The Synthesis and Characterization of Mono- and Dinuclear Cobaloxime Selenocyanate and Thiocyanate Complexes Containing Phosphines, Arsines and Stibines*

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Complexes of the type trans-$[Co(DH)_2(L)X]$ *and* trans-$[(L)Co(DH)_2-X-Co(DH)_2-X]$ *have been synthesized by the reaction between* trans-$[Co(DH)_2(L)Y]$ *and X in a variety of solvents (DH = monoanion of dimethylglyoxime; L = triphenylstibine, triphenylarsine, triphenylphosphine, tri-n-butylstibine; X = $SeCN^-$, SCN^-; Y = Cl^-, Br^-). The formation of mononuclear complexes resulted in solvents of high dielectric, while dinuclear complexes usually resulted in solvents of low dielectric. All of the terminal $SeCN^-$ groups exhibit coordination via the selenium atom, regardless of the nature of L. Several of the terminal SCN^- groups in the mononuclear complexes were N-bound. Little or none of the dinuclear complexes could be produced from N-bound complexes, regardless of solvent dielectric. These results are in accord with the dissociative mechanism proposed for the formation of the dinuclear complexes, i.e., dissociation of the neutral L ligands would be expected to be facilitated by solvents of low dielectric and retarded by the lower trans-effect of the N-bound thiocyanate. The bonding modes adopted by the NCS^- and $NCSe^-$ ions in these complexes are discussed in the context of competing anti-symbiotic and symbiotic effects, respectively.*
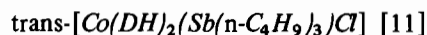
Introduction

The chemistry of cobaloxime pseudohalide complexes of the type trans-$[Co(DH)_2(L)X]^{n-}$ (DH = monoanion of dimethylglyoxime, L = neutral (n = 0) or anionic (n = 1) ligand, X = cyanide, cyanate, thiocyanate or selenocyanate) has provided a fertile field for investigation during the past decade [1–4]. Whereas the cyanide [3], cyanate [4] and selenocyanate [5, 6] ions have been found to behave in a non-ambidentate manner in these complexes, forming Co–CN, Co–NCO and Co–SeCN linkages exclusively, the thiocyanate ion has been shown to form both Co–NCS and Co–SCN linkages, the linkage isomeric ratio depending upon both the nature of the *trans* L ligand [7, 8] and the dielectric constant of the solvent in which the complex is dissolved [9, 10]. With the exception of the cyanate complexes [4], many of these cobaloximes can be converted [3, 4, 6] into pseudohalide-bridged dinuclear complexes of the type trans-$[LCo(DH)_2$-(pseudohalide)-$Co(DH)_2L']$ by two different routes: (1) by reaction [3, 4] between trans-$[Co(DH)_2B$-(pseudohalide)] and trans-$[Co(DH)_2(R)H_2O]$ where B is a nitrogen donor ligand, pseudohalide is either CN^-, NCS^- or $NCSe^-$, and R is an alkyl group, with loss of H_2O, and (2) by reaction [6] of trans-$[Co(DH)_2L(SeCN)]$, where L is a phosphine or a phosphite, with itself in a solvent, such as methylene chloride, having a relatively low dielectric constant, with loss of one of the L ligands.
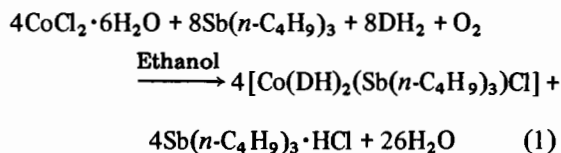
The present work was executed with two goals in mind: (1) to extend the second preparative route to complexes of the thiocyanate ion and (2) to investigate the effects of changing the neutral ligand L in a vertical group, *i.e.*, phosphines, arsines and stibines, on the thiocyanate and selenocyanate linkage isomeric ratios.

Experimental

Preparation of Complexes

trans-$[Co(DH)_2(Sb(n\text{-}C_4H_9)_3)Cl]$ [11]
The reaction scheme for the above complex was as follows:

$$4CoCl_2 \cdot 6H_2O + 8Sb(n\text{-}C_4H_9)_3 + 8DH_2 + O_2$$

$$\xrightarrow{\text{Ethanol}} 4[Co(DH)_2(Sb(n\text{-}C_4H_9)_3)Cl] +$$

$$4Sb(n\text{-}C_4H_9)_3 \cdot HCl + 26H_2O \qquad (1)$$

TABLE I. Properties of *trans*-[Co(DH)$_2$(L)(Y)] Complexes.

L	Y	Color	Yield	Decomposition Temp. (°C)
As(C$_6$H$_5$)$_3$	Br$^-$	dark brown	80%[a]	240–243
Sb(n-C$_4$H$_9$)$_3$	Cl$^-$	red-brown	74%[b]	180–184
Sb(C$_6$H$_5$)$_3$	Cl$^-$	red-brown	78%[b]	216–219

[a]Yield based on Co(NO$_3$)$_2$·6H$_2$O.   [b]Yield based on CoCl$_2$·6H$_2$O.

TABLE II. Preparative Variables for *trans*-[LCo(DH)$_2$-XCN-Co(DH)$_2$XCN] Complexes.

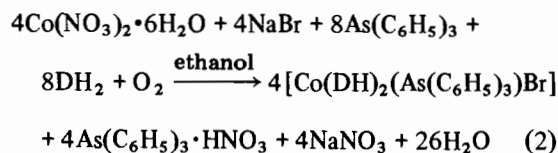| L	X	Vol of Methanol (ml)	Reaction time (hr)	Initial Temp (°C)	Recrystallization Solvent	Length of Exposure (hr)
As(C$_6$H$_5$)$_3$	Se	300	24	~60	CH$_2$Cl$_2$	14
Sb(n-C$_4$H$_9$)$_3$	Se	350	20	~35	CH$_2$Cl$_2$	18
Sb(C$_6$H$_5$)$_3$	S	650	48	~35	C$_6$H$_6$	24

A solution of 2.520 g (10.7 mmol) CoCl$_2$·6H$_2$O and 2.750 g (23.7 mmol) dimethylglyoxime (DH$_2$) was gently heated in 120 ml of absolute ethanol, resulting in the formation of a dark green solution. About 4.6 ml (~20 mmol) of Sb(n-C$_4$H$_9$)$_3$ was added dropwise, and the resulting solution allowed to stir and reach room temperature. A slow color change resulted in the formation of a red-brown solution, and a red-brown precipitate was noted after aeration for one-half hour. The powder was collected via filtration and washed with water, ethanol, and anhydrous diethyl ether.

trans-[Co(DH)$_2$(Sb(C$_6$H$_5$)$_3$)Cl] [11]

The synthesis of this complex was similar to that of the corresponding tri-n-butylstibine complex. A solution of 2.500 g (10.7 mmol) CoCl$_2$·6H$_2$O and 2.753 g (23.7 mmol) dimethylglyoxime was heated and stirred in 100 ml of absolute ethanol. To this solution, 7.680 g (21.8 mmol) of Sb(C$_6$H$_5$)$_3$ was added, followed by the addition of ~50 ml absolute ethanol. The solution was allowed to reach room temperature, followed by aeration for 2 hours. Filtration yielded a red-brown powder which was washed with water, ethanol, and anhydrous diethyl ether.

trans-[Co(DH)$_2$(As(C$_6$H$_5$)$_3$)Br]

The reaction scheme for the above complex was as follows:

$$4Co(NO_3)_2 \cdot 6H_2O + 4NaBr + 8As(C_6H_5)_3 +$$

$$8DH_2 + O_2 \xrightarrow{\text{ethanol}} 4[Co(DH)_2(As(C_6H_5)_3)Br]$$

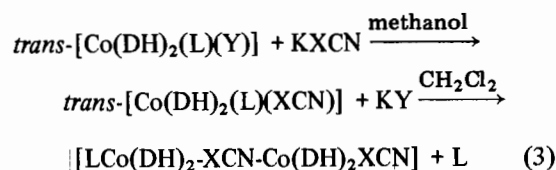$$+ 4As(C_6H_5)_3 \cdot HNO_3 + 4NaNO_3 + 26H_2O \quad (2)$$

A solution of 3.061 g (10.5 mmol) of Co(NO$_3$)$_2$·6H$_2$O, 1.082 g (10.5 mmol) NaBr and 2.749 g (23.7 mmol) dimethylglyoxime in 100 ml of 95% ethanol was heated and stirred, resulting in the formation of a dark green solution. A solution of 6.430 g (21.0 mmol) of As(C$_6$H$_5$)$_3$ in 80 ml of hot 95% ethanol was added in bulk to the green cobalt(II) solution, and the resulting solution allowed to reach room temperature. A stream of air was bubbled through the solution for 1 hour, resulting in the precipitation of a dark brown microcrystalline solid, *trans*-[Co(DH)$_2$(As(C$_6$H$_5$)$_3$)Br]. This product complex was collected via filtration and washed with distilled water, ethanol, and anhydrous diethyl ether.

The properties of the foregoing complexes are shown in Table I.

trans-[LCo(DH)$_2$-XCN-Co(DH)$_2$XCN] (X = S, Se)

The reaction scheme for the dinuclear complexes was as follows:

$$\text{\textit{trans}-}[Co(DH)_2(L)(Y)] + KXCN \xrightarrow{\text{methanol}}$$

$$\text{\textit{trans}-}[Co(DH)_2(L)(XCN)] + KY \xrightarrow{CH_2Cl_2}$$

$$[LCo(DH)_2\text{-XCN-Co}(DH)_2XCN] + L \quad (3)$$

One mmol of *trans*-[Co(DH)$_2$(L)(Y)] (Y = Cl$^-$, Br$^-$) was dissolved, with gentle heating and stirring, in methanol. A second solution containing 1 mmol KXCN, dissolved in ~15 ml of methanol, was added dropwise to the first and allowed to stir at room temperature for a period of one or two days (the triphenylphosphine complex reacts much faster, in about 4 hours). In several cases, the solution

TABLE III. Properties of *trans*-[LCo(DH)$_2$-XCN-Co(DH)$_2$XCN] Complexes.

L	X	Color	Yield[a], %	Decomposition Temp (°C)	Analysis Element	Calc %	Found %
As(C$_6$H$_5$)$_3$	Se	orange brown	not det.	133–136	C	39.36	38.60
					H	4.31	4.04
					N	12.75	12.51
Sb(n-C$_4$H$_9$)$_3$	Se	light beige	39	275–285	C	33.20	32.17
					H	5.48	5.03
					N	12.91	14.21
Sb(C$_6$H$_5$)$_3$	S	dark brown	48	77–85	C	41.12	42.78
					H	4.50	3.85
					N	13.32	not det.

[a]Yield based on *trans*-[Co(DH)$_2$(L)(Y)].

TABLE IV. Preparative Variables for *trans*-[Co(DH)$_2$(L)-CNX] Complexes.

(L)	X	Vol. of Methanol (ml)	Reaction Time (hr)
As(C$_6$H$_5$)$_3$	Se	400	48
Sb(n-C$_4$H$_9$)$_3$	Se	200	24
As(C$_6$H$_5$)$_3$	S	350	24
Sb(n-C$_4$H$_9$)$_3$	S	250	24

turned slightly darker upon the addition of KXCN. The methanol solution was then reduced to dryness on a Rotovap and redissolved in 50–75 ml CH$_2$Cl$_2$

(the Sb(n-C$_4$H$_9$)$_3$ complex was added to ~200 ml benzene). This solution was allowed to stir for up to 24 hours, followed by removal of about half of the solvent. Following filtration to remove the KY by-product, the volume of the solution was further reduced to a few ml. Products were isolated by addition of ~100 ml anhydrous diethyl ether and filtration, then washed with ether after collection. The preparative variables for these compounds are shown in Table II; their properties are tabulated in Table III.

trans-[Co(DH)$_2$(L)(XCN)] (X = S, Se)

Mononuclear cobaloxime complexes were synthesized in a manner similar to that of the dinuclear complexes, except that the recrystallization step in

TABLE V. Properties of *trans*-[Co(DH)$_2$(L)CNX] Complexes.

L	X	Color	Yield[a], %	Decomposition Temp (°C)	Analysis Element	Calc %	Found %
As(C$_6$H$_5$)$_3$	Se	dark brown	73	150–153	C	46.17	46.32
					H	4.45	4.24
					N	9.97	9.75
Sb(n-C$_4$H$_9$)$_3$	Se	dark brown	67	113–116	C	36.60	36.54
					H	6.29	6.17
					N	10.16	9.92
As(C$_6$H$_5$)$_3$	S	light brown	47	186–191	C	49.47	47.00
					H	4.77	4.43
					N	10.68	9.15
Sb(n-C$_4$H$_9$)$_3$	S	red-brown	71	146–147	C	39.27	39.16
					H	6.75	6.65
					N	10.90	11.10

[a]Yield based on *trans*-[Co(DH)$_2$L(Y)].

TABLE VI. Solution and Solid State Infrared Data for trans-[LCo(DH)₂-XCN-Co(DH)₂XCN] Complexes.

L	X	Nitrobenzene solution				Solid State (Nujol mull)			
		ν_{CN} (cm^{-1})		A^a × 10^{-4} (M^{-1} cm^{-2})		ν_{CN} (cm^{-1})		ISR^b Ratio	
		bridging	terminal	bridging	terminal	bridging	terminal	bridging	terminal
P(C₆H₅)₃ [6]	Se	2197	2120	1.8	0.46^d	2192	2121	12.1	3.28^d
As(C₆H₅)₃	Se	2175	2122	1.6	0.70^d	2166	2119	30.7	12.2^d
Sb(n-C₄H₉)₃	Se	2175	2122	1.9	0.68^d	2169	2119	34.4	9.7^d
Sb(C₆H₅)₃	S	2171	2112	0.4^c	1.6^d	2172	2116	2.53^c	7.77^d

^{a}Integrated absorption intensity [15] of ν_{CN} band of sample in nitrobenzene. ^{b}Integrated absorption intensity ratio of ν_{CN} band of sample, using ν_{CN} band of 1,4-dicyanobenzene as internal standard [16, 17]. ^{c}Low value due to partial decomposition. ^{d}S- or Se-bound.

CH₂Cl₂ or benzene was omitted. One mmol of trans-[Co(DH)₂(L)(Y)] (Y = Cl⁻, Br⁻) was dissolved in methanol at ~35 °C. A second solution of ~1 mmol KXCN, dissolved in ~15 ml methanol, was added dropwise to the first and the mixture allowed to stir at room temperature for up to two days. The solution was then reduced on a Rotovap until a precipitate was evident (in several cases, a precipitate formed only after addition of the reduced solution to ~150 ml of distilled water). The products were then isolated via filtration and dried in vacuo. The products may be pulverized and stirred in distilled water if contamination by the salt by-product is suspected. The preparative variables for these compounds are listed in Table IV; their properties are shown in Table V.

[Co(DH)₂P(C₆H₅)₃] was synthesized by the method of Schrauzer and Lee [12]. Trans-[P(C₆H₅)₃-Co(DH)₂-SeCN-Co(DH)₂SeCN] and trans-[Co(DH)₂-(P(C₆H₅)₃)SeCN] were synthesized by the method of Burkhardt and Burmeister [6]. KSeCN was synthesized by the reaction between KCN and Se metal [13].

Physical Measurements

Solid state infrared spectra were recorded on a Perkin-Elmer 180 spectrophotometer with expandable ordinate and abscissa and a range of 4000–200 cm⁻¹. Solid state spectra were measured using potassium bromide plates, spotted with powdered solid samples mixed with Nujol oil. Solution spectra were measured on the same instrument using matched calcium fluoride cells (1.1 mm). Proton nuclear magnetic resonance spectra were recorded on a Perkin-Elmer R-12 spectrometer. Melting points (decomposition temperatures) were measured on a Thomas Hoover capillary melting point apparatus and are uncorrected. Microanalyses were carried out by the Schwartzkopf Microanalytical Laboratory, Woodside, New York 11377.

Results

The effect of solvent dielectric upon the formation of mononuclear and dinuclear selenocyanate complexes has been noted in a previous report [6]. In this study, solvent dielectric has been found to exert a pronounced influence upon the formation of mononuclear and dinuclear thiocyanate complexes as well as the expected results with selenocyanate complexes. Formation of dinuclear species was observed in low dielectric solvents such as methylene chloride or benzene; formation of mononuclear species was observed in high dielectric solvents such as methanol.

The formation of relatively pure dinuclear compounds required the addition of diethyl ether to force the desired product from solution. Allowing the solid to precipitate from solution without ether addition resulted in a mixture of mononuclear and dinuclear products. The reaction of several thiocyanate complexes in low dielectric solvents did not result in the formation of dinuclear complexes; trans-[As(C₆H₅)₃Co(DH)₂-SCN-Co(DH)₂SCN] and trans-[Sb(n-C₄H₉)₃Co(DH)₂-SCN-Co(DH)₂SCN] did not form even when the reaction was carried out in benzene. It should be noted that, of the complexes studied, the triphenylstibine thiocyanate complex was the only dinuclear thiocyanate successfully synthesized. With two exceptions, the mononuclear complexes formed with little complication in methanol. The trans-[Co(DH)₂(As(C₆H₅)₃)SCN] reaction did not result in a pure compound when carried out in methanol or acetonitrile. The occurrence of a ν_{CN} side band at 2124 cm⁻¹ was observed in each case, and is believed to be due to K[Co(DH)₂(SCN)₂] [14]. The synthesis of trans-[Co(DH)₂(Sb(C₆H₅)₃)SCN] in pure form was not achieved in methanol but may form in a higher dielectric solvent. The source of contamination in this case was the dinuclear species.

TABLE VII. Solution and Solid State Infrared Data for *trans*-[Co(DH)$_2$(L)CNX] Complexes.

L	X	Nitrobenzene Solution			Solid State	
		ν_{CN} (cm^{-1})	A^a × 10^{-4} (M^{-1} cm^{-2})	A^b × 10^{-4} (M^{-1} cm^{-2})	ν_{CN} (cm^{-1})	ISR Ratio^c
P(C$_6$H$_5$)$_3$ [6]	Se	2120	0.68^d	0.77^d	2125	2.4^d
As(C$_6$H$_5$)$_3$	Se	2120	0.42^d	0.41^d	2127	2.4^d
Sb(n-C$_4$H$_9$)$_3$	Se	2119	0.89^d	0.81^d	2119	2.6^d
As(C$_6$H$_5$)$_3$	S	2113	0.33^d	0.94^d	2113	6.3^d
Sb(n-C$_4$H$_9$)$_3$	S	2113	5.10^e	7.30^e	2108	22.3^e

^{a}Integrated absorption intensity [15] of ν_{CN} band prior to addition of Co(II). ^{b}Integrated absorption intensity [15] of ν_{CN} band 1 hr after addition of Co(II). ^{c}Integrated absorption intensity ratio of ν_{CN} band of sample using ν_{CN} band of 1,4-dicyanobenzene as internal standard [16, 17]. ^{d}S- or Se-bound. ^{e}N-bound.

Solution infrared studies of the mononuclear and dinuclear complexes were carried out in nitrobenzene at concentrations between 2.5 × 10^{-3} M and 5 × 10^{-3} M. For each compound, two series of spectra were recorded. The first spectra were of a solution composed of the sample in pure solvent. The second series were of sample, solvent and ~2 mol percent [Co(DH)$_2$P(C$_6$H$_5$)$_3$]. After about one hour ~2 vol percent BrCCl$_3$ was added. The Co(II) complex is capable [8] of catalyzing the isomerization of the ambidentate ligands: *trans*-[Co(DH)$_2$L(XCN)] ⇌ *trans*-[Co(DH)$_2$L(NCX)]. BrCCl$_3$ is an oxidant capable [8] of quenching the Co(II) catalyst. In all cases, the solution spectra, after addition of Co(II) and subsequent quenching, showed no significant isomerization (see Tables VI and VII).

Ramsay's method [15] for direct integration was used for the determination of the integrated absorption intensities of the ν_{CN} bands of the complexes in solution. For all of the mononuclear complexes except that of the tri-n-butylstibine thiocyanate complex, the ν_{CN} integrated absorption intensities of the ambidentate ligands were found to fall into the range [16] for S or Se bound compounds. In addition, the terminal thiocyanate and selenocyanate ligands of the dinuclear complexes were all found to be S or Se bound. The tri-n-butylstibine thiocyanate mononuclear complex was found to be N-bound.

Solid state infrared studies were conducted on all mononuclear and dinuclear species using the method of Bailey, *et al.* [17] and 1,4-dicyanobenzene as the internal standard [18]. The choice of this particular standard was made because it does not react with the sample and the ν_{CN} stretch appears in the same grating as the sample, with good resolution. Results from this method (with regard to bonding mode) directly mirror those found by Ramsay's method [15] using the solution infrared data. All

TABLE VIII. Proton NMR Data.

L	X	τ, ppm^a
Mononuclear Compounds		
P(C$_6$H$_5$)$_3$ [6]	Se	7.75
As(C$_6$H$_5$)$_3$	Se	7.66
Sb(n-C$_4$H$_9$)$_3$	Se	7.72
As(C$_6$H$_5$)$_3$	S	7.65, 7.70
Sb(n-C$_4$H$_9$)$_3$	S	7.78
Dinuclear Compounds		
P(C$_6$H$_5$)$_3$ [6]	Se	7.55, 7.62
As(C$_6$H$_5$)$_3$	Se	7.67
Sb(n-C$_4$H$_9$)$_3$	Se	7.68
Sb(C$_6$H$_5$)$_3$	S	7.86

^{a}Relative to tetramethylsilane, 35 °C.

mononuclear complexes were found to be S or Se bound with the exception of the tri-n-butylstibine thiocyanate. Terminal ambidentate ligands in the dinuclear compounds were found to be S or Se bound. The integrated intensity ratios as well as ν_{CN} values for the complexes are found in Tables VI and VII.

A third technique used to characterize these complexes was the use of proton NMR of the dimethylglyoximate methyl resonances, which are sensitive to the nature of the groups present in the axial positions [7, 8]. The results of this study are shown in Table VIII. For all complexes, regardless of whether or not they were mononuclear or dinuclear, only one methyl resonance was noted, except for the triphenylarsine thiocyanate mononuclear and triphenylphosphine selenocyanate dinuclear complexes, which exhibited two. Mononuclear complexes with

only one resonance reflect the fact that only one bonding mode is present. The triphenylarsine thiocyanate proton NMR spectrum indicates about a 5:1 ratio of S (τ = 7.65 ppm) to N (τ = 7.70 ppm) bound thiocyanate. The ordering of chemical shifts is due to the ASIS effect [8] of the nitrobenzene solvent. At least two methyl resonances were expected for the dinuclear complexes since the two glyoximates are in different environments. The appearance of only one band probably is due to the very poor solubility of the compounds in nitrobenzene. The proton NMR spectrum of the triphenylphosphine selenocyanate dinuclear complex indicates an ~2:3 ratio of the downfield peak to the upfield peak.

Discussion

The bonding of the selenocyanate group in trans-[Co(DH)$_2$L(SeCN)] and also the terminal selenocyanate in trans-[LCo(DH)$_2$-SeCN-Co(DH)$_2$SeCN] has been seen to be via the selenium atom, regardless of the nature of the ligand L or the solvent employed. These observations are congruent with those noted before [5, 6], and serve to underscore the pronounced symbiotic effect [19] that the L ligands and the dimethylglyoximates exercise on the selenocyanate.

Conversely, the partial degree of N-bonding exhibited by the mononuclear triphenylarsine thiocyanate complex in solution and the preponderance of N-bonding exhibited by the mononuclear tri-n-butylstibine thiocyanate complex are in accord with an antisymbiotic trend [20] noted previously [8] for three separate series of substituted pyridine, phosphine and phosphite cobaloxime thiocyanate complexes. Our subsequent inability to produce the corresponding dinuclear species from the N-bound tri-n-butylstibine thiocyanate complex can be rationalized in terms of Burmeister and Burkhardt's proposed mechanism [6] for the formation of dinuclear complexes. The hard nitrogen of the thiocyanate, which is relatively low in the trans-influence series, compared to -SCN or -SeCN, fails to labilize the stibine ligand sufficiently well to result in its dissociation and resultant solvation. If dissociation does not occur, a nitrogen atom from a thiocyanate of an intact molecule is unable to attack the exposed cobalt atom to form the bridge, and the mechanism fails to operate.

Once formed, a dinuclear complex can be cleaved in a high dielectric solvent such as acetonitrile.

In an attempt to isolate the complex trans-[Co(DH)$_2$(As(C$_6$H$_5$)$_3$)SeCN] through this procedure, the corresponding dinuclear species was dissolved in acetonitrile with a catalytic amount of Co(II) and a stoichiometric quantity of triphenylarsine. Progress monitored through infrared solution spectra indicated cleavage of the bridging ligand and subsequent formation of an ionic species. The desired mononuclear complex was not isolated.

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