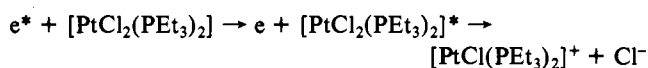
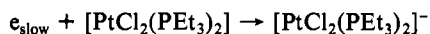


We now address the question of how the species $[\text{PtCl}_2(\text{PEt}_3)_2]^-$ and Cl^- , which according to eq 2, 3, and 4 should be responsible for the formation of $[\text{PtCl}_3(\text{PEt}_3)_2]^-$, are generated in the ion source. The chloride ions can arise, but to a minor extent, from the fragmentation of the negative ions because their abundance is not proportional to that of the molecular and fragment ions and indeed are abundant even in their absence, as can be seen by comparing the abundance of Cl^- under electron impact (100) and electron attachment conditions (72). This behavior suggests that the chloride ions are mainly produced through an ion-pair mechanism:



As for $[\text{PtCl}_2(\text{PEt}_3)_2]^-$ ions, they are abundant when the vapor pressure of the substrate $[\text{PtCl}_2(\text{PEt}_3)_2]$ is relatively high (Cl source configuration) and also under electron attachment conditions ($\text{CH}_4 + \text{N}_2$). These results are indicative of the mechanism of formation



The overall results may be summarized as follows. Under EI conditions abundant Cl^- ions are formed through an ion-pair mechanism. When the pressure of the ion source is relatively high, a five-coordinate adduct is easily produced either by addition of Cl^- to substrate molecule $[\text{PtCl}_2(\text{PEt}_3)_2]$ or, although less likely, by reaction of molecular ions $[\text{PtCl}_2(\text{PEt}_3)_2]^-$ alternatively with Cl^- radicals or complex molecules. The five-coordinate adduct is stable on the time scale of the sector mass spectrometric measurements and does not reveal appreciable decomposition after having left the ion source. An analogous five-coordinate complex, $[\text{PtCl}_2\text{I}(\text{PEt}_3)_2]^-$, is produced in the presence of methyl iodide.

The conclusions of the present work, being obtained under mass spectrometric conditions, do not permit a straightforward extension to reactions in solution. Thus, although we have been able to show that $[\text{PtCl}_3(\text{PEt}_3)_2]^-$ and $[\text{PtCl}_2(\text{PEt}_3)_2]^-$ ions are genuine intermediates, a distinction between transition states and five-coordinate intermediates in substitutions of the type depicted by eq 1 is still to be proven.

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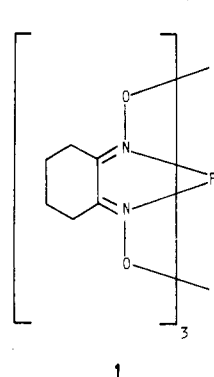
Received June 28, 1984

Synthesis and Characterization of an Iron Clathrochelate Containing an Unreactive Boron-Hydrogen Bond

Sir:

The anion $\text{BH}(\text{OR})_3^-$ has been shown to be a powerful reducing agent.¹ We have incorporated this functionality into a rigid clathrochelate ligand and have found it to be remarkably unreactive. The compound, $[\text{Fe}(\text{NOX})_3(\text{BH})_2]$ (**1**),² is prepared by reacting a mixture of cyclohexanedione dioxime (NOXH_2) and anhydrous ferrous bromide in dry acetonitrile with sodium borohydride. The red-orange solid that precipitates is purified by column chromatography (neutral alumina, methylene chloride solvent) and recrystallized from chloroform/methanol.³ Infrared

(1) Brown, H. C.; Mead, E. J. *J. Am. Chem. Soc.* **1953**, *75*, 6263.
(2) IUPAC name: [Tris(μ -(1,2-cyclohexanedione dioximate)-*O:O*)dihydrodiborato(2-)]-*N,N',N'',N''',N''''*iron(II).



studies reveal a strong terminal B-H stretch at 2490 cm^{-1} along with other bands common to this family of clathrochelates ($\nu_{\text{C}=\text{N}} = 1578$ and 1492 cm^{-1} ; $\nu_{\text{N}-\text{O}} = 1232$ and 1060 cm^{-1} ; $\nu_{\text{B}-\text{O}} = 1203 \text{ cm}^{-1}$).^{4,5} The ^{11}B nuclear magnetic resonance spectrum (Bruker WM 500; 160.47 MHz) consists of a broad symmetrical doublet ($J_{\text{B}-\text{H}} = 120 \text{ Hz}$) centered at -31.9 ppm ($\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ reference), which collapses to a singlet when broad-band proton decoupling is used (See Figure 1). No other ^{11}B resonance is observed, indicating that both boron atoms are in equivalent environments. The ^1H NMR spectrum (Varian T60) in CDCl_3 is dominated by the two broad methylene resonances at 2.90 ppm (β to the oxime nitrogen) and 1.80 ppm (γ to the oxime nitrogen) vs. Me_4Si (internal standard). The hydridic proton's resonance is ill resolved because of the quadrupole broadening of the adjacent boron atom and the interfering overlap of the methylene resonances. UV-visible spectroscopy produces a spectrum reminiscent of other examples of this class of compound^{4,5} with an intense charge-transfer band centered at $22.3 \times 10^3 \text{ cm}^{-1}$ ($\epsilon = 18000 \text{ L/mol}\cdot\text{cm}$; CH_3CN).

Cyclic voltammetric studies⁶ at a platinum electrode in CH_3CN (0.1 M in tetra-*n*-butylammonium fluoroborate) show a quasi-reversible oxidation wave centered at $+0.72 \text{ V}$ (65 mV peak to peak separation, scan rate 100 mV/s) vs. the Ag^0/Ag^+ (0.1 M in CH_3CN) reference electrode. This oxidation is assigned to the $\text{Fe}(\text{II})/\text{Fe}(\text{III})$ couple; however, attempts to synthesize the $\text{Fe}(\text{III})$ clathrochelate electrolytically have failed to produce a stable product. Evidence supporting a metal-centered redox process instead of a ligand-centered process arises from the facts that (1) variations in the ligand system of the iron clathrochelates do not greatly affect the position or the reversibility of the cyclic voltammetric waves⁵ and (2) electrochemical studies of cobalt complexes with identical ligand systems do not produce redox couples other than those that are well established (through electrolytic studies) as being metal centered.⁷

Chemical Reactivity. Brown and co-workers⁸ have shown that the reaction of acetone with sodium triisopropoxyborohydride in diglyme at 0°C is complete in seconds. Attempts to react $[\text{Fe}(\text{NOX})_3(\text{BH})_2]$ with acetone have yielded no reaction after 16 h of reflux. The acid stability of the complex is even more noteworthy. Material isolated from glacial acetic acid after 67 h of reflux still exhibited a strong $\nu_{\text{B}-\text{H}}$ band at 2485 cm^{-1} ; however, some acetate ester formation did occur gradually as evidenced by the appearance of infrared bands typical of esters ($\nu_{\text{C}=\text{O}} = 1730 \text{ cm}^{-1}$; $\nu_{\text{C}-\text{O}} = 1270 \text{ cm}^{-1}$)⁹ in the isolated materials. Studies in concentrated hydrochloric acid indicate that the complex

(3) Anal. Calcd for $\text{C}_{18}\text{H}_{26}\text{B}_2\text{FeN}_6\text{O}_6$: C, 43.24; H, 5.24; N, 16.81. Found: C, 43.04; H, 5.44; N, 16.53.

(4) Jackels, S. C.; Rose, N. J. *Inorg. Chem.* **1973**, *12*, 1232.

(5) Robbins, M. K.; Naser, D. W.; Heiland, J. L.; Grzybowski, J. J. *Inorg. Chem.*, in press.

(6) A Bioanalytical Systems CV-1V cyclic voltammetry instrument was used in conjunction with an H-type cell with a glass frit separating the reference electrode from the working electrode compartment.

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(8) Brown, H. C.; Mead, E. J.; Shoaf, C. J. *J. Am. Chem. Soc.* **1956**, *78*, 3616.

(9) The compound had been dried in vacuo at 110°C to remove any unreacted acetic acid.

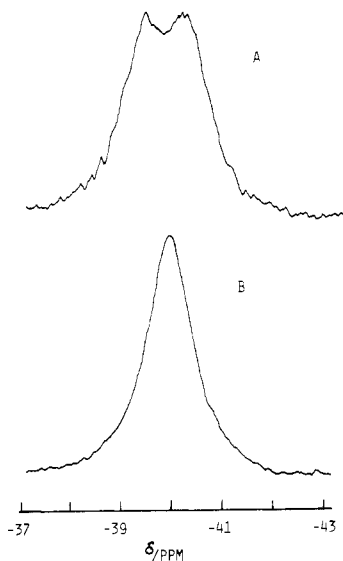


Figure 1. Boron-11 NMR spectrum of $[\text{Fe}(\text{NOX})_3(\text{BH})_2]$ vs. $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$: (A) coupled; (B) proton decoupled.

slowly decomposes, producing a pale yellow solution as has been previously reported for similar clathrochelates without hydridic protons.⁴ Nonetheless, a suspension of $[\text{Fe}(\text{NOX})_3(\text{BH})_2]$ in concentrated HCl that had been stirred for 16 h at 25 °C still yielded a product that contained an intact B-H bond ($\nu_{\text{B-H}} = 2485 \text{ cm}^{-1}$). This degree of acid stability is similar to that found in the $\text{B}_{12}\text{H}_{12}^{2-}$ anion and related compounds.¹⁰

Since the infrared and nuclear magnetic resonance studies show the parameters of the clathrochelate's B-H bond to be comparable to those of other more reactive B-H bonds, it is assumed that the unreactive nature of this bond lies in the steric constraints imposed by the rigid encapsulating ligand. Acid hydrolysis of BH_4^- has been shown to proceed through a five-coordinate BH_5 intermediate prior to loss of H_2 , producing trigonal BH_3 , which rapidly reacts to produce $\text{B}(\text{OH})_4^-$, presumably proceeding through $\text{H}_2\text{B}(\text{OH})_2^-$ and $\text{HB}(\text{OH})_3^-$ intermediates.¹¹ Analogously, it is unlikely that the rigid clathrochelate ligand would readily distort to form pentacoordinate or even more so tricoordinate boron intermediates. In a sense the complex can be viewed as containing a "trapped" monohydroborato intermediate resulting from the "hydrolysis" of the starting borohydride.

Acknowledgment. I wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for supporting this research. Acknowledgment is also made to the NSF Northeast Regional NMR Facility at Yale University, which is funded by the Chemistry Division of the NSF (Grant No. CHE-7916210). The support of a Gettysburg College institutional self-renewal grant is also gratefully acknowledged.

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Received July 30, 1984

Articles

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Electrochemical Oxidation of Zinc Bis(*O,O*-dialkyl phosphorodithioates-*S,S'*) Mediation by 1,1'-Bis(methoxycarbonyl)ferrocene

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Received July 3, 1984

Electrochemical oxidation of zinc bis(*O,O*-diethyl phosphorodithioate-*S,S'*) (**1a**) and zinc bis[*O,O*-bis(1-methylethyl) phosphorodithioate-*S,S'*] (**1b**) in CH_3CN at a glassy-carbon electrode (GCE) using cyclic voltammetry gave irreversible waves with peak potentials of +1.5 V (SCE). Constant-potential oxidation of **1a** at +1.4 V produced the disulfide *O,O,O,O*-tetraethyl thioperoxydiphosphate (**4a**) in nearly quantitative yield via a two-electron process. In contrast, constant-potential oxidation of **1b** at +1.4 V gave only low yields of its corresponding disulfide **4b** (ca. 30%) since **4b** was further oxidized at this potential. The oxidation of **1a** and **1b** at a GCE occurs with a large overpotential. This was demonstrated by oxidizing these compounds in the presence of 1,1'-bis(methoxycarbonyl)ferrocene, which undergoes a one-electron, reversible oxidation at a potential of +0.88 V. A large enhancement of current at this potential was observed when either **1a** or **1b** was added to a solution of this ferrocene mediator. In the presence of the mediator, **1b** could be oxidized at +0.90 V to its disulfide **4b** in high yields (85–90%).

Zinc bis[*O,O*-dialkyl(aryl) phosphorodithioates-*S,S'*] (**1**) have been widely used for quite some time as antioxidants and antiwear agents in lubricating oils. Since the early work of Kennerley and Patterson,¹ these compounds or their decomposition products have been known to catalyze the decomposition of hydroperoxides,²⁻²¹

which are intermediates in the oxidation of hydrocarbons. In spite of numerous studies that have been directed at elucidating the

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