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## Possible Coordination between Halides of Group IV Elements and the Triple Bond of Diethylaminoacetonitrile as Ligand

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Received October 10, 1966

Coordination compounds between diethylaminoacetonitrile and halides of group IV elements have been prepared. The analytical results, the molecular weight determination, and the infrared spectroscopic studies give good evidence of chelate formation through the triple bond of the ligand and the nitrogen of the amino group. The formation of such chelates has been found to be limited to the aminonitriles  $R_2N(CH_2)_nCN$  in which  $n$  was equal to 1 and 2.

### Introduction

Many coordination complexes between the halides of group IV elements and nitriles or dinitriles have been prepared and studied.<sup>1,2</sup> However, none of these compounds has shown evidence of coordination through the triple bond. Harris and Stephenson<sup>3</sup> have previously reported the interesting compound  $[Pt(CH_3CN)_2(NH_3)_4]Cl_2 \cdot H_2O$  in which, on the basis of X-ray analysis, they assumed the methyl cyanide molecules were bonded to the metal atom through the triple bond. However, a recent redetermination of the crystal structure of the above complex has shown<sup>4</sup> normal coordination of two ammonia and of two amidine molecules in a square-planar arrangement,  $[Pt(NH_3)_2(CH_3CNH_2NH)_2]Cl_2 \cdot H_2O$ . It was thought interesting to use the ligand diethylaminoacetonitrile in order to study the possibility of forming chelates in which the triple bond of the  $C \equiv N$  group would be involved. Because of the linearity of the  $-CH_2C \equiv N$  part of the ligand molecule, it was thought impossible to prepare chelates in which there would be normal coordination of the two nitrogen atoms.

### Experimental Section

The experimental setup and the method of preparation of the complexes were quite similar to the ones used previously.<sup>1</sup> The ligands were obtained from the K & K Laboratories and were used as such without further purification. The reactions were performed in a drybox continuously flushed with dry nitrogen. All of the complexes were prepared under similar experimental conditions using methylene chloride as solvent and adding the ligand to an excess of the Lewis acid. The complex with zirconium tetrachloride was obtained by treating it with an excess of ligand in methylene chloride and allowing the reaction to go under magnetic stirring for 3 days. In all cases powders were obtained which were washed with dry methylene chloride and dried *in vacuo* at room temperature. The compound with boron trichloride was prepared by connecting the reaction flask to the nitrogen line and condensing the boron trichloride in the reaction flask kept at about  $-10^\circ$ . The excess boron trichloride was allowed to escape through the nitrogen line and the solvent removed under vacuum at room temperature.

The molecular weight determinations were carried out in nitrobenzene solution by a cryoscopic method. Nitrobenzene was purified according to methods described in literature<sup>5</sup> and its purity was checked by measuring the melting point, which

was found to be in agreement with the literature value. The conductivity was measured with a Radiometer direct-reading conductivity meter, Type CDM 2d No. 47501, and the conductivity cell used was Radiometer Type CDC 114 having pure platinum electrodes. The infrared spectra were determined with a Beckman spectrophotometer, Model IR-8, fitted with sodium chloride optics. The spectra of the complexes were recorded in Nujol mulls using sodium chloride plates. The analytical results, the spectroscopic data, and the molar conductances at  $25^\circ$  are reported in Tables I-III, respectively.

### Discussion

The infrared spectra of the known complexes between group IV elements and nitriles indicate an increase in the  $C \equiv N$  stretching frequency,<sup>1,2</sup>  $\nu(C \equiv N)$ , but in all of the spectra of the compounds prepared with diethylaminoacetonitrile ( $L_A$ ), a decrease varying from 40 to  $100\text{ cm}^{-1}$  is observed (Table II). The possible interpretation of this result is that the triple bond is involved in chelate formation. If we compare our results with the ones obtained by Taufen, *et al.*,<sup>6</sup> and Chatt, *et al.*,<sup>7</sup> who reported a bathochromic effect of approximately 120 and  $200\text{ cm}^{-1}$  of the  $C \equiv C$  stretching vibration of some substituted acetylenes on coordination, it is reasonable to expect that in our compounds the  $C \equiv N$  group is involved in coordination through the triple bond even if the shifts observed are smaller. As a matter of fact, the bond order of the triple bond of a nitrile group will be less reduced than the bond order of the  $-C \equiv C-$  group on coordination because the free electron pair on the nitrogen of the cyano group will tend to share and make up for the drainage of electrons from the triple-bond region on complex formation. Thus the lowering of the  $\nu(C \equiv N)$  to the extent of 40 to  $100\text{ cm}^{-1}$  in the compounds under discussion seems to be reasonable as compared to approximately  $120\text{ cm}^{-1}$  for a monosubstituted acetylene where there is no possibility of any compensation for the lowering of the bond order.

To verify further that the lowering of the  $\nu(C \equiv N)$  on coordination was due to chelation on the triple bond because of steric factors, the ligand ( $L_A$ ) was allowed to react with boron trichloride; the compound obtained

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TABLE I  
ANALYTICAL RESULTS

| Compound  | Mp, °C               | Color           | % metal |       | % halogen |       | Mol wt |       |
|---|----------------------|-----------------|---------|-------|-----------|-------|--------|-------|
|   |                      |                 | Calcd   | Found | Calcd     | Found | Calcd  | Found |
| TiCl <sub>4</sub> (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCH <sub>2</sub> CN   | 130 dec <sup>a</sup> | Greenish gray   | 15.86   | 15.7  | 46.96     | 46.9  | 302.53 | 280   |
| TiBr <sub>4</sub> (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCH <sub>2</sub> CN   | 140 dec <sup>a</sup> | Dark brown      | 9.99    | 9.97  | 66.63     | 66.4  | 470.36 | 440   |
| SnCl <sub>4</sub> (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCH <sub>2</sub> CN   | 115-117              | White           | 31.86   | 31.6  | 38.04     | 37.8  |        |       |
| ZrCl <sub>4</sub> (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCH <sub>2</sub> CN   | 115 dec <sup>a</sup> | Grayish white   | 26.38   | 26.3  | 41.00     | 40.6  |        |       |
| 2BCl <sub>3</sub> (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCH <sub>2</sub> CN   | 52-53                | Yellowish white | 6.23    | 6.0   | 61.25     | 60.5  |        |       |
| TiCl <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub> N(CH <sub>2</sub> ) <sub>2</sub> CN | 120 dec <sup>a</sup> | Brown           | 16.64   | 16.4  | 49.24     | 49.1  |        |       |
| TiCl <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub> N(CH <sub>2</sub> ) <sub>3</sub> CN | 140 dec <sup>a</sup> | Dark brown      | 15.86   | 15.9  | 46.96     | 47.1  |        |       |
| TiCl <sub>4</sub> NCC <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>                     | 235 dec <sup>a</sup> | Yellow          | 15.56   | 15.3  | 46.05     | 46.0  |        |       |

<sup>a</sup> Decomposed by turning black.TABLE II  
THE INFRARED SPECTRA RESULTS IN WAVENUMBER (CM<sup>-1</sup>)<sup>a</sup>

| Compounds   | C≡N str freq<br>(νC≡N) | Shift in C≡N<br>str freq<br>(ΔνC≡N) |
|---|------------------------|-------------------------------------|
| (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCH <sub>2</sub> CN (L <sub>A</sub> )   | 2220 w                 | ...                                 |
| SnCl <sub>4</sub> ·L <sub>A</sub>   | 2180 m                 | -40                                 |
| TiCl <sub>4</sub> ·L <sub>A</sub>   | 2150 m                 | -70                                 |
| TiBr <sub>4</sub> ·L <sub>A</sub>   | 2120 m                 | -100                                |
| ZrCl <sub>4</sub> ·L <sub>A</sub>   | 2140 m                 | -80                                 |
| 2BCl <sub>3</sub> ·L <sub>A</sub>   | 2280 s                 | +60                                 |
|   | 2100 vw                | ...                                 |
| (CH <sub>3</sub> ) <sub>2</sub> N(CH <sub>2</sub> ) <sub>2</sub> CN (L <sub>B</sub> ) | 2240 m                 | ...                                 |
| TiCl <sub>4</sub> ·L <sub>B</sub>   | 2280 m                 | +40                                 |
|   | 2205 s                 | -35                                 |
| (CH <sub>3</sub> ) <sub>2</sub> N(CH <sub>2</sub> ) <sub>3</sub> CN (L <sub>C</sub> ) | 2240 m                 | ...                                 |
| TiCl <sub>4</sub> ·L <sub>C</sub>   | 2285 s                 | +45                                 |

<sup>a</sup> Phase: neat for the ligands and Nujol mulls for the complexes. w, weak; m, medium; s, strong; v, very. A more detailed form of this infrared table has been deposited as Document No. 9221 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting \$1.25 for photoprints or \$1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

TABLE III  
MOLAR CONDUCTANCE OF TiCl<sub>4</sub>·(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NCH<sub>2</sub>C≡N  
IN NITROBENZENE AT 25°

| Concn of adduct, M | Molar conductance, cm <sup>2</sup> mhos/mole |
|--------------------|--|
| 1/128              | 5.74   |
| 1/256              | 5.91   |
| 1/512              | 6.24   |
| 1/1024             | 6.56   |

was 2BCl<sub>3</sub>·L<sub>A</sub> and its infrared spectrum showed a marked increase in ν(C≡N) on coordination. Since the amino and the cyano groups of the ligand molecule coordinate independently to two different boron trichloride molecules, the cyano group uses the free electron pair on the nitrogen for coordination instead of the electrons of the triple bond. We also prepared a compound between titanium tetrachloride and *p*-aminobenzonitrile. This ligand being planar could only coordinate to two different titanium tetrachloride molecules. As expected the ν(C≡N) was increased in the compound indicating normal coordination through the free electron pair on the nitrogen of the cyano group.

To see the effect of lengthening the chain of the ligand, complexes were prepared with 3-dimethyl-

aminopropionitrile (L<sub>B</sub>) and 4-dimethylaminobutyronitrile (L<sub>C</sub>) and titanium tetrachloride. In both cases, one-to-one compounds were obtained, but interesting differences were noted in their infrared spectra. As expected the infrared spectrum of TiCl<sub>4</sub>·L<sub>C</sub> showed only one ν(C≡N) at 2285 cm<sup>-1</sup>, thus indicating normal coordination of the cyano group through the free electron pair on the nitrogen. In this case, the ligand (L<sub>C</sub>) with three CH<sub>2</sub> can easily form a normal chelate even if three atoms of the ligand -CH<sub>2</sub>C≡N are linear. The infrared spectrum of TiCl<sub>4</sub>·L<sub>B</sub> showed two bands in the ν(C≡N) region, one at 2205 cm<sup>-1</sup> and another one weaker in intensity at 2280 cm<sup>-1</sup>. In this complex, normal chelation would still cause tension in the ring and it is possible that there is a competition between two types of compounds, one analogous to TiCl<sub>4</sub>·L<sub>C</sub> having normal coordination of the cyano group but with internal ring tension, and another one analogous to TiCl<sub>4</sub>·L<sub>A</sub> in which chelation takes place through the triple bond. It was not possible, however, to have other evidences of the presence of two compounds, because the compound TiCl<sub>4</sub>·L<sub>B</sub> could not be sublimed and was insoluble in most of the commonly known inert solvents. However the relative intensities of the two bands strongly suggest that the complex analogous to TiCl<sub>4</sub>·L<sub>A</sub> is predominant.

To make sure that our compounds are monomers and true molecular addition compounds, we measured the molecular weights and the conductivity of two of the soluble compounds.

The values of the molecular weights are very important and their determinations were made with great care. The solvent was cautiously purified, the solute was carefully handled in a dry atmosphere for the preparation of solutions, and for any given solution it was possible to repeat the measurements to at least three significant figures. With different solutions however, the results could be repeated to 2% of the reported values in Table I. The results presented here are a little lower than expected and this can be explained by the facts that it is not possible to purify the compounds by recrystallization or sublimation and that some impurities of small molecular weights could still be present in the complexes. In order to see if the low values were the result of dissociation, the infrared spectra of the solutions of the complexes were compared with the infrared spectra of the solution of the pure ligand and ν(C≡N) was observed at 2220 cm<sup>-1</sup> for the

free ligand, at 2150 for  $\text{TiBr}_4 \cdot \text{L}_A$ , and  $2160 \text{ cm}^{-1}$  for  $\text{TiCl}_4 \cdot \text{L}_A$ , but the original band at  $2220 \text{ cm}^{-1}$  has vanished for both solutions of the complexes, thus giving an indication that no appreciable dissociation into the halide and the ligand was happening.

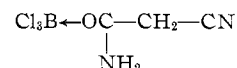
In order to check the possibility of ionization the conductances were measured and the values of molar conductances reported in Table III clearly indicate that ionization is not important in these complexes.

### Conclusion

New coordination complexes of aminonitriles of general formula  $\text{R}_2\text{N}(\text{CH}_2)_n\text{C}\equiv\text{N}$  with some group IV halides have been prepared. The complexes thus prepared are all one-to-one addition compounds.

The complexes in which the aminonitrile was  $(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{C}\equiv\text{N}$  were particularly studied. Their infrared spectra indicated a bathochrome effect of the CN stretching frequency. Since these compounds were

found to be monomeric molecular addition compounds, this bathochrome effect could be attributed either to an inductance effect assuming that the ligand is a monodentate or to a coordination through the triple bond assuming that the ligand is a bidentate. The first of these two possibilities can reasonably be ruled out because in a recent work on complexes of cyanoacetamide<sup>8</sup> we found that in a complex of the composition



coordination of the oxygen of the carbonyl group had no influence on the position of the CN stretching frequency.

**Acknowledgment.**—The authors gratefully acknowledge the continued financial assistance from the National Research Council of Canada.

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## Organosulfur Derivatives of the Metal Carbonyls. IX. Some Transition Metal Derivatives Containing Both $\pi$ -Cyclopentadienyl and Bis(trifluoromethyl)ethylene Dithiolate Ligands<sup>1</sup>

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Received August 18, 1966

Bis(trifluoromethyl)dithietene reacts with  $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{NO}$  to give brown  $[\text{C}_5\text{H}_5\text{Mo}(\text{NO})\text{S}_2\text{C}_2(\text{CF}_3)_2]_2$ . However, the analogous reaction between bis(trifluoromethyl)dithietene and  $\text{C}_5\text{H}_5\text{W}(\text{CO})_2\text{NO}$  gives green  $\text{C}_5\text{H}_5\text{W}[\text{S}_2\text{C}_2(\text{CF}_3)_2]_2$  with the expected magnetic moment for one unpaired electron. The tungsten compound  $\text{C}_5\text{H}_5\text{W}(\text{CO})_3\text{H}$  reacts with bis(trifluoromethyl)dithietene to give primarily brown  $[\text{C}_5\text{H}_5\text{W}(\text{CO})\text{S}_2\text{C}_2(\text{CF}_3)_2]_2$  as well as minor amounts of  $\text{C}_5\text{H}_5\text{W}[\text{S}_2\text{C}_2(\text{CF}_3)_2]_2$ . The manganese compound  $[\text{C}_5\text{H}_5\text{MnCONO}]_2$  reacts with bis(trifluoromethyl)dithietene to give brown volatile paramagnetic  $\text{C}_5\text{H}_5\text{MnNOS}_2\text{C}_2(\text{CF}_3)_2$ . Reaction between  $\text{C}_5\text{H}_5\text{Rh}(\text{CO})_2$  and bis(trifluoromethyl)dithietene gives red  $\text{C}_5\text{H}_5\text{RhS}_2\text{C}_2(\text{CF}_3)_2$ . The red iridium analog of this compound,  $\text{C}_5\text{H}_5\text{IrS}_2\text{C}_2(\text{CF}_3)_2$ , may be obtained from  $\text{C}_5\text{H}_5\text{IrC}_8\text{H}_{12}$  and bis(trifluoromethyl)dithietene. Reductions of some of these  $\pi$ -cyclopentadienyl compounds to anions with alcoholic hydrazine are described. The anions obtained from these reductions, including the previously unreported red-violet  $\{\text{C}_5\text{H}_5\text{W}[\text{S}_2\text{C}_2(\text{CF}_3)_2]_2\}^-$  and green  $\{[(\text{CF}_3)_2\text{C}_2\text{S}_2]_2\text{MnNO}\}^{2-}$ , as well as the known<sup>3</sup> planar species  $\{\text{M}[\text{S}_2\text{C}_2(\text{CF}_3)_2]_2\}^z$  ( $\text{M} = \text{Fe}, z = -1$ ;  $\text{M} = \text{Co}, z = -2$ ;  $\text{M} = \text{Ni}, z = -2$ ) may be isolated as crystalline tetraethylammonium salts. Oxidation of the related brown  $[\text{CH}_3\text{SFeCOC}_5\text{H}_5]_2$  with  $\text{AgSbF}_6$  to the intense blue-green radical cation salt  $[\text{CH}_3\text{SFeCOC}_5\text{H}_5]_2[\text{SbF}_6]$  is described. The mass spectra of numerous  $\pi$ -cyclopentadienylmetal complexes containing  $(\text{CF}_3)_2\text{C}_2\text{S}_2$  ligands are described and discussed.

### Introduction

In 1963 the first reactions between cyclopentadienyl-metal carbonyls and bis(trifluoromethyl)dithietene (I) were described.<sup>4</sup> These reactions yielded the compounds  $[\text{C}_5\text{H}_5\text{MS}_2\text{C}_2(\text{CF}_3)_2]_n$  ( $\text{M} = \text{V}, \text{Cr}, \text{or Mo}, n = 2$ ;  $\text{M} = \text{Co or Ni}, n = 1$ ) for which unusual structures were proposed. One objective of this work was the preparation of  $[\text{C}_5\text{H}_5\text{MS}_2\text{C}_2(\text{CF}_3)_2]_n$  compounds of metals other than the five listed above, since all 24 transi-

tion metals (*i.e.*, three in each column from titanium to copper, inclusive) appear to be suitable candidates for the formation of such compounds albeit of different structures. The structures of these  $[\text{C}_5\text{H}_5\text{MS}_2\text{C}_2(\text{CF}_3)_2]_n$  compounds would be expected to depend drastically upon the electronic configuration and possibly the size of the metal atom. Thus their comparison would be very interesting. This paper describes in detail attempts to prepare  $[\text{C}_5\text{H}_5\text{MS}_2\text{C}_2(\text{CF}_3)_2]_n$  derivatives of the six additional metals tungsten, manganese, iron, ruthenium, rhodium, and iridium. Of these additional six metals only rhodium and iridium have been found to yield compounds of the type  $[\text{C}_5\text{H}_5\text{MS}_2\text{C}_2(\text{CF}_3)_2]_n$  ( $\text{M} = \text{Rh or Ir}, n = 1$ ).

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