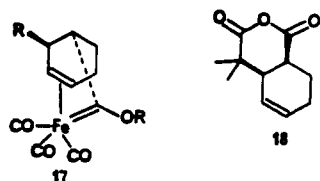
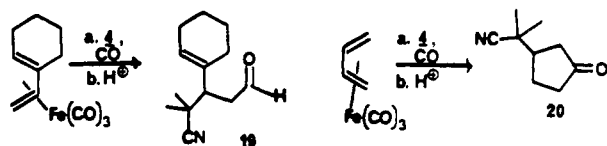


Table I displays the results of a systematic study of complex **2** with a variety of carbanions in the presence of CO.<sup>16</sup> Ketone enolates are apparently not reactive enough to give useful efficiency, but more reactive carbon nucleophiles produce high yields of carbonyl products. The formation of the trans isomer in most cases is consistent with the addition of the nucleophile from the anti direction,<sup>17</sup> followed by CO insertion with retention at the migrating carbon.<sup>7,18</sup> The formation of esters after reaction with the alkyl fluorosulfonates and oxidation is reminiscent of the chemistry of acylchromium pentacarbonyl anions<sup>19</sup> but is not generally observed for the iron analogue.<sup>20</sup> We propose that an (alkylidene)iron intermediate (**17**) forms by O-alkylation of the



proposed acyliron tricarboxylate anion **7** and is oxidized readily to give the esters **11**. Systematic study of this proposal is underway. Under the strong acid quenching conditions, mixtures of cis- and trans-disubstituted cyclohexenes are usually obtained (Table I, entries 1, 6, 8, 14, and 15). These results can be explained by epimerization during acid quenching, giving an equilibrium mixture. In the special case of dilithioisobutyrate (entry 14), ferric chloride treatment appears to oxidize the expected carboxylic acid aldehyde into an anhydride (**18**), and epimerization allows exclusive formation of the cis ring fusion isomer.<sup>9</sup> However, with other quenching techniques, using carbon electrophiles, the pure trans-3,4-disubstituted cyclohexenes are obtained.

The carbonylation process appears to be quite general. For example, the complex from 1-vinylcyclohexene<sup>21</sup> reacts with **4** and CO to give, after protonation, the aldehyde **19** in 71% yield.<sup>9</sup> With



other open chain dienes, preliminary results suggest further reaction of the acyliron intermediates can occur. Under the usual

(16) The general procedures for experiments reported in the table follow. Into a stirred solution of the carbanion (2.7 mmol) in a mixture of THF and HMPA (4:1, v/v; 10 mL) at  $-78^\circ\text{C}$  under argon was passed via syringe needle a stream of carbon monoxide for a period of 1 min, and then the closed system was pressurized to ca. 8 psi as measured by a regulator at the CO cylinder. The system was sealed by means of stopcocks held in place by rubber bands. The neat liquid  $\eta^4$ -(1,3-cyclohexadiene)iron tricarboxylate was added via syringe over 20 s. The mixture was stirred at  $-78^\circ\text{C}$  for 1 h and then at  $25^\circ\text{C}$  for 1 h. After the mixture was cooled to  $-78^\circ\text{C}$  and the pressure was released, the intermediate was quenched with either excess trifluoroacetic acid ( $-78$  to  $25^\circ\text{C}$  over 10 min), methyl iodide (2 h at  $25^\circ\text{C}$ ), alkyl fluorosulfonate/ferric chloride ( $-78$  to  $25^\circ\text{C}$ ), or oxygen/ferric chloride.<sup>12</sup> Filtration of the crude organic product through a short column of silica gel (eluting with hexane/dichloromethane) followed by short-path distillation gave the products listed in the table.

(17) No evidence for the direction of addition of nucleophiles to 1,3-diene ligands has been presented, but anti addition is general for alkene, allyl, cyclohexadienyl, and arene ligands. For a general discussion, see: Collman, J. P.; Hedgedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; pp 303-306.

(18) For a general discussion, see the book cited in ref 17, pp 264-266.

(19) For a general discussion, see: Casey, C. A. In "Transition Metal Organometallics in Organic Synthesis"; Alper, H., Ed.; Academic Press: New York, 1976; p 225.

(20) In general, acyliron tetracarboxylate anions are alkylated at iron (Collman's reaction). The one systematic study of alkylation with alkylating agents of the type used here failed to provide significant yields of the iron-alkylidene species: Fischer, E. O.; Beck, H.-J.; Kreiter, C. G.; Lynch, J.; Müller, J.; Winkler, E. *Chem. Ber.* **1972**, *105*, 162-172. However, phosphine-substituted analogues have been converted to (alkylidene)iron complexes in high yield: Condon, H. L.; Darenbourg, M. *Inorg. Chem.* **1974**, *13*, 506-511.

(21) Dauben, W. G.; Lorber, M. E. *Org. Mass Spectrosc.* **1970**, *3*, 211-218.

conditions,  $\eta^4$ -(1,3-butadiene)Fe(CO)<sub>3</sub><sup>5b</sup> leads to the 3-substituted cyclopentanone **20** in 76% yield.<sup>22</sup> Further development of these processes is underway.

**Acknowledgment.** We are pleased to acknowledge support of this work through a research grant from the National Science Foundation (CHE-7905561) and through a graduate traineeship from the Public Health Service to J.W.H. In addition, NMR facilities at Princeton and Yale, provided partly by grants from the National Science Foundation, were employed in this project.

**Supplementary Material Available:** Spectral and X-ray data for **9** (4 pages). Ordering information is given on any current masthead page.

(22) Cyclopentanone **20** was isolated by short-path distillation ( $80$ – $110^\circ\text{C}$  (0.8 torr)): <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.6–2.2 (m, 7 H), 1.34 (s, 3 H), 1.30 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  2.5.5 (s), 122.7 (s), 45.4 (d), 40.6 (t), 38.2 (t), 25.4 (t), 35.9 (s), 25.1 (q), 24.3 (q); IR (neat) 2980 (s), 2900 (m), 2240 (m), 1740 (s), 1460 (m), 1405 (m), 1395 (m), 1370 (m), 1260 (s) cm<sup>-1</sup>; GC-MS, *m/z* 151 (parent, 7), 89 (3), 83 (38), 69 (5), 56 (9), 55 (100). Anal. Calcd for C<sub>5</sub>H<sub>10</sub>O: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.55; H, 8.68; N, 9.09.

## Mechanism of Ligand Substitution in Mn<sub>2</sub>(CO)<sub>10</sub>

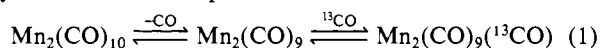
N. J. Coville, A. M. Stolzenberg, and E. L. Muetterties\*

Department of Chemistry, University of California  
Berkeley, California 94720

Received December 30, 1982

By a metal isotope double-labeling procedure, we<sup>1</sup> recently established that thermally initiated ligand substitution reactions of Re<sub>2</sub>(CO)<sub>10</sub> do not involve Re–Re bond cleavage; rather the CO predissociation step Re<sub>2</sub>(CO)<sub>10</sub>  $\rightleftharpoons$  Re<sub>2</sub>(CO)<sub>9</sub> + CO followed by ligand addition to Re<sub>2</sub>(CO)<sub>9</sub> precisely describes the mechanism. We have now established that Mn<sub>2</sub>(CO)<sub>10</sub> substitution reactions<sup>2</sup> are mechanistically analogous to the rhenium systems. These experiments suggest that the Mn–Mn bond energy in Mn<sub>2</sub>(CO)<sub>10</sub> is probably greater than the earlier estimates<sup>3,4</sup> of 16–22 kcal/mol.

Our experiments with <sup>13</sup>CO substitution in Mn<sub>2</sub>(CO)<sub>10</sub> in octane solution at  $120^\circ\text{C}$  and 550–660 torr of <sup>13</sup>CO establish a reaction fully consistent<sup>5</sup> with eq 1 and a half-life of  $45 \pm 10$  min as



compared to a half-life<sup>6a</sup> of 46 min for P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> substitution (Figure 1, supplementary material). To enable an incisive<sup>7</sup> test of thermally initiated Mn–Mn bond scission by a double-labeling procedure under conditions of ligand exchange, Mn<sub>2</sub>(CO)<sub>10</sub> and Mn<sub>2</sub>(<sup>13</sup>CO)<sub>10</sub> were physically mixed and then reacted in octane with <sup>12</sup>CO or with <sup>13</sup>CO at  $120^\circ\text{C}$ . Mass spectrometric analysis of the reaction mixture after varying reaction times evinced no evidence (i.e., buildup of Mn<sub>2</sub>(<sup>12</sup>CO)<sub>6-4</sub>(<sup>13</sup>CO)<sub>4-6</sub> molecules, 394–396 amu range, was less than  $\sim 3\%$ ) that scission of the Mn–Mn bond occurs at significant rates under these conditions of relatively rapid CO exchange (Figure 1). Thus CO ligand

(1) Stolzenberg, A. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1983**, *105*, 822.

(2) For a summary of studies and conclusions regarding Mn<sub>2</sub>(CO)<sub>10</sub> ligand substitution reactions see: Muetterties, E. L.; Burch, R. R.; Stolzenberg, A. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 89–118.

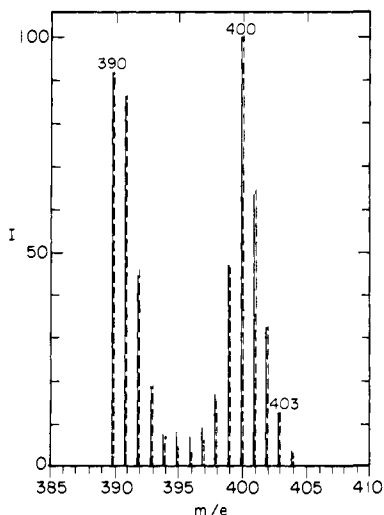
(3) Brown, D. L. S.; Connor, J. A.; Skinner, H. A. *J. Organomet. Chem.* **1974**, *81*, 403.

(4) Connor, J. A.; Zafarani-Moattar, M. T.; Bickerton, J.; El Saied, N. I.; Suradi, S.; Carson, R.; Al Takhin, G.; Skinner, H. A. *Organometallics* **1982**, *1*, 1166–1174.

(5) Assuming a first-order dissociative process with successive dissociation rates statistically corrected for the number of <sup>12</sup>CO groups remaining and that replacement of bound <sup>13</sup>CO by <sup>12</sup>CO is insignificant, the problem is analyzable by a ten-step radioactive decay chain (cf. ref 1). The agreement between experiment and theory was good (Figure 1, supplementary material).

(6) (a) Wawersik, H.; Basolo, F. *Inorg. Chim. Acta* **1969**, *3*, 113. (b) Atwood, J. D. *Inorg. Chem.* **1981**, *20*, 4031 and references therein. (c) Schmidt, S.; Basolo, F.; Troglor, W. *Inorg. Chem.* **1982**, *21*, 1698.

(7) A metal-based isotopic double-labeling procedure is not feasible for manganese because there is only one stable manganese isotope.



**Figure 1.** Mass spectrum of the product obtained from the reaction between  $\text{Mn}_2(^{12}\text{CO})_{10}$ ,  $\text{Mn}_2(^{13}\text{CO})_{10}$ , and  $^{13}\text{CO}$  (76 min, 120 °C). The  $^{13}\text{CO}$  used in these studies was 93.8%  $^{13}\text{C}$ , 9.3%  $^{17}\text{O}$ , and 1.5%  $^{18}\text{O}$ ; accordingly, the  $\text{Mn}_2(^{13}\text{CO})_{10}$  that was prepared from this  $^{13}\text{CO}$  only approached ~94%  $^{13}\text{C}$  content. The simulated spectrum<sup>1,5</sup> for a CO dissociative based reaction using a half-life of 55 min (the range in half-life measurements,  $45 \pm 10$  min, was due to minor temperature variations in the reaction conditions) is shown by dotted lines. Under identical reaction conditions but with an argon atmosphere, there was CO interchange between the manganese dimers. Roughly, 90% of the overall reaction under argon can be described as a pairwise exchange of CO. There was some buildup of mass 395, which can be interpreted as a result of some dissociation, 10%, of the dimer into mononuclear fragments. This could be either from fragmentation (or dimerization) of  $\text{Mn}_2(\text{CO})_{10}$  or of  $\text{Mn}_2(\text{CO})_9$ . Note that the specific molecules  $\text{Mn}_2(^{12}\text{C}^{16}\text{O})_{10}$ ,  $\text{Mn}_2(^{13}\text{C}^{16}\text{O})_{10}$ , and  $\text{Mn}_2(^{12}\text{C}^{16}\text{O})_5(^{13}\text{C}^{16}\text{O})_5$  have the respective amu values of 390, 400, and 395.

exchange in  $\text{Mn}_2(\text{CO})_{10}$  cannot proceed through a rate-determining Mn–Mn bond scission step and is fully consistent with the mechanism outlined in eq 1. Also, there was no major competing (nonproductive with respect to ligand exchange) reaction involving Mn–Mn bond scission at 120–150 °C.<sup>8</sup> We suggest that the Mn–Mn bond energy in  $\text{Mn}_2(\text{CO})_{10}$  substantially exceeds the 22 kcal/mol value most recently estimated<sup>4</sup> (the enthalpy of activation for  $\text{P}(\text{C}_6\text{H}_5)_3$  substitution in  $\text{Mn}_2(\text{CO})_{10}$  is 37 kcal/mol<sup>6a</sup>). Our results confirm the original Wawersik and Basolo<sup>6a</sup> mechanistic proposal for  $\text{Mn}_2(\text{CO})_{10}$  ligand-substitution reactions. This basic mechanistic scheme is also supported by the extensive studies of Atwood and co-workers<sup>6b</sup> and those of Schmidt et al.<sup>6c</sup>

Analogously, the reaction of  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{Mn}_2(^{13}\text{CO})_{10}$  with *tert*-butyl isocyanide showed no evidence of Mn–Mn bond scission in the formation of  $\text{Mn}_2(\text{CO})_9(\text{CNR})$  at 80 °C in benzene solution (Figure 2, supplementary material). Also, this reaction as catalyzed by Pd on charcoal proceeded at 25 °C without (1% or less) Mn–Mn bond scission, (Figure 3, supplementary material). Similar results were obtained with  $\text{Re}_2(^{12}\text{CO})_{10}$  and  $\text{Re}_2(^{13}\text{CO})_{10}$  isocyanide reactions. The half-life of the  $\text{M}_2(\text{CO})_{10}$  uncatalyzed isocyanide reactions are about one-hundredth those for CO or  $(\text{C}_6\text{H}_5)_3\text{P}$  reactions. Accordingly, the mechanism of the isocyanide reaction appears to be different from that for CO or for  $(\text{C}_6\text{H}_5)_3\text{P}$  (eq 1); kinetic analyses of the Mn and Re isocyanide reactions are in progress.

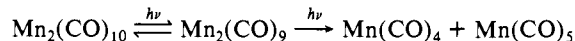
Reaction of  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{Mn}_2(^{13}\text{CO})_{10}$  with  $(\text{C}_6\text{H}_5)_3\text{P}$  in octane at 120 °C was analyzed in the early reaction stages (less than 1 half-life for the fastest<sup>9</sup> reaction of the  $\text{Mn}_2(\text{CO})_9\text{P}(\text{C}_6\text{H}_5)_3$  product with  $^{13}\text{CO}$ ). The mass spectrometric analysis of the residual  $\text{Mn}_2(\text{CO})_{10}$  and the product  $\text{Mn}_2(\text{CO})_9\text{P}(\text{C}_6\text{H}_5)_3$  showed

(8) At 150 °C, there appears to be scission of the Mn–Mn bond, but the percentage contribution of this process to the overall ligand-exchange reaction can be no more than 5%.

(9) Ligand exchange of  $\text{Mn}_2(\text{CO})_9\text{P}(\text{C}_6\text{H}_5)_3$  with phosphines and phosphites was found to be very rapid as was originally reported by Wawersik and Basolo.<sup>6a</sup>

no evidence (1% level) of Mn–Mn bond scission (Figure 4, supplementary material). Analysis of the bis-phosphine product was precluded by the short reaction times and because neither an EI nor a CI mass spectrum could be obtained for this complex.

Irradiation (Pyrex filtered) of the CO reaction with  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{Mn}_2(^{13}\text{CO})_{10}$  clearly established that Mn–Mn bond breaking is a significant process under these conditions although our data do not distinguish between a predominant  $\text{Mn}_2(\text{CO})_{10} \rightarrow 2\text{Mn}(\text{CO})_5$  and a predominant or competing photolytic process<sup>10</sup> of



Quantitative photolysis studies, using labeled Mn (and Re) carbonyls, are in progress to establish whether this reaction is precisely a one-photon process.

The technique employed to distinguish unambiguously between M–CO and M–M bond scission reactions in  $\text{Mn}_2(\text{CO})_{10}$  ligand substitution reactions is applicable generally to polynuclear metal carbonyl complexes, and we are applying this procedure to cobalt, iron, and ruthenium carbonyl complexes.

**Acknowledgment.** This research was supported by the National Science Foundation. N.J.C. thanks the CSIR and the University of the Witwatersrand for financial support while on sabbatical leave. We especially thank Sherri Ogden and Leah Zebre of the UCB Mass Spectrometric Facility for assistance in the mass spectrometric analyses.

**Registry No.**  $\text{Mn}_2(\text{CO})_{10}$ , 10170-69-1;  $\text{P}(\text{C}_6\text{H}_5)_3$ , 603-35-0;  $(\text{CH}_3)_3\text{CNC}$ , 7188-38-7.

**Supplementary Material Available:** Experimental procedure and Figures 1–4 for observed mass spectrometric data in the  $^{13}\text{CO}$ – $\text{Mn}_2(\text{CO})_{10}$  reaction, the  $(\text{CH}_3)_3\text{CNC}$  reaction with  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{Mn}(^{13}\text{CO})_{10}$ , the  $(\text{CH}_3)_3\text{CNC}$  reaction with  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{Mn}(^{13}\text{CO})_{10}$ , catalyzed by Pd on charcoal, and the  $(\text{C}_6\text{H}_5)_3\text{P}$  reaction with  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{Mn}_2(^{13}\text{CO})_{10}$  (7 pages). Ordering information is given on any current masthead page.

(10) See ref 1 and also see: Rothberg, L. J.; Cooper, N. J.; Peters, K. S.; Vaida, V. *J. Am. Chem. Soc.* **1982**, *104*, 3536.

## Birhythmicity and Compound Oscillation in Coupled Chemical Oscillators: Chlorite–Bromate–Iodide System<sup>1</sup>

Mohamed Alamgir and Irving R. Epstein\*

Department of Chemistry  
Brandeis University, Waltham, Massachusetts 02254

Received January 27, 1983

The recent success of systematic approaches to the design of chemical oscillators<sup>2–4</sup> has been accompanied by increased interest in more complex dynamical phenomena such as chemical chaos.<sup>5</sup> Just as the first deliberately designed chemical oscillator<sup>2</sup> was constructed by coupling two bistable systems, one may ask what phenomena might arise if two oscillatory reactions were linked through a common species.

Heilweil et al.<sup>6</sup> and Cooke<sup>7</sup> have investigated the Belousov–

(1) Part 17 in the series Systematic Design of Chemical Oscillators. Part 16: Alamgir, M.; Orbán, M.; Epstein, I. R., submitted for publication in *J. Phys. Chem.*

(2) De Kepper, P.; Epstein, I. R.; Kustin, K. *J. Am. Chem. Soc.* **1981**, *103*, 2133–2134.

(3) Orbán, M.; De Kepper, P.; Epstein, I. R. *J. Am. Chem. Soc.* **1982**, *104*, 2657–2658.

(4) Alamgir, M.; De Kepper, P.; Orbán, M.; Epstein, I. R. *J. Am. Chem. Soc.*, in press.

(5) Turner, J. S.; Roux, J.-C.; McCormick, W. D.; Swinney, H. L. *Phys. Lett.* **1981**, *85A*, 9–12.