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Rearrangement of cyclooctyne to 1,2-cyclooctadiene within the coordination sphere of $CpMn(CO)_2$

Siobhán M. Coughlan and Gilbert K. Yang

Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0744 (USA)

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Abstract

The synthesis of isomeric complexes of $CpMn(CO)_2(C_8H_{12})$ is reported. Reaction of $CpMn(CO)_2THF$ with cyclooctyne yields cyclooctyne complex **1** which has been characterized by ^1H and ^{13}C NMR and infrared spectroscopy. The alkyne carbons exhibit an unusual upfield shift upon coordination. The alkyne moiety in this complex is prone to rearrangement to allene complex **2** which has been characterized by ^1H and ^{13}C NMR and IR spectroscopy. Assignment of each resonance was achieved through 2D COSY NMR experiments. The isomerization of **1** to **2** is accelerated by passing **1** down a silica gel chromatography column. The presumed strain relief upon complexation of the strained alkyne to the metal center is not sufficient to prevent isomerization from occurring.

1. Introduction

A number of complexes of the type $[Mn(\eta^5\text{-}C_5H_4R)(CO)_2(alkyne)]$ have been prepared through the reaction of free alkynes with photochemically generated $CpMn(CO)_2$ [1–3]. Several examples have been documented where rearrangement of alkynes coordinated to manganese [3] and to other metals [4] occurs to give complexes containing η^2-allene or vinylidene ligands. Examples of stable complexes of strained η^2-cycloallenes have been reported by Jones *et al.* [5] and by Visser and Ramakers [6].

Strained alkenes and alkynes are known to be substantially stabilized by complexation to metal centers [7–9]. Complexes of cyclohexyne, cycloheptyne [8] and cyclooctyne [9] have been reported. If coordination of the strained alkyne is substantially favored over coordination of the isomeric allene, then isomerization of the alkyne to the allene might be prevented. In the hope of isolating a Mn-alkyne complex which is stable with respect to such isomerization, we have examined the reaction of a strained alkyne, cyclooctyne, with $CpMn(CO)_2$.

Correspondence to: Dr. G.K. Yang.

2. Results

Reaction of cyclooctyne with a THF solution of $CpMn(CO)_2THF$ at $-50°C$ resulted in slow disappearance of the characteristic red color of $CpMn(CO)_2THF$ and formation of an orange solution. Infrared spectra recorded during this reaction showed loss of the peaks at 1925 and 1845 cm^{-1} attributed to $CpMn(CO)_2(THF)$ and simultaneous growth of three new peaks at 1976, 1964 and 1908 cm^{-1} (THF). Removal of the solvent under reduced pressure yielded a yellow oil. Air-free flash chromatography (silica-60, hexanes) at room temperature yielded a fast moving band identified as $CpMn(CO)_3$ and a slower moving band from which a bright yellow crystalline product could be obtained (**2**). The complexity of both the ^1H and ^{13}C NMR spectra of **2** (Tables 1 and 2) suggested that the symmetry of the cyclooctyne ligand had been disrupted upon complexation to the metal center. Isomerization of the cyclooctyne ligand to an η^2-allene moiety would be consistent with these observations. Thus, **2** was identified as the η^2-1,2-cyclooctadiene complex of $CpMn(CO)_2$ (*vide infra*).

The pure product **2** displays two absorptions in the solution infrared spectrum at 1983 and 1930 cm^{-1} (hexanes) (Table 1) clearly indicating that the product initially observed in the reaction mixture had isomer-

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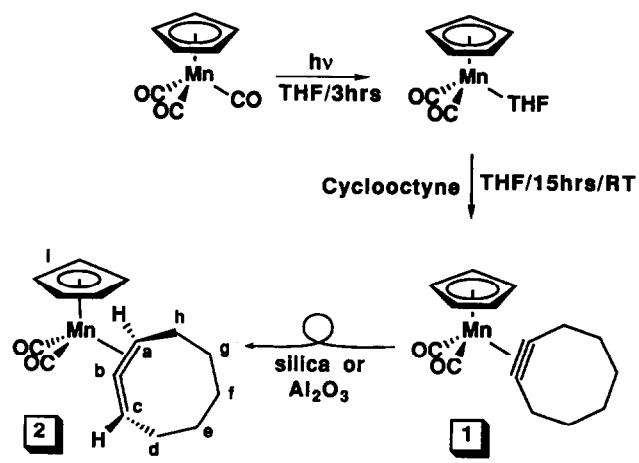
TABLE 1. ^{1}H NMR [a] and infrared [b] data for complexes **1** and **2** at 25°C

Compound	$\delta(^1H)$ppm			ν(CO or C≡C) cm^{-1}
	C_5H_5	CH	CH_2	
1	4.12		2.38(t, J = 5.9) 1.52–1.20(m, CH_2)	1976(m, C≡C) 1964(m, CO) 1908(s, CO)
2	3.98	5.92(q, J = 3.3, H_c) 2.62(m, H_a)	2.46(m, H_d, H_h) 2.19(m, H_d) 1.85(m, H_e, H_f) 1.62(m, H_e, H_g) 1.54(m, H_g) 0.77(m, H_f) 0.54(m, H_h)	1983(s, CO) 1930(s, CO)

[a] Benzene-d_6 solution. Referenced to δ(TMS) = 0.00 ppm. [b] Hexanes solution.

ized. The ^{1}H NMR spectrum (Table 1) exhibits a series of eight multiplets between 0.5 and 2.75 ppm, a very prominent quartet at 5.92 ppm assigned to the unbound allenic proton and an η^5-C_5H_5 resonance at 3.98 ppm.

The $^{13}C\{^1H\}$ NMR spectrum of **2** (Table 2) shows two distinct carbonyl resonances at 233.37 and 232.77 ppm. Two additional low field resonances at 158.97 and 118.8 ppm are observed. The high field region is complex, with six resonances between 38 and 25 ppm. The peaks in the ^{1}H and ^{13}C NMR spectra were assigned by ^{1}H-^{1}H 2D COSY and ^{1}H-^{13}C 2D COSY experiments. The carbon resonating at 158.97 ppm clearly has no protons attached to it and is assigned as the central allenic carbon (C_b), while the carbon at 118.8 ppm is strongly coupled to the free allenic proton resonating at 5.92 ppm and is assigned to this position (C_c). The resonance for the terminal allenic carbon bound to the metal center is observed at 28.28 ppm (C_a) and is strongly coupled to the proton resonating at 2.62 ppm. Consistent with the expectation that the chiral 1,2-cyclooctadiene ligand would render the carbonyl ligands inequivalent, two resonances assigned to carbonyl ligands are observed at ~ 233 ppm.



Scheme 1.

The reaction scheme illustrated in Scheme 1 is proposed for the formation of **2**. Substitution of THF from $CpMn(CO)_2THF$ by cyclooctyne yields the cyclooctyne

TABLE 2. $^{13}C\{^1H\}$ NMR data [a] for complexes **1** and **2** at 25°C recorded in benzene-d_6

Compound	$\delta(^{13}C)$ ppm						
	CO	C_5H_5	$C{\equiv}C$	$\Delta(\delta)$	$C{=}C{=}C$	$C{=}C{=}C$	CH_2
1	233.92	84.67	66.99	−27.01			30.17 29.70 29.07
2	233.37 232.77	85.40			158.97 C_b	118.80 C_c 28.28 C_a	37.64 C_h 36.47 C_d 33.09 C_g 29.44 C_f 26.14 C_e

[a] Referenced to δ(TMS) = 0.00 ppm.

complex **1**. Complex **1** then isomerizes on the silica column to yield the 1,2-cyclooctadiene complex **2** which was isolated in 34% yield. Such acid induced isomerizations have been reported for other metal–alkyne complexes [3,4].

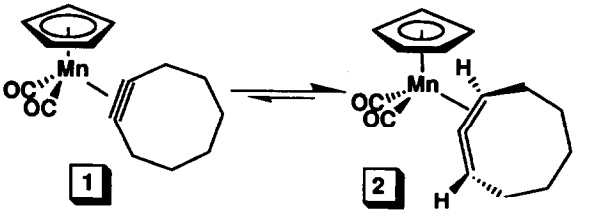
Several attempts were made to purify cyclooctyne complex **1** while avoiding isomerization to allene complex **2**. Room temperature chromatography of the crude product on silica, basic and acidic alumina were all found to yield allene complex **2** exclusively. Successful results were obtained by column chromatography of the crude product on grade III neutral alumina at −81°C (hexane). Although complete separation of cyclooctyne complex **1** from $CpMn(CO)_3$ was difficult to accomplish, we obtained samples of **1** which were sufficiently pure to obtain unambiguous spectroscopic identification of this product. The infrared spectrum of **1** in a solution of hexanes shows two strong absorptions attributed to the two CO stretching modes. The C≡C stretch of the complexed cyclooctyne ligand is seen at 1976 cm^{-1} in comparison to the C≡C stretch in free cyclooctyne at 2230 cm^{-1}. The coordinated cyclooctyne ligand shows an apparent triplet resonance in the ^1H NMR at 2.38 ppm assigned to the protons α to the alkyne functional group. The β and γ protons appear as a broad multiplet at ~ 1.3 ppm.

The $^{13}C\{^1H\}$ NMR spectrum shows equivalent alkyne carbons at 66.99 ppm and three resonances in the alkyl region. In the ^1H coupled ^{13}C NMR spectrum, the alkyne carbons remain a singlet, broadened slightly due to long range C–H coupling. This resonance appears in a region appropriate for alkyne complexes of $CpMn(CO)_2$. These complexes display negative "coordination shifts" ($\Delta(\delta)$) [10*] of the alkyne carbons, *i.e.* the resonance for the coordinated alkyne carbons appears at higher field than the resonance for the free alkyne. Other examples of negative coordination shifts have been seen in cationic metal alkyne complexes [11]. The coordination shift of the cyclooctyne alkyne carbons in **1** is −27.01 ppm.

3. Discussion

Upon coordination to the $CpMn(CO)_2$ moiety, the cyclooctyne ligand in **1** exhibits both an upfield coordination shift of the ^{13}C NMR resonance of the alkyne carbons and a small (~ 150 cm^{-1}) reduction in the C≡C stretching frequency. Chisholm has reported that such spectroscopic changes are observed in complexes where π-backbonding from a filled metal d-orbital to a vacant alkyne π^*-orbital plays only a minor role [4b]. Thus, donation from a filled alkyne π-orbital to a vacant metal orbital is the predominant cyclooctyne–metal bonding interaction in **1**.

The observation of complete isomerization of cyclooctyne complex **1** to allene complex **2** (eqn. (1)) illustrates that coordination of the metal center to the allene moiety is thermodynamically preferred over coordination to the alkyne moiety. From other reports it is evident that, where possible, $CpMn(CO)_2$(alkyne) complexes tend to rearrange to the corresponding allene complexes [3c]. This preference for the allenic structure may be attributed to destabilization of the 18-electron alkyne complexes of $CpMn(CO)_2$ through repulsive interaction of the alkyne $\pi_\perp$ orbital with a filled metal d-orbital [12*]. Since this repulsive interaction is not expected to be present in allene complexes of $CpMn(CO)_2$, the alkyne complex is expected to be destabilized relative to the allenic structure.



(1)

In the cyclooctyne system, we had hoped that strain relief would sufficiently stabilize the cyclooctyne ligand that rearrangement would not be favorable. However, both cyclooctyne and 1,2-cyclooctadiene are strained molecules with estimated strain energies of at least ~ 10 kcal mol^{-1}. Since the strain relief realized upon binding of the 1,2-cyclooctadiene ligand may be comparable to that realized upon binding of the cyclooctyne ligand, stabilization of the alkyne ligand may not be sufficient to overcome the thermodynamic preference towards rearrangement to the allene moiety.

4. Experimental section

4.1. General

All manipulations were carried out under a dry, oxygen-free nitrogen or argon atmosphere using standard vacuum-line or glovebox techniques. ^1H NMR and ^{13}C NMR spectra were recorded on either Bruker AC-250 or AM-360 spectrometers. The ^1H-^{13}C 2D COSY and ^1H-^1H 2D COSY spectra were recorded on the Bruker AM-360 spectrometer. Infrared (IR) spectra were recorded on a Perkin-Elmer IR-281 or IBM System 9000 FTIR spectrometer. Solvents were purified by standard methods and were distilled under nitrogen and used immediately. Irradiations were carried out in Pyrex vessels using a water-jacketed 450 W

* Reference number with asterisk indicates a note in the list of references.

Hanovia high-pressure mercury vapor lamp. Column chromatography was carried out either on silica gel-60 (E. Merck, 230–400 mesh) or neutral aluminum oxide (Aldrich, 50 mesh). Microanalysis was performed by Galbraith Laboratories, Knoxville, TN. Cyclooctyne was synthesized according to literature procedures [13].

4.2. Preparation of $CpMn(CO)_2$(1,2-cyclooctadiene) (2)

A solution of $CpMn(CO)_3$ (0.27 g, 1.34 mmol) in 250 ml of freshly distilled THF was irradiated at 0°C. Carbon monoxide was periodically removed under a vacuum. After 1 h, an IR spectrum of the reaction mixture showed a strong ν(CO) absorption at 1845 cm^{-1} for the THF complex, $CpMn(CO)_2$(THF) in addition to residual absorptions at 2029 and 1925 cm^{-1} for the unreacted $CpMn(CO)_3$. Further irradiation for another 2 h intensified the absorptions from $CpMn(CO)_2$THF relative to $CpMn(CO)_3$. Cyclooctyne (0.17 ml, 1.34 mmol) was added dropwise at room temperature to the solution of $CpMn(CO)_2$THF in THF. After 18 h of stirring, the deep orange solution was concentrated under reduced pressure and chromatographed on a silica gel column prepared with hexane. Elution with hexane afforded two fractions. These were in order, $CpMn(CO)_3$, and the complex **2** (ν(CO) 1983 and 1930 cm^{-1}). Yield of **2**: 130 mg (0.46 mmol, 34.1%). NMR data are given in Tables 1 and 2. Anal. Found: C, 63.38; H, 6.09. $C_{15}H_{17}MnO_2$ calc.: C, 63.38; H, 6.03%.

4.3. Preparation of $CpMn(CO)_2$(cyclooctyne) (1)

$CpMn(CO)_3$ (0.20 g, 1.00 mmol) was irradiated at −30°C in freshly distilled diethyl ether for 4.5 h. Carbon monoxide gas was removed at hourly intervals, while keeping the reaction solution as cold as possible. Cyclooctyne (0.09 g, 0.80 mmol) was vacuum transferred into the reaction solution and the resulting mixture was stirred for 18 h at −20°C. The ether solution was dried under a vacuum and the residue was triturated with hexane to extract the product. The crude product was chromatographed at −81°C on grade III neutral alumina eluted with hexanes. Fractions containing $CpMn(CO)_3$ were collected first, followed by fractions containing $CpMn(CO)_2$(cyclooctyne) (**1**). The solution infrared spectrum of **1** (hexanes) had characteristic bands at 1976, 1964 and 1908 cm^{-1}, with trace amounts of the starting material $CpMn(CO)_3$ present (ν(CO) 2029 and 1925 cm^{-1}). NMR data are given in Tables 1 and 2.

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