

The Reaction of Alkyl Halides with the Bis(1,2-Dicyanoethylene-dithiolato)lead(II) Ion

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The reaction of the bis(1,2-dicyanoethylene-dithiolato)lead(II) ion, $Pb(mnt)_2^{2-}$, with various organohalides has been examined and found to yield the halo(1,2-dicyanoethylenedithiolato)lead(II) ion $Pb(mnt)X^-$ ($X = Br, I$) and the 1,2-di(alkylmercapto) 1,2-dicyanoethylene, R_2mnt ($R = 1^\circ, 2^\circ$ alkyl). Qualitative rate studies have shown that the alkylation proceeds much faster for $Pb(mnt)_2^{2-}$ than for Na_2mnt .

Introduction

It has been observed that certain transition metal complexes of 1,2-dithiolato ligands can be alkylated with alkyl halides [1–4]. These reactions proceed in cases where the formal oxidation state of the metal is such that the complex could be approximated as having coordinated dianionic ligands, e.g. $Ni[S_2C_2(C_6H_5)_2]_2^{2-}$ [1]. Therefore, the sulfur atoms could be expected to be centers of nucleophilic attack [1]. If this suggestion is true, then we felt it would be of interest to extend these studies to main group dithiolato complexes where the anionic nature of the ligand might be expected to be more pronounced [5]. We chose to study the bis(1,2-dicyanoethylenedithiolato)lead(II) complex since the ligand should show considerable anionic character in this system and the structure of the complex is expected to be similar to that exhibited by the bisdithiolato Group VIII complexes [6].

Experimental

Materials and Measurements

Disodium dicyanoethylene-1,2-dithiolate [7] (Na_2mnt^b) and bistetrabutylammonium bis(dicyanoethylene-1,2-dithiolato)lead(II) [6] were prepared

by previously reported procedures. Commercially available alkyl halides were used without further purification. NMR measurements were recorded on a JEOL C60-HL spectrophotometer. Infrared spectra were obtained on a Beckman IR-20A spectrophotometer. Analyses were performed by the Robertson Laboratory. Molecular weights were determined mass spectrophotometrically using a Perkin-Elmer RMU-6D spectrometer.

Reaction of CH_3I with $[(C_4H_9)_4N]_2Pb(mnt)_2$

A solution of 2.18 g (0.00225 mol) of $[(C_4H_9)_4N]_2Pb(mnt)_2$ in 20 ml of methanol was treated with 0.71 g (0.005 mol) of CH_3I and allowed to stir for fifteen minutes at room temperature. During this time, a precipitate was obtained and isolated by filtration. The yellow crystalline solid, m.p. 174 °C, was isolated in nearly quantitative yield and was shown to be $[(C_4H_9)_4N]Pb(mnt)I$. *Anal.* Calcd for $[(C_4H_9)_4N]Pb(mnt)I$: C, 33.46, H, 5.07. Found: C, 33.51, H, 5.01%. The solvent was removed from the filtrate under reduced pressure and the resulting dark orange paste was dried *in vacuo* over $CaSO_4$. The crude material was placed in a Soxhlet apparatus and extracted with pentane. The resulting pentane solution was reduced, under reduced pressure, to a volume of about 2 ml. The remaining solvent was removed by passing a stream of nitrogen gas over the solution. The resulting solid was sublimed (0.05 mm, 80–85 °C) to give 0.31 g of a yellow powder. The product was identified as *cis*-1,2-di(methylmercapto)-1,2-dicyanoethylene, $(CN)_2C_2(SCH_3)_2$, m.p. 99 °C (lit. [8] 99 °C). *Anal.* Calcd for $C_6H_6N_2S_2$: C, 42.32, H, 3.56, N, 16.45, mol wt, 170. Found: C, 42.45, H, 3.71, N, 16.43%, mol wt 170. Based on the assumption that one mol of the $Pb(mnt)_2^{2-}$ ion ultimately provides one mol of the mnt ion in the reaction, a yield of 81% is obtained.

Reaction of Other Organohalides with $[(C_4H_9)_4N]_2Pb(mnt)_2$

A variety of organohalides were used in place of methyl iodide using the procedure described above. In cases where a reaction occurred (as indicated by

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^b Mnt is an abbreviation of the trivial name maleonitriledithiolate for the dicyanoethylene-1,2-dithiolate ion, $S_2C_2(CN)_2^{2-}$.

TABLE I. Qualitative Rate Studies of Alkylation of Coordinated and Uncoordinated Mnt.

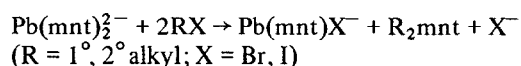
Reaction Mixture ^a	Time ^b	(CH ₃) ₂ mnt/CH ₃ I ^c
CH ₃ I + Pb(mnt) ₂ ²⁻	immediately upon mixing	7.8
	5	8.1
	7	14.5
	8	21.3
CH ₃ I + Na ₂ mnt	immediately upon mixing	0.09
	2	0.08
	10	0.08
	15	0.09

^aSolutions of equal volumes, initially containing 0.0024 mol of each reactant.^bMinutes. ^cRatio of peaks in NMR spectra.

formation of the Pb(mnt)X⁻ ion), the alkylated dithiolate was left as a crude oil. The identity of the oil was established by nmr spectroscopy. Reactive organohalides include: ethyl iodide, ethyl bromide, sec-butyl iodide, n-octyl iodide, and α -bromotoluene. Organohalides which were unreactive under the conditions employed in this study include: n-butyl chloride, tert-butyl chloride, tert-butyl iodide, bromobenzene, and iodobenzene.

Results and Discussion

The isolation of the two major products indicates that the reaction exhibits the following stoichiometry:



Although the Pb(mnt)Br⁻ ion has been reported in the reaction lead diacetate with Na₂mnt in the presence of tetrabutylammonium bromide [6], the Pb(mnt)I⁻ ion has not previously been prepared. The dimethylated dithiolate, (CH₃)₂mnt, has previously been prepared by alkylation of Na₂mnt [8]. The melting point, infrared spectrum and nmr spectrum of the (CH₃)₂mnt prepared in this study were identical to those for a sample prepared *via* the previously reported method [8].

In comparing the results of the alkylation of Pb(mnt)₂²⁻ with similar studies on group VIII dithiolato complexes [1-4], one observes both similarities and differences. In the transition metal complexes, the alkylated dithiolate remains coordinated to the metal and the halide may [3] or may not [1,4] be coordinated depending on the system involved. In the lead complex, the metal-sulfur interaction is presumably weaker than in the transition metal complexes where extensively electron delocalization can occur [2]. Therefore, the reduction of the negative charge on sulfur is

sufficient to cause dissociation of the lead-(CH₃)₂mnt bond. This dissociation is probably favored by the insolubility of [(C₄H₉)₄N]Pb(mnt)I. Furthermore, some alkylated dithiolates are known to be poor donors [9]. Attempts at alkylation of Ni(mnt)₂²⁻ have previously been shown to be unsuccessful [1]. The observed lack of reactivity was ascribed to the inductive effect of the cyano group reducing the sulfur nucleophilicity [1]. In the present case, this electron drain is counterbalanced by the increased anionic nature of the ligand when bonded to lead(II).

The most significant question which arises from this study is the role of the metal ion in these reactions. In order to probe this question, a qualitative rate study of the alkylation of the mnt moiety with and without a coordinated lead(II) ion was conducted. The reaction can be monitored by following the changes in the intensity of the (CH₃)₂mnt (δ = 2.73) and CH₃I (δ = 2.15) NMR signals in deuterioacetone. A summary of these studies is found in Table I. The coordination of a lead(II) ion to the mnt unit clearly leads to a drastic rate increase. Our qualitative rate study was conducted in acetone and it has been shown that orders of nucleophilicity can vary with solvent [10]. However, we observe rapid reaction of methyl iodide with the Pb(mnt)₂²⁻ in methanol (see Experimental) whereas the reaction of Na₂mnt with methyl iodide in methanol takes several hours. Thus it appears that the change in solvent doesn't result in a change in order of nucleophilicities in this case. It has been shown that the reactivity of various nucleophiles toward methyl iodide in methanol increases with the softness of the nucleophile [11]. Since the lead(II) ion is a borderline acid [12], it is not clear *a priori* how lead(II) coordination will alter the basic site. If no other effects were operative, it would appear that the lead(II) ion increases the softness of the ligand sulfur centers. However, one could also envision an interaction between the lead atom in Pb(mnt)₂²⁻ and

the iodine atom in methyl iodide which would lead to a polarization of the carbon-iodine bond. This polarization would increase the susceptibility of the methyl iodide to nucleophilic attack.

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