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Bisdecarbonylation of *o*-Carbomethoxybenzoylpentacarbonylmanganese(I)

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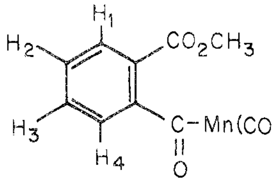
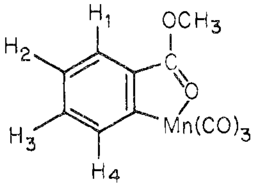
o-Carbomethoxybenzoylpentacarbonylmanganese(I), **1a**, was prepared by reaction of $NaMn(CO)_5$ with the corresponding acid chloride. **1a** undergoes bisdecarbonylation in $CHCl_3$ at 50° to give *o*-carbomethoxyphenyltetracarbonylmanganese(I), **2a**, in which the carbomethoxy group acts as a chelating ligand. No monodecarbonylated material was observable by spectral means. Decarbonylation of **1a** in the presence of 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, ETPO, gives only the ETPO substitution product *o*-carbomethoxybenzoyl(ETPO)tetracarbonylmanganese(I), **1b**. The rate of disappearance of **1a** in the presence of ETPO is independent of ETPO concentration.

Introduction

In the course of studying the reactions of lithium reagents with acylpentacarbonylmanganese compounds, we required a sample of *o*-carbomethoxybenzoylpentacarbonylmanganese(I), **1a**. This compound was found to lose two molecules of carbon monoxide slowly at 25° to give *o*-carbomethoxyphenyltetracarbonylmanganese(I), **2a**, in which the carbomethoxy group acts as a chelating ligand. Several compounds containing a chelating carbonyl group have been obtained previously by less straightforward routes.[1] A related imine analog of **2a** has also been reported.[2] Here we present our findings concerning the rate and mechanisms of the conversion of **1a** to **2a**.



1a, L = CO
b, L = ETPO



2a, L = CO
b, L = ETPO

ETPO = 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane

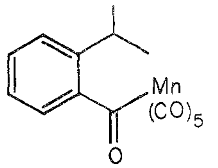
Results

1a was prepared in 60% yield from *o*-carbomethoxybenzoyl chloride and $NaMn(CO)_5$ in tetrahydrofuran (THF) at 0°. The infrared spectrum of **1a** (Table I) contained bands at 1728 cm^{-1} due to the carbomethoxy group and 1630 cm^{-1} due to the benzoylmanganese moiety. In addition, five bands were observed in the metal carbonyl region. The nmr spectrum of **1a** is remarkable in that all four aromatic hydrogens have widely different chemical shifts and give rise to first-order multiplets (Figure 1). The assignment of the H_1 and H_4 resonances in **1a** was made on the basis of chemical shift comparisons with closely related compounds. The downfield resonance at δ 7.97 was assigned to H_1, the proton adjacent to the ester group; for comparison, the proton adjacent to the ester group appears at δ 7.70 in dimethyl phthalate, at δ 7.77 in methyl *o*-isopropylbenzoate, **3**, and at δ 8.05 in methyl benzoate. The upfield resonance of **1a** at δ 7.19 was assigned to H_4, the proton ortho to the acylmanganese group; for comparison, the ortho protons in benzoylpentacarbonylmanganese appear at δ 7.46 and the proton ortho to the acylmanganese group in **3** appears at δ 7.2. The chemical shifts of H_2 and H_3 were assigned on the basis of ^1H-decoupling experiments. Irradiation of H_1 at δ 7.97 led to the collapse of the H_2 resonance at δ 7.45 from a doublet of triplets to a double of doublets (J = 7.5 Hz, J' = 1.5 Hz) while the H_3 resonance at δ 7.73 collapsed from a doublet of triplets to a triplet (J = 7.5 Hz).

Table I. Infrared Spectra

Compd	Str freq, cm^{-1}
1a[a]	2118 m, 2063 m, 2025 s, 2014 s, 1999 s, 1728 w, 1630 w
1b[b]	2086 m, 2018 s, 1994 s, 1718 w, 1600 w, 1591 w
2a[a]	2085 m, 1997 s, 1947 s, 1617 w, 1610 m, 1578 w
2b[b]	2024 s, 1953 s, 1908 s, 1612 m
3[b]	2115 m, 2050 m, 2025 s, 2006 s, 1635 m

[a] Heptane. [b] $CHCl_3$.



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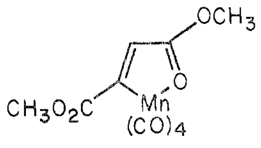

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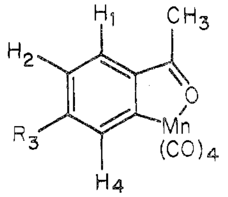


5a, R_3 = H
b, R_3 = CH_3

1a undergoes bisdecarbonylation slowly at 25° in acetone to give high yields of **2a**. Pyrolysis of neat **1a** at 90° on a vacuum line gave a 95% yield of **2a** and a 124% yield of CO based upon 2 mol of CO/mol of **1a**. The infrared spectrum of **2a** (Table I) contains a band at 1610 cm^{-1} due to the coordinated ester group (shifted from 1728 cm^{-1} for the uncoordinated ester of **1a**) and three strong CO bands due to the $Mn(CO)_4$ moiety. In the related compound **4**, Booth has observed the coordinated ester carbonyl frequency at 1591 cm^{-1}.[1b]

In the 100-MHz nmr spectrum of **2a**, the chemical shifts of the four aromatic protons were widely separated and first-order splitting patterns were observed (Figure 1 and Table II). The assignment of chemical shifts was simplified since Kaesz has recently reported the nmr spectrum of a series of related compounds, including **5a** and **5b**, obtained by the pyrolysis of $CH_3Mn(CO)_5$ in the presence of substituted acetophenones.[1a] The chemical shift of H_4 moves downfield from δ 7.24 in **1a** to δ 7.96 in **2a** due to the deshielding effect of the neighboring Mn atom in **2a**. A comparison of the mass spectra of **1a** and **2a** clearly indicates the conversion from an

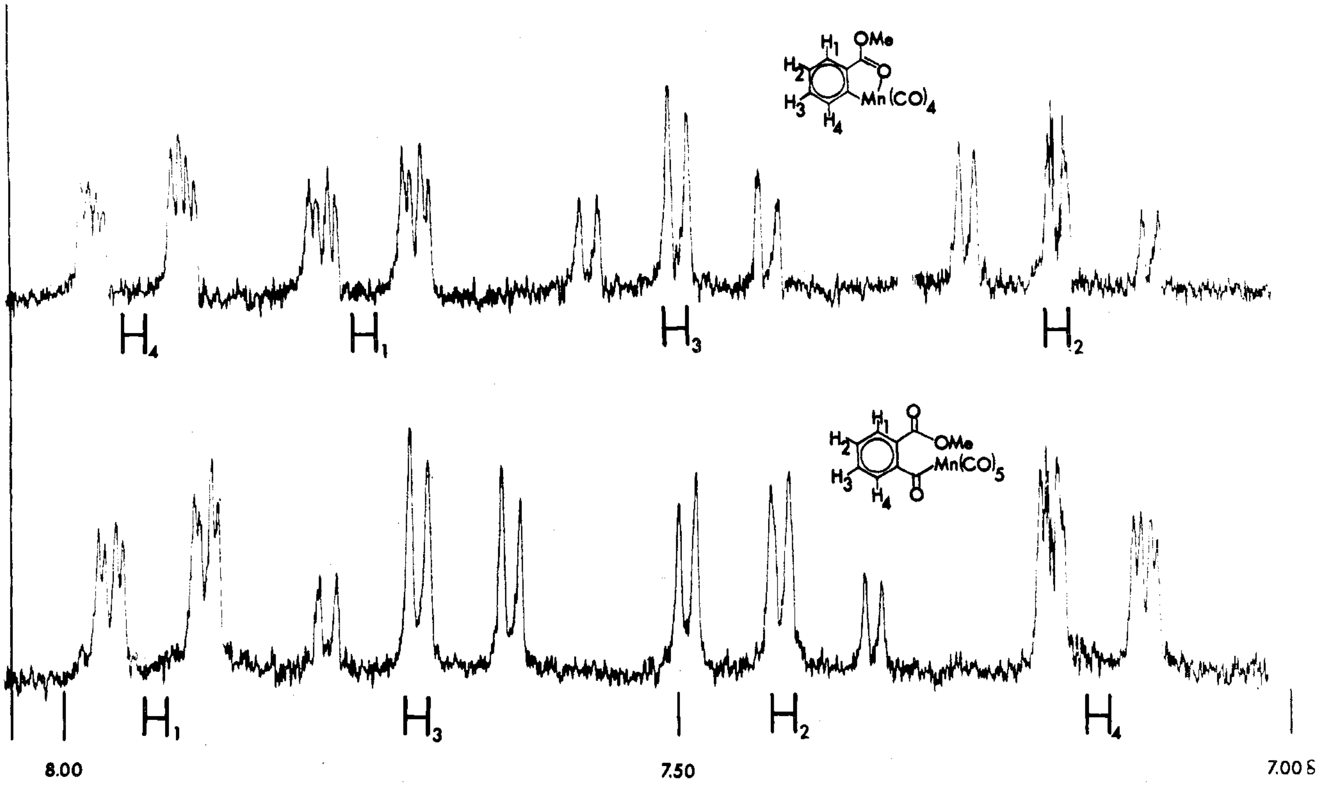


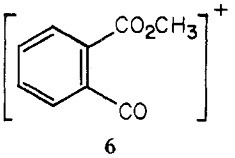
Figure 1. Aromatic region of 100-MHz ^{1}H nmr spectra of **1a** and **2a** in acetone-d_6.

Table II. 100-MHz Nmr Spectra (δ)

Compd	H_1	H_2	H_3	H_4	Other resonances	Coupling constants, Hz
1a[a]	7.93 ddd	7.42 td	7.71 td	7.16 ddd	3.89 (s) OCH_3	$J_{12} = 7.7, J_{13} = 1.4,$ $J_{14} = 0.5, J_{23} = 7.5,$ $J_{24} = 1.5, J_{34} = 7.6$
1b[a]	7.89 dd	7.37 td	7.66 td	7.24 dd	0.87 (t, $J = 8.0$ Hz) CH_2CH_3 1.36 (q, $J = 8.0$ Hz) CH_2CH_3 3.84 (s) OCH_3 4.46 (d, $J_{P-H} = 5.0$ Hz) OCH_2	$J_{12} = 8.0, J_{13} = 1.0,$ $J_{23} = 7.8, J_{24} = 1.5,$ $J_{34} = 7.8$
2a[a]	7.75 ddd	7.19 td	7.50 td	7.94 ddd	4.08 (s) OCH_3	$J_{12} = 7.6, J_{13} = 1.5,$ $J_{14} = 0.6, J_{23} = 7.5,$ $J_{24} = 1.2, J_{34} = 7.3$
2b[a]	7.53 ddd	6.96 tt	7.24 td	7.86 dddd	0.76 (t, $J = 7.5$ Hz) CH_2CH_3 1.21 (q, $J = 7.5$ Hz) CH_2CH_3 3.91 (s) OCH_3 4.11 (d, $J_{P-H} = 4.5$ Hz) OCH_2	$J_{12} = 7.5, J_{13} = 1.5,$ $J_{14} = 0.6, J_{23} = 7.2,$ $J_{24} = 1.2, J_{34} = 7.2,$ $J_{P-H_2} = 1.3, J_{P-H_4} = 1.8$
5a[b]	7.83 dd	7.17 td	7.41 td	8.09 dd	2.6 (s) $COCH_3$	$J_{12} = 7.5, J_{13} = 1.5,$ $J_{14} = 0.7, J_{23} = 7.0,$ $J_{24} = 1.1, J_{34} = 7.0$
5b[c]	7.73	6.94		7.90		$J_{12} = 7.7, J_{24} = 1.5$
3	Multiplet (*ca.* 7.2)				1.21 (septet, $J = 7.0$ Hz) 3.06 (d, $J = 7.0$ Hz)	

[a] Recorded in acetone-d_6. [b] Reference 1a. [c] H. D. Kaesz, private communication.

aroylmanganese compound to an arylmanganese compound since the peak due to ion **6** (m/e 163) which is 62% of the base peak in **1a** is conspicuously absent (<2%) in the mass spectrum of **2a**.



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The decarbonylation of **1a** to **2a** in $CHCl_3$ was studied by nmr in evacuated sealed tubes with *p*-di-*tert*-butylbenzene as an internal standard. The reaction was followed by monitoring the disappearance of the methoxy signal of **1a** at δ 3.89. The methoxy resonance of the product, **2a**, was found at δ 3.98 and no intermediate could be detected. The first-order rate plot for the reaction was slightly curved; the rate of reaction slowed down during the course of the decarbonylation as the pressure of CO in the tube increased to 4 atm.

The effect of CO pressure on the rate of bisdecarbonylation of more dilute solutions of **1a** in sealed tubes was studied by infrared spectroscopy. The band at 2120 cm^{-1} was used to monitor the disappearance of **1a** since it was cleanly separated from other bands of starting material and products. In the absence of added CO, the CO pressure in the sealed tubes at half-reaction was calculated to be ~0.15 atm. The rate of bisdecarbonylation of **1a** under 1.4 and 2.5 atm of CO in sealed tubes was also studied by infrared spectroscopy (Table III). Under all these conditions, no curvature in the first-order rate plots could be detected. The rate of bisdecarbonylation of **1a** was slowed by a factor of 6.3 under 2.5 atm of CO.

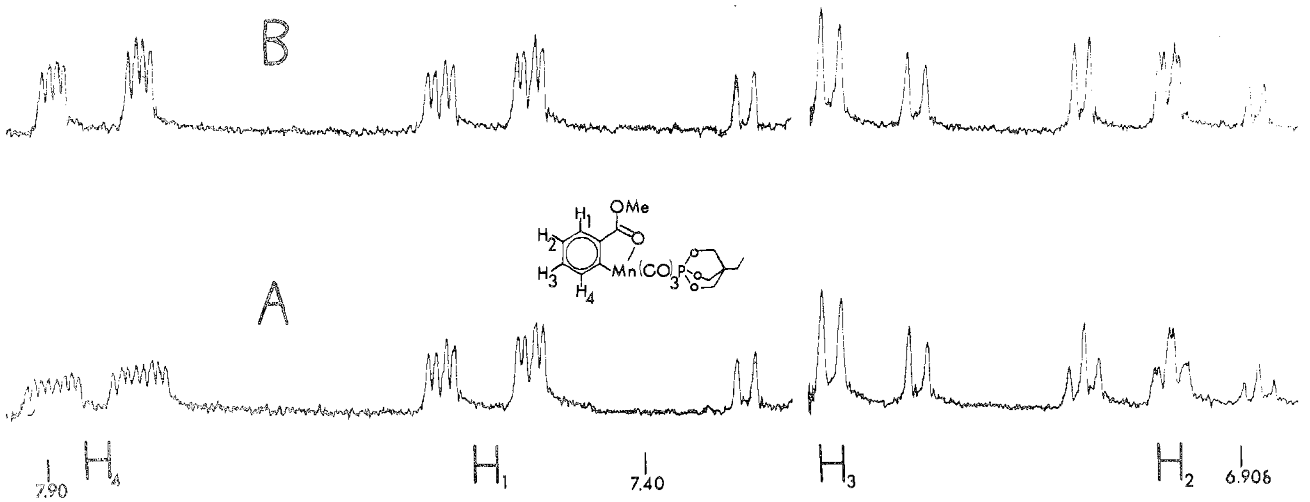


Figure 2. (A) Aromatic region of 100-MHz ^1H nmr spectrum of **2b** in acetone-d_6. (B) ^{31}P-Decoupled ^1H nmr spectrum of **2b**.

Table III. Effect of CO Pressure on Bisdecarbonylation of **1a** at 50.87° in $CHCl_3$[a]

Run	CO pressure, atm	10^4k,[d] sec^{-1}
1	~0.15[b,c]	3.96 ± 0.15
2	1.4	1.03 ± 0.05
3	2.5	0.63 ± 0.02

[a] Disappearance of **1a** was followed by observing the band at 2120 cm^{-1} in the infrared spectrum of **1a**; initial concentration of **1a** was ~0.06 *M*. [b] CO pressure developed at half-reaction in the absence of added CO. [c] The sealed tubes were shaken to achieve equilibration of CO between the gas phase and solution; rates were a factor of ~2 slower in the absence of shaking. [d] Least-squares first-order rate constants ± standard deviation.

In an effort to trap an intermediate such as **7** (Scheme I), **1a** was refluxed in $CHCl_3$ with 2 equiv of the bicyclic phosphite ETPO for 30 min. ETPO was used as the ligand since it was known to give stable complexes of the type $C_6H_5COMn(CO)_4ETPO$.[4] A pale yellow solid obtained was identified as the ETPO substitution product, **1b**, on the basis of spectral data. The ir spectrum (Table I) showed bands at 1718 and 1600 cm^{-1} for the ester carbonyl and acylmanganese carbonyl, respectively. The metal carbonyl region of the spectrum contains a medium-intensity band at 2086 cm^{-1} and two strong bands at 2018 and 1994 cm^{-1}, indicating a *cis*-$Mn(CO)_4$ unit[3,4] in **1b**. The nmr spectrum of **1b** is very similar to that of **1a** with the addition of resonances for the ligand (Table II).

The kinetics of the reaction of **1a** with ETPO were studied by ir (Table IV) using the same technique as used to measure the rate of decarbonylation of **1a**. The rate of the substitution reaction was independent of ETPO concentration and was not significantly different from the rate of decarbonylation of **1a** in the absence of added CO.

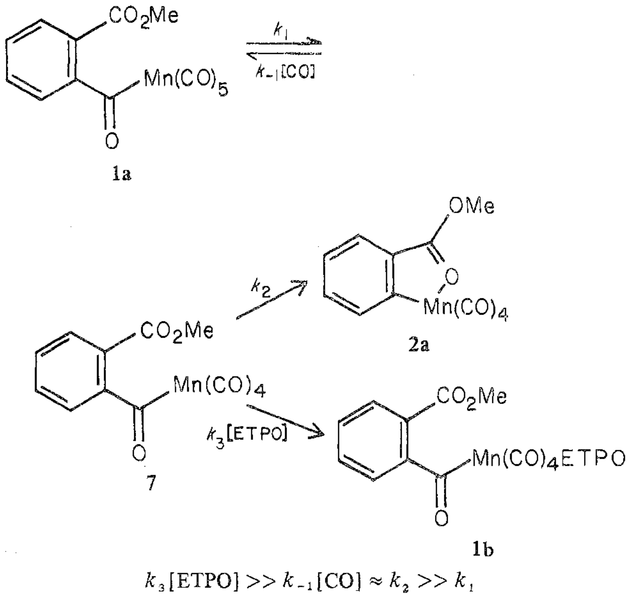
The reaction of **1a** with ETPO to give **1b** was quite clean. **2a**, which has a strong band at 1947 cm^{-1} and can be detected at <5%, was not present in the reaction mixture. Similarly, the absence of absorption at 1908 cm^{-1} indicated the absence of **2b** in the reaction mixture. An authentic sample of **2b** was prepared in 70% yield by refluxing **2a** and ETPO in $CHCl_3$ for 1 hr. **2b** was also obtained from prolonged heating of **1b** in $CHCl_3$. The ir spectrum of **2b**, as expected, shows a coordinated carbonyl at 1612 cm^{-1} and three metal carbonyl bands of similar intensity (Table I). The nmr spectrum of **2b** was surprisingly more complex in the aromatic region than that of **2a** (Table II). Phosphorus decoupling experiments demonstrated that the additional complexity is due to ^{31}P coupling. Broad-band irradiation of ^{31}P collapsed the H_4 signal at δ 7.86 from a doublet of doublet of doublet of doublets to a doublet of doublet of doublets (J_{P-H_4} = 1.8 Hz) (Figure 2). At the same time the H_2 signal at δ 6.96 collapsed from a triplet of triplets to a triplet of doublets (J_{P-H_2} = 1.3 Hz). The $^{31}P-H_2$ coupling is a remarkable example of six-bond $^{31}P-^1H$ coupling. There was no noticeable ^{31}P coupling to H_1 and H_3.

Table IV. Effect of ETPO Concentration on Substitution of **1a** at 50.87° in $CHCl_3$[a,b]

Run	[**1a**], *M*	[ETPO], *M*	10^4k,[c] sec^{-1}
1	0.061	0.065	3.40 ± 0.18
2	0.061	0.183	3.49 ± 0.15
3	0.061	0.216	3.22 ± 0.10
4	0.061	0.562	3.41 ± 0.12

[a] The disappearance of **1a** was followed by observing the band at 2120 cm^{-1}. [b] The only product observed by ir was **1b**. [c] Least-squares first-order rate constants ± standard deviation.

Scheme I



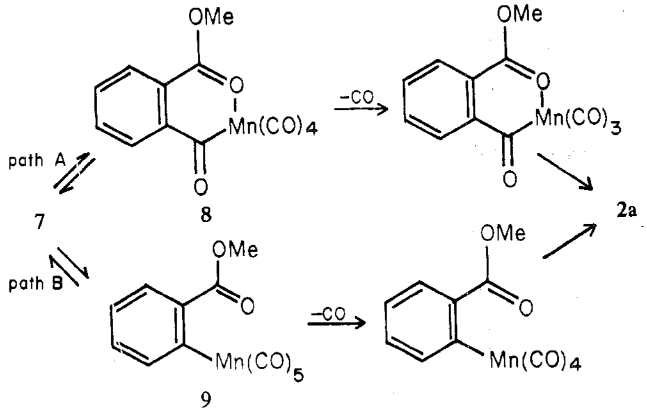
$k_3[ETPO] >> k_{-1}[CO] \approx k_2 >> k_1$

An attempt to prepare **1a** by carbonylation of **1b** at 25° and 1000 psi of CO for 4 days gave only **1b**[5].

Discussion

All of our data on the bisdecarbonylation and ETPO substitution reactions of **1a** are consistent with the mechanism shown in Scheme I.[6] The rate of ETPO substitution of **1a** is

Scheme II



first order in **1a** and is independent of the concentration of ETPO between 0.06 and 0.56 *M*. This is consistent with a rate-determining loss of a coordinated carbon monoxide to give an intermediate with the elemental composition of **7** which then is rapidly and completely trapped by ETPO to give **1b**. Since none of the bisdecarbonylated material **2a** was formed in the ETPO substitution reactions, the rate of capture of intermediate **7** by ETPO must be much faster than loss of a second CO from **7** ($k_3[\mathrm{ETPO}] \gg k_2$). In a related study of the ETPO substitution of benzoylpentacarbonylmanganese(I), Haszeldine found that the rate of substitution was similarly independent of ETPO concentration and that only substitution products were obtained.[7]

In the absence of ETPO, bisdecarbonylaton of **1a** gives **2a**. No monodecarbonylated species such as **7** were detectable by ir or nmr; consequently, the loss of a second CO from intermediate **7** must be much faster than the rate of formation of **7** ($k_2 \gg k_1$). The rate of bisdecarbonylation of **1a** in the absence of added CO is not significantly different from the rate of ETPO substitution of **1a**. This is consistent with a rate-limiting formation of the same intermediate, **7**, in both reactions.

The bisdecarbonylation of **1a** was retarded by CO pressure as would be expected from Scheme I. At 2.5 atm of CO, the rate of recapture of CO by intermediate **7** to regenerate **1a** was calculated to be 6.2 times faster than loss of CO from **7** to give bisdecarbonylation product **2a**.

The unique feature of the bisdecarbonylation of **1a** is that intermediate **7** undergoes the loss of a second molecule of CO at a much faster rate than loss of the first CO from **1a**. The rapid loss of CO from **7** is possibly intramolecularly assisted by the ester group which becomes coordinated to manganese in the bisdecarbonylated product **2a**.

Two mechanistic routes can be considered for the decarbonylation of intermediate **7** to **2a** (Scheme II). The two pathways differ only in the timing of CO loss and aryl migration. Path A involves loss of CO followed by migration of the aryl group to manganese, while path B involves aryl migration prior to loss of CO. The key finding that the loss of a second CO from intermediate **7** is *more rapid* than loss of the first CO from **1a** can be accommodated by either pathway if certain suppositions concerning each reaction sequence are made. Path A requires that the coordinated carbomethoxy group in **8** be more effective than coordinated CO in **1a** in promoting decarbonylation. This does not appear reasonable since **2a** which has a coordinated carbomethoxy group undergoes ETPO substitution more slowly than $C_6H_5Mn(CO)_5$. Path B requiries that the decarbonylation of **9** be accelerated by the neighboring carbomethoxy group either *via* steric destabilization of **9** or *via* direct nucleophilic assistance of the loss of CO. At present, we have no direct evidence which distinguishes path A from path B. We are now attempting to synthesize compounds similar to **9** to determine whether neighboring carbomethoxy groups can accelerate decarbonylation.

Experimental Section

General Data. Infrared spectra were recorded on a Digilab FTS-20 Fourier transform interferometer and on Perkin-Elmer 267 and Beckman IR-8 spectrophotometers. Ultraviolet spectra were recorded on a Cary 15 spectrophotometer. Nmr spectra were recorded on Jeol MH100 (100 MHz) and Varian XL-100 (100 MHz) spectrometers; ^{31}P-decoupling experiments were performed on the Varian XL-100. Mass spectra were run on a AEI-MS9 spectrometer at 70 eV with direct insertion of solid samples. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. Chloroform was purified before use in kinetic studies by passage through alumina. Melting points were obtained on a Hoover capillary melting point apparatus and are uncorrected.

***o*-Carbomethoxybenzoylpentacarbonylmanganese(I), 1a.** A THF solution of $NaMn(CO)_5$ (6 ml, 0.6 *M*, 3.6 mmol) was added to *o*-carbomethoxybenzoyl chloride[8] (0.800 g, 4.0 mmol) in 10 ml of THF at 0°. The solution was stirred at 0° for 1 hr and solvent removed on a rotary evaporator. The residue was dissolved in methylene chloride, filtered, and purified by preparative tlc (silica gel, chloroform). A yellow band (R_f 0.6) was collected and recrystallized from pentane at −25° to give 0.58 g (1.62 mmol, 45%) of **1a**: mp 70–72°; uv λ_{max}(hexane) 215 (ϵ 46,500) and 285 nm (sh, ϵ 8020); *m/e* 302 (7), 246 (7), 218 (16), 191 (10), 190 (100), 163 (62), 160 (25), 136 (22), 132 (40), 105 (70), 77 (44).

Anal. Calcd for $C_{14}H_7MnO_8$: C, 46.95; H, 2.00; Mn, 15.34. Found: C, 46.92; H, 1.87; Mn, 15.40.

***o*-Carbomethoxyphenyltetracarbonylmanganese(I), 2a.** **1a** (0.09 g, 0.251 mmol) was heated to 120–125° at 0.1 mm in a vacuum sublimation apparatus. Within 10 min all material had sublimed to a cold finger. Preparative thin-layer chromatography (silica gel, benzene) followed by sublimation (70°, 0.1 mm) gave 0.05 g (66%) of **2a**: mp 115–120° dec; uv λ_{max}(hexane) 210 (sh, ϵ 29,400), 234 (ϵ 22,800), and 352 nm (ϵ 2760); *m/e* 302 (9), 246 (6), 218 (20), 191 (9), 190 (100), 160 (24), 136 (22), 132 (32), 105 (73), 77 (39); calcd molecular ion ($C_{12}H_7MnO_6$) 301.9623, found 301.9630.

Anal. Calcd for $C_{12}H_7MnO_6$: C, 47.71; H, 2.33; Mn, 18.18. Found: C, 47.40; H, 2.25; Mn, 17.97.

A 146-mg (0.41-mmol) sample of **1a** was heated to 85–90° on a vacuum line. Carbon monoxide evolution was followed by measuring the increase in pressure. A total of 1.01 mmol of carbon monoxide (40 mm, 124% of the theoretical amount based on two CO's per **1a**) was evolved; **2a** was obtained in 95% yield.

***o*-Isopropylbenzoylpentacarbonylmanganese(I), 3.** A THF solution of $NaMn(CO)_5$ (15 ml, 0.58 *M*, 8.7 mmol) was added to *o*-isopropylbenzoyl chloride[9] (1.71 g, 9.4 mmol) in 10 ml of ether at 0°. The solution was stirred under nitrogen for 3 hr at 25°. Solvent was removed on a rotary evaporator and the residue was dissolved in equal amounts of methylene chloride and water. The organic layer was dried ($MgSO_4$), filtered, and concentrated. Column chromatography (silica gel, hexane) gave a fraction which was further purified by sublimation (25°, 0.5 mm) and preparative thin-layer chromatography (silica gel, 10:90 ether–pentane) to give a white solid, **3**: mp 56–57°; *m/e* 314 (2) 286 (3), 258 (5), 230 (3), 223 (2), 202 (5), 175 (2), 174 (19), 172 (3), 158 (3), 149 (2), 148 (8), 147 (28), 133 (3), 130 (3), 129 (5), 121 (3), 120 (30), 119 (5), 118 (4), 117 (4), 106 (8), 105 (100); calcd $(M - CO)^+$ ($C_{14}H_{11}MnO_5$) 313.9987, found 313.9975.

***cis-o*-Carbomethoxybenzoyltetracarbonyl(ETPO)manganese(I), 1b.** A solution of **1a** (62.3 mg, 0.174 mmol) and ETPO (29.0 mg, 0.179 mmol) in 6 ml of chloroform was refluxed 1 hr. Preparative thin-layer chromatography (silica gel, ether) gave 43.6 mg (51%) of **1b**, mp 58–68°.

***cis-o*-Carbomethoxyphenyltricarbonyl(ETPO)manganese, 2b.** A solution of **2a** (50.8 mg, 0.168 mmol) and ETPO (65 mg, 0.40 mmol) in 3 ml of chloroform was refluxed for 1 hr. Preparative tlc (silica gel, benzene) gave 51.6 mg (70%) of a bright yellow powder, **2b**: mp 148–154° dec; *m/e* 436 (2), 353 (3), 352 (19), 211 (3), 190 (100), 160 (12), 136 (14), 133 (7), 132 (24), 124 (4), 118 (6), 117 (4), 109 (4), 106 (5), 105 (75); calcd molecular ion ($C_{17}H_{18}MnO_8P$) 436.0120; found 436.0103.

Kinetic Studies of the Decarbonylation of 1a by Ir. Samples were prepared in degassed chloroform in tubes sealed under various amounts of CO. Chloroform was purified immediately before use by filtration through alumina. Pressures of CO reported are corrected for temperature difference. Run 1 (Table III) was sealed *in vacuo* (0.1 mm). Samples for run 2 were prepared by sealing the tubes under 0.84 atm of CO at −78°; the pressure calculated at 50.8° is 1.4 atm. Samples for run 3 were sealed under 0.59 atm of CO at −196°; the pressure calculated at 50.8° is 2.5 atm.

The samples were immersed in a constant-temperature bath at 50.87 ± 0.02°. For run 1, the sealed tubes were shaken to achieve equilibration of CO between the gas phase and solution. Rates were slower by a factor of 2 in the absence of shaking. The reaction was quenched at −78° and samples stored at −25° until the scale-expanded (5 times) ir spectrum could be obtained on the PE 267. Examination of the ir spectra indicated **2a** was the product. Rates are based on a single run of at least five points.

Kinetic Studies of the Reaction of 1a with ETPO. Samples were prepared in degassed chloroform in sealed tubes. The samples were immersed in a constant-temperature bath at 50.87 ± 0.02°. The reaction was quenched at −78° and samples stored at −25° until the high-resolution Fourier transform ir spectrum could be obtained. The disappearance of the band at 2120 cm^{-1} of **1a** was used to determine the rate. Examination of the ir spectrum of the samples indicated **1b** was the sole product in runs 1–4 (Table IV).

Acknowledgment. We thank Mr. Terry Burkhardt for obtaining Varian XL-100 nmr spectra. Financial support from the National Science Foundation (Grants No. GP-32160 and GP-41259X) is gratefully acknowledged.

Registry No. **1a**, 53897-19-1; **1b**, 53897-17-9; **2a**, 53897-12-4; **2b**, 53897-18-0; **3**, 53897-20-4; NaMn(CO)$_5$, 13859-41-1; *o*-carbomethoxybenzoyl chloride, 4397-55-1; *o*-isopropylbenzoyl chloride, 53881-34-8.

References and Notes

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Magnetic Ordering of Mono(diimine)iron(II) Chlorides. $Fe(2,2'\text{-bipy})Cl_2$ and $Fe(5,5'\text{-}(CH_3)_2\text{-}2,2'\text{-bipy})Cl_2$

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The temperature and magnetic field dependences of the Mössbauer spectra of $Fe(2,2'\text{-bipy})Cl_2$ (prepared in solution) show the compound to be a ferromagnet with a Curie temperature of ~4 K, V_{zz} positive, and $H_{hf} = -60$ kOe. A similar study of the methyl-substituted derivative $Fe(5,5'\text{-}(CH_3)_2\text{-}2,2'\text{-bipy})Cl_2$ (prepared by vacuum thermolysis) indicates this complex to be a slowly relaxing paramagnet over the range ~11–2 K with V_{zz} positive and $H_{hf} = -211$ kOe. These results correlate with susceptibility studies and far- and near-infrared spectra which show $Fe(2,2'\text{-bipy})Cl_2$ to be a chain polymer containing six-coordinate iron(II) while the dimethyl derivative is probably a dimer for which the iron coordination number is 5. When $Fe(2,2'\text{-bipy})Cl_2$ is prepared by low-temperature vacuum thermolysis of $[Fe(2,2'\text{-bipy})_3]Cl_2$, the resulting system does not order sharply as in the case of the solution preparation but otherwise appears to have the same structure. Mössbauer spectra show that high-temperature thermolysis results in partial breaking of the chloro bridging of polymeric $Fe(2,2'\text{-bipy})Cl_2$ to give a system of the same empirical formula but with a lower coordination number for the iron atoms.

I. Introduction

Ferromagnetic ordering in transition metal–organic ligand systems is not common. However, in a recent susceptibility study,[1] $Fe(phen)Cl_2$ was observed to order ferromagnetically with a Curie temperature $T_c = 8 \pm 2$ K, a Curie–Weiss constant $C = 3.8$ emu/mol, and a paramagnetic Curie temperature $\Theta = +12$ K. In this paper we use Mössbauer spectroscopy to consider the effects of replacing the phenanthroline ligand by other diimines, specifically as in $Fe(2,2'\text{-bipy})Cl_2$ and the methyl-substituted derivative $Fe(5,5'\text{-}(CH_3)_2\text{-}2,2'\text{-bipy})Cl_2$, and to measure T_c precisely. At the present time, the techniques involved in the preparation of these systems do not lend themselves to the formation of appropriate single crystals for direct X-ray structure determination or other single-crystal studies and the measurements reported here refer to powder materials. As we will show below, the addition of the methyl substituents considerably alters the magnetic properties. The $Fe(2,2'\text{-bipy})Cl_2$ is ferromagnetic and structurally similar[2] to the $Fe(phen)Cl_2$. The $Fe(5,5'\text{-}(CH_3)_2\text{-}2,2'\text{-bipy})Cl_2$ is paramagnetic and has a different structure. We present spectroscopic data from which we infer that the ferromagnetic materials have a chloro-bridged polymeric chain structure, while the paramagnetic compound has a dimeric structure with five-coordinate iron sites. The effects of preparative technique and thermal annealing on the magnetic ordering of $Fe(2,2'\text{-bipy})Cl_2$ and $Fe(phen)Cl_2$ are also briefly discussed.

II. Experimental Section

Both $Fe(phen)Cl_2$ and $Fe(2,2'\text{-bipy})Cl_2$ were prepared in solution using the method of Dwyer.[3] In this preparation, the complex is rapidly precipitated when a warm aqueous hydrochloric acid solution containing a tenfold excess of ferrous chloride is decanted directly onto the finely ground solid ligand. Attempts to grow single crystals of these complexes by conventional solution methods result in disproportionation of the mono(diimine) complex to more stable species such as $[Fe(2,2'\text{-bipy})_3]^{2+}$.

It is also possible to prepare $Fe(2,2'\text{-bipy})Cl_2$ by (10 hr) vacuum (~10 μ) thermolysis[4] of $[Fe(2,2'\text{-bipy})_3]Cl_2$ at 145° with subsequent loss of 2 mol of ligand. The X-ray powder patterns as well as near-infrared and visible electronic spectra of the foregoing solution and thermolysis preparations of $Fe(2,2'\text{-bipy})Cl_2$ are identical. This and Mössbauer spectra at 300 and 78 K suggest that the systems are isomorphous and have essentially the same molecular structure.

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