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## Synthesis and Characterization of Neutral Thiocyanato- and Selenocyanato-Bridged Cobaloximes

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Pseudohalides react with alkylcobaloximes to produce labile complexes  $[\text{Co}(\text{dmgH})_2(\text{CNX})(\text{R})]^-$  ( $\text{X} = \text{O}, \text{S}, \text{Se}$ ) where the linkage isomer preference is dependent upon X, the alkyl group R, and the solvent. Isomer equilibration occurs rapidly in solution and is not influenced by cobalt(II) catalysis. The inert pseudohalide complexes  $\text{Co}(\text{dmgH})_2(\text{CNS})(\text{B})$  and  $\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{B})$  were found to react with alkylcobaloximes  $\text{Co}(\text{dmgH})_2(\text{R})(\text{H}_2\text{O})$  and  $\text{Co}(\text{dmgH})_2(\text{R})$  to form neutral pseudohalide-bridged dicobaloximes  $(\text{R})\text{Co}(\text{dmgH})_2-(\text{CNS})-\text{Co}(\text{dmgH})_2(\text{B})$  and  $(\text{R})\text{Co}(\text{dmgH})_2-(\text{NCSe})-\text{Co}(\text{dmgH})_2(\text{B})$  for various combinations of alkyl groups R and nitrogen donor ligands B. The corresponding cyanato-bridged dicobaloximes could not be prepared. Product characterization is by  $^1\text{H}$  NMR and IR spectroscopies, vapor-phase osmometry, and elemental analysis. Pseudohalide bridging is established to occur by remote bonding of the two cobaloximes to the N and S or Se atoms of the pseudohalide. Both linkage isomers of the thiocyanato-bridged system have been prepared and characterized. Only the isomer shown above has been prepared and characterized for the selenocyanato system. This is consistent with the existence of a single isomer for the inert terminally bound compounds  $\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{B})$ . The ligand-bridged dicobaloximes were found to partially dissociate in chloroform according to the reaction  $(\text{CNX}^- = \text{NCS}^-, \text{SCN}^-, \text{NCSe}^-)$   $(\text{R})\text{Co}(\text{dmgH})_2-(\text{CNX})-\text{Co}(\text{dmgH})_2(\text{B}) \rightarrow \text{Co}(\text{dmgH})_2(\text{R}) + \text{Co}(\text{dmgH})_2(\text{CNX})(\text{B})$ . The degree of dissociation is dependent on R, CNX, and B; more stable dimers are formed with  $\text{R} = \text{CF}_3^-$  than  $\text{CH}_3^-$  and with  $\text{B} = \text{py}$  than  $\text{pip}$ . Comparison with the previously reported analogous cyano-bridged dicobaloximes establishes the following order of decreasing stability with respect to the dissociation reaction (the line indicates the donor atom bonded to the  $\text{Co}(\text{dmgH})_2(\text{B})$  end of the dimer):  $\text{NC}^- > \text{NCS}^- > \text{NCSe}^- > \text{SCN}^- \gg \text{OCN}^-$ . In the presence of trace quantities of cobalt(II) the reaction of  $\text{Co}(\text{dmgH})_2(\text{CNS})(\text{B})$  or  $\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{B})$  with  $\text{Co}(\text{dmgH})_2(\text{R})$  produces oligomers of the form  $(\text{R})\text{Co}(\text{dmgH})_2-[(\text{CNX})\text{Co}(\text{dmgH})_2]_n(\text{CNX})\text{Co}(\text{dmgH})_2(\text{B})$  ( $n = 2, 3; \text{X} = \text{S}, \text{Se}$ ). Similar oligomer formation is observed when solid samples of the ligand-bridged dimer are dissolved in chloroform in the presence of trace quantities of cobalt(II). A mechanism involving cobalt(II) catalysis is proposed for the oligomer formation reaction.

### Introduction

The ability of pseudohalides to form bridges between transition-metal complexes is well documented.<sup>1-4</sup> Several recent papers dealing with cobalt(III) which are relevant to this study have appeared in the literature.<sup>5-10</sup> We are interested in synthesizing and characterizing stable neutral pseudohalide-bridged complexes of cobaloximes, particularly those in which bridged linkage isomers are accessible. These complexes are of interest in elucidating the mode of ligand bridging (adjacent or remote) and the influence of the pseudohalide and nonbridging trans ligands on complex stability. Interest in pseudohalide-bridged complexes may also arise from the role of these ligands in inner-sphere electron-transfer reactions.<sup>11</sup>

This report concerns the synthesis and characterization of a series of thiocyanato- and selenocyanato-bridged dicobaloximes of the general formula  $(\text{R})\text{Co}(\text{dmgH})_2(\text{CNX})\text{Co}(\text{dmgH})_2(\text{B})$  (I), where  $\text{X} = \text{S}$  or  $\text{Se}$ ,  $\text{R} = \text{CH}_3^-$  or  $\text{CF}_3^-$ , and  $\text{B} = \text{py}$ ,  $\text{pip}$ ,  $\text{py-3-Cl}$ ,  $\text{NH}_3$ , or  $\text{NH}_2\text{-pr}$  in various combinations.<sup>12</sup> In addition, pseudohalide-bridged oligomers of the general formula  $(\text{R})\text{Co}(\text{dmgH})_2-[(\text{CNX})\text{Co}(\text{dmgH})_2]_n(\text{CNX})\text{Co}(\text{dmgH})_2(\text{B})$  (II) are also described for  $\text{X} = \text{S}$  or  $\text{Se}$ . The pseudohalide-bridged dicobaloximes are analogous to our earlier report on the corresponding cyano-bridged dicobaloximes.<sup>13</sup> A preliminary report of some of these results has been made.<sup>14</sup>

### Experimental Section

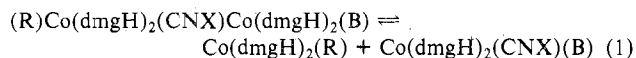
**Physical Methods.**  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , and  $n\text{-C}_6\text{H}_{14}$  were refluxed over  $\text{CaH}_2$  and distilled under dry  $\text{N}_2$  prior to use.  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{BrCCl}_3$  (Aldrich Gold Label) were stored over Linde 4A molecular sieves. All solutions containing alkylcobaloximes or  $\text{BrCCl}_3$  were kept from direct exposure to light. Satisfactory elemental analyses were obtained for all compounds, except where noted, by MHW Laboratories, Garden City, Mich.

IR spectra were obtained over the region 4000–200  $\text{cm}^{-1}$  with a Perkin-Elmer Model 621 spectrophotometer. Solution IR spectra were obtained using matched 0.5-mm and 1.0-mm KBr cells. Solid-state IR spectra were obtained from KBr disks. Spectra were calibrated

against polystyrene (1944.0 and 906.7  $\text{cm}^{-1}$ ) and  $\text{CO}_2$  (2350.0  $\text{cm}^{-1}$ ). The integrated absorption band intensities,  $A$ , for  $\nu_{\text{CN}}$  vibrations of coordinated thiocyanate and selenocyanate were determined from solution IR spectra according to the method of Ramsey.<sup>15</sup> An  $A$  value of ca.  $10^5 \text{ M}^{-1} \text{ cm}^{-2}$  indicates N-bonded SCN, and an  $A$  value of ca.  $10^4 \text{ M}^{-1} \text{ cm}^{-2}$  indicates S-bonded SCN.<sup>4,16</sup> A modification of this method was used to obtain the corresponding solid-state  $\nu_{\text{CN}}$  absorption band intensities,  $A_s$ , relative to the intensity of the absorption arising from the NO linkage of the dimethylglyoxime ligand at ca. 1230  $\text{cm}^{-1}$ .<sup>17</sup> It has been established that  $A_s$  values  $\geq 2$  indicate N-bonded SCN and  $A_s$  values  $\leq 1$  indicate S-bonded SCN.<sup>17</sup> An independent check of this classification was made by using salicylic acid as an internal standard<sup>3,4</sup> for both linkage isomers of  $\text{Co}(\text{dmgH})_2(\text{CNS})(\text{py})$ . Similar  $A$  and  $A_s$  ranges were used to identify linkage isomers for coordinated selenocyanate.

$^1\text{H}$  NMR spectra were recorded in deuterated solvents at 29 °C with a Jeol Model JNH-MH-100 spectrometer. Anhydrous samples were prepared using a freeze-pump-thaw technique and sealed on a vacuum line. Spectra are referenced to internal  $\text{Me}_4\text{Si}$ .

Molecular weights were determined by vapor-pressure osmometry in dry  $\text{CHCl}_3$  or dry  $\text{CH}_2\text{Cl}_2$  containing 1 vol %  $\text{BrCCl}_3$ , using a Metrolab Model 301 A osmometer. Each solvent run was calibrated separately with diphenyl as a standard over the concentration range from 0.005 to 0.4 M. Calibration curve precision was within 2%. The percent dissociation for the ligand-bridged complexes, for the assumed equilibrium reaction 1, was calculated using eq 2, where X is the



$$X = (M_{\text{AB}} - \bar{M}) / \bar{M} \times 100 \% \quad (2)$$

percent dissociation,  $M_{\text{AB}}$  is the theoretical molecular weight of  $(\text{R})\text{Co}(\text{dmgH})_2(\text{CNX})\text{Co}(\text{dmgH})_2(\text{B})$ , and  $\bar{M}$  is the experimentally observed molecular weight. The agreement between measured molecular weights starting with the ligand-bridged complexes and those starting with equimolar solutions of reactants is  $\pm 10 \text{ g/mol}$ . The uncertainty in calculated percent dissociation data is  $\pm 2\%$ .

**Preparation of Complexes.** The compounds  $\text{Co}(\text{dmgH})_2(\text{R})(\text{H}_2\text{O})$  ( $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7$ ),<sup>18</sup>  $\text{Co}(\text{dmgH})_2(\text{CH}_3)$ ,<sup>18</sup>  $\text{Co}(\text{dmgH})_2(\text{CH}_3)(\text{S}(\text{CH}_3)_2)$ ,<sup>18</sup>  $\text{Co}(\text{dmgH})_2(\text{CF}_3)(\text{H}_2\text{O})$ ,<sup>13</sup> and  $\text{Co}(\text{dmgH})_2(\text{NCO})(\text{py})$ <sup>18</sup> were prepared as described in the literature. Syntheses

of  $\text{Co}(\text{dmgH})_2(\text{CHBr}_2)(\text{L})$  ( $\text{L} = \text{H}_2\text{O}, \text{S}(\text{CH}_3)_2$ ) were by published procedures for analogous compounds.<sup>18,19</sup> **Caution:** The cobaloxime compounds described here containing the dibromomethyl ligand were found to be shock and temperature sensitive.

**$\text{Co}(\text{dmgH})_2(\text{CF}_3)$ .** An analyzed sample of  $\text{Co}(\text{dmgH})_2(\text{CF}_3)(\text{H}_2\text{O})$ <sup>13</sup> was heated to 130 °C ( $10^{-5}$  torr) for 30 h to produce the completely dehydrated compound. The IR spectrum exhibited the characteristic  $\text{dmgH}$  and  $\text{CF}_3$  absorptions and no absorptions due to coordinated or lattice  $\text{H}_2\text{O}$ . The compound was found to be hygroscopic. <sup>1</sup>H NMR spectra obtained at 29 °C in dry  $\text{CDCl}_3$  exhibited four equal-intensity signals in the  $\text{dmgH}$  methyl region. This is interpreted as being due to the formation of the dimer  $[\text{Co}(\text{dmgH})_2(\text{CF}_3)]_2$ , similar to that observed at low temperatures for  $[\text{Co}(\text{dmgH})_2(\text{CH}_3)]_2$ .<sup>20</sup> <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 4 vol %  $\text{BrCCl}_3$ , 29 °C):  $\delta$  1.98, 2.19, 2.42, 2.45.

**$[\text{AsPh}_4][\text{Co}(\text{dmgH})_2(\text{CH}_3)(\text{CNX})]$  ( $\text{X} = \text{S}, \text{Se}, \text{O}$ ).** In a typical synthesis  $\text{Co}(\text{dmgH})_2(\text{CH}_3)(\text{S}(\text{CH}_3)_2)$ , 0.5 g (1.4 mmol), and  $[\text{AsPh}_4]\text{SCN}$ , 0.8 g (1.8 mmol), were dissolved in 100 mL of dry ethanol with stirring at room temperature. Addition of anhydrous ether, 50 mL, caused precipitation of an orange powder which was isolated by filtration. The product was recrystallized from ethanol/ether, washed with ether, and dried in vacuo. The yield was ca. 90%. Similar procedures were used to synthesize the analogous selenocyanato and cyanato complexes.

**$[\text{AsPh}_4][\text{Co}(\text{dmgH})_2(\text{CF}_3)(\text{CNS})]$ .** In a typical synthesis 0.25 g (0.7 mmol) of  $\text{Co}(\text{dmgH})_2(\text{CF}_3)$  was suspended in 75 mL of dry  $\text{CHCl}_3$ . Upon addition of 0.60 g (1.4 mmol) of  $[\text{AsPh}_4]\text{SCN}$  the reactants dissolved. The slow addition of dry hexane resulted in the separation of the product as an oil, which was dissolved in 50 mL of dry ethanol and was then precipitated with anhydrous ether. The product was collected by filtration, washed with anhydrous ether, and dried in vacuo.

**$[\text{AsPh}_4][\text{Co}(\text{dmgH})_2(\text{CF}_3)(\text{CNSe})]$ .** In a typical synthesis 0.31 g (0.9 mmol) of  $\text{Co}(\text{dmgH})_2(\text{CF}_3)$  was suspended in 75 mL of dry  $\text{CHCl}_3$ . Upon addition of 0.84 g (1.8 mmol) of  $[\text{AsPh}_4]\text{SeCN}$  the reactants dissolved. The slow addition of 300 mL of anhydrous ether resulted in the precipitation of a solid product which contained both ionic and coordinated selenocyanate. The solid was suspended in 75 mL of dry ethanol and was then filtered to collect the solid product which was washed with anhydrous ether and dried in vacuo.

**$[\text{AsPh}_4][\text{Co}(\text{dmgH})_2(\text{CF}_3)(\text{NCO})]$ .** In a typical synthesis 0.31 g (0.9 mmol) of  $\text{Co}(\text{dmgH})_2(\text{CF}_3)$  was suspended in 100 mL of  $\text{CHCl}_3$ . Upon addition of 0.38 g (0.9 mmol) of  $[\text{AsPh}_4]\text{NCO}$  the reactants dissolved. The slow addition of hexane resulted in the precipitation of the product which was collected by filtration, washed with anhydrous ether, and dried in vacuo.

**$[\text{AsPh}_4][\text{Co}(\text{dmgH})_2(\text{CHBr}_2)(\text{CNS})]$ .** In a typical synthesis 1.0 g (1.9 mmol) of  $\text{Co}(\text{dmgH})_2(\text{CHBr}_2)(\text{S}(\text{CH}_3)_2)$  was suspended in 50 mL of dry ethanol at room temperature. Upon addition of 1.0 g (2.4 mmol) of  $[\text{AsPh}_4]\text{SCN}$  the reactants dissolved. After being stirred for 15 min at room temperature, the solution was filtered to remove a fine blue powder which was identified by its IR spectrum as  $[\text{AsPh}_4]_2[\text{Co}(\text{NCS})_4]$ . The filtrate was gradually diluted with 300 mL of anhydrous ether which resulted in the precipitation of the product. The product was collected by filtration, washed with anhydrous ether, and dried in vacuo.

**$[\text{AsPh}_4][\text{Co}(\text{dmgH})_2(\text{CHBr}_2)(\text{CNSe})]$ .**  $\text{Co}(\text{dmgH})_2(\text{CHBr}_2)(\text{S}(\text{CH}_3)_2)$ , 1.0 g (1.9 mmol), and  $[\text{AsPh}_4]\text{SeCN}$ , 1.5 g (3.0 mmol), were dissolved in 50 mL of reagent grade  $\text{CHCl}_3$  at room temperature with stirring. The addition of excess dry hexane precipitated an olive colored powder that was collected by filtration, washed with anhydrous ether, and air-dried. An IR spectrum indicated that the solid sample contained both coordinated and ionic selenocyanate. The olive colored powder, 1 g, was suspended in 50 mL of dry ethanol and stirred at room temperature for 10 min. The suspension was then filtered to collect solid material that was identified as  $[\text{AsPh}_4]_2[\text{Co}(\text{NCSe})_4]$  by its IR spectrum. The filtrate was diluted with 250 mL of anhydrous ether which resulted in the precipitation of  $[\text{AsPh}_4][\text{Co}(\text{dmgH})_2(\text{CHBr}_2)(\text{CNSe})]$  contaminated with  $[\text{AsPh}_4]\text{SeCN}$ . Further dilution with anhydrous ether to a total solution volume of 500 mL and cooling to -78 °C resulted in precipitation of the desired product as a brick red powder. The product was collected by filtration, washed with anhydrous ether, and dried in vacuo.

**$[\text{AsPh}_4][\text{Co}(\text{dmgH})_2(\text{CHBr}_2)(\text{NCO})]$ .**  $\text{Co}(\text{dmgH})_2(\text{CHBr}_2)(\text{S}(\text{CH}_3)_2)$ , 0.80 g (1.5 mmol), and  $[\text{AsPh}_4]\text{NCO}$ , 0.80 g (1.8 mmol), were stirred in 125 mL of dry ethanol at room temperature for 15 min. The solution was then filtered to remove a small amount of

undissolved residue. The filtrate was diluted with 375 mL of anhydrous ether and cooled to 0 °C to yield a precipitate, which was collected by filtration and identified as  $[\text{AsPh}_4]_2[\text{Co}(\text{NCO})_4]$  by its IR spectrum. Further dilution of the filtrate with anhydrous ether to a total solution volume of 1 L resulted in the precipitation of the product as a tan-yellow powder that was collected by filtration, washed with anhydrous ether, and dried in vacuo.

**$\text{Co}(\text{dmgH})_2(\text{CNS})(\text{B})$ .** The thiocyanato complexes where B is py or pip were prepared by literature methods.<sup>18</sup> The N- and S-bonded isomers were separated by fractional recrystallization from a  $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$  solvent mixture containing ca. 1 vol %  $\text{BrCCl}_3$  to prevent isomer equilibration. The N-bonded isomer was significantly less soluble than the S-bonded isomer. Isomer purity was established by <sup>1</sup>H NMR spectra in  $\text{CD}_2\text{Cl}_2$ .

**$\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{B})$ .** The selenocyanato complexes where B is py, pip, py-3-Cl,  $\text{NH}_3$ , or  $\text{NH}_2\text{-pr}$  were prepared in an analogous manner. In a typical preparation, 5.76 g (23.1 mmol) of  $\text{Co}(\text{C}_6\text{H}_5\text{COO})_2 \cdot 4\text{H}_2\text{O}$  was dissolved in 50 mL of  $\text{H}_2\text{O}$  at 55 °C in a  $\text{N}_2$  atmosphere and added to 5.37 g (46.3 mmol) of dimethylglyoxime dissolved in 175 mL of 70 vol %  $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$  at 55 °C, also in a  $\text{N}_2$  atmosphere.  $\text{KSeCN}$ , 7.30 g (50.7 mmol), dissolved in 50 mL of  $\text{H}_2\text{O}$  was then added to the reaction mixture, which was aerated at room temperature for 3 h with stirring. The solution was then filtered to remove a brown residue. A molar equivalent or a slight excess of the desired ligand B was added to the filtrate which resulted in  $\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{B})$  precipitating from the reaction mixture in 50–85% yield. Equivalent results were obtained by first isolating  $[\text{Co}(\text{dmgH})_2(\text{SeCN})_2]^-$  as the  $\text{Na}^+$  or  $\text{K}^+$  salt and then redissolving the complex for reaction with the desired ligand B. The crude reaction products were washed with water, ethanol, and ether. The solvents used for recrystallizations were as follows: B = py,  $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$ ; B = pip or py-3-Cl,  $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$ ; B =  $\text{NH}_3$ ,  $(\text{CH}_3)_2\text{CO}$ ; B =  $\text{NH}_2\text{-pr}$ ,  $(\text{CH}_3)_2\text{CO}/\text{C}_6\text{H}_{14}$ . All recrystallized products were dried in vacuo and analyzed as  $\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{B})$ , except for the case when B =  $\text{NH}_3$  where the hydrate  $\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{NH}_3) \cdot \frac{1}{2}\text{H}_2\text{O}$  was formed.  $\text{BrCCl}_3$  was not used in the synthesis of the selenocyanato complexes since there was no evidence for selenocyanate isomerization.

**$(\text{R})\text{Co}(\text{dmgH})_2(\text{CNX})\text{Co}(\text{dmgH})_2(\text{B})$ .** Synthesis of ligand-bridged dimeric complexes of this formula where  $\text{R} = \text{CH}_3^-$  or  $\text{CF}_3^-$ ,  $\text{X} = \text{S}$ , and B = py or pip and where  $\text{R} = \text{CH}_3^-$  or  $\text{CF}_3^-$ ,  $\text{X} = \text{Se}$ , and B = py, pip,  $\text{NH}_3$ , py-3-Cl, or  $\text{NH}_2\text{-pr}$  were carried out in a similar manner. The basic technique involved dissolving ca. 1 mmol of  $\text{Co}(\text{dmgH})_2(\text{R})$  with ca. 1 mmol of  $\text{Co}(\text{dmgH})_2(\text{CNX})(\text{B})$  in  $\text{CHCl}_3$  containing ca. 5 vol %  $\text{BrCCl}_3$  at room temperature. The solution was then concentrated in vacuo and dry hexane was added to induce precipitation of the product. Recrystallization was carried out in  $\text{CHCl}_3/\text{C}_6\text{H}_{14}$  solvent mixtures containing a few vol %  $\text{BrCCl}_3$ . All manipulations were carried out in a darkened room under rigorously dry conditions by using a vacuum line or Schlenk tubes under a dry  $\text{N}_2$  purge. Isomerically pure thiocyanato complexes  $\text{Co}(\text{dmgH})_2(\text{CNS})(\text{B})$  were used in all syntheses, as established by their <sup>1</sup>H NMR spectra in  $\text{CH}_2\text{Cl}_2$ . Isomerization prior to reaction to form the ligand-bridged complex was prevented by treatment with  $\text{BrCCl}_3$  simultaneous with dissolution in  $\text{CHCl}_3$ . Although selenocyanato-cobaloximes,  $\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{B})$ , were not observed to isomerize, ligand-bridged syntheses were carried out in the presence of  $\text{BrCCl}_3$  to prevent oligomer formation.

Isolation of the ligand-bridged complexes was by selective precipitation of the less soluble dimeric product upon the addition of  $\text{C}_6\text{H}_{14}$ . This resulted in the isolation of pure ligand-bridged dimeric products, except in those cases where  $\text{Co}(\text{dmgH})_2(\text{NCS})(\text{B})$  was a reactant. The solubility of the N-bonded isomers of  $\text{Co}(\text{dmgH})_2(\text{CNS})(\text{B})$  is significantly less than that of the S-bonded isomers. As a result, it was difficult to isolate pure samples of  $(\text{R})\text{Co}(\text{dmgH})_2\text{SCNCo}(\text{dmgH})_2(\text{B})$ , since its solubility was similar to that of  $\text{Co}(\text{dmgH})_2(\text{NCS})(\text{B})$ . Other data also suggest that this ligand-bridged linkage isomer is unstable with respect to dissociation. As a result, satisfactory elemental analyses were not obtained for this dimeric ligand-bridged linkage isomer.

In a typical preparation  $\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{py})$ , 0.33 g (0.7 mmol), and  $\text{Co}(\text{dmgH})_2(\text{CH}_3)$ , 0.21 g (0.7 mmol), were placed in a dry Schlenk tube, and 5 mL of  $\text{BrCCl}_3$  and 120 mL of freshly distilled  $\text{CHCl}_3$  were added under a purge of dry  $\text{N}_2$ . The reaction mixture was stirred at room temperature until all of the reactants dissolved. The resulting solution was concentrated to a 30-mL volume under reduced pressure, and ca. 130 mL of dry hexane was added with

stirring. The orange-brown precipitate was collected by filtration, washed with dry hexane, and dried in vacuo.

Characterization is by elemental analysis,  $^1\text{H}$  NMR and IR spectroscopies (see Results), and vapor-pressure osmometry (see above) which shows partial dissociation in  $\text{CHCl}_3$  containing 1 vol %  $\text{BrCCl}_3$  at 37 °C. Experimental molecular weights and theoretical molecular weights are as follows.  $(\text{R})\text{Co}(\text{dmgH})_2(\text{NCS})\text{Co}(\text{dmgH})_2(\text{B})$ : R =  $\text{CH}_3^-$ , B = py, 590 (731); R =  $\text{CH}_3^-$ , B = pip, 600 (737); R =  $\text{CF}_3^-$ , B = pip, 690 (791).  $(\text{R})\text{Co}(\text{dmgH})_2(\text{SCN})\text{Co}(\text{dmgH})_2(\text{B})$ : R =  $\text{CH}_3^-$ , B = py, 538 (731); R =  $\text{CH}_3^-$ , B = pip, 490 (737); R =  $\text{CF}_3^-$ , B = pip, 620 (791).  $(\text{R})\text{Co}(\text{dmgH})_2(\text{NCSe})\text{Co}(\text{dmgH})_2(\text{B})$ : R =  $\text{CH}_3^-$ , B = pip, 590 (783); R =  $\text{CF}_3^-$ , B = pip, 700 (837).

$(\text{R})\text{Co}(\text{dmgH})_2[\text{-(CNX)Co}(\text{dmgH})_2]_n(\text{CNX)Co}(\text{dmgH})_2(\text{B})$ . Ligand-bridged oligomers were isolated with the following composition: when X = Se, B = py, py-3-Cl,  $\text{NH}_3$ ,  $\text{NH}_2$ -pr, or pip, and R =  $\text{CH}_3^-$ ,  $\text{C}_2\text{H}_5^-$ , or  $n\text{-C}_3\text{H}_7^-$ ; when X = S, B = py or pip, and R =  $\text{CH}_3^-$ ,  $\text{C}_2\text{H}_5^-$ , or  $n\text{-C}_3\text{H}_7^-$ . These oligomeric compounds were synthesized in two ways. In one route the synthesis was carried out as described above for the ligand-bridged dimer, but without the addition of  $\text{BrCCl}_3$ . Depending on the solubility properties of the oligomer, as dictated by R, B, and X, the oligomer gradually precipitated without any solvent removal or addition of  $\text{C}_6\text{H}_{14}$ . In other cases where precipitation was induced either by concentration or by the addition of hexane, care was taken not to precipitate the dimer compound  $(\text{R})\text{Co}(\text{dmgH})_2(\text{CNX})\text{Co}(\text{dmgH})_2(\text{B})$ .

The polymeric complexes were also prepared by dissolving the corresponding ligand-bridged dimer in  $\text{CHCl}_3$  or  $\text{CH}_2\text{Cl}_2$ , but without adding  $\text{BrCCl}_3$ . Precipitation occurred by adjusting the concentration or by adding  $\text{C}_6\text{H}_{14}$ . Anhydrous conditions were used to prevent the isolation of  $\text{Co}(\text{dmgH})_2(\text{R})(\text{OH}_2)$  along with the oligomer.

Due to the variation in oligomer chain length ( $n$ ) elemental analyses were not obtained. Characterization was by IR and  $^1\text{H}$  NMR spectra. IR spectra (KBr) exhibited a strong broad absorption at  $2170\text{ cm}^{-1}$ , typical dmgh absorptions, and only weak absorptions for the ligand B. Although the solid oligomers were insoluble in  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$ , they were completely dissolved by the addition of ca. 1 vol % pyridine. By consideration of its  $^1\text{H}$  NMR spectrum the dissolved product was identified as  $\text{Co}(\text{dmgH})_2(\text{R})(\text{py})$  and  $\text{Co}(\text{dmgH})_2(\text{CNX})(\text{py})$  in the ratio 1:3–4. This established the composition of the oligomer and  $n$  as 2–3.

A typical synthesis was as follows:  $(\text{CH}_3)\text{Co}(\text{dmgH})_2(\text{NCSe})\text{Co}(\text{dmgH})_2(\text{py})$ , 0.50 g (0.6 mmol), was placed in a reaction tube on a high-vacuum line. Dry  $\text{CH}_2\text{Cl}_2$ , 50 mL, was distilled onto the sample and stirred at room temperature until dissolved. The solution was then concentrated to 20 mL, and 10 mL of dry  $\text{C}_6\text{H}_{14}$  was added. The polymeric product was slowly precipitated, collected by filtration, washed with anhydrous ether, and dried in vacuo. The molecular weight by vapor-pressure osmometry was 1200.

## Results

**Characterization of Terminally Bound Pseudohalocobaloximes.  $\text{Co}(\text{dmgH})_2(\text{CNX})(\text{B})$ .** The syntheses of pseudohalide-containing cobaloximes with uncharged nitrogen donor ligands are described in the Experimental Section. For the thiocyanate complexes with B = py or pip, both the N- and S-bonded isomers were prepared and isolated from  $\text{CH}_2\text{Cl}_2$  in the presence of  $\text{BrCCl}_3$ . Isomer separation was made possible by the lower solubility of the N-bonded form.  $\text{BrCCl}_3$  (4 vol %) was present to scavenge trace quantities of cobalt(II) which are known to catalyze  $\text{N} \rightleftharpoons \text{S}$  isomerization of coordinated thiocyanate.<sup>21,22</sup> The  $^1\text{H}$  NMR spectra for  $\text{Co}(\text{dmgH})_2(\text{CNS})(\text{B})$  exhibited dimethylglyoximate methyl resonances which were clearly distinguishable for the N- and S-bonded isomers in  $\text{CH}_2\text{Cl}_2$  and  $\text{PhNO}_2$  solvents, as was previously reported for  $\text{Co}(\text{dmgH})_2(\text{CNS})(t\text{-Bupy})$ .<sup>22</sup> These data are listed in Table I. This allowed the isomeric purity of the compounds to be established to within 5%. Assignment of the bonding mode as -NCS or -SCN was made for each isomer from solid-state and solution IR integrated absorption intensity data using the thiocyanate  $\nu_{\text{CN}}$  absorption band. These data are listed in Table II. Integrated intensity data obtained in  $\text{CHCl}_3$  solution containing  $\text{BrCCl}_3$  ( $A$ ) are consistent with solid-state data ( $A_s$ ), indicating that isomerization did not occur on dissolution or reprecipitation of the

**Table I.** Proton Magnetic Resonance Data for  $\text{Co}(\text{dmgH})_2(\text{CNX})(\text{B})$

compd	dmgH methyl resonance <sup>a</sup>		
	$\text{CDCl}_3$	$\text{CH}_2\text{Cl}_2$	$\text{PhNO}_2$
$\text{Co}(\text{dmgH})_2(\text{NCS})(\text{py})$	2.44 <sup>b</sup>	2.43 <sup>b</sup>	2.47
$\text{Co}(\text{dmgH})_2(\text{SCN})(\text{py})$	2.44 <sup>b</sup>	2.41 <sup>b</sup>	2.54
$\text{Co}(\text{dmgH})_2(\text{NCS})(\text{pip})$	2.59 <sup>b</sup>	2.57 <sup>b</sup>	2.57
$\text{Co}(\text{dmgH})_2(\text{SCN})(\text{pip})$	2.59 <sup>b</sup>	2.55 <sup>b</sup>	2.70
$\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{py})$	2.45 <sup>b</sup>	2.36 <sup>b</sup>	2.52
$\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{pip})$	<i>e</i>	2.48 <sup>c</sup>	2.54
$\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{py-3-Cl})$	2.41 <sup>b</sup>	2.36 <sup>c</sup>	2.60
$\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{NH}_3)$	<i>e</i>	<i>e</i>	2.46
$\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{NH}_2\text{-pr})$	<i>e</i>	2.43 <sup>c</sup>	
$\text{Co}(\text{dmgH})_2(\text{NCO})(\text{py})$	2.32 <sup>b</sup>	2.30 <sup>d</sup>	

<sup>a</sup> Chemical shift data in  $\text{CDCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , and  $\text{PhNO}_2$  solvents at 29 °C expressed in  $\delta$  units downfield from internal  $\text{Me}_4\text{Si}$ .

<sup>b</sup> Containing 4 vol %  $\text{BrCCl}_3$ . <sup>c</sup> Data obtained at 34 °C.

<sup>d</sup> Acetone- $d_6$  at 29 °C. <sup>e</sup> Reliable data not obtained due to low solubility.

complexes in the presence of  $\text{BrCCl}_3$ . The N-bonded thiocyanate complexes also exhibited a characteristic  $\nu_{\text{CS}}$  IR absorption at  $837\text{ cm}^{-1}$ , which was absent in the S-bonded isomer.<sup>1,4</sup>

Selenocyanato complexes  $\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{B})$  were prepared with a variety of ligands B.  $^1\text{H}$  NMR (Table I) and IR (Table II) spectra indicate that each compound was isolated in a single isomeric form. All complexes are assigned the Se-bonding mode on the basis of integrated intensity data for the  $\nu_{\text{CN}}$  absorption band (Table II). Data obtained in solution ( $A$ ) are in the expected range for Se-bonded selenocyanate<sup>4,9</sup> and solid-state data ( $A_s$ ) are comparable to those obtained for S-bonded thiocyanate, as expected. Repeated attempts to make the corresponding N-bonded isomers by a variety of synthetic routes were unsuccessful.

$\text{Co}(\text{dmgH})_2(\text{NCO})(\text{py})$  was prepared as a single isomer as evidenced by a single  $^1\text{H}$  NMR signal for the dimethylglyoximate methyl group in  $\text{CDCl}_3$  and acetone- $d_6$  solvents.  $^1\text{H}$  NMR and IR data are presented in Tables I and II. Neither the frequency nor the intensity of the  $\nu_{\text{CN}}$  absorption band for coordinated cyanate is as definitive for isomer assignments as for coordinated thiocyanate or selenocyanate.<sup>4</sup> However, we assign the bonding mode as N bonded for  $\text{Co}(\text{dmgH})_2(\text{NCO})(\text{py})$  on the basis of a  $\nu_{\text{CO}}$  absorption at  $1341\text{ cm}^{-1}$  and an  $A$  value for  $\nu_{\text{CN}}$  which is consistent with other N-bonded cyanates.<sup>4,23</sup>

$[\text{Co}(\text{dmgH})_2(\text{CNX})(\text{R})]^-$ . The synthesis and isolation of alkylcobaloximes containing pseudohalide ligands are described in the Experimental Section for  $\text{OCN}^-$ ,  $\text{SCN}^-$ , and  $\text{SeCN}^-$  with  $\text{CH}_3^-$ ,  $\text{CF}_3^-$ , and  $\text{CHBr}_2^-$  trans alkyl groups. For  $\text{SCN}^-$  and  $\text{SeCN}^-$ , these alkylcobaloximes tend to form linear pseudohalide-bridged dimers when dissolved in solution, as evidenced by  $^1\text{H}$  NMR spectra (Table III) which exhibit two new equally intense dmgh methyl resonances that cannot be assigned to either terminally bound linkage isomer. For methylcobaloxime the corresponding axial methyl resonances are also observed. Weak linear bridge formation was also suggested by  $^1\text{H}$  NMR data for  $[\text{Co}(\text{dmgH})_2(\text{CF}_3)(\text{NCO})]^-$ . These observations are analogous to a previous report of ligand-bridged dimer formation in certain alkylcobaloximes containing  $\text{SCN}^-$ ,  $\text{N}_3^-$ , or  $\text{CN}^-$ .<sup>7</sup> The dimers are in equilibrium with both isomeric forms of the monomer (except for cyanate where only the N-bonded form was observed). Dimer formation can be suppressed in the presence of excess pseudohalide.

Evidence that both linkage isomers of the monomeric (pseudohalo)alkylcobaloximes  $[\text{Co}(\text{dmgH})_2(\text{CNX})(\text{R})]^-$  (X = S, Se) are present in solution may be obtained from  $^1\text{H}$  NMR data listed in Table IV. Two dmgh methyl resonances were observed in all cases and when R =  $\text{CH}_3^-$  the corre-

**Table II.** Infrared C-N Stretching Frequency for the Compounds  $\text{Co}(\text{dmgH})_2(\text{CNX})(\text{B})$ ,  $\text{Ph}_4\text{As}[\text{Co}(\text{dmgH})_2(\text{CNX})(\text{R})]$ , and  $(\text{R})\text{Co}(\text{dmgH})_2(\text{CNX})\text{Co}(\text{dmgH})_2(\text{B})$ 

compd	$\nu_{\text{CN}}, \text{cm}^{-1}$ <sup>a</sup>				compd	$\nu_{\text{CN}}, \text{cm}^{-1}$ <sup>a</sup>			
	KBr	$A_{\text{T}}^b$	soln	$10^{-4}A^c$		KBr	$A_{\text{T}}^b$	soln	$10^{-4}A^c$
(A) $\text{Co}(\text{dmgH})_2(\text{CNX})(\text{B})$									
$\text{Co}(\text{dmgH})_2(\text{NCS})(\text{py})$	2130	2.4	2120 <sup>f</sup>	10 <sup>f</sup>	$\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{pip})$	2122	0.4	2121 <sup>g</sup>	0.6 <sup>g</sup>
$\text{Co}(\text{dmgH})_2(\text{SCN})(\text{py})$	2120	1.0	2112 <sup>f</sup>	1.3 <sup>f</sup>	$\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{py-3-Cl})$	2119	0.2	2121 <sup>g</sup>	0.5 <sup>g</sup>
$\text{Co}(\text{dmgH})_2(\text{NCS})(\text{pip})$	2112	3.6	2121 <sup>f</sup>	9.4 <sup>f</sup>	$\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{NH}_3)$	2122 <sup>d</sup>	0.4 <sup>d</sup>	2122 <sup>f</sup>	<i>h</i>
$\text{Co}(\text{dmgH})_2(\text{SCN})(\text{pip})$	2116	0.6	2112 <sup>f</sup>	1.7 <sup>f</sup>	$\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{NH}_2\text{-pr})$	2121	0.4	<i>h</i>	<i>h</i>
$\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{py})$	2116	0.2	2121 <sup>g</sup>	0.6 <sup>g</sup>	$\text{Co}(\text{dmgH})_2(\text{NCO})(\text{py})$	2190 <sup>e</sup>	3.0	2188 <sup>e,f</sup>	23 <sup>f</sup>
(B) $\text{Ph}_4\text{As}[\text{Co}(\text{dmgH})_2(\text{CNX})(\text{R})]$									
$\text{Ph}_4\text{As}[\text{Co}(\text{dmgH})_2(\text{NCS})\text{-}(\text{CH}_3)]$			2115 <sup>f</sup>		$\text{Ph}_4\text{As}[\text{Co}(\text{dmgH})_2(\text{CNSe})\text{-}(\text{CHBr}_2)]$	2105	0.4		
$\text{Ph}_4\text{As}[\text{Co}(\text{dmgH})_2(\text{SCN})\text{-}(\text{CH}_3)]$	2110 <sup>i</sup>	2.4	2107 <sup>f</sup>		$\text{Ph}_4\text{As}[\text{Co}(\text{dmgH})_2(\text{CNSe})\text{-}(\text{CF}_3)]$	2111	1.4		
$\text{Ph}_4\text{As}[\text{Co}(\text{dmgH})_2(\text{CNS})\text{-}(\text{CHBr}_2)]$	2106	2.5			$\text{Ph}_4\text{As}[\text{Co}(\text{dmgH})_2(\text{NCO})\text{-}(\text{CH}_3)]$	2224	3.2		
$\text{Ph}_4\text{As}[\text{Co}(\text{dmgH})_2(\text{CNS})\text{-}(\text{CF}_3)]$	2115	1.8			$\text{Ph}_4\text{As}[\text{Co}(\text{dmgH})_2(\text{NCO})\text{-}(\text{CHBr}_2)]$	2225	sh		
$\text{Ph}_4\text{As}[\text{Co}(\text{dmgH})_2(\text{NCSe})\text{-}(\text{CH}_3)]$			2103 <sup>f</sup>		$\text{Ph}_4\text{As}[\text{Co}(\text{dmgH})_2(\text{NCO})\text{-}(\text{CF}_3)]$	2226	3.5		
$\text{Ph}_4\text{As}[\text{Co}(\text{dmgH})_2(\text{SeCN})\text{-}(\text{CH}_3)]$	2094 <sup>j</sup>	1.8	2116 <sup>f</sup>						
(C) $(\text{R})\text{Co}(\text{dmgH})_2(\text{CNX})\text{Co}(\text{dmgH})_2(\text{B})$									
$(\text{CH}_3)\text{Co}(\text{dmgH})_2(\text{NCS})\text{Co}(\text{dmgH})_2(\text{py})$	2157		2149 <sup>f</sup>		$(\text{CH}_3)\text{Co}(\text{dmgH})_2(\text{NCSe})\text{Co}(\text{dmgH})_2(\text{pip})$	2154			
$(\text{CH}_3)\text{Co}(\text{dmgH})_2(\text{SCN})\text{Co}(\text{dmgH})_2(\text{py})$	2161		2156 <sup>f</sup>		$(\text{CH}_3)\text{Co}(\text{dmgH})_2(\text{NCSe})\text{Co}(\text{dmgH})_2(\text{py-3-Cl})$	2153			
$(\text{CH}_3)\text{Co}(\text{dmgH})_2(\text{NCS})\text{Co}(\text{dmgH})_2(\text{pip})$	2153				$(\text{CH}_3)\text{Co}(\text{dmgH})_2(\text{NCSe})\text{Co}(\text{dmgH})_2(\text{NH}_3)^k$	2142	br	2144 <sup>k</sup>	
$(\text{CH}_3)\text{Co}(\text{dmgH})_2(\text{SCN})\text{Co}(\text{dmgH})_2(\text{pip})$	2150				$(\text{CH}_3)\text{Co}(\text{dmgH})_2(\text{NCSe})\text{Co}(\text{dmgH})_2(\text{NH}_2\text{-pr})$	2152	br		
$(\text{CF}_3)\text{Co}(\text{dmgH})_2(\text{NCS})\text{Co}(\text{dmgH})_2(\text{pip})$	2162	br	2156 <sup>f</sup>		$(\text{CF}_3)\text{Co}(\text{dmgH})_2(\text{NCSe})\text{Co}(\text{dmgH})_2(\text{py})$	2169			
$(\text{CF}_3)\text{Co}(\text{dmgH})_2(\text{SCN})\text{Co}(\text{dmgH})_2(\text{pip})$	2160		2167 <sup>f</sup>		$(\text{CF}_3)\text{Co}(\text{dmgH})_2(\text{NCSe})\text{Co}(\text{dmgH})_2(\text{pip})$	2167			
$(\text{CH}_3)\text{Co}(\text{dmgH})_2(\text{NCSe})\text{Co}(\text{dmgH})_2(\text{py})$	2158		2145 <sup>f</sup>						

<sup>a</sup> C-N stretching frequency for coordinated  $\text{SCN}^-$ ,  $\text{SeCN}^-$ , or  $\text{OCN}^-$ . <sup>b</sup>  $A_{\text{T}}$  is defined as the solid-state intensity of the XCN ligand absorption relative to the intensity of the NO absorption at ca. 1230  $\text{cm}^{-1}$  arising from the dmGH ligand. See the Experimental Section. <sup>c</sup> The integrated absorption band intensity ( $\text{M}^{-1} \text{cm}^{-2}$ ) as determined by the method of Ramsay.<sup>15</sup> <sup>d</sup> Data obtained from hemihydrate crystalline sample. <sup>e</sup> Broad absorption with a shoulder at 2250  $\text{cm}^{-1}$ . <sup>f</sup> Dry  $\text{CHCl}_3$  solution at  $10^{-3}$  M containing 4 vol %  $\text{BrCCl}_3$  and 1-mm path length KBr cells. <sup>g</sup> Dry  $\text{CH}_2\text{Cl}_2$  solution at  $10^{-2}$  M and 0.5-mm path length cells; identical  $\nu_{\text{CN}}$  data obtained in  $\text{CHCl}_3$  solution containing  $\text{BrCCl}_3$ . <sup>h</sup> Reliable data not obtained due to low solubility. <sup>i</sup> The sample is a mixture of N- and S-bonded forms. <sup>j</sup> The sample is a mixture of N- and Se-bonded forms. <sup>k</sup> Dry DMF.

sponding axial methyl signals were also observed. The thiocyanate and selenocyanate complexes could only be isolated as the mixed-linkage isomers due to the lability of the alkylcobaloximes, an apparent lack of any strong bonding preference by the alkylcobaloxime, and similar solubility properties for both isomers. Mixed-linkage isomers were observed even when product isolation was carried out in the presence of  $\text{BrCCl}_3$ .

<sup>1</sup>H NMR signal assignments for the N- and X-bonded isomers are based on the following reasoning. For the isomers of  $[\text{Co}(\text{dmgH})_2(\text{CNX})(\text{CH}_3)]^-$  ( $\text{X} = \text{S}, \text{Se}$ ) the upfield axial methyl resonance is assigned to the N-bonded isomer. This is consistent with previous literature assignments for  $[\text{Co}(\text{dmgH})_2(\text{CNS})(\text{CH}_3)]^-$ <sup>7</sup> and relative chemical shifts for axial protons of other cobaloximes containing N- and S-donor anionic ligands.<sup>24,25</sup> Identical assignments are made for the selenocyanato complexes since the magnetic substituent effects of  $-\text{NCS}$  and  $-\text{NCSe}$  and  $-\text{SCN}$  and  $-\text{SeCN}$  are expected to be similar.<sup>24,25</sup> Assignment of an equatorial dmGH methyl group signal to that of the corresponding axial methyl group in  $[\text{Co}(\text{dmgH})_2(\text{CNX})(\text{CH}_3)]^-$  was made on the basis of the required peak areas. This established the dmGH methyl group for the N-bonded isomer to be upfield relative to that of the

corresponding S- or Se-bonded isomer. These same relative chemical shifts were used for the N/S and N/Se isomer assignments in the complexes containing  $\text{CHBr}_2^-$  or  $\text{CF}_3^-$  ligands, as shown in Table IV.

Using the <sup>1</sup>H NMR chemical shift assignments given in Table IV, we were able to determine the relative N/X isomer ratios for the alkylcobaloximes in different solvents. These data are shown in Table V. The isomerization equilibria were rapidly established and were independent of the presence of  $\text{BrCCl}_3$ . These results are consistent with a previous report<sup>22</sup> of increased stabilization of N-bonded thiocyanate in aprotic solvents of increasing dielectric constant and therefore lend additional support to our <sup>1</sup>H NMR chemical shift assignments for the different isomeric forms. Data in Table V also show that the addition of water, a protic solvent, enhances the stabilities of S-bonded thiocyanate and Se-bonded selenocyanate, relative to the corresponding N-bonded form. This is consistent with previous observations for inert (thiocyanato)cobaloximes<sup>22</sup> and pentacyanocobaltate(III) ion containing thiocyanato or selenocyanato.<sup>26</sup> The variation in N/Se ratio with solvent reported here is the reverse of that found for complexes of Pt(II) and Pd(II).<sup>27</sup> However, it should be noted that opposite solvent influences were found for the

**Table III.** Proton Magnetic Resonance Data for Ligand-Bridged Dicobaloximes<sup>a</sup>

compd	Co-CH <sub>3</sub> <sup>b</sup>	dmgH	
		CH <sub>3</sub> <sup>c</sup>	CH <sub>3</sub> <sup>d</sup>
(CH <sub>3</sub> )Co(dmgh) <sub>2</sub> (NCS)Co-(dmgh) <sub>2</sub> (py)	0.76	2.32	2.46
(CH <sub>3</sub> )Co(dmgh) <sub>2</sub> (SCN)Co-(dmgh) <sub>2</sub> (py)	0.83	2.26	2.54
(CH <sub>3</sub> )Co(dmgh) <sub>2</sub> (NCS)Co-(dmgh) <sub>2</sub> (pip)	0.73	2.27	2.58
(CH <sub>3</sub> )Co(dmgh) <sub>2</sub> (SCN)Co-(dmgh) <sub>2</sub> (pip)	0.80	2.22	2.66
(CF <sub>3</sub> )Co(dmgh) <sub>2</sub> (NCS)Co-(dmgh) <sub>2</sub> (py)		2.36	2.39
(CF <sub>3</sub> )Co(dmgh) <sub>2</sub> (SCN)Co-(dmgh) <sub>2</sub> (py)		2.26	2.50
(CF <sub>3</sub> )Co(dmgh) <sub>2</sub> (NCS)Co-(dmgh) <sub>2</sub> (pip)		2.36	2.55
(CF <sub>3</sub> )Co(dmgh) <sub>2</sub> (SCN)Co-(dmgh) <sub>2</sub> (pip)		2.28	2.67
(CH <sub>3</sub> )Co(dmgh) <sub>2</sub> (NCSe)Co-(dmgh) <sub>2</sub> (py)	0.78	2.29	2.43
(CH <sub>3</sub> )Co(dmgh) <sub>2</sub> (NCSe)Co-(dmgh) <sub>2</sub> (pip)	0.74 <sup>e</sup>	2.20 <sup>e</sup>	2.48 <sup>e</sup>
(CH <sub>3</sub> )Co(dmgh) <sub>2</sub> (NCSe)Co-(dmgh) <sub>2</sub> (py-3-Cl)	0.74 <sup>e</sup>	2.21 <sup>e</sup>	2.37 <sup>e</sup>
(CF <sub>3</sub> )Co(dmgh) <sub>2</sub> (NCSe)Co-(dmgh) <sub>2</sub> (py)		2.41	2.44
(CF <sub>3</sub> )Co(dmgh) <sub>2</sub> (NCSe)Co-(dmgh) <sub>2</sub> (pip)		2.34	2.45
[(CH <sub>3</sub> )Co(dmgh) <sub>2</sub> (NCS)Co-(dmgh) <sub>2</sub> (CH <sub>3</sub> )] <sup>h</sup>	0.62, <sup>f</sup> 0.83 <sup>g</sup>	2.18 <sup>f</sup>	2.18 <sup>g</sup>
[(CF <sub>3</sub> )Co(dmgh) <sub>2</sub> (NCS)Co-(dmgh) <sub>2</sub> (CF <sub>3</sub> )] <sup>h</sup>		2.26 <sup>f</sup>	2.37 <sup>g</sup>
[(CH <sub>3</sub> )Co(dmgh) <sub>2</sub> (NCSe)Co-(dmgh) <sub>2</sub> (CH <sub>3</sub> )] <sup>h</sup>	0.58, <sup>f</sup> 0.78 <sup>g</sup>	2.15 <sup>f</sup>	2.15 <sup>g</sup>
[(CF <sub>3</sub> )Co(dmgh) <sub>2</sub> (NCSe)Co-(dmgh) <sub>2</sub> (CF <sub>3</sub> )] <sup>h</sup>		2.15 <sup>f</sup>	2.21 <sup>g</sup>

<sup>a</sup> CDCl<sub>3</sub> solvent containing 8 vol % BrCCl<sub>3</sub> at 29 °C, chemical shift values are in δ units downfield from Me<sub>4</sub>Si. <sup>b</sup> Chemical shift of axial CH<sub>3</sub> group bonded to cobalt. <sup>c</sup> Chemical shift of dmgh CH<sub>3</sub> group bound to the alkylcobaloxime end of the dimer. <sup>d</sup> Chemical shift of dmgh CH<sub>3</sub> group bound to the ligand cobaloxime end of the dimer. <sup>e</sup> Data obtained at 34 °C. <sup>f</sup> Signal due to cobaloxime bonded to N end of ligand bridge. <sup>g</sup> Signal due to cobaloxime bonded to S or Se end of ligand bridge. <sup>h</sup> Ph<sub>4</sub>As<sup>+</sup> salt.

**Table IV.** Proton Magnetic Resonance Data for Ph<sub>4</sub>As[Co(dmgh)<sub>2</sub>(CNX)(R)]<sup>a</sup>

compd	δ, CDCl <sub>3</sub>		δ, PhNO <sub>2</sub>	
	Co-CH <sub>3</sub>	dmgh-CH <sub>3</sub>	Co-CH <sub>3</sub>	dmgh-CH <sub>3</sub>
[Co(dmgh) <sub>2</sub> (NCS)(CH <sub>3</sub> )] <sup>-</sup>	0.51	2.09	0.88	2.35
[Co(dmgh) <sub>2</sub> (SCN)(CH <sub>3</sub> )] <sup>-</sup>	0.84	2.20	1.35	2.57
[Co(dmgh) <sub>2</sub> (NCSe)(CH <sub>3</sub> )] <sup>-</sup>	0.51	2.09	0.88	2.33
[Co(dmgh) <sub>2</sub> (SeCN)(CH <sub>3</sub> )] <sup>-</sup>	0.84	2.20	1.33	2.58
[Co(dmgh) <sub>2</sub> (NCS)(CHBr <sub>2</sub> )] <sup>-</sup>		2.15		2.33
[Co(dmgh) <sub>2</sub> (SCN)(CHBr <sub>2</sub> )] <sup>-</sup>		2.20		2.52
[Co(dmgh) <sub>2</sub> (NCSe)(CHBr <sub>2</sub> )] <sup>-</sup>		2.12		2.33
[Co(dmgh) <sub>2</sub> (SeCN)(CHBr <sub>2</sub> )] <sup>-</sup>		2.20		2.54
[Co(dmgh) <sub>2</sub> (NCS)(CF <sub>3</sub> )] <sup>-</sup>		2.13		2.45
[Co(dmgh) <sub>2</sub> (SCN)(CF <sub>3</sub> )] <sup>-</sup>		2.21		2.65
[Co(dmgh) <sub>2</sub> (NCSe)(CF <sub>3</sub> )] <sup>-</sup>		2.14		2.31
[Co(dmgh) <sub>2</sub> (SeCN)(CF <sub>3</sub> )] <sup>-</sup>		2.21		2.52

<sup>a</sup> Chemical shift data in CDCl<sub>3</sub> and PhNO<sub>2</sub> solvents at 29 °C expressed in δ units downfield from internal Me<sub>4</sub>Si.

thiocyanate bonding mode with class "a" and class "b" metals.<sup>3,26</sup>

Well-resolved solution IR spectra could not be obtained in all cases due to the lability of the complexes and the tendency for ligand bridge dimer formation. The addition of excess pseudohalide eliminated bridge formation, but then this resulted in a strong ionic pseudohalide ν<sub>CN</sub> absorption which

**Table V.** Equilibrium Ratio of [Co(dmgh)<sub>2</sub>(NCX)(R)]<sup>-</sup>/[Co(dmgh)<sub>2</sub>(XCN)(R)]<sup>-</sup> (X = S, Se) for Different Alkyl Groups and Solvents<sup>a</sup>

isomer ratio	solvent		
	CDCl <sub>3</sub>	PhNO <sub>2</sub>	Me <sub>2</sub> SO- <sub>d</sub> <sub>6</sub>
[Co(dmgh) <sub>2</sub> (NCS)(CH <sub>3</sub> )] <sup>-</sup> /[Co(dmgh) <sub>2</sub> (SCN)(CH <sub>3</sub> )] <sup>-</sup>	4.0	6.7	>100
[Co(dmgh) <sub>2</sub> (NCS)(CHBr <sub>2</sub> )] <sup>-</sup> /[Co(dmgh) <sub>2</sub> (SCN)(CHBr <sub>2</sub> )] <sup>-</sup>	2.6	5.8	>100
[Co(dmgh) <sub>2</sub> (NCS)(CF <sub>3</sub> )] <sup>-</sup> /[Co(dmgh) <sub>2</sub> (SCN)(CF <sub>3</sub> )] <sup>-</sup>	(1.7) <sup>b</sup>	(3.0) <sup>b</sup>	>100
[Co(dmgh) <sub>2</sub> (NCSe)(CH <sub>3</sub> )] <sup>-</sup> /[Co(dmgh) <sub>2</sub> (SeCN)(CH <sub>3</sub> )] <sup>-</sup>	2.0	5.1	>100
[Co(dmgh) <sub>2</sub> (NCSe)(CHBr <sub>2</sub> )] <sup>-</sup> /[Co(dmgh) <sub>2</sub> (SeCN)(CHBr <sub>2</sub> )] <sup>-</sup>	(1.3) <sup>b</sup>		
[Co(dmgh) <sub>2</sub> (NCSe)(CF <sub>3</sub> )] <sup>-</sup> /[Co(dmgh) <sub>2</sub> (SeCN)(CF <sub>3</sub> )] <sup>-</sup>	1.0	1.5	>100
[Co(dmgh) <sub>2</sub> (NCSe)(CHBr <sub>2</sub> )] <sup>-</sup> /[Co(dmgh) <sub>2</sub> (SeCN)(CHBr <sub>2</sub> )] <sup>-</sup>	0.5	0.9	>100
[Co(dmgh) <sub>2</sub> (NCSe)(CF <sub>3</sub> )] <sup>-</sup> /[Co(dmgh) <sub>2</sub> (SeCN)(CF <sub>3</sub> )] <sup>-</sup>	(0.4) <sup>b</sup>	(0.6) <sup>b</sup>	

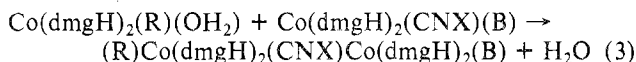
<sup>a</sup> As determined by <sup>1</sup>H NMR signal integration; estimated precision ±10%. Data obtained at 29 °C in dry solvents containing 1 equiv of cobaloxime and 3 equiv of Ph<sub>4</sub>As[CNX]. <sup>b</sup> Data obtained with the addition of 1 equiv of H<sub>2</sub>O.

overlapped with that of the coordinated pseudohalide. Also since the integrated intensity of the N-bonded pseudohalide is about 10 times that of the S- or Se-bonded isomer, the definition of the weaker ν<sub>CN</sub> absorption band is reduced. However, resolution of the ν<sub>CN</sub> absorption was achieved for [Co(dmgh)<sub>2</sub>(CH<sub>3</sub>)(CNSe)]<sup>-</sup> and [Co(dmgh)<sub>2</sub>(CH<sub>3</sub>)(CNS)]<sup>-</sup> in CHCl<sub>3</sub>, so that isomer assignments could be made on the basis of relative peak intensities and N/X ratios obtained from <sup>1</sup>H NMR data. The solid-state integrated absorption intensities (A<sub>s</sub>) reflect the mixed N/X isomer ratio found in CHCl<sub>3</sub>, the solvent from which the complexes were isolated. These results are summarized in Table II.

The monomeric cyanate complexes of the alkylcobaloximes (R = CH<sub>3</sub><sup>-</sup>, CF<sub>3</sub><sup>-</sup>, CHBr<sub>2</sub><sup>-</sup>) exhibit only one dmgh methyl <sup>1</sup>H NMR signal, suggesting that a single isomer is present. This is assumed to be the N-bonded form due to the marked tendency for cyanate to coordinate through the N atom<sup>2</sup> and the weaker affinity of alkylcobaloximes for O donors relative to N- and S-donor atoms.<sup>28</sup> The solid-state integrated absorption intensity data (A<sub>s</sub>) for ν<sub>CN</sub> are consistent with N bonding. (See Table II.)

#### Characterization of Pseudohalide-Bridged Dicobaloximes.

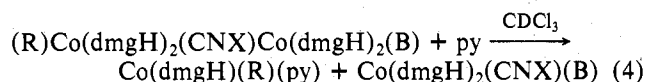
The synthesis of thiocyanato and selenocyanato ligand bridged dicobaloximes is based on the reaction of a kinetically labile alkylcobaloxime with an inert cobaloxime containing an isomerically pure coordinated pseudohalide (eq 3). No dimer



formation was observed to occur for the corresponding cyanatocobaloxime. These reactions were carried out in chloroform in the presence of BrCCl<sub>3</sub> to prevent isomerization of the pseudohalide ligand.<sup>21,22</sup> The equilibrium position of reaction 3 is shifted further to the right under anhydrous conditions where H<sub>2</sub>O can no longer act as a competing ligand. All data reported here are for vigorously dried solvents and the anhydrous form of the alkylcobaloxime Co(dmgh)<sub>2</sub>(R). In most cases solid products were isolated by precipitation upon addition of hexane. Synthetic procedures and product isolation are described in the Experimental Section.

Evidence for a chemical reaction upon mixing Co(dmgh)<sub>2</sub>(R) and Co(dmgh)<sub>2</sub>(CNX)(B) was obtained from IR and <sup>1</sup>H NMR spectra and vapor-phase osmometry. Since isolation of a solid product was by precipitation from a mixed solvent and not solvent evaporation and since the reactants have significantly different solubilities, elemental analysis of the precipitated product also verifies reaction 3.

Dimer formation was established in each case by  $^1\text{H}$  NMR spectra obtained in  $\text{CDCl}_3$  solvent containing 1 vol %  $\text{BrCCl}_3$ . Similar spectra were obtained from redissolved solid reaction products and solutions containing equivalent amounts of reactants. The product of reaction 3 exhibits two new dmGH methyl resonances of equal intensity, one in the region  $\delta$  2.0–2.3 and another at  $\delta$  2.3–2.7. In those cases where  $\text{R} = \text{CH}_3^-$  a new axial methyl resonance also appears. Support for attributing a dimeric structure to the product shown in reaction 3 comes from the equal intensity of the new oxime resonances. Also,  $^1\text{H}$  NMR spectra show that addition of pyridine to the product of reaction 3 produces equal amounts of  $\text{Co}(\text{dmGH})_2(\text{R})(\text{py})$  and  $\text{Co}(\text{dmGH})_2(\text{CNX})(\text{B})$  (eq 4). These



data demonstrate that the products from reaction 3 contain equivalent numbers of  $\text{Co}(\text{dmGH})_2(\text{R})$  and  $\text{Co}(\text{dmGH})_2(\text{CNX})(\text{B})$  units, which supports dimer formation.

$^1\text{H}$  NMR data for the dimeric complexes  $(\text{R})\text{Co}(\text{dmGH})_2(\text{CNX})\text{Co}(\text{dmGH})_2(\text{B})$  are presented in Table III. The upfield dmGH methyl group resonance is assigned to the alkylcobaloxime end of the dimer. This is qualitatively consistent with the relative dmGH methyl group chemical shifts ( $\text{CDCl}_3$ ) of alkylcobaloxime pseudohalide complexes, which occur from  $\delta$  2.0 to  $\delta$  2.3 (Table IV), and of neutral ligand cobaloxime pseudohalide complexes, which occur more downfield from  $\delta$  2.3 to  $\delta$  2.6 (Table I). It is noteworthy that in  $(\text{CH}_3)\text{Co}(\text{dmGH})_2(\text{CNS})\text{Co}(\text{dmGH})_2(\text{py})$  and  $(\text{CH}_3)\text{Co}(\text{dmGH})_2(\text{CNS})\text{Co}(\text{dmGH})_2(\text{pip})$  the chemical shift for the dmGH and axial methyl resonances move in opposite directions upon changing from one bridging ligand linkage isomer to the other. This is presumably due to anisotropic effects of the cobalt.

Molecular weight data were obtained for selected compounds by vapor-phase osmometry. These data were collected in  $\text{CHCl}_3$  containing  $\text{BrCCl}_3$  for crystalline products of reaction 3 and for equivalent molar quantities of the reactants mixed in the osmometer (see Experimental Section). The results were the same in both cases. Results are presented in Table VI which reflect the degree of dissociation of the dimer according to eq 1.

The primary evidence for dimerization occurring through the pseudohalide ligand comes from IR spectra obtained in  $\text{CHCl}_3$  solution and as KBr disks. These data are presented in Table II. In both cases  $\nu_{\text{CN}}$  for  $(\text{R})\text{Co}(\text{dmGH})_2(\text{CNS})\text{Co}(\text{dmGH})_2(\text{B})$  and  $(\text{R})\text{Co}(\text{dmGH})_2(\text{CNSe})\text{Co}(\text{dmGH})_2(\text{B})$  was in the range 2149–2167 and 2140–2169  $\text{cm}^{-1}$ , respectively. This is higher in energy than either of the corresponding terminally bound pseudohalide complexes  $\text{Co}(\text{dmGH})_2(\text{CNX})(\text{B})$  or  $[\text{Co}(\text{dmGH})(\text{R})(\text{CNX})]^-$ . Pseudohalide ligands which simultaneously bond to two transition-metal ions have been found to exhibit higher energy  $\nu_{\text{CN}}$  absorption bands than the corresponding singly coordinated pseudohalide.<sup>3,4,6,9,10</sup> In some cases this has been verified by X-ray diffraction determinations of molecular structure.<sup>8</sup> The cyano-bridged dicobaloximes which are analogous to the compounds described here but contain a cyanide bridge between the two cobalt(III) ions exhibit a similar increase in  $\nu_{\text{CN}}$  upon dimer formation.<sup>13</sup>

Evidence to support the remote ligand bridge formation  $\text{Co}-\text{N}-\text{C}-\text{X}-\text{Co}$  rather than adjacent bonding through the N or X atom may be obtained from  $^1\text{H}$  NMR and IR data.  $^1\text{H}$  NMR spectra provide direct evidence for remote pseudohalide bridge formation in the organodicobaloxime complexes  $[(\text{R})\text{Co}(\text{dmGH})_2(\text{CNX})\text{Co}(\text{dmGH})_2(\text{R})]^-$ . These data are shown in Table III. Bridge formation results in two new dmGH methyl signals and, when  $\text{R} = \text{CH}_3^-$ , two new axial methyl signals. These data may be interpreted as either remote ligand

bridge formation or the formation of equal amounts of both adjacent bridge structures. The equal stability required in the latter case is highly unlikely.

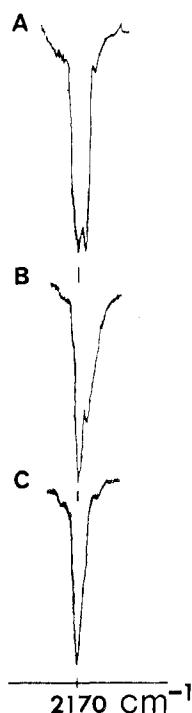
In the case of the thiocyanato complexes  $\text{Co}(\text{dmGH})_2(\text{CNS})(\text{B})$ , which were shown to exhibit linkage isomerism,  $^1\text{H}$  NMR and IR data demonstrate that each isomer reacts with the alkylcobaloxime to produce a single pseudohalide-bridged product and that the product differs depending on whether the N- or S-bonded complex is used as the starting material (Tables II and III). Since adjacent bridge formation through the N atom of thiocyanate is highly unlikely (as evidenced by the absence of neutral cyanato bridge formation), these data are best interpreted in terms of the remote pseudohalide bridge geometry as shown above. The single available Se-bonded isomer of the (selenocyanato)cobaloximes  $\text{Co}(\text{dmGH})_2(\text{SeCN})(\text{B})$  was found to react with an alkylcobaloxime to produce a single selenocyanato-bridged dicobaloxime, as shown by IR and  $^1\text{H}$  NMR spectra.

Remote pseudohalide bridge formation, then, allows for the possibility of isomers. Both bridging isomers were found for the thiocyanato complexes. No pseudohalide isomerization was found to occur upon dimer formation. This was established by reacting the pseudohalide-bridged dimer with py (eq 4) and by demonstrating that the  $\text{Co}(\text{dmGH})_2(\text{CNX})(\text{B})$  ( $\text{X} = \text{S}, \text{Se}$ ) released was the same linkage isomer as found in the reactant, by comparison of  $^1\text{H}$  NMR spectra in  $\text{CH}_2\text{Cl}_2$ . For this reason the bridge linkage isomer is assigned to be that of the inert reactant  $\text{Co}(\text{dmGH})_2(\text{CNX})(\text{B})$ . This is also consistent with only one pseudohalide ligand bridge isomer being observed for the selenocyanato systems.

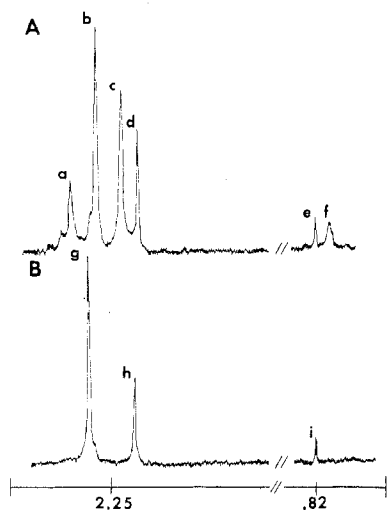
For the thiocyanato complexes the differences in energies of the  $\nu_{\text{CN}}$  band for the two ligand-bridged linkage isomers are the same as for the corresponding terminally bound compounds  $\text{Co}(\text{dmGH})_2(\text{CNS})(\text{B})$  (Table II). A quantitative assessment of  $\nu_{\text{CN}}$  band intensities for the ligand-bridged complexes was not possible due to partial dissociation in solution and a broadening of  $\nu_{\text{NO}}$  in the solid state as a result of nonequivalent dimethylglyoximate groups in the dimer. However,  $\nu_{\text{CN}}$  bandwidths (KBr) at half-height for  $(\text{R})\text{Co}(\text{dmGH})_2(\text{NCX})\text{Co}(\text{dmGH})_2(\text{B})$  ( $\text{X} = \text{S}, \text{Se}$ ) were 10–20  $\text{cm}^{-1}$ , while those for  $(\text{R})\text{Co}(\text{dmGH})_2(\text{SCN})\text{Co}(\text{dmGH})_2(\text{B})$  were 30–40  $\text{cm}^{-1}$ . This is qualitatively in agreement with the integrated peak intensities for the corresponding terminally bound complexes  $\text{Co}(\text{dmGH})_2(\text{CNX})(\text{B})$ .

**Characterization of Pseudohalide-Bridged Cobaloxime Oligomers.** When the synthesis of pseudohalide-bridged dicobaloximes was carried out in  $\text{CHCl}_3$  in the absence of  $\text{BrCCl}_3$ , a secondary reaction was observed. This is illustrated in Figures 1 and 2 for the case where  $\text{R} = \text{CH}_3^-$ ,  $\text{B} = \text{py}$ , and  $\text{X} = \text{Se}$ . Figure 1 shows the  $\nu_{\text{CN}}$  region of the IR spectrum less than 1 min after mixing  $10^{-2}$  M  $\text{CHCl}_3$  solutions of  $\text{Co}(\text{dmGH})_2(\text{CH}_3)$  and  $\text{Co}(\text{dmGH})_2(\text{SeCN})(\text{py})$ . A  $\nu_{\text{CN}}$  maximum at 2145  $\text{cm}^{-1}$  due to the formation of  $(\text{CH}_3)_3\text{Co}(\text{dmGH})_2(\text{NCSe})\text{Co}(\text{dmGH})_2(\text{py})$  is evident, along with a higher energy absorption maximum at 2170  $\text{cm}^{-1}$ . Three minutes after mixing, the higher energy band has increased in intensity and the lower energy band decreased in intensity. In less than 10 min only the  $\nu_{\text{CN}}$  absorption at 2170  $\text{cm}^{-1}$  is present.

Figure 2 shows  $^1\text{H}$  NMR spectra for the same system in  $\text{CDCl}_3$  in the absence of  $\text{BrCCl}_3$ . Spectrum A shows the characteristic resonances for  $(\text{CH}_3)_3\text{Co}(\text{dmGH})_2(\text{NCSe})\text{Co}(\text{dmGH})_2(\text{py})$  and  $\text{Co}(\text{dmGH})_2(\text{CH}_3)(\text{py})$ , with an additional signal in the dmGH methyl region at  $\delta$  2.50. Only those signals due to  $(\text{CH}_3)_3\text{Co}(\text{dmGH})_2(\text{NCSe})\text{Co}(\text{dmGH})_2(\text{py})$  are present under similar conditions with  $\text{BrCCl}_3$  present. The new signal at  $\delta$  2.50 and those due to  $\text{Co}(\text{dmGH})_2(\text{CH}_3)(\text{py})$  increase in intensity, while those signals due to  $(\text{CH}_3)_3\text{Co}(\text{dmGH})_2$ -



**Figure 1.** IR spectra in  $\nu_{\text{CN}}$  region after mixing equivalent molar quantities of  $\text{Co}(\text{dmgH})_2(\text{CH}_3)$  (ca. 0.02 M) and  $\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{py})$  (ca. 0.02 M) in dry  $\text{CHCl}_3$ : (A) <1 min after mixing, (B) 3 min after mixing, (C) 10 min after mixing. Absorption maxima are at 2145 and 2170  $\text{cm}^{-1}$ .



**Figure 2.** (A)  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  of a sample equivalent with that described in Figure 1: (a)  $\delta$  2.50 dmgH methyl resonance due to oligomer (see text); (b)  $\delta$  2.35, (c)  $\delta$  2.21 due to dmgH methyl groups of  $(\text{CH}_3)\text{Co}(\text{dmgH})_2(\text{NCSe})\text{Co}(\text{dmgH})_2(\text{py})$ ; (d)  $\delta$  2.11, (e)  $\delta$  0.82 due to dmgH and axial methyl groups of  $\text{Co}(\text{dmgH})_2(\text{CH}_3)(\text{py})$ ; (f)  $\delta$  0.75 due to axial methyl group of  $(\text{CH}_3)\text{Co}(\text{dmgH})_2(\text{NCSe})\text{Co}(\text{dmgH})_2(\text{py})$ . (B)  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  of the solid material obtained from solution A after addition of py: (g)  $\delta$  2.36 due to dmgH methyl groups of  $\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{py})$ ; (h)  $\delta$  2.11, (i)  $\delta$  0.82 due to dmgH and axial methyl groups of  $\text{Co}(\text{dmgH})_2(\text{CH}_3)(\text{py})$ . The integration ratio g/h is ca. 3–4:1.

$(\text{NCSe})\text{Co}(\text{dmgH})_2(\text{py})$  decrease in intensity, with increasing time. Eventually, precipitation of the species which is responsible for the signal at  $\delta$  2.50 occurs. A  $\text{CDCl}_3$  suspension of the precipitate dissolves on treatment with pyridine. The  $^1\text{H}$  NMR spectrum of such a solution is given in part B of Figure 2. This shows  $^1\text{H}$  NMR signals which correspond to  $\text{Co}(\text{dmgH})_2(\text{CH}_3)(\text{py})$  and  $\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{py})$  in a 1:3–4 ratio.

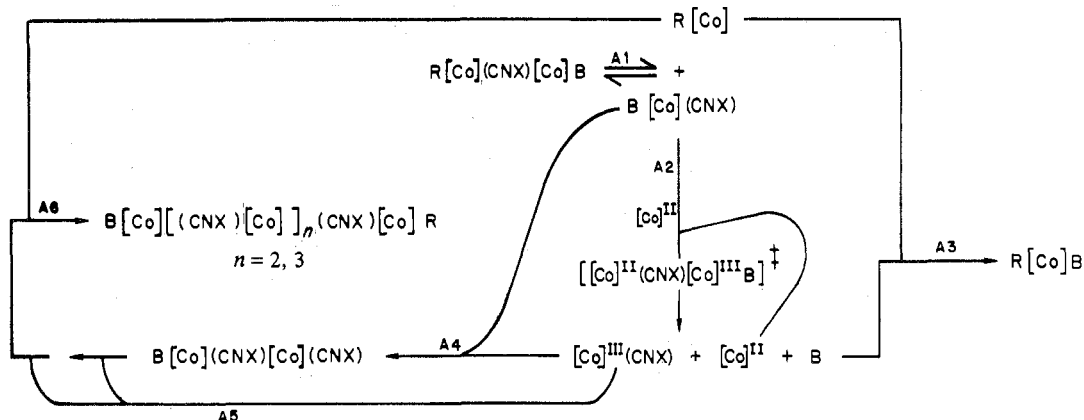
The product of reaction 3 ( $\text{R} = \text{CH}_3^-$ ,  $\text{B} = \text{py}$ ,  $\text{X} = \text{Se}$ ) in the absence of  $\text{BrCCl}_3$  is a pseudohalide-bridged oligomer of the form  $(\text{CH}_3)\text{Co}(\text{dmgH})_2[-(\text{NCSe})\text{Co}(\text{dmgH})_2-]_n-(\text{NCSe})\text{Co}(\text{dmgH})_2(\text{py})$  ( $n = 2, 3$ ). Evidence for pseudohalide bridge formation comes from IR spectra which exhibit a  $\nu_{\text{CN}}$  absorption at 2170  $\text{cm}^{-1}$ , which is in the range found for selenocyanato-bridged dimers. Chain length ( $n = 2, 3$ ) is established from the ratio of products  $\text{Co}(\text{dmgH})_2(\text{CH}_3)(\text{py})$  and  $\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{py})$  formed upon oligomer cleavage by reaction with pyridine. Diminished-intensity pyridine IR absorptions (relative to the monomer or dimer) are also consistent with oligomer formation. Vapor phase osmometry data show a molecular weight in excess of 1200 g/mol, which also supports oligomer formation.

Similar results were obtained for other dimer formation reactions carried out in the absence of  $\text{BrCCl}_3$  ( $\text{R} = \text{CH}_3^-$ ,  $\text{CF}_3^-$ ,  $\text{C}_2\text{H}_5^-$ ,  $n\text{-C}_3\text{H}_7^-$ ,  $i\text{-C}_3\text{H}_7^-$ ;  $\text{B} = \text{py}$ -3-Cl,  $\text{NH}_3$ , pip;  $\text{X} = \text{S}$ , Se). All oligomers exhibited a dmgH methyl resonance at ca.  $\delta$  2.50 in  $\text{CDCl}_3$  prior to precipitation and a  $\nu_{\text{CN}}$  absorption at 2170 ( $\pm 2$ )  $\text{cm}^{-1}$  in  $\text{CHCl}_3$  solution and as a KBr disk. Oligomer cleavage by treatment of a  $\text{CHCl}_3$  suspension with pyridine gave  $\text{Co}(\text{dmgH})_2(\text{R})(\text{py})$  and  $\text{Co}(\text{dmgH})_2(\text{CNX})(\text{B})$  as the exclusive products in a 1:3–4 ratio, as determined by  $^1\text{H}$  NMR spectra. No oligomer formation was observed in the attempted synthesis of cyanate-bridged dicobaloximes, which is consistent with the weak tendency for cyanate to form linear bridged complexes.

## Discussion

The observation of a single linkage isomer being formed for the complexes  $\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{B})$  ( $\text{B} = \text{py}$ , pip, py-3-Cl,  $\text{NH}_3$ ,  $\text{NH}_2\text{-pr}$ ) is consistent with data reported for a similar series of (selenocyanato)cobaloximes.<sup>9,10</sup> Mixed linkage isomer formation for selenocyanato complexes of cobalt(III) has been observed previously,<sup>26,29</sup> but there are fewer examples than found for thiocyanato complexes. The (alkyl)(selenocyanato)cobaloximes,  $[\text{Co}(\text{dmgH})_2(\text{CNSe})(\text{R})]^-$ , reported here exhibit linkage isomerism which is influenced by the trans alkyl ligand and the solvent. Similar behavior was observed for the corresponding thiocyanato complexes. The influence of the counterion was not investigated.

The ligand-bridged dimeric complexes reported here were synthesized according to reaction 3 in the presence of the oxidizing agent  $\text{BrCCl}_3$ . In the absence of  $\text{BrCCl}_3$ , trace quantities of  $\text{Co}(\text{II})$  are known to be present.<sup>21,22</sup> Under these conditions pseudohalide-bridged oligomer formation was observed. Scheme I is a proposed mechanism for oligomer formation which is consistent with our data. Reaction A1 shows the dissociation of the ligand-bridged dimer, which is consistent with osmotic pressure, IR, and  $^1\text{H}$  NMR data. Reaction A2 is the  $\text{Co}(\text{II})$ -catalyzed formation of the coordinatively unsaturated  $\text{Co}(\text{dmgH})_2(\text{CNX})$  (produced as a transient species). Evidence for this step comes from the observation that oligomer formation does not occur in the absence of trace quantities of  $\text{Co}(\text{II})$  (as established by the addition of trace amounts of  $\text{Co}(\text{II})$  or by carrying out the reaction in the absence of  $\text{BrCCl}_3$ ). We tentatively propose an inner-sphere electron-transfer for step A2. This is consistent with our observation that oligomer formation does not occur in the corresponding cyano complexes, the cyanide group being a less efficient electron-transfer agent. It is probable that electron transfer occurs via adjacent attack at least in the case of the selenocyanato complexes since cleavage of the oligomer results in the formation of the original linkage isomer  $\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{B})$ , which does not isomerize in the presence of  $\text{Co}(\text{II})$ . Reaction A2 is further established by  $^1\text{H}$  NMR spectra which demonstrate the formation of  $\text{Co}(\text{dmgH})_2(\text{R})(\text{B})$ , presumably via reaction A3. (See for example Figure 2.) Reactions A4 and A5 are chain-building steps with lig-

Scheme I<sup>a</sup>

<sup>a</sup> [Co]<sup>+</sup> = Co(dmgh)<sub>2</sub><sup>+</sup>.

Table VI. Percent Dissociation for Ligand-Bridged Dicobaloximes<sup>a</sup>

compd	% dissocn
(CH <sub>3</sub> )Co(dmgh) <sub>2</sub> (NCS)Co(dmgh) <sub>2</sub> (py)	24
(CH <sub>3</sub> )Co(dmgh) <sub>2</sub> (SCN)Co(dmgh) <sub>2</sub> (py)	36
(CH <sub>3</sub> )Co(dmgh) <sub>2</sub> (NCS)Co(dmgh) <sub>2</sub> (pip)	23
(CH <sub>3</sub> )Co(dmgh) <sub>2</sub> (SCN)Co(dmgh) <sub>2</sub> (pip)	50
(CH <sub>3</sub> )Co(dmgh) <sub>2</sub> (NCSe)Co(dmgh) <sub>2</sub> (pip)	33
(CF <sub>3</sub> )Co(dmgh) <sub>2</sub> (NCS)Co(dmgh) <sub>2</sub> (pip)	15
(CF <sub>3</sub> )Co(dmgh) <sub>2</sub> (SCN)Co(dmgh) <sub>2</sub> (pip)	20
(CF <sub>3</sub> )Co(dmgh) <sub>2</sub> (NCSe)Co(dmgh) <sub>2</sub> (pip)	20
(CH <sub>3</sub> )Co(dmgh) <sub>2</sub> (NC)Co(dmgh) <sub>2</sub> (py)	0
(CH <sub>3</sub> )Co(dmgh) <sub>2</sub> (NC)Co(dmgh) <sub>2</sub> (pip)	0

<sup>a</sup> See Experimental Section for a discussion of the method used.

and-bridge formation at the coordinatively unsaturated cobalt. Reaction A6 is the oligomer termination step. Oligomer molecular weight is most likely determined by relative concentrations and solubility properties.

In the absence of trace quantities of Co(II), the ligand-bridged dimeric complexes reported here are stable with respect to oligomer formation. However, dissociation does occur as shown in reaction A1 of Scheme I. The degree of dissociation is dependent upon the bridging ligand and the trans ligands R and B. More stable dimers are formed with R = CF<sub>3</sub><sup>-</sup> than CH<sub>3</sub><sup>-</sup> and with B = py than pip, as determined by osmotic-pressure and <sup>1</sup>H NMR competition measurements. This is in qualitative agreement with stability variations found for the corresponding cyano-bridged complexes (R)Co(dmgh)<sub>2</sub>(NC)Co(dmgh)<sub>2</sub>(B).<sup>13</sup> Percent dimer dissociation data listed in Table VI and competition experiments monitored by <sup>1</sup>H NMR spectra such as described in Figure 3 indicate the following variation in the stability of the complexes (R)Co(dmgh)<sub>2</sub>(L)Co(dmgh)<sub>2</sub>(B) as a function of the ligand bridge L (the line indicates the donor atom attached to the Co(dmgh)<sub>2</sub>(B) end of the dimer):



This sequence, based on a homologous series, is in agreement with the known bridging abilities of the pseudohalides.<sup>1,2</sup> This series also reflects the relative affinity of the labile alkylcobaloxime end of the dimer for various pseudohalide donor atoms, as seen in Table V. For a series of substituted-pyridine complexes with a particular alkylcobaloxime, it has been reported that the stability of the complex increases with the proton basicity of the substituted pyridine.<sup>28,30</sup> For a series of acidocobaloximes, we have found that the relative basicities of the free end of a coordinated ambidentate ligand decrease in the following order:<sup>17</sup> -CN > -SCN >> -NCS. These observations are in agreement with the relative order of dimer stability shown above for the complexes (R)Co(dmgh)<sub>2</sub>-

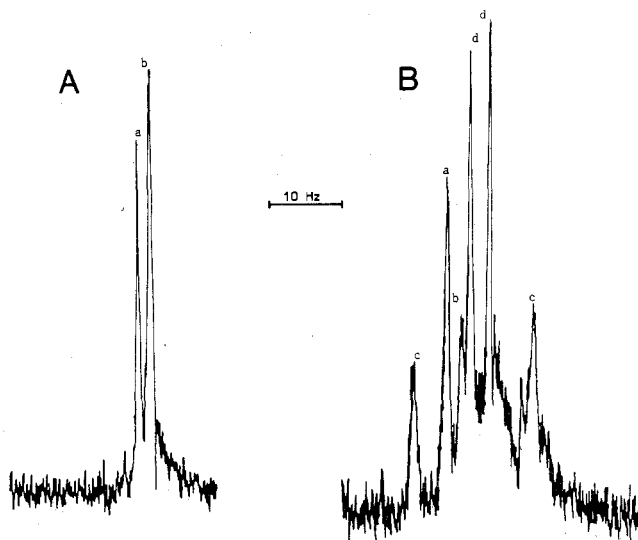


Figure 3. (A) <sup>1</sup>H NMR spectrum in CH<sub>2</sub>Cl<sub>2</sub> of Co(dmgh)<sub>2</sub>(NCS)(py) ((a) δ 2.44) and Co(dmgh)<sub>2</sub>(SCN)(py) ((b) δ 2.42) showing resolved dmgh methyl resonances. (B) Addition of Co(dmgh)<sub>2</sub>(CF<sub>3</sub>) to isomer mixture shown in (A). Spectrum shows preferential formation of the more stable ligand-bridged isomer (CF<sub>3</sub>)Co(dmgh)<sub>2</sub>(NCS)Co(dmgh)<sub>2</sub>(py) having equal-intensity dmgh methyl resonances d (δ 2.35, 2.39), relative to the isomer (CF<sub>3</sub>)Co(dmgh)<sub>2</sub>(SCN)Co(dmgh)<sub>2</sub>(py) having equal-intensity dmgh methyl resonances c (δ 2.50, 2.26). The spectrum also shows a concomitant greater decrease in signal b due to Co(dmgh)<sub>2</sub>(SCN)(py) relative to that of a due to Co(dmgh)<sub>2</sub>(NCS)(py). (Spectra A and B were obtained in the presence of BrCCl<sub>3</sub>.)

(L)Co(dmgh)<sub>2</sub>(B). Our inability to prepare cyanate-bridged complexes of this type is consistent with the tendency for this ligand to form the more sterically hindered adjacent ligand bridge geometry (if a bridge is formed at all)<sup>31</sup> and the lesser affinity of cobaloximes for oxygen donors.<sup>28</sup>

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**Registry No.** Co(dmgh)<sub>2</sub>(NCS)(py), 30235-61-1; Co(dmgh)<sub>2</sub>(SCN)(py), 30032-62-3; Co(dmgh)<sub>2</sub>(NCS)(pip), 68646-02-6; Co(dmgh)<sub>2</sub>(SCN)(pip), 57383-07-0; Co(dmgh)<sub>2</sub>(SeCN)(py), 58340-22-0; Co(dmgh)<sub>2</sub>(SeCN)(pip), 68646-01-5; Co(dmgh)<sub>2</sub>(SeCN)(py-3-Cl), 68646-00-4; Co(dmgh)<sub>2</sub>(SeCN)(NH<sub>3</sub>), 68645-99-8; Co(dmgh)<sub>2</sub>(SeCN)(NH<sub>2</sub>-pr), 68645-98-7; Co(dmgh)<sub>2</sub>(NCO)(py), 30786-24-4; Ph<sub>4</sub>As[Co(dmgh)<sub>2</sub>(NCS)(CH<sub>3</sub>)],



43065-08-3;  $\text{Ph}_4\text{As}[\text{Co}(\text{dmgH})_2(\text{SCN})(\text{CH}_3)]$ , 43065-12-9;  $\text{Ph}_4\text{As}[\text{Co}(\text{dmgH})_2(\text{NCS})(\text{CHBr}_2)]$ , 68645-97-6;  $\text{Ph}_4\text{As}[\text{Co}(\text{dmgH})_2(\text{SCN})(\text{CHBr}_2)]$ , 68645-95-4;  $\text{Ph}_4\text{As}[\text{Co}(\text{dmgH})_2(\text{NCS})(\text{CF}_3)]$ , 68645-93-2;  $\text{Ph}_4\text{As}[\text{Co}(\text{dmgH})_2(\text{SCN})(\text{CF}_3)]$ , 68645-91-0;  $\text{Ph}_4\text{As}[\text{Co}(\text{dmgH})_2(\text{NCSe})(\text{CH}_3)]$ , 68645-89-6;  $\text{Ph}_4\text{As}[\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{CH}_3)]$ , 68646-25-3;  $\text{Ph}_4\text{As}[\text{Co}(\text{dmgH})_2(\text{NCSe})(\text{CHBr}_2)]$ , 68646-23-1;  $\text{Ph}_4\text{As}[\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{CHBr}_2)]$ , 68646-21-9;  $\text{Ph}_4\text{As}[\text{Co}(\text{dmgH})_2(\text{NCSe})(\text{CF}_3)]$ , 68646-19-5;  $\text{Ph}_4\text{As}[\text{Co}(\text{dmgH})_2(\text{SeCN})(\text{CF}_3)]$ , 68646-17-3;  $\text{Ph}_4\text{As}[\text{Co}(\text{dmgH})_2(\text{NCO})(\text{CH}_3)]$ , 68646-15-1;  $\text{Ph}_4\text{As}[\text{Co}(\text{dmgH})_2(\text{NCO})(\text{CHBr}_2)]$ , 68646-13-9;  $\text{Ph}_4\text{As}[\text{Co}(\text{dmgH})_2(\text{NCO})(\text{CF}_3)]$ , 68646-11-7;  $(\text{CH}_3)\text{Co}(\text{dmgH})_2(\text{NCS})\text{Co}(\text{dmgH})_2(\text{py})$ , 68646-09-3;  $(\text{CH}_3)\text{Co}(\text{dmgH})_2(\text{SCN})\text{Co}(\text{dmgH})_2(\text{py})$ , 68646-08-2;  $(\text{CH}_3)\text{Co}(\text{dmgH})_2(\text{NCS})\text{Co}(\text{dmgH})_2(\text{pip})$ , 68646-07-1;  $(\text{CH}_3)\text{Co}(\text{dmgH})_2(\text{SCN})\text{Co}(\text{dmgH})_2(\text{pip})$ , 68646-06-0;  $(\text{CF}_3)\text{Co}(\text{dmgH})_2(\text{NCS})\text{Co}(\text{dmgH})_2(\text{py})$ , 68646-05-9;  $(\text{CF}_3)\text{Co}(\text{dmgH})_2(\text{SCN})\text{Co}(\text{dmgH})_2(\text{py})$ , 68646-04-8;  $(\text{CF}_3)\text{Co}(\text{dmgH})_2(\text{NCS})\text{Co}(\text{dmgH})_2(\text{pip})$ , 68646-03-7;  $(\text{CF}_3)\text{Co}(\text{dmgH})_2(\text{SCN})\text{Co}(\text{dmgH})_2(\text{pip})$ , 68646-40-2;  $(\text{CH}_3)\text{Co}(\text{dmgH})_2(\text{NCSe})\text{Co}(\text{dmgH})_2(\text{py})$ , 68646-39-9;  $(\text{CH}_3)\text{Co}(\text{dmgH})_2(\text{NCSe})\text{Co}(\text{dmgH})_2(\text{pip})$ , 68646-38-8;  $(\text{CH}_3)\text{Co}(\text{dmgH})_2(\text{NCSe})\text{Co}(\text{dmgH})_2(\text{py}-3\text{-Cl})$ , 68646-37-7;  $(\text{CH}_3)\text{Co}(\text{dmgH})_2(\text{NCSe})\text{Co}(\text{dmgH})_2(\text{NH}_3)$ , 68646-36-6;  $(\text{CH}_3)\text{Co}(\text{dmgH})_2(\text{NCSe})\text{Co}(\text{dmgH})_2(\text{NH}_2\text{-pr})$ , 68646-35-5;  $(\text{CF}_3)\text{Co}(\text{dmgH})_2(\text{NCSe})\text{Co}(\text{dmgH})_2(\text{py})$ , 68646-34-4;  $(\text{CF}_3)\text{Co}(\text{dmgH})_2(\text{NCSe})\text{Co}(\text{dmgH})_2(\text{pip})$ , 68646-33-3;  $\text{Ph}_4\text{As}[(\text{CH}_3)\text{Co}(\text{dmgH})_2(\text{NCS})\text{Co}(\text{dmgH})_2(\text{CH}_3)]$ , 43065-20-9;  $\text{Ph}_4\text{As}[(\text{CF}_3)\text{Co}(\text{dmgH})_2(\text{NCS})\text{Co}(\text{dmgH})_2(\text{CF}_3)]$ , 68646-32-2;  $\text{Ph}_4\text{As}[(\text{CH}_3)\text{Co}(\text{dmgH})_2(\text{NCSe})\text{Co}(\text{dmgH})_2(\text{CH}_3)]$ , 68646-30-0;  $\text{Ph}_4\text{As}[(\text{CF}_3)\text{Co}(\text{dmgH})_2(\text{NCSe})\text{Co}(\text{dmgH})_2(\text{CF}_3)]$ , 68715-75-3;  $\text{Co}(\text{dmgH})_2(\text{CF}_3)$ , 68646-28-6;  $\text{Co}(\text{dmgH})_2(\text{CF}_3)(\text{H}_2\text{O})$ , 59493-04-8;  $[\text{Co}(\text{dmgH})_2(\text{CF}_3)]_2$ , 68646-27-5;  $\text{Co}(\text{dmgH})_2(\text{CH}_3)(\text{S}(\text{CH}_3)_2)$ , 25482-40-0;  $\text{Co}(\text{dmgH})_2(\text{CHBr}_2)(\text{S}(\text{CH}_3)_2)$ , 68646-26-4;  $\text{Co}(\text{dmgH})_2(\text{CH}_3)$ , 36609-02-6;  $\text{Co}(\text{dmgH})_2(\text{CH}_3)(\text{py})$ , 23642-14-0.

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## Chemistry of Ring-Bridged Bis( $\eta^5$ -cyclopentadienyl) Ligands. Derivatives of $\alpha, \alpha'$ -Dicyclopentadienyl-*m*-xylene

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The synthesis of the ligand  $\alpha, \alpha'$ -dicyclopentadienyl-*m*-xylene (**1**) is reported. **1** was found to polymerize readily; however, reaction with sodium hydride, before extensive polymerization had occurred, gave the dianion of disodium (*m*-phenylenedimethylene)dicyclopentadienide (**2**). **2** was used to prepare additional derivatives of the type  $m\text{-C}_6\text{H}_4(\text{CH}_2\text{C}_5\text{H}_4\text{R})_2$ , where  $\text{R} = \text{CH}_3$  or  $\text{Si}(\text{CH}_3)_3$ . The thermolysis of  $\text{Mo}(\text{CO})_6$  and the photolysis of  $\text{W}(\text{CO})_6$  with dianion **2** in tetrahydrofuran generated  $m\text{-C}_6\text{H}_4(\text{CH}_2\text{C}_5\text{H}_4\text{M}(\text{CO})_3)_2^{2-}$ , where  $\text{M} = \text{Mo}$  (**5**) and  $\text{W}$  (**6**). These metallo dianions were reacted with alkyl halides to prepare  $m\text{-C}_6\text{H}_4(\text{CH}_2\text{C}_5\text{H}_4\text{M}(\text{CO})_3\text{R})_2$ , where  $\text{M} = \text{Mo}$  and  $\text{W}$  and  $\text{R} = \text{CH}_3$  and  $\text{CH}_2\text{CH}_3$ . The chemistry of the bridged molybdenum derivatives was examined in more detail with  $\text{R} = \text{H}$ , I derivatives being prepared. The hydrido derivative was found to reduce 1,3-pentadiene and phenylacetylene with the subsequent formation of complex **14**,  $m\text{-C}_6\text{H}_4[\text{CH}_2\text{C}_5\text{H}_4\text{Mo}(\text{CO})_3]_2$ . A better preparation of **14** involved the reaction of 1,2-dibromoethane with dianion **5** in a 1:1 ratio. Photolysis of the methylmolybdenum derivative in the presence of triphenylphosphine affords  $m\text{-C}_6\text{H}_4[\text{CH}_2\text{C}_5\text{H}_4\text{Mo}(\text{CO})_2\text{CH}_3\text{P}(\text{C}_6\text{H}_5)_3]_2$ .

### Introduction

We have made a preliminary report<sup>1</sup> of the preparation and chemistry of  $\alpha, \alpha'$ -dicyclopentadienyl-*m*-xylene (**1**)  $m\text{-C}_6\text{H}_4(\text{CH}_2\text{C}_5\text{H}_5)_2$ . This ligand belongs to the class of covalently linked bis(cyclopentadiene) ligands  $\text{Z}(\text{C}_5\text{H}_5)_2$  which can be used to prepare linked bimetallic complexes of the type  $\text{Z}(\eta^5\text{-C}_5\text{H}_4\text{ML}_n)_2$  where L is the extensive group of ligands that binds with metal cyclopentadiene units. Several linked

complexes which are derived from the  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  systems have been prepared:  $[\eta^5\text{-C}_5\text{H}_4\text{CR}_1\text{R}_2\text{CR}_1\text{R}_2\text{-}\eta^5\text{-C}_5\text{H}_4]\text{Fe}_2(\text{CO})_4$  where  $\text{R}_1 = \text{H}$ ,  $\text{R}_2 = \text{N}(\text{CH}_3)_2^{2a,c}$  and  $\text{R}_1 = \text{R}_2 = \text{CH}_3^{2b,c}$  and  $(\text{CH}_3)_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2]_2$ .<sup>1,3</sup> Additionally complexes of the silicon-bridged system which do not contain a metal-metal bond have been reported:<sup>4</sup>  $(\text{CH}_3)_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{M}(\text{CO})_3]_2$  where  $\text{M} = \text{Mn}$  or  $\text{Re}$  and  $(\text{CH}_3)_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Co}(\text{CO})_2]_2$ . In this paper the details of the preparation