta^3\text{-}C_3H_4(1\text{-}Cl))Mn(CO)_3(PPh_3)$, 96021-49-7; $(\eta^3\text{-}C_3H_4(2\text{-}Cl))Mn(CO)_3(P(n\text{-}Bu)_3)$, 96021-50-0; $(\eta^3\text{-}C_3H_4(1\text{-}t\text{-}Bu))Mn(CO)_3(PPh_3)$, 96021-51-1; $(\eta^3\text{-}C_3H_4(2\text{-}t\text{-}Bu))Mn(CO)_3(PPh_3)$, 96021-52-2; $(\eta^3\text{-}C_3H_4(2\text{-}t\text{-}Bu))Mn(CO)_3(P(n\text{-}Bu)_3)$, 96021-53-3; $(\eta^3\text{-}C_3H_3(1,1\text{-}Me_2))Mn(CO)_3(PPh_3)$, 96021-54-4; $(\eta^3\text{-}C_3H_3(1,2\text{-}Ph_2))Mn(CO)_3(PPh_3)$, 96021-55-5; $(\eta^3\text{-}C_3H_3(1,2\text{-}Ph_2))Mn(CO)_3(PMe_2Ph)$, 96021-56-6; $(\eta^3\text{-}C_3H_3(1,2\text{-}Ph_2))Mn(CO)_3(PCy_3)$, 96021-57-7; $(\eta^3\text{-}C_3H_5)Mn(CO)_2(PMe_2Ph)_2$, 96021-58-8; $(\eta^3\text{-}C_3H_5)Mn(CO)_2(P(OEt)_3)_2$, 76294-46-7; $(\eta^3\text{-}C_3H_5)Mn(CO)_4$, 33307-28-7; $KMn(CO)_5$, 15693-51-3; $KMn(CO)_4(PMe_2Ph)$, 96021-59-9; $KMn(CO)_4(PPh_3)$, 67204-49-3; 1,3-dichloropropene, 542-75-6; 2,3-dichloro-1-propene, 78-88-6; 1-chloro-2-butene, 591-97-9; 4-bromo-2-butenonitrile, 42879-03-8; 1-bromo-4,4-dimethyl-2-pentene, 62946-91-2; 3-bromo-2-*tert*-butyl-1-propene, 3854-52-2; 1-chloro-3-methyl-2-butene, 10071-60-0; 3-chloro-1,2-diphenyl-1-propene, 1794-49-6; allyl chloride, 107-05-1.

Supplementary Material Available: Supplemental kinetic data for reactions of eq 3, 5, asnd 6 (5 pages). Ordering information is given on any current masthead page.

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