Articles

Probing the Chemistry of Organomanganese Complexes. A Kinetic Study on the Demetalation of Manganacycles and Correlation of the Kinetic Parameters with Manganese-55 Chemical Shifts

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Demetalation of a series of unsaturated manganacycles was performed to ascertain the relationship between the electronic nature of the metalacycle substituents and the rate of demetalation. For aryl-substituted metalacycles, Hammett analysis of the observed rate constants for demetalation correlated with the Hammett σ^+ constant indicating that resonance, as well as inductive, effects stabilize the transition state for the demetalation. The activation parameters for demetalation of the phenyl derivative are $\Delta H^* = 11.1 \pm 0.87$ kcal mol^{-1} and $\Delta S^* = -25.6 \pm 2.9$ cal mol^{-1} K^{-1}. A correlation of the rates of demetalation of these complexes and their ^{55}Mn chemical shift is observed that suggests that there is a relationship between the factors that influence the chemical shift of the metal and the factors that control the energy of the transition state for demetalation. This relationship is discussed.

Introduction

Alkylmanganese pentacarbonyl complexes have been shown to be useful for the synthesis of a variety of carbonyl derivatives via the intermediacy of manganacycles 3 (Scheme I).[1] An integral feature of these studies was removal of the organic ligand from the metal complex. The mechanism by which this process occurs its important since it is often the final step in transition-metal-mediated organic synthesis.[1,2] The results described herein focus on the mechanism of the demetalation process of manganacycles derived from sequential insertion of methylmanganese(I) pentacarbonyl (1) and alkynes 2a-e. We report the kinetic parameters for this transformation which provide insight into the nature of the transition state for demetalation. Additionally, a correlation of the rate constants for demetalation with the manganese-55 nuclear magnetic resonance chemical shift of the manganacycles is demonstrated. The relationship between a kinetic (rate constant) and a molecular ground-state parameter (chemical shift) can be utilized to evaluate the influence of ligand substitution on the electronic characteristics of the metal center and to determine how these changes affect the chemical reactivity of the complexes.

Demetalation of unsaturated manganacycles 3 is accomplished by treatment with acid in acetonitrile at room temperature, and preliminary studies have demonstrated that substituents on the manganacycle influence the ratio of products 4 and 5 formed (see Scheme I), as well as the rate of demetalation. For manganacycles with aryl substituents on the carbon bearing manganese (3a-e), electron-donating groups on the aromatic ring favor formation of enone 4 over butenolide 5, while the opposite trend is observed when the aromatic ring is substituted with electron-withdrawing groups. An alkyl substituent on the

carbon bearing manganese leads to the exclusive formation of butenolide. A direct correlation of the enone/butenolide product ratios and metal chemical shift is not possible in a discussion of the alkyl- and aryl-substituted manganacycles since an alkyl substituent is electron-donating only in an inductive sense, while an aryl substituent has both inductive and resonance contributions (vide infra).

We had proposed in the preliminary study of this reaction that demetalation of manganacycle 3 occurred by reversible protonation of C-4 followed by partitioning of the resulting cationic carbene complex into either the enone by hydride migration or the butenolide product involving a CO insertion manifold (see Scheme II).[1f] The existence of rapid, reversible protonation step is supported by a deuterium-incorporation experiment.[1f] A detailed kinetic analysis of the demetalation reaction was undertaken because it was anticipated that the analysis would support the proposed mechanism and provide insight into the nature of the transition state for this unique demetalation process.

Results and Discussion

A series of aryl-substituted manganacycles was synthesized by reaction of 1 and the appropriate phenylacetylene derivative 2a-e.[1] Preliminary investigation of

(1) (a) DeShong, P.; Slough, G. A. *Organometallics* **1984**, *3*, 636. (b) DeShong, P.; Slough, G. A. *J. Am. Chem. Soc.* **1985**, *107*, 7788. (c) DeShong, P.; Slough, G. A.; Rheingold, A. L. *Tetrahedron Lett.* **1987**, *28*, 2229. (d) DeShong, P.; Slough, G. A.; Sidler, D. R. *Tetrahedron Lett.* **1987**, *28*, 2233. (e) DeShong, P.; Slough, G. A.; Elango, V. *Carbohydr. Res.* **1987**, *171*, 342. (f) DeShong, P.; Sidler, D. R.; Rybczynski, P. J.; Slough, G. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 2575. (g) DeShong, P.; Sidler, D. R. *J. Org. Chem.* **1988**, *53*, 4892. (h) DeShong, P.; Slough, G. A.; Sidler, D. R.; Rybczynski, P. J.; von Philipsborn, W.; Kunz, R.; Bursten, B. E.; Clayton, T. W. Jr. *Organometallics* **1989**, *8*, 1381.

(2) Collman, J. P.; Hegedus, L. A.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 433-440.

[†] Summer Undergraduate Research Participant, 1987.

Scheme I. Synthesis and Reaction of Unsaturated Manganacycles
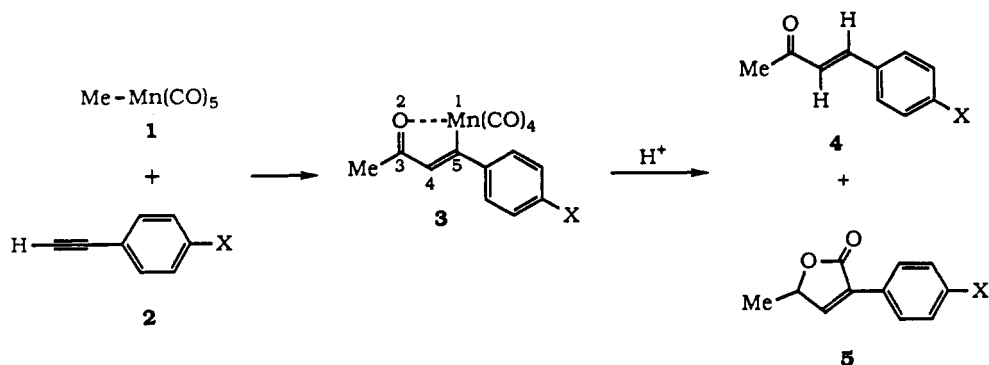
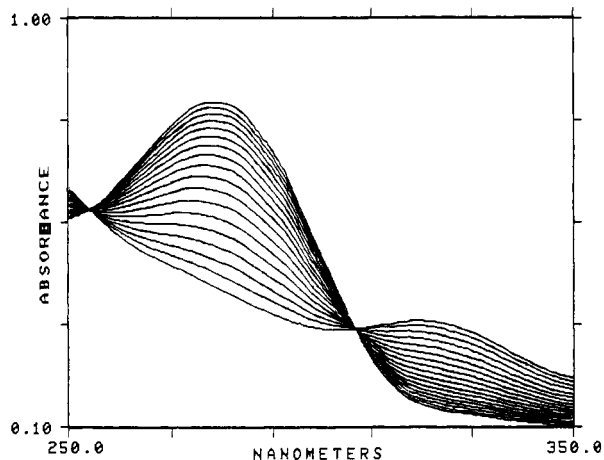
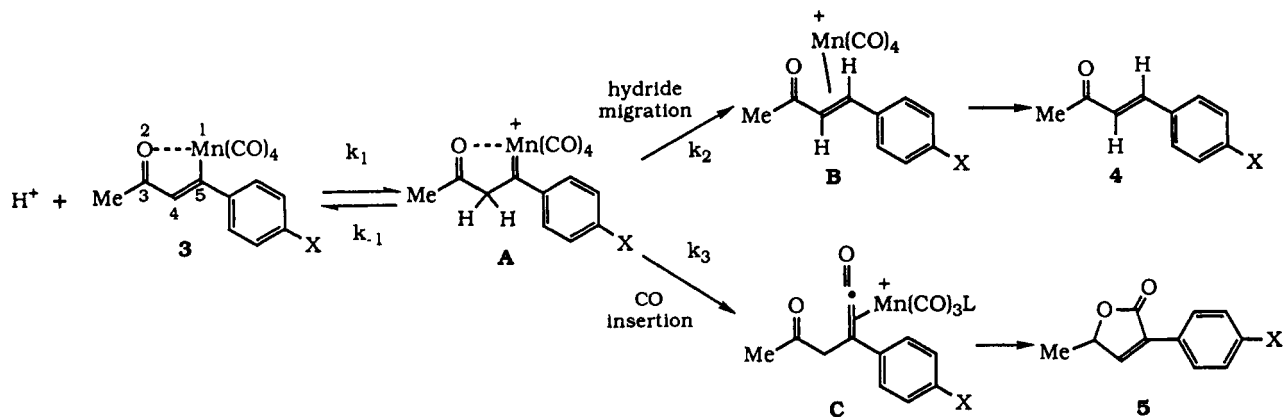**Scheme II. Demetalation of Unsaturated Manganacycles**

**Figure 1.** Ultraviolet spectra (A vs t) for the demetalation of 3c at 30.0 °C.

the rate of demetalation as a function of acid concentration demonstrated that the reaction was unimolecular in manganacycle and that changes in acid concentration had no effect on the process. Therefore, under standard demetalation conditions, the manganacycle must exist exclusively in the protonated form A, and the observed rate constant for demetalation will be dependent only on k_2 and k_3 and not on the magnitude of either of the rate constants in the preequilibrium. Subsequently, reaction rates for demetalation were determined with excess acid[3] at 30.0 °C, and the absorbances for starting material and products, respectively, were monitored through 5 half-lives by ultraviolet spectroscopy. Observed rate constants (k_{obs}) are

Table I. Observed Rate Constants at 30.0 °C

entry	reactant	k_{obs}, h^{-1}	av k_{obs} ± std dev
1	3a, X = OMe	0.515	0.502 ± 0.019
		0.509	
		0.529	
		0.486	
		0.476	
		0.500	
2	3b, X = Me	0.279	0.261 ± 0.018
		0.265	
		0.276	
		0.265	
		0.248	
		0.233	
3	3c, X = H	0.163	0.155 ± 0.006
		0.157	
		0.152	
		0.160	
		0.151	
		0.147	
4	3d, X = Cl	0.123	0.120 ± 0.003
		0.119	
		0.122	
		0.120	
		0.116	
		0.121	
5	3e, X = NO$_2$	0.034	0.033 ± 0.003
		0.036	
		0.030	
6	6	0.440	0.442 ± 0.005
		0.439	
		0.448	
7	7		

(3) The demetalation has been shown to be unimolecular, dependent upon [manganacycle].

the sum of the rate constants k_2 and k_3[4] for the pseudo-first-order process and were determined from the change
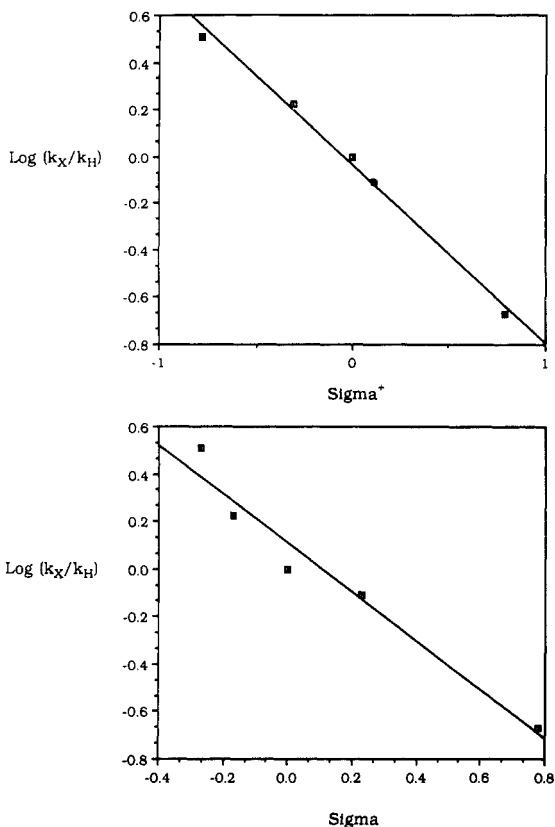
Figure 2. Hammet plots. Plots of log k_{obs} vs Hammett σ^+ and σ constants.

in absorbances for reactant and product, respectively. The ultraviolet spectra shown in Figure 1 are representative of these transformations.

The influence of aryl substituents on the Gibb's energy change of demetalation of manganacycle **3c** was evaluated by using the Hammett equation (see Table I).[5] Plots of the ln (k_{obs}/k_H) vs Hammett σ^+ and σ constants in Figure 2 demonstrate a better linear correlation of the data with Hammett σ^+ constants, indicating that the transition state is stabilized by both inductive and resonance effects. The slope of the correlation (ρ) is -0.76, which confirms the qualitative observation that electron-donating groups enhance the rate of the demetalation reaction. The magnitude of the slope indicates that the rate is not heavily dependent upon the electronic characteristics of the aryl substituent. From this analysis it was concluded that in the transition state C-5 carries minimal charge and suggests that the transition state for demetalation resembles intermediates B/C rather than A (see Scheme II).

In addition to phenylacetylene-derived manganacycles, the rates of demetalation were determined for the manganacycles **6** and **7** arising from 1 with 1-hexyne or methyl propiolate (Table I), respectively. The observed rate constant for demetalation of **6** demonstrates that the alkyl-substituted manganacycle eliminates the metal faster than all but the fastest of the phenyl-substituted com-

Table II. Observed Rate Constants for 3c at Variable Temperatures

entry	temp, °C	k_{obs}, h⁻¹	av k_{obs} ± std dev
1	40.0	0.304	0.306 ± 0.005
		0.311	
		0.302	
2	30.0	0.163	0.155 ± 0.006
		0.157	
		0.152	
		0.160	
		0.151	
		0.147	
3	21.0	0.085	0.087 ± 0.006
		0.079	
		0.081	
		0.096	
		0.088	
		0.090	
4	15.0	0.049	0.060 ± 0.011
		0.053	
		0.049	
		0.066	
		0.066	
		0.077	

plexes. Attempts to determine the demetalation rate of manganacycle **7** were unsuccessful due to decomposition of the complex during the extended times required to affect demetalation.[6] Qualitatively, these results are consistent with the observation from the aryl series that electron-donating groups enhance demetalation rates, while electron-withdrawing groups retard the rate.

The kinetic results are consistent with the mechanism for demetalation proposed in Scheme II and indicate that the aryl ring stabilizes the transition state for demetalation by resonance and inductive effects. We speculate that the transition state for demetalation has the π-system of the aryl ring aligned with the developing π-systems of the intermediates B and C.[7] Additional evidence supporting this hypothesis is presented below.

In addition to Hammett analysis, an Arrhenius analysis of the demetalation of manganacycle **3c** was performed to determine the activation parameters for the demetalation (see Table II). In the case of manganacycle **3a**, the rate constant k_3 is approximately equal to zero since negligible quantities of butenolide **5** are produced with this substrate. Accordingly, k_{obs} is proportional exclusively to k_2,[3] and the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ obtained from the Eyring equation rate are for the process leading to enone formation only.

Plots of the variable temperature data for manganacycle **3a** yield an enthalpy of activation of 11.1 ± 0.87 kcal mol⁻¹ and an entropy of activation of -25.6 ± 2.9 cal mol⁻¹ K⁻¹, which corresponds to a Gibb's energy of activation of 18.8 ± 1.9 kcal mol⁻¹ at 30.0 °C. These results are also consistent with the mechanism proposed in Scheme II. The magnitude of the entropy term demonstrates that the transition state is highly ordered as anticipated from the results of the Hammett study. For instance, the transition state for the transformation of A to B must be highly ordered since the hydride must migrate across one face of the developing π-system while the metal traverses the alternate face. An analogous situation can be imagined for the insertion of carbon monoxide into A to afford ketene complex C.

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(4) For the mechanistic proposal indicated in Scheme II having a rapid preequilibrium $(k_1, k_{-1} \gg k_2, k_3)$, the expression for the observed rate constant under pseudo-first-order reaction conditions is normally

$$k_{obs} = (k_2 + k_3)(k_1/k_{-1})[\text{H}^+]$$

However, because the manganacycle exists exclusively in the protonated form, then [manganacycle 3] ≈ [A]. In the kinetic investigations involving manganacycle **3c**, $k_3 \approx 0$ since only traces of the butenolide are produced in the demetalation reaction.

(5) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*; Plenum: New York, 1984; pp 179–190.

(6) After long periods under standard demetalation conditions, the starting material had undergone extensive decomposition but had produced a negligible amount of the expected products. Apparently the rate is so slow $(t_{1/2} > 75$ h) that competing pathways predominate.

(7) A detailed computational analysis of ground-state conformational preferences of manganacycle **3c** and potential transition state geometries is in progress in Professor Bursten's laboratories at The Ohio State University.
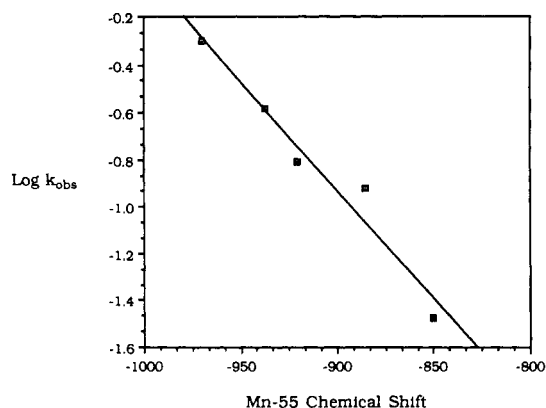
Mn-55 Chemical Shift

Figure 3. Plot of log k_{obs} vs Mn-55 chemical shift.

During the course of the kinetic investigation it was noted that the manganese-55 chemical shifts of the respective complexes correlated with the logarithm of the observed rate constants for demetalation as indicated in Figure 3. This result demonstrated that factors affecting the chemical shift of the complexes also influence the kinetic parameters (rate constant) for demetalation and that the chemical shift data can be applied as a probe of the electronic structure of the metal center in this transformation. Previous studies by Hegedus,[8a] von Philipsborn,[8b] and Mason[8c] had demonstrated that transition-metal NMR spectroscopy could be utilized to study the catalytic activity among transition-metal complexes of Cr, Co, and Mo, respectively. In addition, Hegedus has demonstrated that *relative* reactivity of chromium complexes can be correlated to the line width of the ^{53}Cr resonances. Our results are the first example in which kinetic data have been correlated with the transition-metal NMR chemical shift of manganese complexes.

The chemical shift of heavy-atom nuclei, ^{55}Mn in this instance, is dependent on several features of the complex such as symmetry of electron distribution in the complex and ligand field splitting.[1h,8c] Therefore, unlike the situation with light nuclei of spin $^1/_2$ such as ^1H and ^{13}C, a priori predictions of chemical shift in metal complexes do not follow the trends commonly observed with the spin $^1/_2$ nuclei in which an increase in electron density on the nucleus results in an increase in the shielding of the nucleus.[9] We speculate that the correlation observed between the chemical shift of manganese and the log k_{obs} is the result of an interplay of two separate factors. From an extension of the earlier study of Bursten and Clayton performed in collaboration with our laboratory, it was anticipated that an aryl substituent at C-5 influences the paramagnetic contribution to the chemical shift of the metal in both a resonance and inductive fashion.[1h] The inductive contribution is expected to dominate in this system and the chemical shift of the metal should accordingly move upfield with electron-donating substituents, as is observed. On the other hand, the kinetic results indicate that both inductive *and* resonance considerations play a significant role in the transition state for demetalation since the rates give a linear correlation with Hammett σ^+ constants. In this instance, electron-donating

substituents on the aryl group stabilize the transition state for demetalation by making the developing π-system of the transition state, which resembles B/C in Scheme II, a better donor, thereby lowering the energy of activation for demetalation. Although a definitive treatment of the chemical shift correlation with the kinetic data awaits further computational studies on this system,[7] this kinetic study has demonstrated that manganese-55 nuclear magnetic resonance spectroscopy can be employed to provide insight into the demetalation reactions of manganacycles. It is anticipated that manganese-55 NMR spectroscopy may be a valuable method of probing the mechanism of other reactions in these systems.

Experimental Section

General Experimental Procedures. Melting points were taken in Kimax soft-glass capillary tubes by using a Thomas-Hoover Uni-Melt capillary melting point apparatus (Model 6406 K) equipped with a calibrated thermometer.

Magnetic resonance (^1H and ^{13}C NMR) spectra were recorded on Varian Associates analytical NMR spectrometer (Model EM-360), a Bruker WP-200, IBM AF-200, or IBM AM-400 spectrometer. Chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane. Coupling constants (J values) are given in hertz, and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). The spin multiplicities for off-resonance decoupled (ORD) carbon NMR are indicated in the same manner. It should be noted that only poorly resolved proton NMR spectra could be obtained from some manganacycle complexes. Deuterated NMR solvents contained 99.0–99.8% deuterium in the indicated position. ^{55}Mn NMR spectra were recorded on a Varian XL-200 or IBM AM-400 spectrometer in ca. 0.2 M solutions. δ (Mn) values (± 10 ppm) are reported relative to an external reference of saturated aqueous $KMnO_4$ at δ 0.0 or an internal reference of $Mn_2(CO)_{10}$ at δ -2287.

Infrared spectra were recorded on a Perkin-Elmer Model 281 diffraction grating spectrophotometer or a Nicolet 5DXC Fourier transform infrared spectrophotometer. Band positions are given in reciprocal centimeters (cm^{-1}) and are listed as br (broad), vs (very strong), s (strong), m (medium), or w (weak).

Mass spectral data were obtained on a Kratos MS-950 double-focusing high-resolution spectrometer, a VG 7070E spectrometer, or on a Finnigan 3200 twin EI and CI quadrupole mass spectrometer equipped with a Finnigan 6000 computer. The chemical ionization gas was methane unless specified otherwise. Elemental analyses were performed by Micro-Tech laboratories, Skokie, IL.

Ultraviolet (UV) spectra were recorded on a Gilford Response spectrophotometer. Wavelengths (λ) are reported in nanometers. Solvent systems and molar extinction coefficients (ϵ) are reported for each spectrum.

Thin-layer chromatography (TLC) was performed on 0.25-mm Merck silica-coated glass plates, with the compounds being identified in one or more of the following manners: UV (254 nm, unless otherwise specified), iodine, sulfuric acid, or vanillin/sulfuric acid charring. Preparative thin-layer chromatography (PLC) was performed on 0.5- or 2.0-mm Merck silica-coated plates. Flash chromatography was performed using thick-walled glass columns and "medium-pressure" silica (Merck, 32–63 μm). Radial chromatography was performed on a chromatotron (Harrison Research Inc., Palo Alto, CA). Analytical high-performance liquid chromatography (HPLC) was performed utilizing a Milton Roy Constametric II liquid chromatograph equipped with a Spectro Monitor III variable-wavelength UV detector. Gas chromatography was performed on a Hewlett-Packard Model 5890A chromatograph equipped with a 0.20 mm × 25 m cross-linked methylsilicone capillary column and flame ionization detector. Helium was the carrier gas.

All solvents were distilled from calcium chloride before use unless noted otherwise. Tetrahydrofuran (THF), diethyl ether, and pentane were distilled from sodium/benzophenone ketyl. Acetonitrile was distilled from calcium hydride. All reagents were distilled, recrystallized, or chromatographed prior to use unless

(8) (a) Hafner, A.; Hegedus, L. S.; deWeck, G.; Hawkins, B.; Dötz, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 8413. (b) von Philipsborn, W. *Pure Appl. Chem.* **1986**, *58*, 513 and references cited therein. (c) Green, J. C.; Grieves, R. A.; Mason, J. *J. Chem. Soc., Dalton Trans.* **1986**, 1313.

(9) In a preliminary report on manganese-55 NMR spectroscopy we have demonstrated that subtle changes in the σ-donating and π-accepting characteristics of phosphines can induce either upfield (lower frequency) or downfield (higher frequency) changes in the chemical shift.[1h]

otherwise noted. Glassware used in the reactions described below was dried in an oven at 120 °C and assembled under an inert atmosphere of nitrogen or argon. Manganese carbonyl was obtained from Strem Chemical Co. (catalog no. 25-1330) and was sublimed prior to use. All reactions using sodium (pentacarbonyl)manganate(I) were performed in airless Schlenk glassware under an atmosphere of argon.

The high-pressure apparatus consisted of a hydraulically pressurized autoclave containing castor oil. Pressures were determined directly from a gauge attached to the autoclave. High-pressure reactions were conducted in disposable plastic tuberculin syringes sealed with a luer lock cap. Details of the reaction apparatus have been previously described.[1]

General Procedure for the Reaction of Methylmanganese Pentacarbonyl with Alkynes. A solution of methylmanganese pentacarbonyl (0.7–1.0 mmol) and alkyne (1.05–1.2 equiv) in Et_2O (20 mL) was stirred in the dark at atmospheric pressure under N_2 for the specified time. The solution was concentrated in vacuo and purified by flash chromatography to afford the adduct.

Reaction of Methylmanganese Pentacarbonyl and 4-(Methoxyphenyl)acetylene. (*OC*-6-23)-Tetracarbonyl[1-(4-methoxyphenyl)-3-oxo-1-butenyl-*C*^{1}*O*^{3}]manganese (3a). The solution was stirred for 24 h, and the adduct (36 mg, 55%) was isolated as a yellow/orange solid. Recrystallization from pentane afforded a yellow/orange powder: mp 85–87 °C; R_f = 0.36, 8:1 hexanes/EtOAc; IR (CCl_4) 3000 (w), 2028 (m), 1997 (vs), 1948 (vs); ^{1}H NMR ($CDCl_3$) δ 7.32 (d, J = 14.0, 2 H), 6.88 (s, 1 H), 6.82 (d, J = 14.0, 2 H), 3.71 (s, 3 H), 2.25 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 213.5, 161.0, 141.8, 134.0, 130.0, 113.8, 55.4, 26.3; ^{55}Mn NMR (C_6D_6, 298 K) δ –970 ($W_{1/2}$ = 32.5 kHz); mass spectrum, m/z (rel intensity, percent) 342 (M^+, 6), 286 (4), 258 (11), 230 (100); mass spectrum, m/z 341.9942 (calcd for $C_{15}H_{11}O_6Mn$ 341.9936); UV (CH_3CN) λ_{max} 345 (ϵ 1.69 × 10^4).

Reaction of Methylmanganese Pentacarbonyl and 4-(Methylphenyl)acetylene. (*OC*-6-23)-Tetracarbonyl[1-(4-methylphenyl)-3-oxo-1-butenyl-*C*^{1}*O*^{3}]manganese (3b). The solution was stirred for 48 h, and the adduct (304 mg, 76%) was isolated as a yellow/orange solid. Recrystallization from hexane/EtOAc afforded a yellow/orange powder: mp 79–80 °C; R_f = 0.51, 10:1 hexanes/EtOAc; IR (CCl_4) 2080 (s), 1995 (vs), 1950 (s); ^{1}H NMR ($CDCl_3$) δ 7.33 (d, J = 8.0, 2 H), 7.23 (d, J = 8.0, 2 H), 7.00 (s, 1 H), 2.40 (s, 3 H), 2.36 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 213.9, 139.2, 134.8, 129.1, 125.6, 26.2, 21.2; ^{55}Mn NMR (C_6D_6, 298 K) –937 ($W_{1/2}$ = 25.0 kHz); mass spectrum, m/z (rel intensity, percent) 326 (M^+, 2), 270 (54), 242 (14), 214 (M^+ – 4 CO, 100), 151 (26), 115 (10), 55 (41); mass spectrum, m/z 214.0189 (M^+ – 4 CO; calcd. for $C_{11}H_{11}OMn$: 214.0190); UV (CH_3CN) λ_{max} 331 (ϵ 1.11 × 10^4).

Reaction of Methylmanganese Pentacarbonyl and Phenylacetylene. (*OC*-6-23)-Tetracarbonyl[3-oxo-1-phenyl-1-butenyl-*C*^{1}*O*^{3}]manganese (3c). The solution was stirred for 48 h, and the adduct (305 mg, 63%) was isolated as an orange solid. Recrystallization from pentane at –78 °C afforded a yellow/orange solid: mp 62–64 °C; R_f = 0.52, 4:1 hexanes/EtOAc; IR (CCl_4) 3060 (w), 2083 (s), 1996 (vs), 1951 (vs), 1575 (m); ^{1}H NMR ($CDCl_3$) δ 7.40 (s, 5 H), 7.00 (s, 1 H), 2.38 (s, 3 H); ^{13}C NMR (C_6D_6) δ 250.4, 219.6, 214.5, 211.3, 149.8, 136.4, 134.8, 129.7, 127.5, 126.4, 26.4; ^{55}Mn NMR (C_6D_6, 298 K) δ –920 ($W_{1/2}$ = 21.5 kHz); mass spectrum, m/z (rel intensity, percent) 312 (M^+, 5), 256 (8), 228 (18), 200 (100); mass spectrum, m/z 311.9835 (M^+, calcd for $C_{14}H_9O_5Mn$ 312.1500), 200.0024 (M^+ – 4 CO, calcd for $C_{10}H_9OMn$ 200.1100); UV (CH_3CN) λ_{max} 326 (ϵ 1.25 × 10^4).

Reaction of Methylmanganese Pentacarbonyl and 4-(Chlorophenyl)acetylene. (*OC*-6-23)-Tetracarbonyl[1-(4-chlorophenyl)-3-oxo-1-butenyl-*C*^{1}*O*^{3}]manganese (3d). The solution was stirred for 24 h, and the adduct (195 mg, 89%) was isolated as a yellow solid. Recrystallization from pentane afforded a yellow powder: mp 98–100 °C; R_f = 0.57, 4:1 hexanes/EtOAc; IR (CCl_4) 3000 (w), 2085 (s), 2003 (vs), 1952 (vs), 1461 (s); ^{1}H NMR ($CDCl_3$) δ 7.34 (m, 4 H), 6.98 (s, 1 H), 2.38 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 255.1, 214.5, 210.0, 147.9, 135.5, 134.6, 128.6, 126.5, 26.5; ^{55}Mn NMR (C_6D_6, 298 K) δ –885 ($W_{1/2}$ = 25.0 kHz); mass spectrum, m/z (rel intensity, percent) 348 (M^+ + 2, 3), 346 (M^+, 9), 292 (6), 290 (16), 264 (11), 262 (33), 236 (88), 234 (M^+ – 4 CO, 100), 101 (24), 75 (36), 70 (91); mass spectrum, m/z 347.9806 (M^+ + 2, calcd for $C_{14}H_8O_5ClMn$ 347.9806), 345.9441 (M^+, calcd for

$C_{14}H_8O_5MnCl$ 345.9444); UV (CH_3CN) λ_{max} 322 (ϵ 1.03 × 10^4).

Reaction of Methylmanganese Pentacarbonyl and 4-(Nitrophenyl)acetylene. (*OC*-6-23)-Tetracarbonyl[1-(4-nitrophenyl)-3-oxo-1-butenyl-*C*^{1}*O*^{3}]manganese (3e). The solution was stirred for 7 days, and the adduct (188 mg, 85%) was isolated as an orange powder. Recrystallization from pentane at 0 °C afforded the adduct as orange needles: mp 126–127 °C (dec); R_f = 0.38, 4:1 hexanes/EtOAc; IR (CCl_4) 2087 (m), 1999 (s), 1956 (s); ^{1}H NMR ($CDCl_3$) δ 8.27 (d, J = 8.0, 2 H), 7.40 (d, J = 8.0, 2 H), 7.01 (s, 1 H), 2.43 (s, 3 H); ^{13}C NMR (C_6D_6) δ 245.8, 219.0, 215.5, 213.7, 210.4, 155.8, 147.7, 136.6, 124.9, 123.9, 26.0; ^{55}Mn NMR (C_6D_6, 298 K) δ –850 ($W_{1/2}$ = 26.0 kHz); mass spectrum, m/z (rel intensity, percent) 357 (M^+, 6), 301 (6), 273 (22), 245 (M^+ – 4CO, 100); mass spectrum, m/z 244.9884 (M^+ – 4 CO, calcd for $C_{10}H_8NO_3Mn$ 244.9885); UV (CH_3CN) λ_{max} 325 (ϵ 1.35 × 10^4).

Reaction of Methylmanganese Pentacarbonyl and 1-Hexyne. (*OC*-6-23)-Tetracarbonyl[1-methyl-1-oxo-2-heptenyl-*C*^{3}*O*^{1}]manganese (6). The solution was stirred for 41 h and the adduct (80 mg, 23%) was isolated as a bright yellow oil: R_f = 0.56, 10:3 hexanes/CH_2Cl_2; IR (CCl_4) 2900 (w), 2040 (m), 1990 (s); ^{1}H NMR (C_6D_6) δ 6.54 (s, 1 H), 3.06 (m, 2 H), 1.63 (m, 5 H), 1.30 (m, 2 H), 0.90 (m, 3 H); ^{13}C NMR (C_6D_6) δ 134.9, 132.0, 47.9, 31.5, 25.5, 22.9, 14.0; ^{55}Mn NMR (C_6D_6, 298 K) δ –1010 ($W_{1/2}$ = 20.5 kHz); mass spectrum, m/z (rel intensity, percent) 177 (9), 153 (85), 124 (61), 111 (47), 97 (49), 80 (84), 67 (41), 55 (100); mass spectrum, m/z 292.015 (calcd for $C_{12}H_{13}O_5Mn$ 292.014).

General Procedure for the High-Pressure Preparation of Alkyne Adducts. A solution of alkymanganese pentacarbonyl complex (ca. 0.7–0.8 mmol) and alkyne (1.05–1.2 equiv) in solvent (1.0 mL) was pressurized as indicated. The reaction mixture was depressurized, the reaction vessel was rinsed with EtOAc, and the combined organics were concentrated in vacuo. Adducts were purified by flash chromatography.

Reaction of Methylmanganese Pentacarbonyl and Methyl Propiolate (7). A solution of methylmanganese pentacarbonyl and 296 propiolate in Et_2O was pressurized to 5 kbar or kept at atmospheric pressure for 72 h, and the adduct (400 mg, 93%) was isolated as a yellow oil: R_f = 0.45 in 4:1 hexane/EtOAc; IR (CCl_4) 3000 (w), 2950 (w), 2090 (m), 2000 (vs), 1960 (vs), 1720 (m), 1325 (m), 1200 (m); ^{1}H NMR ($CDCl_3$) δ 7.15 (s, 1 H), 3.86 (s, 3 H), 2.38 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 231.5 (s), 218.6 (s), 216.7 (s), 213.1 (s), 208.4 (s), 175.2 (s), 136.4 (d), 51.8 (q), 27.2 (q), quaternary carbon not observed; ^{55}Mn NMR (C_6D_6, 296 K) δ –821 ($W_{1/2}$ = 18.0 kHz); mass spectrum, m/z (rel intensity, percent 294 (M^+, 2), 238 (3), 210 (3), 182 (M^+ – 4 CO, 13), 152 (23), 124 (84), 110 (11), 86 (24), 80 (100), 55 (99); mass spectrum, m/z 293.9563 (M^+, calcd for $C_{10}H_7O_7Mn$ 293.9572).

General Method for the Demetalation of Unsaturated Manganacycles under Acidic Conditions: Determination of Rate Constants and Half-Lives. Rate constant (k) and half-life ($t_{1/2}$) data for the demetalation of unsaturated manganacycles were determined by triplicate runs of the following procedure and were reported as average values.

An aliquot (1.00 mL) of a solution of manganacycle (1.0–1.5 mg) in CH_3CN (10.00 mL) was diluted to 10.00 mL with CH_3CN. A portion of this solution (3.00 mL) was placed in a quartz UV cuvette. A solution of anhydrous HCl in CH_3CN (100.0 μL, 3.7% w/w) was added to the manganacycle and reference (3.00 mL of CH_3CN) cells.

Both the disappearance of manganacycle and the appearance of product were monitored by UV absorbance. Absorbance values (A) were recorded until dA/dt approached 0 (through at least 5 half-lives).

Reaction rates for demetalation were determined by using 100-fold excess acid at the indicated constant temperature. The data were fit to the following equations for reactant and product, respectively:

$$A_t = A_0(1 - \exp(-k_{obs}t)) + C$$

$$A_t = A_0 \exp(-k_{obs}t) + C$$

In these equations A_t and A_0 are absorbance at time (t) and time zero, respectively, k_{obs} is the observed rate constant, and C is a constant related to the total change in the absorbance. Data fits were made by using Systat.

Supplementary Material Available: Plots of exponential decay/growth of ultraviolet absorbances for manganacycles **3a–e** (4 pages). Ordering information is available on any current masthead.

Silica-Bound Sulfonic Acid Catalysts

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The catalytic activity of colloidal silica sulfonic acid for the hydrolyses of diazinon [diethyl 2-isopropyl-6-methyl-4-pyrimidinyl phosphorothioate] and triphenylmethyl fluoride was compared with that of silica gel sulfonic acids, gel and macroporous poly(styrenesulfonic acids), powdered and soluble Nafion, *p*-toluenesulfonic acid, and hydrochloric acid. For diazinon hydrolysis, the colloidal catalyst was only slightly less active than the soluble strong acid catalysts and 2.8 times more active than any of the other heterogeneous catalysts. The silica gel and polymeric sulfonic acid catalysts had similar activities. For triphenylmethyl fluoride hydrolysis all of the catalysts were only weakly active.

Introduction

Heterogeneous strong acid catalysts such as poly(styrenesulfonic acid) ion-exchange beads[1-3] and Nafion[4-7] can be separated easily from reaction mixtures and used under flow conditions, and they often give purer products and fewer side reactions than homogeneous acids. Aliphatic[8] and aromatic[9-12] sulfonic acids bound to silica gel have also been used as ion exchangers, but little is known about their use as acid catalysts.

Many heterogeneous catalysts are less active for fast reactions than the corresponding homogeneous catalysts because the reaction rates are limited by the transport of reactant to the active sites on the particle surface. The rate of a reaction that is limited only by mass transfer is directly proportional to the particle surface area.[13] One approach to high surface area heterogeneous catalysts is to use porous supports such as silica and macroporous polymers. Another approach is to use colloidal sized particles as the catalyst support. Since surface area is

Scheme I

Scheme II

inversely proportional to particle size, by decreasing the particle size, the mass transfer limitations can be reduced and the catalyst should become more active. High activity of colloidal catalysts has been found with phase-transfer catalysts,[14] polystyrene latexes containing only surface sulfonic acid groups,[15] colloidal palladium,[16] colloids modeled after enzymes,[17-19] and transition-metal oxidation

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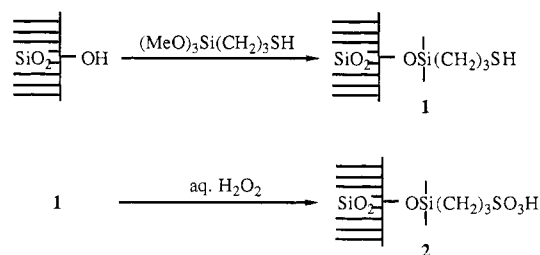
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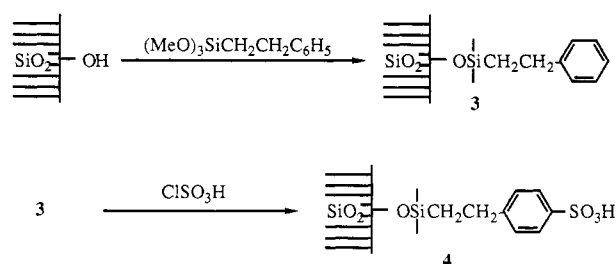(11) Unger, K.; Nyamah, D. *Chromatographia* **1974**, *7*, 63–68.

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