ment proceeds by a concerted 3,2 peroxyl radical mechanism. Furthermore, the transfer of chirality across the allyl system during rearrangement suggests a model for the rearrangement in acyclic peroxyls in which substituents on the allyl system occupy pseudoequatorial positions in an envelopelike transition-state structure. The proposed mechanism for rearrangement and the suggested transition-state structure are shown in Scheme I. Such a transition-state model suggests that the stereochemistry of the product stereogenic center should depend on the geometry of the double bonds in the reactant and product hydroperoxides.

The observed stereochemical course of the concerted 3,2 peroxyl radical rearrangement is of interest with regard to eicosanoid biosynthesis. Allyl and dienyl hydroperoxides are important intermediates in the arachidonic acid cascade, and the observation of highly stereoselective allyl hydroperoxide rearrangements suggests the possibility of such concerted rearrangements in the biosynthesis of these compounds.[14]

Acknowledgment. Supported by a grant from the NIH (HL 17921). P.H.D was supported by an NCI Fellowship (CA08282-02) and J.K.K. by an NIEHS Toxicology postdoctoral award (ES07031).

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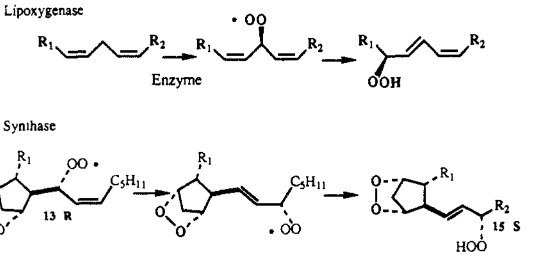
[14] The 3,2 peroxyl rearrangement can be proposed in the biosynthesis of lipoxygenase and prostaglandin products. A lipoxygenase mechanism involving conversion of a nonconjugated hydroperoxide (or peroxyl) to the conjugated diene product would not compromise stereochemistry as is also the case for rearrangement of an intermediate 13-hydroperoxide in the biosynthesis of PGG. In PG biosynthesis, the first oxygen would be delivered to carbon 13 of the chain and rearrange to the 11-peroxy. Following cyclization of the peroxyl, the second oxygen would also be delivered to carbon 13 and rearrange to the 15-hydroperoxide product. In this mechanism both oxygens are delivered to the same face of the same carbon in the chain.



Metal-Ligand Bond Dissociation Energies in CpMn(CO)$_2$L Complexes

Jane K. Klassen, Matthias Selke, Amy A. Sorensen, and Gilbert K. Yang*

Department of Chemistry
University of Southern California
Los Angeles, California 90089-0744

Received October 23, 1989

The photochemical ligand substitution reactions of CpMn(CO)$_3$ have been well studied and are synthetically very useful routes to substituted CpMn(CO)$_2$L complexes.[1] In contrast, CpMn(CO)$_3$ is inert toward thermal substitution.[2,3] In an effort to understand the thermodynamic reasons for this reactivity, we have examined Mn-L bond dissociation energies in a number of manganese complexes by time-resolved photoacoustic calorimetry.

Table I. Enthalpic and Kinetic Data for the Reaction of CpMn(CO)$_3$ with L in Heptane Solution According to Scheme I[a]

ligand	CpMn(CO)$_3$ $\Delta H_{\text{Mn-CO}}$, kcal/mol	CpMn(CO)$_2$L ΔH_2 (-BDE Mn-L), kcal/mol	$k_2 \times 10^{-6}$, L/(mol s)
THF	46.2 ± 1.2	-16.1 ± 1.4	4.4 ± 0.1
acetone	47.8 ± 1.7	-17.4 ± 1.0	3.6 ± 0.4
cis-cyclooctene	47.6 ± 1.4	-24.5 ± 2.3	2.3 ± 0.4
Bu$_2$S	45.3 ± 1.4	-28.7 ± 2.2	8.2 ± 0.5
P(OMe)$_3$[b]			7.1
PPh$_3$[b]			11
average	46.7 ± 1.7		

[a] Errors are given as 1 standard deviation of the scatter in the data. [b] See ref 9.

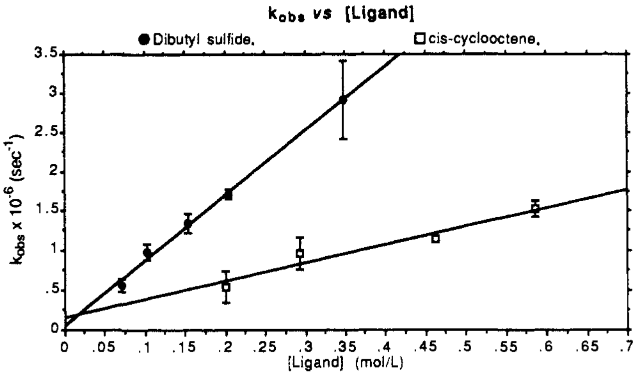


Figure 1. Plot of k_{obsd} vs [ligand] for the reaction of CpMn(CO)$_2$S with *cis*-cyclooctene and Bu$_2$S at 25 ± 1 °C in *n*-heptane. For *cis*-cyclooctene, $r^2 = 0.93$; for Bu$_2$S, $r^2 = 0.996$. Other data is given in Table I. Error bars are the greater of the standard deviation calculated from the scatter in the data and ±10%.

Upon irradiation with light (<~400 nm), CpMn(CO)$_3$ readily dissociates one CO ligand with a quantum yield[4] of 0.65 (Scheme I). In good donor solvents such as THF, the initially formed CpMn(CO)$_2$ is stabilized as the solvated intermediate CpMn(CO)$_2$S.[1] Substitution of the solvent molecule from this intermediate by "good" ligands such as phosphines and olefins occurs readily, leading to the corresponding CpMn(CO)$_2$L complexes. This reaction scheme is ideal for examination by photoacoustic calorimetry (PAC), which has been used to examine the energetics and kinetics in a number of organic and inorganic systems.[5] The PAC experiment detects, by way of the resulting thermal expansion, the heat released into solution from reactions initiated by absorption of a short pulse of laser light. From comparison of the amplitude and phase of this signal to a reference signal, both the enthalpy and kinetics of the reactions under study may be obtained. The results of the photoacoustic experiments on CpMn(CO)$_3$ performed in *n*-heptane solution are shown in Table I. The ligand concentrations were varied from ~0.1 to ~0.5 M. Consistent with the mechanism shown in Scheme I, the Mn-CO bond dissociation energies ($\Delta H_{\text{Mn-CO}}$) were constant within the concentration range used and were constant between the different ligands. The strength of the Mn-CO bond in CpMn(CO)$_3$ is remarkably high when compared to other known

Scheme I

$$\text{CpMn(CO)}_3 \xrightarrow[\Delta H_{\text{Mn-CO}},\ \text{"fast"}]{337.1\ \text{nm}} \text{CpMn(CO)}_2\text{S} \xrightarrow[\Delta H_2,\ k_2,\ \text{"slow"}]{+\text{L}} \text{CpMn(CO)}_2\text{L}$$

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* Author to whom correspondence should be addressed.

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metal–CO bond strengths[6,7] but is consistent with the observed reluctance of this species to undergo thermal CO substitution reactions.

In agreement with the observations that $\mathrm{CpMn(CO)_2THF}$ is thermally sensitive and is readily substituted by a variety of ligands,[1] the Mn–THF bond was found to be relatively weak. In comparison, *cis*-cyclooctene and $\mathrm{Bu_2S}$ form substantially stronger Mn–L bonds and the resulting complexes are correspondingly more stable. Complexes of both of these ligands can be isolated by displacement of THF from $\mathrm{CpMn(CO)_2THF}$ and decompose only above room temperature.[2,8]

The rate constants k_{obsd} for the coordination of L to $\mathrm{CpMn(CO)_2S}$ displayed first-order dependences on the concentration of the incoming ligand. Plots of k_{obsd} vs. [ligand] for *cis*-cyclooctene and $\mathrm{Bu_2S}$ are shown in Figure 1. The rate constants are all very large, which demonstrates the reactivity of the $\mathrm{CpMn(CO)_2S}$ intermediate toward donor molecules when weakly solvated by hydrocarbon solvents. Poliakoff et al.[9] obtained similar results upon examining the rates of reaction of $\mathrm{P(OMe)_3}$ and $\mathrm{PPh_3}$ with $\mathrm{CpMn(CO)_2S}$ in *n*-heptane solution using time-resolved IR spectroscopy (Table I).

From the data in Table I, we expected the $\mathrm{Mn{-}SBu_2}$ bond to be 4.2 ± 3.0 kcal/mol *stronger* than the Mn–*cis*-cyclooctene bond. To confirm this, we examined the equilibrium between the corresponding manganese complexes **1** and **2**.

$$\underset{\mathbf{1}}{\mathrm{CpMn(CO)_2}(cis\text{-}\mathrm{C_8H_{14}})} + \mathrm{SBu_2} \rightleftharpoons \underset{\mathbf{2}}{\mathrm{CpMn(CO)_2(SBu_2)}} + cis\text{-}\mathrm{C_8H_{14}}$$

Both of these complexes are known to undergo thermal substitution near 100 °C via clean first-order kinetics.[2,8] Since the equilibrium constant was expected to heavily favor the $\mathrm{SBu_2}$ complex **2**, we ran the experiments under high concentrations of *cis*-cyclooctene, in either neat *cis*-cyclooctene (7.7 M) or 1.2 M solutions of *cis*-cyclooctene in heptane, with identical results.[10] The van't Hoff plot of the equilibrium data obtained between 80 and 120 °C gave $\Delta H = -2.9 \pm 1$ kcal/mol and $\Delta S = 3.6 \pm 2$ eu. This value for ΔH is very close to the -4.2 ± 3 kcal/mol that we predicted on the basis of the individual bond strengths for the *cis*-cyclooctene complex **1** and the $\mathrm{SBu_2}$ complex **2** determined by photoacoustic calorimetry. The degree to which these two very different techniques agree attests to the accuracy of the photoacoustic technique in determining metal–ligand bond dissociation energies.

An estimate of the strength of the heptane–Mn interaction can be obtained from consideration of information in the literature and our data. Angelici and Loewen[2] have studied the ligand substitution of the *cis*-cyclooctene complex **1** by $\mathrm{PPh_3}$ in methylcyclohexane solution. Similarly, Butler and Sawai[8] have studied the ligand substitution of the $\mathrm{SBu_2}$ complex **2** by $\mathrm{P(O\text{-}}n\mathrm{\text{-}Bu)_3}$ in methylcyclohexane solution. Both reactions proceed by purely dissociative pathways.

$$\underset{\mathbf{1}}{\mathrm{CpMn(CO)_2}(cis\text{-}\mathrm{C_8H_{14}})} + \mathrm{PPh_3} \rightarrow \mathrm{CpMn(CO)_2(PPh_3)} + cis\text{-}\mathrm{C_8H_{14}}$$

$$\Delta H^{\ddagger} = 34.9 \pm 0.7 \text{ kcal/mol};\ \Delta S^{\ddagger} = 27.5 \pm 2.0 \text{ eu}$$

$$\underset{\mathbf{2}}{\mathrm{CpMn(CO)_2(SBu_2)}} + \mathrm{P(O\text{-}}n\mathrm{\text{-}Bu)_3} \rightarrow \mathrm{CpMn(CO)_2(P(O\text{-}}n\mathrm{\text{-}Bu)_3)} + \mathrm{SBu_2}$$

$$\Delta H^{\ddagger} = 36 \pm 1 \text{ kcal/mol};\ \Delta S^{\ddagger} = 22 \pm 1 \text{ eu}$$

In methylcyclohexane solution, the activation enthalpies for these reactions are respectively 10 and 7 kcal/mol *greater* than the corresponding Mn–L bond strengths in heptane. Assuming little difference between methylcyclohexane and heptane, this implies that the Mn–heptane interaction is close to 8 or 9 kcal/mol. This is similar to the 10 kcal/mol Cr–heptane interaction in $\mathrm{(CO)_5Cr{-}heptane}$[5c] and the 9.6 kcal/mol W–ethane interaction in $\mathrm{(CO)_5W{-}ethane}$.[11] The sum of Mn–heptane interaction (8–9 kcal/mol) and the solution-phase Mn–CO bond dissociation energy (46.7 kcal/mol) gives 55 kcal/mol as an estimate of the *gas-phase* Mn–CO bond dissociation energy in $\mathrm{CpMn(CO)_3}$. Further experiments are necessary to confirm the magnitude of the Mn–heptane interaction.

Acknowledgment. We acknowledge the National Institutes of Health (GM-42704-01), the University of Southern California Faculty Research and Innovation Fund, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this research.

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Poly(thiophosphazenes): New Inorganic Macromolecules with Backbones Composed of Phosphorus, Nitrogen, and Sulfur Atoms

Jeffrey A. Dodge, Ian Manners, and Harry R. Allcock*

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

Gerhard Renner and Oskar Nuyken*

Makromolekulare Chemie I, Universität Bayreuth
Universitätsstrasse 30, D-8580 Bayreuth, West Germany

Received November 3, 1989

Macromolecules that possess backbones consisting entirely of inorganic elements are of considerable current interest from the viewpoint of both their unusual physical properties and their potential function as precursors to ceramic materials.[1-8] However, to date, relatively few well-characterized classes of these materials have been prepared.

Classical polyphosphazenes are a broad, well-established class of inorganic macromolecules with backbones of alternating phosphorus and nitrogen atoms. Their main method of synthesis involves the ring-opening polymerization of hexachlorocyclotriphosphazene (**1**) followed by replacement of the halogen atoms of **2** by organic, inorganic, or organometallic units. This has provided access to a wide variety of stable and useful materials.[9-11]

We are currently exploring the polymerization behavior of cyclic species analogous to **1** but containing skeletal heteroatoms in

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