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Note

Reaction of [*fac*-$(CO)_3(dppe)Mn(OH_2)]BF_4$ with ^{13}CO and conversion of the resulting tetracarbonyl to labeled isocyanato complexes

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Abstract

When ^{13}CO is bubbled into a CH_2Cl_2 solution of [*fac*-$(CO)_3(dppe)Mn(OH_2)]BF_4$ (dppe = $Ph_2PCH_2CH_2PPh_2$), the aqua ligand is replaced by the CO to give the tetracarbonyl, $[(CO)_3(^{13}CO)(dppe)Mn]BF_4$ (**1**) in which the labeled CO appears exclusively at the site originally occupied by the aqua ligand. Treatment of this aqua complex with NaN_3 leads to an approximate 50:50 mixture of isocyanates corresponding to attack, with equal probability, at either the labeled CO or its axial partner. Neither of the two CO groups *trans* to the P atoms in the tetracarbonyl are affected. © 2000 Published by Elsevier Science S.A. All rights reserved.

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1. Introduction

The octahedral Mn(I) complex [*fac*-$(CO)_3(dppe)$-$Mn(OH_2)]BF_4$ is readily prepared by a simple, high-yield two step procedure [1].

$$Mn_2(CO)_{10} + \text{dppe} + \text{1-pentanol} \rightarrow fac\text{-}(CO)_3(\text{dppe})MnH \quad (1)$$

$$fac\text{-}(CO)_3(\text{dppe})MnH + HBF_4 \rightarrow [fac\text{-}(CO)_3(\text{dppe})Mn(OH_2)]BF_4 \quad (2)$$

Owing to the facial geometry and the presence of the chelating phosphorus atoms, the aqua ligand must occupy an axial position *trans* to CO. We have shown that the aqua ligand in this complex is readily replaced at room temperature by a wide variety of neutral as well as anionic ligands to give the corresponding complexes with functional groups σ-bonded to the Mn [2]. The chemistry of some such functional groups has proven to be substantially different from that of the corresponding functional groups in traditional organic chemistry, obviously reflecting the influence of the transition metal [3,4]. The aqua ligand in [*fac*-$(CO)_3(dppe)Mn(OH_2)]BF_4$ is readily exchanged with D_2O with the retention of facial geometry so that even were the reaction to proceed by dissociation of the ligand, the new ligand occupies the position of the departing ligand. However, when the aqua ligand is replaced by CO, the resulting tetracarbonyl complex, $[(CO)_4(dppe)Mn]BF_4$, contains two different geometric sets of COs, one set of two, each *trans* to a P atom, and the other set of two axial COs *trans* to each other. It might be assumed that when an azido group attacks a carbonyl of the tetracarbonyl complex, either of the two now essentially symmetry equivalent axial COs would be attacked to give the identical isocyanato complex provided scrambling does not occur. In order to test this assumption, several experiments with ^{13}CO were conducted and are reported herein.

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2. Experimental

[*fac*-$(CO)_3$(dppe)$Mn(OH_2)$]BF_4 was prepared from *fac*-$(CO)_3$(dppe)MnH as described in the literature [1]. *fac*-$(CO)_3$ (dppe)Mn(NCO) was also prepared in accordance with the literature [5]. ^{13}CO (99%) was purchased from Aldrich. Solvents were used as received.

2.1. Preparation of [$(CO)_4$(dppe)Mn]BF_4

This tetracarbonyl was previously prepared from *fac*-$(CO)_3$(dppe)MnH without, however, isolating the aqua intermediate [6]. In this procedure, the pure aqua complex, [*fac*-$(CO)_3$(dppe)$Mn(OH_2)$]BF_4 (0.138 g, 0.215 mmol), was placed in a round bottomed flask and 20 ml of CH_2Cl_2 was added and the solution stirred. A very quick evacuation was performed and a needle was then inserted and CO was bubbled through the solution for approximately 3 min. The solution was stirred overnight (ca. 18 h) to give [$(CO)_4$(dppe)Mn]BF_4. Isolation techniques were the same as those previously reported and the spectral data match those previously reported [5,6].

Table 1
Mass spectroscopy results (*m*/*z*) [a]

Parent compound	Fragment	^{13}C incorporation
	C_{29}, [$(CO)_3$(dppe)Mn]$^+$, 537	*Ratio 538:537*
[$(CO)_4$(dppe)Mn]BF_4	Theory	0.32
	Observed	1.2
[$(CO)_3(^{13}CO)$(dppe)-Mn]BF_4 (**1**)	Observed	1.5
	C_{27}, [(dppe)Mn(NCO)]$^+$, 495	*Ratio 496:495*
fac-$(CO)_3$(dppe)-Mn(NCO)	Theory	0.30
	Observed	0.33
Mixture of *fac*-$(CO)_3$(dppe)-Mn($N^{13}CO$) (**2**), $(CO)_2(^{13}CO)$(dppe)-Mn(NCO) (**3**)	Theory: 100% ($N^{13}CO$)	∞ (no 495)
	50% ($N^{13}CO$), 50% (NCO)	1.30
	25% ($N^{13}CO$), 75% (NCO)	0.63
	Observed	1.28

[a] All ratios include appropriate contributions from the natural abundance of ^{13}C in the fragments. Theoretical ratios were calculated based on Table 2.2 of Ref. [7].

2.2. Preparation of [$(CO)_3(^{13}CO)$(dppe)Mn]BF_4 (1)

Compound **1** was prepared from [*fac*-$(CO)_3$(dppe)$Mn(OH_2)$]BF_4 according to the directions given for [$(CO)_4$(dppe)Mn]BF_4 (see Section 2.1) with the following exceptions: ^{13}CO was bubbled through a solution of the aqua complex (0.152 g, 0.237 mmol) for ca. 1 min and the solution was stirred for ca. 24 h. Crystalline [$(CO)_3(^{13}CO)$(dppe)Mn]BF_4 (**1**) (0.123 g, 0.189 mmol), was obtained from a CH_2Cl_2–hexane mixture.

2.3. Stirring [$(CO)_4$(dppe)Mn]BF_4 with ^{13}CO

The tetracarbonyl, [$(CO)_4$(dppe)Mn]BF_4 (0.107 g), was placed in a round bottomed flask and approximately 20 ml of CH_2Cl_2 was added and the solution was stirred. A very quick evacuation was performed and a needle was then inserted and ^{13}CO was bubbled through the solution for ca. 1 min. The solution was stirred under the ^{13}CO and monitored by IR for a total of 4 days. There was no evidence of a reaction.

2.4. Reaction of [$(CO)_3(^{13}CO)$(dppe)Mn]BF_4 with NaN_3 to give labeled isocyanates

The reaction conditions were similar to the literature preparation for unlabeled *fac*-$(CO)_3$(dppe)Mn(NCO) [5]. [$(CO)_3(^{13}CO)$(dppe)Mn]BF_4 (0.103 g, 0.158 mmol) was dissolved in 20 ml of methanol and NaN_3 was added (0. 11 g, 0. 17 mmol). The mixture was stirred for 1 day. The solvent was removed by rotary evaporation and the resulting solids were extracted with benzene. The benzene solution was concentrated and hexane was added. On cooling yellow crystals (0.058 g) resulted.

2.5. Mass spectra

Mass spectra were recorded on a Kratos MS-25 high-performance mass spectrometer. Spectra of the unlabeled complexes, [$(CO)_4$(dppe)Mn]BF_4 and *fac*-$(CO)_3$(dppe)Mn(NCO), were used for comparison with the mass spectra of the products isolated in Sections 2.2 and 2.4. The relevant data are found in Table 1.

2.6. IR spectra

IR spectra were recorded on a Perkin–Elmer Spectrum One FTIR instrument employing 1.0 mm NaCl liquid cells. IR data for all reactions are found in Table 2. The Perkin–Elmer instrument was utilized to determined peak areas after a deconvolution program was employed to separate overlapping bands.

Table 2
Infrared spectra, ν (cm^{-1}) in CH_2Cl_2

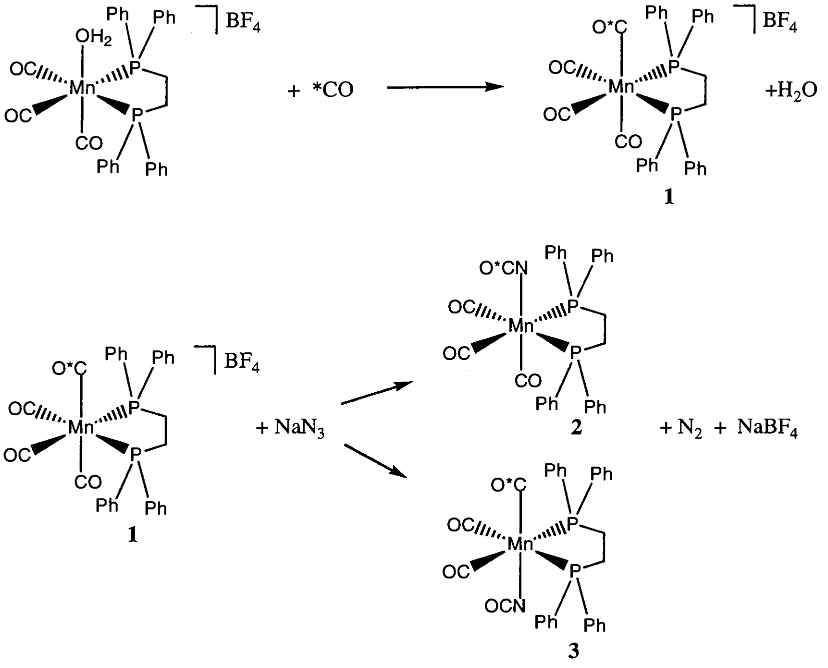
[(CO)$_4$(dppe)Mn]BF$_4$ [a]				
Carbonyl groups	2093 vs	2024 sh	2014 vs	1998 vs
*[(CO)$_3$(^{13}CO)(dppe)Mn]BF$_4$ (**1**)*				
Carbonyl groups	2081 vs	2023 sh	1996 vs	1985 vs
fac-(CO)$_3$(dppe)Mn(NCO) [b]				
NCO	2240s			
Carbonyl groups	2028 vs	1957 vs	1919 vs	
*Mixture of fac-(CO)$_3$(dppe)Mn(N^{13}CO) (**2**) and (CO)$_2$(^{13}CO)(dppe)Mn(NCO) (**3**)*				
				Area (%$T\times cm^{-1}$)
$N^{13}CO$	2182 s			−2156
NCO	2240 s			−2165
Carbonyl groups	2026 vs	1956 vs	1919 s	1881 s

[a] The IR data for $[(CO)_4(dppe)Mn]BF_4$ have been reported previously [5].

[b] Complete IR data in C_6H_6 for *fac*-$(CO)_3(dppe)Mn(NCO)$ [5] and in CH_2Cl_2 for the carbonyl groups have been reported previously [9].

3. Results and discussion

When unlabelled tetracarbonyl is prepared by our standard procedure and then treated with ^{13}CO, no incorporation of the label is observed indicating that once formed the monolabeled tetracarbonyl will not undergo further exchange with ligated COs, i.e. no complex with multi-labeled COs need be considered. When the labeled tetracarbonyl **1** (Scheme 1) is prepared and treated with NaN_3 to produce the corresponding isocyanato complex, the question arises as to which of the two sets of coordinated COs is attacked. The reaction of the azide with the CO proceeds via a pathway analogous to the Curtius rearrangement, where the CO originally attacked by the azide results in an isocyanato group in the same geometric position. If the attack were to occur exclusively on the labeled CO, at the position originally occupied by the aqua ligand, then 100% of the isocyanato group should be the labeled isocyanate **2** (Scheme 1), and no labeled COs should remain. However, if the attack of the azide were to occur equally on either of the axial COs then half of the isocyanato groups would contain the label and the other half of the label would still be on the axial CO; 50% of **2** and 50% of **3** (Scheme 1). If attack of N_3^- were on the equatorial COs of **1** (Scheme 1), the resulting isocyanato complex would have a *mer*-configuration, but this possibility need not be considered because only the *fac*-isomer is obtained. Another possibility should be mentioned. If during a dissociative



Scheme 1.

displacement of the aqua ligand, the three remaining COs somehow became equivalent before the fourth and labeled CO became ligated, then the isocyanato group formed subsequently would contain only one quarter of the label; 25% of **2**. Although the chelating phosphine would make such a pentacoordinate intermediate unlikely, it is a conceivable intermediate. The question then is what percentage of the NCO group is $N^{13}CO$? 100% if only the labeled CO is attacked; 50% if the labeled CO and its axial partner CO are equally attacked; or 25% if all four COs become equivalent before attack. In order to answer this question, infrared and mass spectra of the reaction products were obtained and the results are discussed below.

3.1. Mass spectra

The relevant mass spectra data are summarized in Table 1. None of the complexes exhibit a molecular ion ($M^{+\bullet}$) peak. All peak numbers are m/z values.

The spectrum of the non-labeled tetracarbonyl contains the peak 537, corresponding to the fragment $[(CO)_3(dppe)Mn]^+ = (M^{+\bullet} - CO)$. The 538:537 peak intensity ratio is 1.2 while the expected value for a C29 fragment is 0.32 [7]. This higher than expected ratio observed is due to contributions from the incorporation of hydrogen, i.e. $\{[(CO)_3(dppe)Mn]^+ + H\}$. The labeled tetracarbonyl **1** has a 538:537 peak intensity ratio of 1.5. This increase in the ratio from 1.2 to 1.5 indicates incorporation of ^{13}CO but a quantitative comparison is not possible owing to the $\{[(CO)_3(dppe)Mn]^+ + H]\}$ interference and the fact that we cannot determine which of the four COs is lost. Hence, attention was directed to the isocyanato spectra.

The pure, unlabelled isocyanate, *fac*-$(CO)_3(dppe)Mn(NCO)$, has the fragment peak 537, $[(CO)_3(dppe)Mn]^+ = (M^{+\bullet} - NCO)$, and again its 538:537 peak intensity ratio shows interference from $\{[(CO)_3(dppe)Mn]^+ + H]\}$ and accordingly this ratio is not useful. However, the fragment peak 495, $[(NCO)(dppe)Mn]^+ = (M^{+\bullet} - 3CO)$, is also observed for the unlabeled isocyanato complex and the 496:495 peak intensity ratio is consistent with the 496:495 peak intensity ratio for a C_{27} fragment. This ratio was used to obtain the quantitative information required to answer the question of what percentage of the NCO group is $N^{13}CO$ in the mixture of isocyanato complexes. The observed and theoretical ratios are shown in Table 1 and clearly indicate that an approximate 50:50 mixture of **2** and **3** are found in the reaction mixture. Therefore, we conclude that no ligand rearrangement occurs in the substitution of the aqua ligand in [*fac*-$(CO)_3(dppe)Mn(OH_2)]BF_4$ by CO and that the two axial COs in the resulting tetracarbonyl are indistinguishable in their reaction with the azide.

3.2. IR spectra

Comparison of the IR data (Table 2) of the unlabelled tetracarbonyl with the monolabeled tetracarbonyl **1** show that as expected, all of the CO stretching frequencies in **1** are shifted to lower frequencies by isotopic labeling.

The IR of the products from the reaction of the labeled tetracarbonyl **1** with NaN_3 clearly show stretches for both the NCO in **3** (2240 cm^{-1}) and $N^{13}CO$ in **2** (2182 cm^{-1}). If one assumes as a first-order approximation that the isotope effect is associated exclusively with $^{13}C{=}O$ in $N{=}^{13}C{=}O$ a shift to lower frequency of approximately 51 cm^{-1} is predicted. Similarly, if one assumes that the isotope effect is associated exclusively with $N{=}^{13}C$ in $N{=}^{13}C{=}O$ a shift to lower frequency of approximately 48 cm^{-1} is predicted [8]. The observed shift of 58 cm^{-1} is, therefore, not unreasonable. In order to quantify the relative amounts of **2** and **3**, a deconvolution was performed to eliminate the slight overlap of the peaks. The areas of the isocyanato bands were calculated and found to be very similar indicating a mixture of approximately 50% **2** and 50% **3**, a conclusion consistent with the mass spectral analysis.

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