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Probing the Chemistry of Organomanganese Complexes. A Kinetic Study of the Role of Coordinate Bonds in a Demetalation Reaction.

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Abstract The kinetics of demetalation of a series of aryl-substituted manganacycles was measured to ascertain the relationship between the electronic nature of the manganacycle substitutents and the strength of the coordinate bond between the carbonyl oxygen and the metal center. Hammett and Arrhenius analyses were performed on these complexes and the activation parameters for demetalation were determined. These analyses were consistent with a mechanism (Scheme 4) in which the coordinate manganese-oxygen bond is highly broken in the transition state for demetalation. Correlation of the kinetic data with the Mn-55 chemical shifts of the manganacycles was not possible in this system.

Introduction

In recent years it has been demonstrated that alkylmanganese pentacarbonyl complexes (**1**) are useful for the synthesis of a variety of carbonyl derivatives as indicated in Scheme 1.[1] For example, photodemetalation of manganacycle **2** prepared from the reaction of complex **1** and methyl acrylate can afford either keto-ester **3** or enone **4** in high yield depending upon the reaction conditions. Similarly, enone **6** is the product of acid-catalyzed demetalation of unsaturated manganacycle **5**; while butenolide **7** is produced by treatment of manganacycle **5** with a reducing agent.

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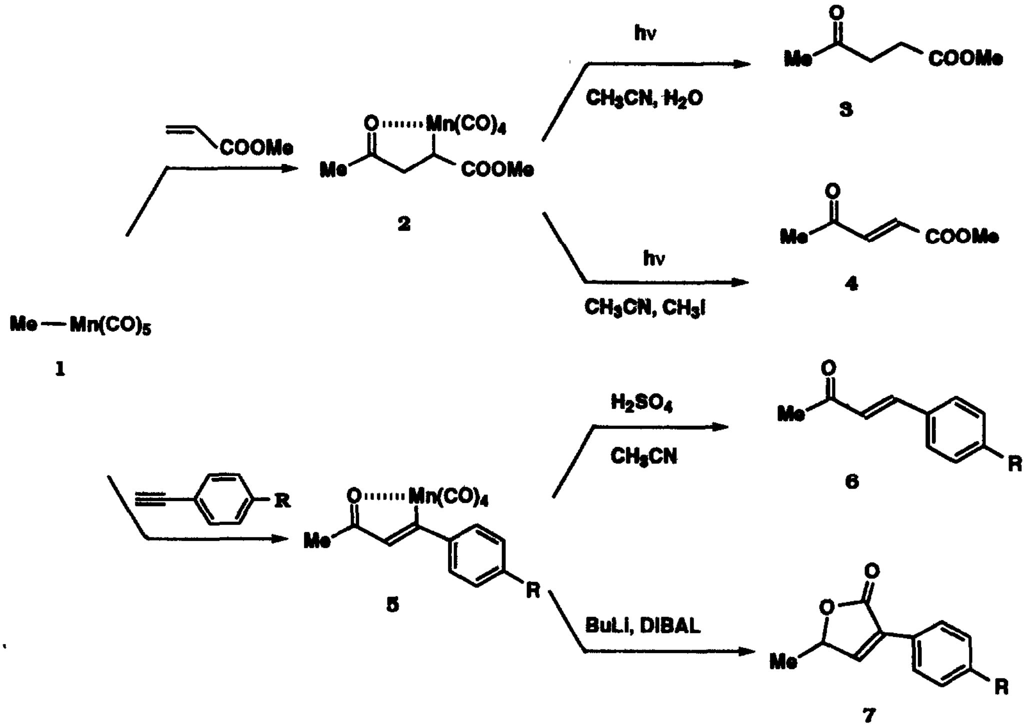
Scheme 1

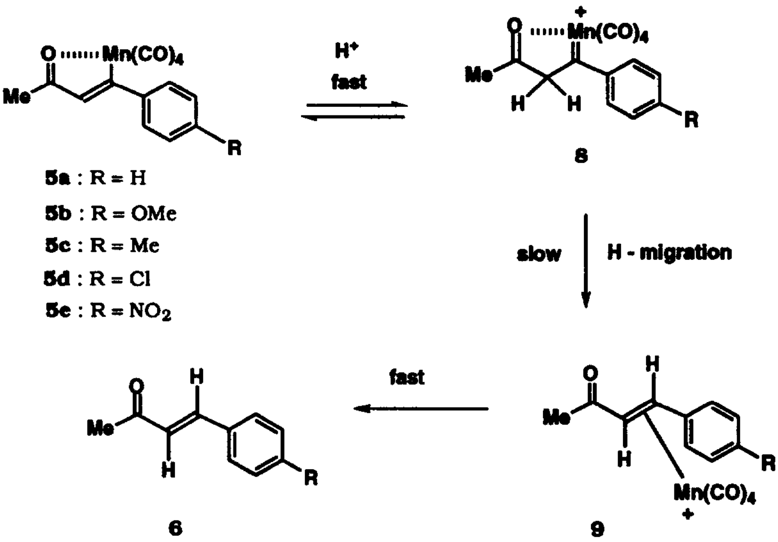


In addition to evaluating the scope and limitations of this methodology with regard to synthetic applications, the mechanism of these novel demetalation processes has been investigated extensively with the expectation that this information would be applicable to extending the demetalation methodology to new carbon-carbon bond forming processes. Recently, we have reported that the photodemetalation reaction leading to formation of derivatives **3** and **4** proceeds *via* the intermediacy of a paramagnetic manganese species.[2]

From an earlier investigation, we proposed that the acid-catalyzed demetalation of unsaturated manganacycle **5** occurs by the mechanism indicated in Scheme 2.[3] This mechanistic proposal was supported by three pieces of evidence. First, an Arrhenius analysis of the demetalation reaction demonstrated that the activation parameters were $\Delta H^{\neq} = 11.1 \pm 0.87$ kcal/mole and $\Delta S^{\neq} = -25.6 \pm 2.9$ cal/mole-K for complex **5a**. Secondly, the Hammett analysis of the demetalation of complexes **2a**-**2e** (see Scheme 2) correlated with σ^+ constants and gave a ρ value of -0.76.

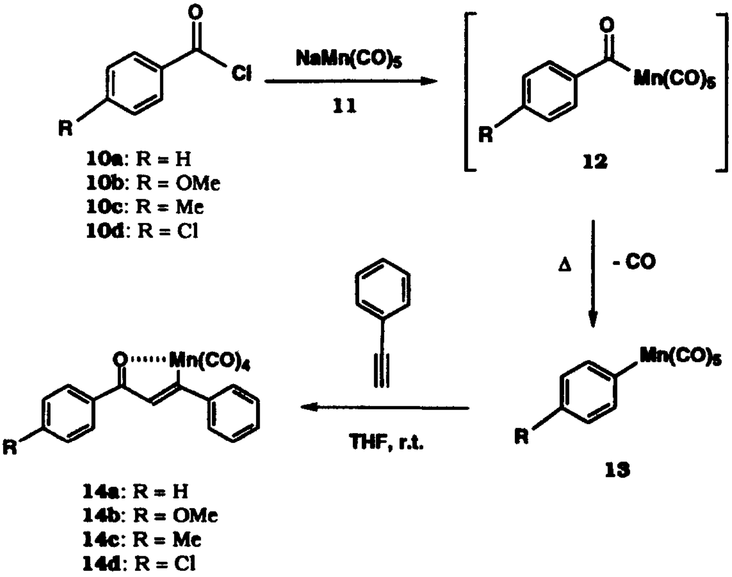
The last piece of evidence supporting the mechanistic hypothesis was the correlation of the rate constant ($\log k_{obs}$) with the Mn-55 chemical shift of the respective manganacycles **2a**-**2e**. We attributed this correlation to the ability of the substituent on the aromatic ring to affect the paramagnetic contribution of the Mn-55 nucleus.[1h,3] This result was particularly exciting because it was the first time that a correlation between a kinetic parameter and the chemical shift of Mn-55 had been observed.[3]

Scheme 2



In the proposed mechanism for the demetalation of manganacycle **5** shown in Scheme 2, the rate-determining step is conversion of cationic complex **8** to π-complex **9** which occurs with rupture of two bonds: the carbon–manganese bond and the manganese-oxygen coordinate bond. The studies summarized above had demonstrated that breaking of the carbon-manganese bond was a key feature in the rate determining step as evidenced by the ρ-value of -0.76 in the Hammett analysis.[1h] However, the fate of the coordinate metal-oxygen bond cleavage in the rate determining step could not be assessed from the

Scheme 3



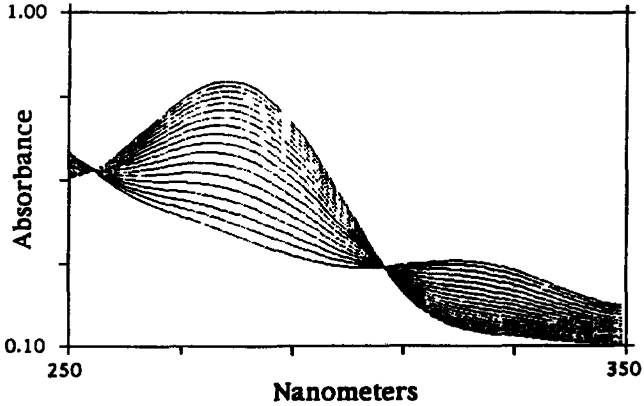
existing data. Accordingly, the kinetic study of the demetalation of manganacycles **14** (Scheme 3) described in this paper was undertaken to ascertain the extent of manganese-oxygen bond cleavage that occurs in the transition state. Also, having demonstrated that Mn-55 chemical shifts could be correlated with the kinetic constants for the earlier demetalation process,[1h] it was anticipated that this technique could be extended as a mechanistic probe to these related systems.

Results and Discussion

Manganacycles **14a-d** were prepared by sequential insertion of the respective phenylmanganese pentacarbonyl derivative (**13**) with phenylacetylene by standard procedures.[1f] In turn, the aryl complexes were prepared from the coupling of the corresponding benzoyl chloride derivative **10** and sodium manganate (**11**)[4] to afford benzoyl complex **12** which underwent spontaneous deinsertion of carbon monoxide.[5,9]

The kinetics of the demetalation of manganacycles **14a-d** were measured spectrophotometrically and a representative ultraviolet spectrum is provided in Figure 1. The change in absorbance of the starting materials (*ca.* 350 nm) and products (*ca.* 310 nm) was measured through five (5) half-lives and the observed rate constants were determined as described previously.[3] Rate constants for the pseudo-first order process[6] are summarized in Table 1.

Figure 1. Ultraviolet Spectrum for Demetalation of Manganacycle **14a** at 30.0 C.



The presence of isosbestic points in the spectrum (Figure 1) indicate that the transformation is a state-to-state process in which there were no kinetically significant intermediates. The influence of the *para*-substituent on the rate of reaction indicated that electron-donating groups increase the rate of the demetalation reaction, and that electron-withdrawing groups decrease the rate of demetalation (Table 1). However, the influence of the *para*-substituent on the kinetics of demetalation is slight.

A Hammett analysis of the kinetic results was performed also. Plots of log (k_{obs}/k_H) *vs.* σ and σ^+ (Figures 2 and 3, respectively) show a better correlation with the Hammett σ^+ constants indicating that *resonance and inductive* effects contribute to stabilization of the charge in the transition state proceeding from complex **8** to π-complex **9**. The small magnitude of ρ for this demetalation (0.21), however, suggests that the manganese-oxygen coordinate bond is extensively broken in the transition state because the *para*-substituents' effects are slight, even for strongly electron-donating groups such a methoxy.

Table 1. Observed Rate Constants for Demetalation of Manganacycles **14** at 25.0 °C.

Entry	Reactant	k_{obs}, h^{-1}	k_{obs}	$t_{1/2}$, h^{-1}
1	**14a**, X=Cl	0.487 0.356 0.522 0.454 0.473	0.458 ± 0.005	1.513
2	**14b**, X=H	0.451 0.523 0.432 0.496 0.556	0.491 ± 0.008	1.412
3	**14c**, X=Me	0.511 0.595 0.564 0.559 0.633	0.575 ± 0.024	1.205
4	**14d**, X=MeO	0.702 0.688 0.725 0.728 0.712	0.711 ± 0.043	0.975

Figure 2. Hammett Plot of log (k_{obs}/k_H) *vs.* Hammett σ Constants.

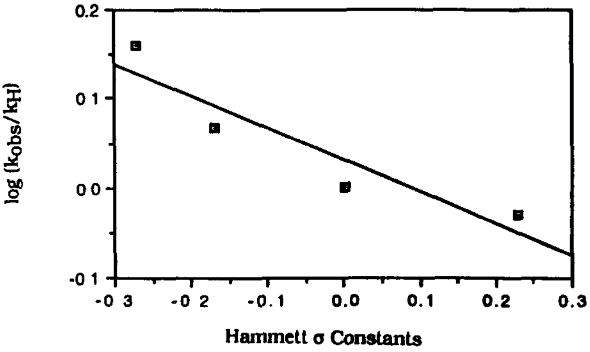
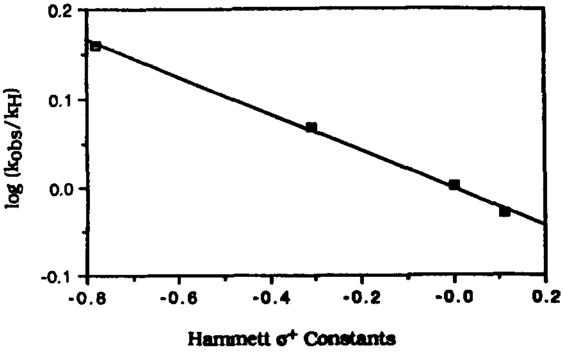


Figure 3. Hammett Plot of log (k_{obs}/k_H) *vs.* Hammett σ⁺ Constants.



Further insight into the mechanism of demetalation was obtained from an Arrhenius analysis to determine the activation parameters for the process. Demetalation of manganacycle **14a** was performed at five temperatures (Table 2), and the activation parameters were calculated using the Eyring equation.[7] Analysis of the variable temperature data yielded an enthalpy of activation of 10.9 ± 1.1 kcal/mol, an entropy of activation of -23.4 ± 1.2 cal/mol, and a Gibb's energy of activation of 17.9 ± 1.4 kcal/mol. Rybczynski reported that demetalation of a similar system, manganacycle **5** (R=H, Scheme 1), displayed an enthalpy of activation 11.1 ± 0.9 kcal/mol, entropy of activation -25.6 ± 2.9 cal/mol-K, and a Gibb's energy of activation of 18.8 ± 1.9 kcal/mol.[3] The activation parameters for the two demetalation reactions of manganacycles **5a** and **14a** are identical within the error limits of the experiments and suggest that the demetalation in both systems proceeds by an analogous mechanism.

Table 2. Rate Constants for Demetalation of Manganacycle **14a**.

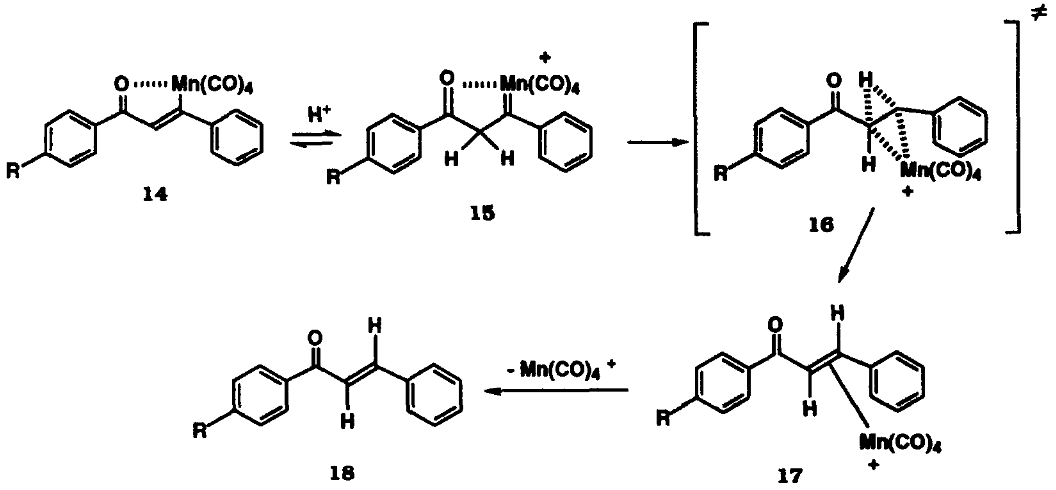
Entry	T (± 0.1 °C)	k_{obs}, h^{-1}	av k_{obs}	$t_{1/2}$, h^{-1}
1	10.0	0.210	0.203 ± 0.002	3.415
		0.202		
		0.215		
		0.210		
		0.182		
2	25.0	0.451	0.491 ± 0.008	1.412
		0.523		
		0.432		
		0.496		
		0.556		
3	30.0	0.608	0.671 ± 0.008	1.033
		0.733		
		0.990		
		0.507		
		0.518		
4	35.0	1.093	0.945 ± 0.026	0.733
		0.891		
		0.796		
		1.012		
		0.930		
5	45.0	1.998	1.998 ± 0.048	0.347
		2.066		
		2.130		
		1.950		
		1.863		

The large negative value of the entropy of activation observed in the demetalation of manganacycle **14a** indicates the presence of a highly ordered transition state during the rate-determining step. This result is consistent with the mechanism proposed in Scheme 4 in which transition state **16** involves simultaneous 1,2-migration of hydride and cleavage of the carbon-manganese bond.

The kinetic results are also consistent with direct protonation of the carbon-manganese bond with concomitant liberation of the metal. This mechanistic hypothesis can be discounted, however, since deuterium labelling experiments indicate that there is a fast, equilibrium protonation process occurring consistent with the mechanism indicated in Scheme 4.[3]

The Hammett analysis discussed above indicated that the coordinate bond of cationic complex **15** was extensively broken in the transition state (*vide supra*). One potential reason for the high degree of order observed in the transition state should be that the π-systems of the two aryl rings align with the developing carbon-carbon π-bond of intermediate **17**.

Scheme 4



Previous studies of demetalation processes in manganacycles had demonstrated that the kinetic data could be correlated with the chemical shifts of the Mn-55 nucleus of complexes such as **14**.[3] These results indicated that factors affecting the chemical shift of the complexes also influence the kinetic parameters for demetalation. This correlation furnished insight concerning the electronic structure of the metal center in this transformation. Accordingly, extension of the Mn-55 NMR technique to this study was undertaken. The results are summarized in Table 3. The Mn-55 chemical shift of the *p*-methoxy manganacycle **14b** could not be measured due to extreme broadening (>40 KHz) of the signal. In this series of complexes, the Mn-55 chemical shifts are virtually identical within experimental error and do not correlate with the experimental log (k_{obs}/k_H) values.

Table 3. Mn-55 Chemical Shifts of Manganacycles **14**.

Manganacycle	δ Mn-55
14a (R = H)	-925 (± 20 ppm)
14b (R = OMe)	a
14c (R = Me)	-880 (± 20 ppm)
14d (R = Cl)	-900 (± 20 ppm)

a: The signal was too broad to be measured, >40 KHz.

Previous studies by Hegedus,[8a] von Philipsborn,[8b,c] and Mason[8d] had shown that transition metal NMR spectroscopy could be employed to study the reactivity of metal complexes of Cr, Co, Rh, and Mo, respectively. Also, Hegedus had demonstrated that the *relative* reactivity of various Cr-complexes correlated to the line width of Cr-53 resonances.

The lack of correlation with the rate data and chemical shifts of the metal nucleus as was determined in the earlier demetalation study was particularly discouraging. However, upon reflection, it is a result that should have been anticipated. In the previous study of demetalation reactions, we were able to demonstrate that the substituent effects on the kinetics of demetalation were significant (ρ -0.79) while in this case the ρ-value was less pronounced (-0.21). As was described above, cleavage of the coordinate bond between the carbonyl oxygen and the metal is not an important feature in the transition state of this demetalation process. Accordingly, when comparing the Mn-55 chemical shifts in the manganacycles series **5** and **14**, it appears that the substituent effects are of the same magnitude; however, they cannot be determined accurately because of the extreme line widths of the Mn-55 signals.

The conclusion that is drawn from this portion of the study is that the chemical shift of the metal can only be exploited to provide insight into the demetalation process when the bonds being cleaved in the rate-determining step are bonds involving the metal. Further studies in support of this hypothesis are underway and will be reported in due course.

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Experimental Section

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

Magnetic resonance (^1H and ^{13}C) spectra were recorded on either a Bruker WP-200 or AM 400 spectrometer. Chemical shifts are reported in parts per million downfield from tetramethylsilane. Spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Deuterated NMR solvents contained 99-99.8% deuterium in the indicated position. Mn-55 chemical shifts were measured in benzene-d_6 on an IBM AM-400 and AMX-600 spetrometers in *ca.* 0.2M solutions at 300 K. δ(Mn) values (± 20 ppm) were determined relative to an internal refernce of $Mn_2(CO)_{10}$ at δ -2287 and are reported relative to $KMnO_4$ (δ 0).

Infrared spectra were recorded on a Nicolet 5DXC Fourier transform infrared spectrometer. Band positions are given in reciprocal centimeters (cm^{-1}) and are listed as vs (very strong), s (strong), m (medium), w (weak), and sh (shoulder).

All reactions were performed in oven dried glassware (110 °C) using freshly distilled solvents and reagents. All reactions were performed in airless Schlenk glassware under an inert atmosphere of nitrogen unless otherwise indicated.

General Procedure for the Preparation of *p*-R-Phenylmanganese Pentacarbonyl Complexes. Complexes **13a-d** were prepared according to the method of Beck et al.[9]

Na/Hg amalgam (1%) was prepared in a 50 mL Schlenk flask by adding Na (0.16 g, 6.96 mmol) in small (~20 mg) portions with stirring to Hg (1.4 mL, 0.093 mmol) in 5 mL THF. After allowing the reaction to cool (~15 minutes), $Mn_2(CO)_{10}$ (1.0 g, 2.5 mmol) was added along with 15 mL THF to give an dark green solution. The reaction mixture was stirred under nitrogen for *ca.* 1 h, yielding a solution of sodium pentacarbonylmanganate (**11**). This solution was added via cannula (leaving the Hg behind) to ~4.5 mmol of the appropriate para-substituted benzoyl chloride derivative. The reaction mixture was allowed to stir under nitrogen in the dark for the recorded time. The reaction mixture was then opened to air and filtered through celite. Concentration *in vacuo* yielded crude products which were purified by flash column chromatography on silica gel unless noted otherwise. All products were >95% pure by tlc, HPLC, and/or ^{13}C NMR analysis unless noted otherwise.

Phenylmanganese pentacarbonyl (**13a**, R=H): Reaction mixture was stirred for 24 h. The product (yellow crystals) was purified by column chromatography (6" 25 mm silica gel flash column) with hexane to yield white-yellow crystals. Recrystalization from pentane gave 731 mg (53%) of complex **13a** (R=H) as white crystals: m.p. 51-52 °C[5,9]; Rf = 0.30 in hexane; IR (CCl_4) 2115 (m), 2019 (vs), 1997 (s) cm^{-1}.

p-Methoxyphenylmanganese pentacarbonyl (**13b**, R=OMe): Reaction mixture was stirred for 18 h. The product (yellow-brown oil) decomposed during chromatorgraphy on silica gel (hexane:EtOAc 9:1); accordingly, the crude product was utilized in manganacycle formation without purification: IR (CCl_4) 2083(w), 2045 (s), 2013(w), 1997 (s), 1941 (m).

p-Methylphenylmanganese pentacarbonyl (**13c**, R=Me): Reaction mixture was stirred for 18 h. The product (yellow-brown oil) decomposed on during chromatography on silica gel (hexane:EtOAc 9:1); accordingly, the crude product was utilized in manganacycle formation without purification: IR (CCl_4) 2055 (w), 2046 (w), 2013 (m), 1981 (w).

p-Chlorophenylmanganese pentacarbonyl (**13d**, R=Cl): Reaction mixture was stirred for 18 h. After filtration and concentration, the product (yellow crystals) was purified by column chromatography (6" 25mm hexane) to yield white-yellow crystals. Recrystalization from pentane gave 887 mg (53%) of white crystals of chloro-complex **13d** (R=Cl) : m.p. 69-70 °C; Rf = 0.29 in hexane; IR (CCl_4) 2116 (m), 2022 (vs), 2001 (s); ^1H NMR (C_6D_6) 7.2-7.0 (m).

General Procedure for Preparation of *Para*-Substituted Manganacycles 14.

Complexes **14a-d** were prepared according to the methods developed previously in this laboratory.[1]

A solution of *para*-substituted phenylmanganese pentacarbonyl (**13**) (~0.367 mmol) and phenylacetylene (1.0-1.4 equiv.) in Et_2O (20 mL) was stirred in the dark under nitrogen for the indicated time. The solution was purified by flash column chromatography on silica to afford the adduct in a purity of >95% as judged by tlc, HPLC, and/or ^{13}C NMR analysis.

Manganacycle **14a**: The solution was stirred at room temperature for 72 h, and the adduct was isolated as an orange semisolid (94 mg, 68%). Rf = 0.18 hexane; IR (CCl_4) 2082.6 (m), 1998.3 (vs), 1950.4 (s); ^1H NMR (C_6D_6) 7.1 (m, 6H), 7.46 (s, 1H), 7.47 (dd, 2H, J=1.2, 6.8), 7.68 (dd, 2H, J= 1.4, 8.3); ^{13}C NMR ($CDCl_3$) 178.0, 137.0, 135.7, 134.1, 133.1, 130.8, 129.6, 129-128 (m), 126.9, 123.3, 120.2; ^{55}Mn NMR (C_6D_6) -925 ± 20.

Manganacycle **14b**: The solution was stirred at room temperature under nitrogen in the dark for 72 h, and the adduct (35%) was isolated as an unstable, brown-orange oil. Rf = 0.17 hexane; IR (CCl_4) 2081 (w), 1997 (s), 1949 (m); ^1H NMR ($CDCl_3$): 3.87 (s, 3H), 6.90 (m, 3H), 7.44 (m, 6H), 7.64 (s, 1H), 7.93 (d, 2H, J=8.8); ^{13}C NMR ($CDCl_3$) 203.4, 150.5, 139.1, 131.8, 131.4, 128-127 (m), 125.2, 114.1, 55.6; ^{55}Mn NMR (C_6D_6): signal was too broad to measure; >40 KHz.

Manganacycle **14c**: The solution was stirred at room temperature under nitrogen in the dark for 72 h, and the adduct (5c) (65%) was isolated as an brown-orange oil. Rf = 0.18 hexane; IR (CCl_4) 2082 (w), 1997 (s), 1949 (m); ^1H NMR ($CDCl_3$): 2.41(s, 3H), 7.43 (m, 7H), 7.67 (s, 1H), 7.90 (d, 2H, J=8.3); ^{55}Mn NMR (C_6D_6): -880 ± 20.

Manganacycle 14d: The solution was stirred at room temperature under nitrogen in the dark for 72 h, and the adduct isolated as an brown-orange solid (77 mg, 51%). Rf =0.20 hexane; IR (CCl_4) 2083 (m), 1996 (vs), 1953 (s); ^1H NMR ($CDCl_3$): 7.45 (m, 7H), 7.66 (s, 1H), 7.95 (d, 2H, J=8.6); ^{55}Mn NMR (C_6D_6): -900 ± 20.

General Procedure for the Demetalation of Unsaturated Manganacycles under Acidic Conditions: Rate constants (k) and half-life ($t_{1/2}$) data for demetalation of manganacycles **14a-d** were determined by quintuplet runs of the following procedure and were reported as average values (see Tables 1 and 2).

An aliquot (2.5 mL) of a solution of the appropriate manganacycle (2.0 mg) in CH_3CN (10.0 mL) was diluted to 10.00 mL with CH_3CN. The solution was maintained at the desired temperature (±0.1 °C) in a constant temperature bath. A portion of this solution was placed in a temperature-controlled UV cuvette. Anhydrous H_2SO_4 (0.100 mL) was added to the cuvette and the solution was shaken for *ca.* 3 s. Both the disappearence of the manganacycle and the appearance of the product were monitored. The wavelength followed for the manganacycle and the products were *ca.* 350 nm and 310 nm, respectively. Absorbance values (A) were recorded until dA/dt approached 0 (approximately 5 half-lives). Rate constants were calculated using Systat®.

References and Notes

1. (a) DeShong, P.; Slough, G.A. *Organometallics* **1984**, *3*, 636. (b) DeShong, P.; Slough, G. A. ; Elango, V. *J. Am. Chem. Soc.* **1985**, *107*, 7788. (c) DeShong, P.; Slough, G. A.; Rheingold, A. L. *Tetrahedron Lett.* **1987**, *28*, 2229. (d) DeShong, P.; Sidler, D. R.; Slough, G.A.*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. W.; Bursten, B. E.; Clayton, T. W., Jr. *Organometallics* **1989**, *8*, 1381.

2. Smith, L. J.; DeShong, P.; Lessen, T. A. "Demetalation of Organomanganese Complexes. The First Example of a High Spin Mn(I) Species.", submitted to *J. Am. Chem. Soc.*

3. DeShong, P.; Sidler, D.R.; Rybczynski, P.J.; Ogilvie, A. A.; von Philipsborn, W. *J. Org. Chem.* **1989**, 54, 5432.

4. Drew, D.; Darensbourg, M.Y.; Darensbourg, D. J. *J. Organomet. Chem.* **1975**, *85*, 73.

5. Coffield, T.H.; Kozikowski, J.; Closson, J. *J. Org. Chem.* **1957**, *22*, 598.

6. The demetalation reaction had been shown to be a first-order process under these kinetic conditions; see reference 3 for details.

7. Eyring, H. *J. Chem. Phys.* **1935**, *3*, 107.

8. (a) Hafner, A.; Hegedus, L.S.; deWeck, G.; Hawkins, B.; Dötz, K.J. *J. Am. Chem. Soc.* **1988**, *110*, 8413. (b) von Philipsborn, W. *Pure Appl. Chem.* **1986**, *58*, 513; and references cited therein. (c) Koller, M.; von Philipsborn, W. *Organometallics.* **1992**, *11*, 467. (d) Green, J. C.; Grieves, R. A.; Mason, J. *J. Chem. Soc., Dalton Trans.* **1986**, 1313.

9. Beck, W.; Hieber, W.; Tengler, H. *Chem. Ber.* **1961**, *94*, 862.