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Synthesis and characterization of $M[Mn(CO)_4DF]$ and $M[Mn(CO)_4DM]$ ($M = Li$, Na, $(PPh_3)_2N$; DF = dimethyl fumarate, DM = dimethyl maleate) and the role of these complexes in the isomerization of free DM to DF

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Abstract

The complexes $M[Mn(CO)_4DF]$ (**1**) and $M[Mn(CO)_4DM]$ (**2**) ($M = Li$ (**a**), Na (**b**), $(PPh_3)_2N$ (PPN) (**c**); DF = dimethyl fumarate, DM = dimethyl maleate) were prepared by photochemical reactions of $M[Mn(CO)_5]$ with the appropriate olefin, or by the metathesis reactions of (Li or Na)$[Mn(CO)_4DF]$ and (Li or Na)$[Mn(CO)_4DM]$ with [PPN]Cl. They were characterized by a combination of elemental analysis and IR and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. Complexes **1a**, **1b**, **2a**, and **2b** catalyze the isomerization of free DM to DF in THF under reflux for 2–4 days. By contrast, **1c** and **2c** are catalytically inactive under comparable experimental conditions. Studies on the catalyzed isomerization revealed that **1a** and **1b** exchange ligated DF with free DM in THF at 47–50°C over several days, whereas **1c** does not. All three complexes **2a**, **2b**, and **2c** isomerize to **1a**, **1b**, and **1c**, respectively, in THF at 45–55°C over several days. From these rather qualitative results it is suggested that the catalyzed isomerization of free DM to DF proceeds by incorporation of DM in the coordination sphere of **1**, conversion of the resultant **2** back to **1**, and replacement of ligated DF by free DM.

Introduction

One of the earliest reports of photochemical substitution reactions of metal carbonyl anions was in 1971, when phosphine, arsine, and stibene derivatives of $[M(CO)_6]^-$ ($M = V$, Nb, and Ta) were prepared [1]. Until recently, no ligands other than σ-donor molecules, e.g., phosphines, had been used in such reactions. In 1987, our laboratory reported on the facile substitution of CO in $Na[Co(CO)_4]$ by the activated olefins dimethyl fumarate (DF) and dimethyl maleate (DM) by either photochemical or thermal means [2]. These reactions are interesting, since an olefin normally would not be expected to react readily with electron-rich metal carbonyl anions. However, because of their electronegative substituents, these olefin ligands are capable of stabilizing the anionic substitution products. To

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investigate these types of reactions further, another metal carbonyl anion system was sought. Pentacarbonylmanganate(1 −) was considered a good candidate, since it is known to undergo photoinduced substitution reactions [3]. In this paper we describe the substitution chemistry of pentacarbonylmanganate(1 −) with the activated olefins dimethyl fumarate (DF) and dimethyl maleate (DM). The isomerization of DM to DF catalyzed by $M[Mn(CO)_4(DF \text{ or } DM)]$ where M = Li or Na is also presented and discussed.

Experimental

General procedures and measurements

All reactions and manipulations of air-sensitive compounds were carried out under an atmosphere of purified Ar by use of standard procedures [4]. Elemental analyses for C and H were performed by Galbraith Laboratories, Inc., Knoxville, TN. Infrared (IR) spectra were recorded on a Perkin-Elmer Model 283B grating spectrophotometer in a solution cell with CaF_2 windows and were calibrated with polystyrene. ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on a Bruker AM-250 spectrometer, and the chemical shifts are given in ppm downfield from the internal standard Me_4Si. Irradiation reactions were carried out in a quartz Schlenk tube with sixteen 254-nm lamps in a Rayonet photochemical reactor.

Materials

All solvents were dried and degassed before use. Tetrahydrofuran (THF) was distilled from potassium-benzophenone, dichloromethane from CaH_2, hexane and pentane from potassium metal, and diethyl ether from sodium-potassium alloy, all under an argon atmosphere. Dimanganese decacarbonyl was obtained from Pressure Chemical Co. or Strem Chemical Co. and used without further purification. Dimethyl maleate (DM) and dimethyl fumarate (DF) were purchased from Aldrich Chemical Co. DM was further purified by distillation. Bis(triphenylphosphine) nitrogen(1 +) chloride ([PPN]Cl) was used as received commercially. The method of Gladysz [5] was adopted for the preparation of $M[Mn(CO)_5]$ (M = Li or Na). Both carbonylate salts were prepared and used as 0.019 *M* THF solutions. The concentration of the solution is based on the assumption of complete reduction of $Mn_2(CO)_{10}$ (0.15 g, 0.38 mmol, 40 ml of THF). Sodium pentacarbonylmanganate(1 −) was also prepared by reduction of a THF solution of $Mn_2(CO)_{10}$ with 1% sodium amalgam and used as a 0.019 *M* THF solution. The method of Wrighton was employed for the synthesis of $PPN[Mn(CO)_5]$ [3].

Preparation of $M[Mn(CO)_4DF]$ (1)

All of the following preparative reactions were monitored by IR spectroscopy by following the disappearance of the ν(CO) absorptions of $[Mn(CO)_5]^-$ (e.g., at 1898 (vs) and 1863 (vs) cm^{-1} when M = Na [6]).

(i) $Li[Mn(CO)_4DF]$ (1a). In a quartz Schlenk tube, DF (0.11 g, 0.76 mmol) and 40 ml of a 0.019 M THF solution of $Li[Mn(CO)_5]$ (0.76 mmol) are combined, placed in the Rayonet photochemical reactor, and irradiated for 4–5 h or until the reaction is complete as monitored by IR spectroscopy. The bright yellow solution is transferred from the quartz vessel into another Schlenk tube where the solvent is

removed under vacuum to give an orange oil. The orange oil is further purified by dissolution in CH_2Cl_2 and addition of hexane. After the reaction mixture is kept for approximately 24 h at 10°C, a yellow solid containing THF precipitates: IR (THF) ν(CO) 2026 (m), 1936 (vs), 1889 (s), 1685 (w), 1633 (m) cm^{-1}; ^1H NMR (acetone-d_6) δ 3.63 (m, THF), 3.49 (s, Me), 2.62 (s, CH), 1.79 (m, THF).

*(ii) Na[Mn(CO)$_4$DF] (**1b**).* The title complex is prepared in a manner analogous to that described above for Li[Mn(CO)$_4$DF] (**1a**) by using DF (0.11 g) and 40 ml of a 0.019 *M* solution of Na[Mn(CO)$_5$]. After the reaction is complete, **1b** is isolated as a yellow oil by removal of THF. It can be further purified by dissolving the yellow oil in CH_2Cl_2 and adding a layer of hexane. After this mixture is stored at 10°C for at least 24 h, a yellow solid precipitates and is isolated by decanting away the solvent. After drying under vacuum the product still contains THF: IR (THF) ν(CO) 2023 (m), 1934 (s), 1888 (s), 1688 (w), 1650 (w) cm^{-1}; ^1H NMR (acetone-d_6) δ 3.63 (THF), 3.47 (s, Me), 2.66 (s, CH), 1.79 (m, THF).

*(iii) PPN[Mn(CO)$_4$DF] (**1c**).* The title complex was prepared by two methods. In the first, PPN[Mn(CO)$_5$] (0.56 g, 0.76 mmol) and DF (0.11 g, 0.76 mmol) are dissolved in 40 ml of THF, and the resulting solution is placed in a quartz vessel and irradiated for 4–6 h or until the reaction is complete. The THF solution of the product is concentrated to approximately 2 ml, and hexane is added to induce precipitation, which takes place overnight at 10°C. A yellow solid isolated in this manner (0.43 g, 67%) can be recrystallized from CH_2Cl_2/Et_2O to give dull yellow crystals.

The second method consists of metathesis between either **1a** or **1b** and [PPN]Cl. Generally, an equimolar (0.76 mmol) mixture of the appropriate lithium or sodium salt of the manganate complex and [PPN]Cl is stirred in 40 ml of THF for 1 h. The solution is filtered to remove the LiCl or NaCl, and the filtrate is collected. It is then worked-up as described above: IR (THF) ν(CO) 2018 (m), 1931 (vs), 1981 (sh), 1877 (s), 1685 (m) cm^{-1}; ^1H NMR (acetone-d_6) δ 7.7–7.4 (m, Ph), 3.51 (s, Me), 2.63 (s, CH); $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 177.8 (CO_2), 140–133 (Ph), 49.9 (Me), 32.7 (CH). Anal. Found: C, 65.06; H, 4.21. $C_{46}H_{38}MnNO_8P_2$ calcd.: C, 65.02; H, 4.51%.

*Preparation of M[Mn(CO)$_4$DM] (**2**)*

As in the synthesis of **1**, all reactions were monitored by IR spectroscopy.

*(i) Li[Mn(CO)$_4$DM] (**2a**).* This reaction is conducted similarly to that for the preparation of **1a**, using DM (0.095 ml, 1.150 g/ml, 0.76 mmol) and 40 ml of 0.019 *M* THF solution of Li[Mn(CO)$_5$] (0.76 mmol). In the ensuing workup, the orange oil product is dissolved in minimum CH_2Cl_2, and to this solution is added hexane. The mixture is kept for several days at 10°C, during which time the product goes into CH_2Cl_2/hexane, leaving an oil residue, which is discarded. The solution is evaporated to dryness to afford **2a** as a yellow powder containing THF: IR (THF) ν(CO) 2032 (m), 1938 (vs), 1903 (s), 1670 (m) cm^{-1}; ^1H NMR (acetone-d_6) δ 3.63 (m, THF), 3.56 (s, Me), 2.37 (s, CH), 1.79 (m, THF).

*(ii) Na[Mn(CO)$_4$DM] (**2b**).* The procedure is essentially identical with that for **1b**, except that DM (0.095 ml, 1.150 g/ml, 0.76 mmol) is used in place of DF. The product is isolated as a yellow solid that contains THF: IR (THF) ν(CO) 2026 (m), 1935 (s), 1923 (s), 1899 (s), 1692 (m) cm^{-1}; ^1H NMR (acetone-d_6) δ 3.63 (m, THF), 3.58 (s, Me), 2.33 (s, CH), 1.79 (m, THF).

(iii) PPN[Mn(CO)$_4$DM] (2c). As for **1c**, two synthetic methods were employed In the photochemical one, **2c** is isolated in 62% yield (0.40 g) by irradiation of 40 ml of a THF solution of PPN[Mn(CO)$_5$] (0.56 g, 0.76 mmol) and DM (0.095 ml, 1.150 g/ml, 0.76 mmol) for 4–6 h. Unlike **1c**, the yellow solid **2c** could not be recrystallized. In the metathesis method, the procedure is strictly analogous to that for **1c**. Spectroscopic data for **2c**: IR (THF) ν(CO) 2020 (m), 1934 (s), 1909 (m), 1875 (s), 1717 (w) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 7.7–7.6 (Ph), 3.53 (s, Me), 2.21 (s, CH); ^{13}C{^{1}H} NMR (acetone-d_6) δ 179.5 (CO_2), 140–130 (Ph), 49.9 (Me), 32.4 (CH). Anal. Found: C, 64.65; H, 4.16. $C_{46}H_{38}MnNO_8P_2$ calcd.: C, 65.02; H, 4.51%.

Reactions of M[Mn(CO)$_4$DF] (1) and M[Mn(CO)$_4$DM] (2)

All reactions were carried out in a 25–50 ml round-bottom flask equipped with a side-arm, stir bar, and a condenser. The reactions were monitored by IR and ^{1}H NMR spectroscopies. When decomposition products begin to hinder ^{1}H NMR measurements, 2–5 ml of the reaction solution is syringed out and added to an equimolar amount of [PPN]Cl. The mixture is stirred, and the resulting precipitate is allowed to settle. The solution is then transferred to another flask, evaporated to dryness, and the residue (**1c** or **2c**) is dissolved in acetone-d_6 for a ^{1}H NMR measurement.

(i) Isomerization of DM to DF. In a typical reaction, a THF solution (20 ml) of the manganate complex **1** or **2** (0.38 mmol) and DM (0.095 ml, 0.76 mmol) is maintained at reflux temperature for 2–4 days. For **1a**, **1b**, **2a**, and **2b**, the reaction mixture is treated with [PPN]Cl before ^{1}H NMR analysis. Because of the paramagnetic nature of decomposition products, quantitative analysis of these reaction mixtures was not attempted.

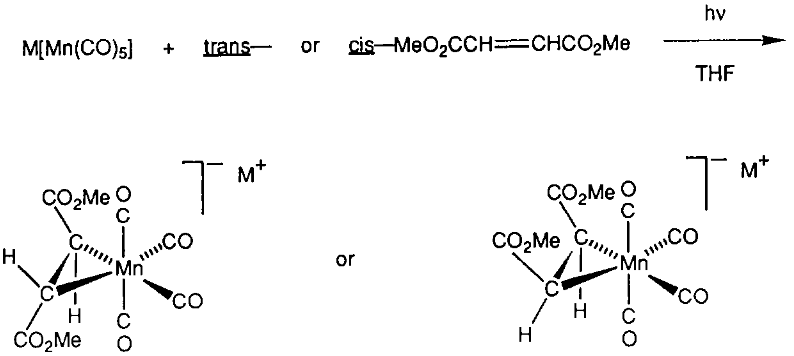
(ii) Olefin exchange reactions. In a representative reaction, 15 ml of a 0.019 *M* THF solution of **1a**, **1b**, or **1c** (0.28 mmol) and 0.070 ml of DM (0.56 mmol) are combined in a Schlenk flask and heated at ca. 50°C. The reaction is monitored by IR and ^{1}H NMR spectroscopies.

(iii) Isomerization of complexes. Typically, 15 ml of a 0.019 *M* THF solution of **2a**, **2b**, or **2c** is heated at ca. 55°C as the reaction is monitored by IR and ^{1}H NMR spectroscopies.

Results and discussion

Preparation and characterization of M[Mn(CO)$_4$DF] (1) and M[Mn(CO)$_4$DM] (2)

Salts of [Mn(CO)$_5$]$^-$ react with the activated olefins DF and DM under photolytic conditions in THF solution to give the monosubstituted complexes M[Mn(CO)$_4$DF] (**1**) and M[Mn(CO)$_4$DM] (**2**), respectively (eq. 1). In this manner were prepared the manganate compounds **1** and **2** where M = Li (**1a**, **2a**), Na (**1b**, **2b**), and $(PPh_3)_2N$ (PPN) (**1c**, **2c**). The PPN$^+$ salts of **1** and **2** can also be synthesized by the metathesis reactions of **1a** or **1b** and **2a** or **2b**, respectively, with [PPN]Cl in THF. Only complexes **1c** and **2c** could be prepared analytically pure. They were isolated as yellow solids, which decompose very slowly over several months when stored at ambient temperature. The Li$^+$ and Na$^+$ salts of **1** and **2** were obtained as air-sensitive yellow solids, which can be kept intact for long periods of time under Ar at 0°C. Their ^{1}H NMR spectra show the presence of



1 2 (I)

cation-coordinated THF even after prolonged drying under vacuum. Although the analytical data of **1a**, **1b**, **2a**, and **2b** were not satisfactory because of a variable amount of THF present, the IR and ^{1}H NMR spectra were clean and matched extremely well those of **1c** and **2c**, thus establishing the identity of the manganate anions therein.

Spectroscopic data for **1** and **2**, given in the Experimental section, are in complete accord with the proposed formulations. In the IR metal-carbonyl ν(CO) region, three or four bands are observed at 2032–1875 cm^{-1} with medium to very strong intensity. In addition, two and one carboxylate ν(CO) absorptions are generally noted for complexes **1** and **2**, respectively, at 1717–1633 cm^{-1} with weak to medium intensity. The bands at 2032–1875 cm^{-1} occur at higher energy than those of the corresponding M[Mn(CO)$_5$] [3,6]. A similar shift was noted previously for Na[Co(CO)$_3$DF] and Na[Co(CO)$_3$DM] compared to Na[Co(CO)$_4$] [7]. It indicates that the olefins DF and DM are superior π-acceptor ligands, which compete favourably with CO for π electrons of the metal. In fact, the values of ν(CO) for **1** and **2** are unrealistically high for manganese(I –) compounds [3,6]. It appears that a better formulation of these complexes is as manganacyclopropane species, with the metal being formally manganese(I). This bonding description is supported by the observed shift to lower energy of the carboxylate ν(CO) bands of DF and DM upon complexation to manganese in **1** and **2** (ν(CO) 1731 (m) and 1740 (m), 1733 (m) cm^{-1} for free DF and DM, respectively).

The number of metal-carbonyl ν(CO) bands occurring in the IR spectra of **1** and **2** (three or four) does not unambiguously distinguish between axially- (approximately C_{3v}) and equatorially-substituted (C_{2v}) trigonal-bipyramidal structures for **1** and **2**. This is because for the former structure the degeneracy of the *E* mode (in C_{3v}) will most likely be removed owing to axial perturbation by the olefin. Thus, in each case, four absorption bands are expected [8–10]. A number of related iron(0) complexes Fe(CO)$_4$(olefin), including Fe(CO)$_4$(DF) and Fe(CO)$_4$(DM), have been reported also to exhibit three or four metal-carbonyl ν(CO) bands in their IR spectra [11]. X-ray crystallographic analyses of several Fe(CO)$_4$(olefin) complexes, including Fe(CO)$_4$(fumaric acid) [12], have revealed that the olefin is positioned equatorially in an essentially parallel arrangement [13]. This corresponds to a distorted *cis*-Fe(CO)$_4$(X)$_2$ octahedral structure, assuming metallacyclopropane formalism. The same geometry is proposed for complexes **1** and **2**.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **1** and **2** indicate strong interaction between the manganese and each of the olefins, in agreement with the IR data. Thus, proton resonances of the CH groups of **1** and **2** occur at δ 2.66–2.62 and 2.37–2.21, respectively, at considerably higher fields than the corresponding resonances of the free olefin (δ 6.84 and 6.38 [11]). Somewhat smaller upfield shifts for the CH protons were noted earlier for $Na[Co(CO)_3DM]$ (δ 3.20) [7] and for $Fe(CO)_4(DF)$ (δ 3.68) and $Fe(CO)_4(DM)$ δ 3.64) [11]. By contrast, the position of the signal of the Me protons changes much less upon coordination of the olefin (e.g., δ 3.80 for free DF [11], δ 3.51–3.47 for **1**), as is to be expected. All of the ^1H NMR spectra show only one CH and one Me resonance, indicating that the olefin is symmetrically bonded to the manganese and that coordination of the counterion does not disturb this symmetry. It was noted previously for $Na[Co(CO)_3DM]$ and $Na[Co(CO)_2(DF)_2]$ that a doubling of signals occurs for the aforementioned groups, but only in the less polar solvents CD_2Cl_2, $CDCl_3$, and THF-d_8 [7]. The use of polar acetone-d_6 in this study is not expected to result in a similar behaviour.

The resonances of the CH carbons in the $^{13}C\{^1H\}$ NMR spectra of **1c** and **2c** occur at δ 32.7 and 32.4, respectively. These chemical shifts correspond to δ 133.5 (DF) [14] and 130.1 (DM) [15] for the free ligands, again a large upfield change upon complex formation. The magnitude of the observed upfield shifts of the proton and carbon resonances of DF and DM upon formation of **1** and **2** points to a substantial amount of metal-to-olefin π bonding and is consistent with the proposed manganacyclopropane formulation for these complexes.

Catalyzed isomerization of DM to DF

The isomerization of DM to DF was observed during an investigation of the synthesis and reactivity of complexes **1** and **2**. Interestingly, this isomerization is catalyzed by the Li^+ and Na^+ salts of the manganate anions, **1a**, **1b**, **2a**, and **2b**, but not by the PPN^+ salts, **1c** and **2c**. It was of interest to investigate the role of the counterion and possibly to elucidate the mechanism of this process. A quantitative investigation of the isomerization was precluded by the slow rate of the reaction; at room temperature, several weeks are required to completely convert DM to DF. In an attempt to increase the rate, the reactions were carried out at elevated temperatures (45 to 68°C). Unfortunately, although the isomerization proceeds faster, complexes **1** and **2** start to decompose at these temperatures. For example, in THF at reflux, complete isomerization of a twofold excess of DM by **1a** or **2a** occurs in 48 h. The manganate complexes, however, are substantially destroyed. The decomposition products, which could not be identified, hindered spectroscopic measurements which were necessary even for a semiquantitative investigation of this system. Despite these difficulties, it was possible to carry out a qualitative study of the conversion of DM to DF by examining the relative rate and the effect of the counterion on the isomerization itself and on several closely related reactions.

From the experimental standpoint, it was necessary to monitor the concentrations of **1** and **2** as well as of free DF and DM during the reaction. Although IR spectroscopy proved qualitatively useful in distinguishing between the isomeric

Table 1

Results of the isomerization experiments of DM to DF by complexes **1** and **2** in THF at reflux temperature

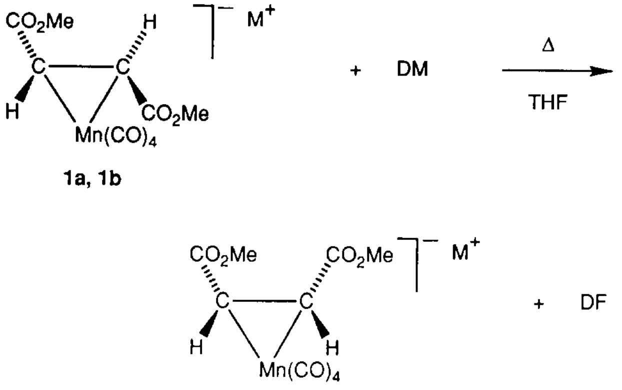
Reactants	Results
1a, DM	After 2 days complete isomerization of free DM to DF occurred. Some decomposition of **1a** also took place.
2a, DM	After 2 days complete isomerization of free DM to DF occurred along with isomerization of **2a** to **1a**. Some decomposition also took place.
1b, DM	After 4 days complete isomerization of DM to DF occurred. Some decomposition of **1b** also took place.
2b, DM	After 4 days isomerization of DM to DF occurred along with isomerization of **2b** to **1b**. Some decomposition also took place
1c, DM	After 4 days there was no change except for a small amount of decomposition of **1c**.
2c, DM	After 4 days no isomerization of DM to DF occurred. Isomerization of **2c** to **1c** and some decomposition took place.

complexes **1** and **2** (but not between free DF and DM in these mixtures), ^{1}H NMR spectroscopy provided better quantitative data. Because of gradual decomposition of the manganate complexes at the temperatures of these experiments, considerable broadening of the NMR signals was noted as reaction proceeded. To make measurements possible, **1a**/**2a** and **1b**/**2b** present in solution were converted to the corresponding PPN$^+$ salts **1c**/**2c**, which were then readily analyzed by ^{1}H NMR spectroscopy. Concentrations of free DF and DM were determined along with those of **1c** and **2c** by this method.

In planning a series of meaningful experiments to learn more about the isomerization of DM to DF by **1** or **2**, two general mechanistic possibilities were considered. The actual isomerization could occur (a) in the coordination sphere or (b) outside the coordination sphere of the metal complex. If any pathway of type (a) is operative, then free DM must replace the DF in **1**, the resulting **2** must isomerize to **1**, and the DF in **1** must again be replaced with DM; the two processes—substitution and isomerization—are each required to occur no slower than the catalyzed isomerization of free olefin. If these conditions are not satisfied, then the isomerization proceeds by a pathway (b). To distinguish between pathways (a) and (b), studies were conducted of (i) catalyzed isomerization (by **1** and **2**) of DM to DF, (ii) olefin exchange reactions of **1** and **2**, and (iii) isomerization of complexes **1** and **2**.

(i) Isomerization of DM to DF. Table 1 provides a summary of results on the isomerization of DM to DF by the various complexes **1** and **2** in THF at reflux. Under comparable experimental conditions, no conversion occurs of DF to DM.

Two general observations are noteworthy. (a) The Li$^+$ salts of **1** and **2**, viz. **1a** and **2a**, are more effective catalysts for the isomerization than the corresponding Na$^+$ salts, **1b** and **2b**, while the PPN$^+$ salts, **1c** and **2c**, are completely ineffective. However, **2c** undergoes conversion to **1c** (entry 6). (b) Use of **2a** and **2b** leads not only to the isomerization of free DM to DF, but also to the isomerization of **2a** to **1a** and **2b** to **1b** (entries 2 and 4). A discussion of these results is deferred until section (iv) in order to consider other relevant experiments presented in (ii) and (iii).



1a, 1b

2a, 2b

(2)

(ii) Olefin exchange reactions. Substitution of DF in each of **1a**, **1b**, and **1c** by DM was investigated in THF solution at 45–50°C (eq. 2). The results of these experiments are presented in Table 2.

The first two entries summarize the reactions of **1a** with DM. In both cases, substitution reaches completion before any significant decomposition is noted. Under the conditions employed, which are less forcing than those for experiment 1 in Table 1, no isomerization of **2a** to **1a** is observed. To confirm this finding, two control experiments were conducted by heating a solution of **2a** and free DM. The results, shown as entries 3 and 4 in Table 2, indicate that although some decomposition occurs, neither **2a** nor free DM undergoes isomerization. On going from the Li^+ to the Na^+ salt of **1** (i.e. from **1a** to **1b**, entry 5), olefin exchange also occurs but the rate of substitution is slower, and significant decomposition takes place before complete conversion to **2b** is realized. The PPN^+ salt, **1c**, does not appear to undergo olefin exchange with DM.

It is of interest that the Li^+ salt **1a**, which is a more effective catalyst for the isomerization of DM to DF than the Na^+ salt **1b**, also exchanges olefin at a faster rate. The observed reactivity order in substitution, Na^+ salt $\gg$ PPN^+ salt, reflects the same dependence on counterion as that of $M[Co(CO)_4]$ [2] and $M[HFe(CO)_4]$ [16]. Accordingly, neither $PPN[Co(CO)_4]$ nor $PPN[HFe(CO)_4]$ undergoes ligand exchange; however, the Na^+ salts of both of these complexes readily participate in

Table 2

Substitution of DM in complexes **1**

Reactants	[Mn complex] (*M*)	[DM] (*M*)	Temp. (°C)	No. of days	Results
1a, DM	0.019	0.037	47	7	Formation of **2a** complete by IR
1a, DM	0.019	0.19	50	3	Formation of **2a** complete by IR
2a, DM	0.019	0.037	47	8	No change except some decomposition
2a, DM	0.019	0.19	50	6	No change except some decomposition
1b, DM	0.025	0.05	45	20	1:1 **1b**/**2b** by ^1H NMR
1c, DM	0.019	0.038	45	11	No change except some decomposition

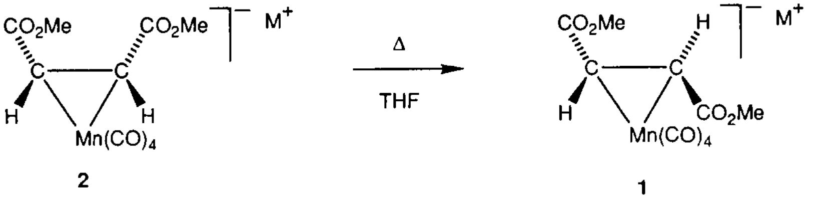
Table 3

Isomerization of **2** to **1**

Complex	Concentration (M)	Temp. (°C)	No. of days	Results
2a	0.026	55	9	2:1 **1a**/**2a** by ^{1}H NMR spectroscopy
2b	0.026	55	13	1.4:1 **1b**/**2b** by ^{1}H NMR spectroscopy
2c	0.019	45	8	4:1 **1c**/**2c** by ^{1}H NMR spectroscopy

substitution reactions. This difference in reactivity has been attributed to ion-pairing phenomena, with the small Na^+ ion—and particularly the Li^+ ion—interacting strongly with the carbonylmetallate ion and facilitating ligand dissociation [17]. Although it has not been established in this study whether the exchange reactions of **1** with DM follow a dissociative or an associative mechanism, the former is considered to be much more likely from the observed reactivity dependence on counterion. Ligand exchange reactions of other carbonylmetallate systems have been shown to follow dissociative mechanisms [17]. In addition to the foregoing, we cannot dismiss the possibility that the actual ligand exchange occurs in 17-electron neutral species derived from **1a** and **1b** by one-electron oxidation with appropriate decomposition products present in the reaction mixture.

(iii) Isomerization of complexes. The isomerization of the maleato complexes **2a**, **2b**, and **2c** to the corresponding fumarato complexes **1** in THF solution at 45–55°C (eq. 3) was followed by ^{1}H NMR spectroscopy. The results are given in Table 3. Under similar conditions, there is no observable reverse reaction, i.e. of **1** to **2**.

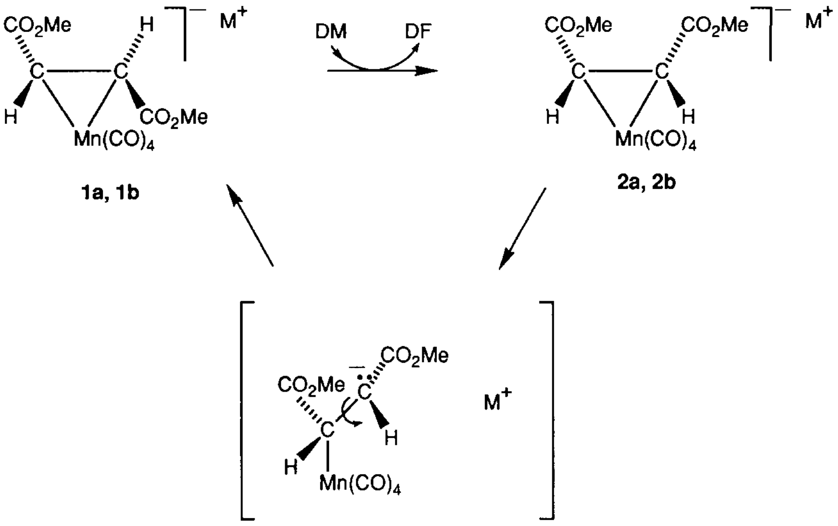


(3)

All three complexes **2a**, **2b**, and **2c** undergo isomerization. Since the isomerization is very slow, temperatures somewhat higher than those for the olefin exchange reactions were used for **2a** and **2b**. Also, decomposition of the complexes necessitated termination of the experiments before complete isomerization occurred. The isomerization reaction of **2c** proceeds at somewhat lower temperature and at a faster rate than that of **2a** and **2b**. This may in part be due to the higher solubility of **1c** compared to **2c** providing a driving force. The difference in solubility observed for the PPN^+ fumarate and maleate complexes is not apparent for the Li^+ and Na^+ counterparts.

It is proposed that the isomerization proceeds by slippage of the η^2-olefin–manganese bond to give an alkyl-manganese complex, in which the negative charge on the β-carbon atom of the alkyl ligand receives stabilization by the adjacent ester group (cf. Scheme 1). Rotation about the CH–CH bond and reverse of the slippage lead to the formation of the fumarato complex, **1**.

(iv) Mechanism of the isomerization of DM to DF. The foregoing results on reactions of **1** and **2** are consistent with pathway (a) for the catalyzed isomerization



Scheme 1.

of DM to DF. This pathway, consisting of the two reactions investigated—olefin exchange and complex isomerization—is depicted in Scheme 1.

An important requirement for the catalysis in point is that complexes **1** undergo olefin exchange. It is seen in Table 1 that the Li^+ and Na^+ salts of the fumarate complex, viz. **1a** and **1b**, respectively, which exchange ligated DF with free DM (Table 2), catalyze the isomerization of DM to DF. By contrast, the corresponding PPN^+ salt **1c**, which does not undergo such an exchange (Table 2), is devoid of catalytic activity (Table 1).

The second essential requirement for the catalysis of the conversion of DM to DF is that complexes **2** undergo isomerization to **1**. This has been confirmed for the three maleate complexes **2a**, **2b**, and **2c** (Table 3). For **2a** and **2b**, the isomerization requires somewhat higher temperatures and longer reaction times than the corresponding olefin exchange of **1a** and **1b** (but not than the catalyzed isomerization of DM to DF (cf. Table 1), which is consistent with pathway (a)). Thus it is the slow step of the catalytic cycle in Scheme 1.

Because of the qualitative nature of this study, the role of the counterion could not be fully elucidated. The PPN^+ salts **1c** and **2c** do not catalyze the isomerization of DM to DF since they do not undergo olefin exchange. As for comparisons between the Li^+ salts **1a** and **2a** and the Na^+ salts **1b** and **2b**, the former give cleaner reactions in shorter times. The reasons for this behaviour are not entirely obvious, but a possible explanation lies in the greater covalency of the M–O bonds for lithium, which may stabilize the alkyl-manganese intermediate in the isomerization of **2** to **1**. However, because of the observed isomerization of the PPN^+ salt **2c** to **1c**, such an interaction is not the only important contributing factor.

The isomerization of dialkyl maleates to the corresponding fumarates is a well studied reaction that is catalyzed by many reagents, most of which are general catalysts for *cis–trans* isomerization of olefins [18]. Many examples of *cis–trans* isomerization catalyzed by metal complexes are known as well, including several of the conversion of DM to DF [19–21]. Maleate-to-fumarate isomerization was also observed in the synthesis of $Na[Co(CO)_2(DF)_2]$ from $Na[Co(CO)_4]$ and excess DM in THF at reflux, but was not investigated with respect to mechanism [7].

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