

to provide a diminished susceptibility to electrophilic attack may partly account for the observed stabilization.³⁰

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Registry No. H₃GeSCF₃, 68457-15-8; H₂Ge(SCF₃)₂, 68457-16-9; H₃GeSeCF₃, 68457-17-0; H₂Ge(SeCF₃)₂, 68457-18-1; H₃Ge(SeCF₃)Br, 68457-19-2; Ge₂H₅SCF₃, 68457-20-5; Ge₂H₅SeCF₃, 68457-21-6; Hg(SeCF₃)₂, 60129-77-3; Hg(SCF₃)₂, 21259-75-6; GeH₃I, 13573-02-9; GeH₃Br, 13569-43-2; AgSCF₃, 811-68-7; GeH₂Br₂, 13769-36-3; GeH₂I₂, 14694-31-6; Ge₂H₅I, 19021-93-3.

References and Notes

- (1) Communicated in part at the 33rd Northwest Regional Meeting of the American Chemical Society, Seattle, June 1978.
- (2) C. H. Van Dyke, "Preparative Inorganic Reactions", Vol. 6, W. L. Jolly, Ed., Interscience, New York, 1971, p 157.
- (3) G. A. Gibbon, Y. Rousseau, C. H. Van Dyke, and G. J. Mains, *Inorg. Chem.*, **5**, 114 (1966).
- (4) S. Cradock, E. A. V. Ebsworth, and D. W. H. Rankin, *J. Chem. Soc. A*, 1628 (1969).
- (5) J. E. Drake and C. Riddle, *J. Chem. Soc. A*, 1573 (1969).
- (6) J. W. Anderson, G. K. Barker, J. E. Drake, and M. Rodger, *J. Chem. Soc., Dalton Trans.*, 1716 (1973).
- (7) P. C. Angus and S. R. Stobart, *J. Chem. Soc., Dalton Trans.*, 2342 (1975).
- (8) J. E. Drake and R. T. Hemmings, *Can. J. Chem.*, **51**, 302 (1973).
- (9) J. E. Drake and C. Riddle, *Q. Rev., Chem. Soc.*, **24**, 263 (1970).
- (10) K. M. Mackay and P. J. Roebuck, *J. Chem. Soc.*, 1195 (1964); K. M. Mackay, P. Robinson, E. J. Spanier, and A. G. MacDiarmid, *J. Inorg. Nucl. Chem.*, **28**, 1377 (1966).
- (11) K. M. Mackay, R. D. George, P. Robinson, and R. Watt, *J. Chem. Soc. A*, 1920 (1968).
- (12) S. R. Stobart, *Chem. Commun.*, 999 (1970).
- (13) L. M. Dennis, R. B. Corey, and R. W. Moore, *J. Am. Chem. Soc.*, **46**, 657 (1924).
- (14) H. J. Emel us and D. E. MacDuffie, *J. Chem. Soc.*, 2597 (1961).
- (15) E. H. Man, D. D. Coffman, and E. L. Muettterties, *J. Am. Chem. Soc.*, **81**, 3575 (1959).
- (16) J. W. Dale, H. J. Emel us, and R. N. Haszeldine, *J. Chem. Soc.*, 2939 (1958); H. J. Emel us and M. J. Dunn, *J. Inorg. Nucl. Chem.*, **27**, 752 (1965).
- (17) C. J. Marsden, *J. Fluorine Chem.*, **5**, 401 (1975).
- (18) A. G. MacDiarmid, *Q. Rev., Chem. Soc.*, **10**, 208 (1956).
- (19) M. E. Redwood and C. J. Willis, *Can. J. Chem.*, **43**, 1893 (1965).
- (20) E. J. Spanier and A. G. MacDiarmid, *J. Inorg. Nucl. Chem.*, **31**, 2976 (1969).
- (21) A. J. Downs and E. A. V. Ebsworth, *J. Chem. Soc.*, 3516 (1960); E. A. V. Ebsworth, H. J. Emel us, and N. Welcman, *J. Chem. Soc.*, 2290 (1962).
- (22) E. A. V. Ebsworth, S. G. Frankiss, and A. G. Robiette, *J. Mol. Spectrosc.*, **12**, 299 (1964).
- (23) J. T. Wang and C. H. Van Dyke, *Chem. Commun.*, 612 (1967).
- (24) G. K. Barker, J. E. Drake, and R. T. Hemmings, *J. Chem. Soc., Dalton Trans.*, 450 (1974).
- (25) C. H. Van Dyke and A. G. MacDiarmid, *Inorg. Chem.*, **3**, 1071 (1964).
- (26) K. M. Mackay, P. Robinson, and R. D. George, *Inorg. Chim. Acta*, **1**, 236 (1967).
- (27) W. L. Jolly, *J. Am. Chem. Soc.*, **85**, 3083 (1963).
- (28) See for example R. Demuth, J. Apel, and J. Grobe, *Spectrochim. Acta, Part A*, **34**, 357 (1978).
- (29) K. M. Mackay and K. J. Sutton, *J. Chem. Soc. A*, 2312 (1968); K. M. Mackay, S. T. Hosfield, and S. R. Stobart, *J. Chem. Soc. A*, 3250 (1970).
- (30) For a discussion of factors which may be responsible for the stabilizing effect of fluorocarbon ligands in metal complex chemistry see R. S. Nyholm, *Q. Rev., Chem. Soc.*, **24**, 1 (1970).
- (31) Relative ion abundance data are available from the authors on request.

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Reactions of Primary Alkylantimony Compounds. Formation of the Macromolecular Species (RSb)_x and (RSbI_{0.4})_x

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Reactions of the primary alkylstibines CH₃SbH₂, C₂H₅SbH₂, and n-C₄H₉SbH₂ with organosilicon chlorides or HCl produce a pale green macromolecular species with a metallic sheen analyzing as (RSb)_x while the same stibines with iodine-containing reagents, I₂, ICl, Cl₄, and (CH₃)₂AsI, produce a purple-black species, (RSbI_{0.4})_x. With CH₃AsCl₂, the stibines yield only the all-arsenic macromolecule (CH₃As)_x and RSbCl₂. No evidence for the formation of cyclooligomers of antimony is found.

Introduction

Low-dimensional organometallic macromolecules warrant study as potential sources of new materials with unusual electrical properties.¹ Earlier studies of a homoatomic ladder-structure catenate of arsenic, (CH₃As)_x,^{2,3} exposed a rich variety of thermal and photoconductivity properties^{4,5} that encouraged us to extend this study to antimony.

Few reports exist of compounds which analyze satisfactorily as multiples of the unit RSb; those that do are restricted to cyclooligomers with sterically demanding phenyl⁶ or *tert*-butyl⁷ R groups. Previous reports of high-molecular-weight organoantimony catenates invariably describe products containing excess antimony.^{8,9} In two earlier papers we briefly reported procedures which provide the (CH₃Sb)_x polymer, specifically the reactions of CH₃SbH₂ with dibenzylmercury¹⁰ and with sulfur monochloride.¹¹ The present study concerns the reactions of primary alkylstibines with elemental halogen, halocarbons, and organometallic halides.

Since our primary interest was a study of the ability of the RSb unit to form macromolecular compositions, it was im-

portant that the primary alkylarsenic reagents be as free as possible from potentially chain-terminating dialkyl derivatives and chain-branching antimony trihalide. The results of our study of both existing and novel procedures to obtain high-purity organoantimony monomers is described in a recent review.¹²

Results

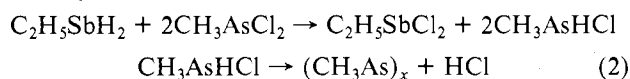
Reactions of Alkylstibines. Primary alkylstibines react rapidly with iodine, iodine monochloride, or carbon tetraiodide in benzene to form a microcrystalline purple-black solid and alkyldiiodostibine. A ¹H NMR spectrum of the reaction mixture within 1 min of combination shows a complete absence of alkylstibine. The ¹H NMR spectrum is consistent with RSbI₂ formation: R = Me, singlet at δ 1.84; R = Et, δ 1.95 (quartet) 1.65 (triplet) (³J_{HH'} = 7 Hz). After opening of the reaction tube and removal of the purple-black solid by filtration, evaporation of solvent affords a bright yellow crystalline solid identified as RSbI₂. The purple-black solid showed consistent C, H, and I percentages near the empirical composition RSbI_{0.4} (or R₅Sb₅I₂). We are seeking crystals large

enough for X-ray structural analysis and electrical property characterization. No iodine could be displaced from $\text{CH}_3\text{SbI}_{0.4}$ by heating at 50 °C in vacuo (0.1 mmHg) for 2 days; in contrast, attempts to form this material by exposing crystals of halogen-free $(\text{RSb})_x$ to iodine vapor (~ 1 mmHg at 40 °C) result in rapid and complete destruction of the original material.¹³

As monitored by ^1H NMR spectroscopy, alkylstibines combine with CCl_4 to form CHCl_3 and RSbCl_2 , but in contrast to alkylarsines,³ no Sb-Sb condensation products are found even when CH_3SbH_2 is in excess of the ratio shown in eq 1.



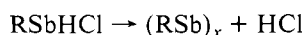
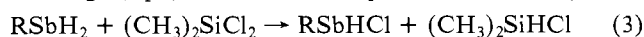
Ethylstibine and CH_3AsCl_2 undergo rapid hydrogen-chlorine exchange followed by slow HCl elimination to form the all-arsenic ladder homopolymer $(\text{CH}_3\text{As})_x$. No other solid products were formed, and no antimony or ethyl group incorporation in $(\text{CH}_3\text{As})_x$ could be detected by mass spectrometry.



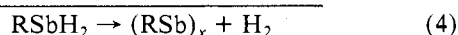
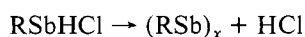
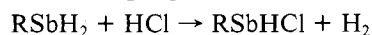
There was no ^1H NMR evidence for the formation of $\text{C}_2\text{H}_5\text{SbHCl}$. With $(\text{CH}_3)_2\text{AsI}$, CH_3SbH_2 produces $(\text{C}_2\text{H}_5)_2\text{AsH}$, $(\text{CH}_3)_2\text{AsAs}(\text{CH}_3)_2$, and solid $\text{CH}_3\text{SbI}_{0.4}$; no CH_3SbI_2 or CH_3SbHI was found.

The reactions of RSbH_2 with three organosilicon chlorides, $(\text{CH}_3)_2\text{SiCl}_2$, $(\text{CH}_3)_3\text{SiCl}$, and $(\text{C}_6\text{H}_5)_3\text{SiCl}$, provided $(\text{RSb})_x$ without apparent halogen incorporation. In each reaction, a crystalline solid with a pale green metallic luster and the formula $(\text{RSb})_x$ was isolated. An X-ray diffraction powder pattern shows no bands in common with the major bands of elemental antimony. This polymeric compound is, in appearance, quite different from previously reported black materials with the claimed formula $(\text{RSb})_x$ which are obtained from the thermal decomposition of RSbH_2 .^{8,9,14} We also isolated this black, amorphous material and found that it slowly turns gray in the presence of air and moisture. It is very likely a mixture of finely divided antimony metal and a variety of $(\text{CH}_3\text{Sb})_x$ modifications. (X-ray powder patterns of these amorphous materials frequently show the major bands of elemental antimony.) In contrast, the new pale green solid is indefinitely air stable and consists of small, well-formed crystals.

These reactions of CH_3SbH_2 with organosilicon chlorides were monitored by ^1H NMR. Initially, a small amount of HCl is formed, but it eventually disappears. The concentrations of the silicon compounds remain nearly constant (within experimental error) at their initial levels. Only the concentration of CH_3SbH_2 decreases with time until it is consumed. On opening the reaction tube, we observed a pressure due to a noncondensable gas (hydrogen). These reactions can, therefore, better be described as catalytic. The initial formation of HCl is believed to occur via a halogen-hydrogen exchange (eq 3). Then the HCl produced can catalyze the



decomposition of RSbH_2 (eq 4). With regard to reaction 3,



it should be noted that CH_3AsH_2 and $(\text{CH}_3)_2\text{SiCl}_2$ do not undergo H/Cl exchange even at 100 °C.

We also found that CH_3SbH_2 reacts directly with HCl in a 2:1 molar ratio to give the same shiny pale green solid,

$(\text{CH}_3\text{Sb})_x$. The reaction, however, was much faster and the rapid formation of solid in the reaction tube precluded ^1H NMR monitoring.

Although we were unable to demonstrate with certainty the preparation of *n*-butylstibine due to its very rapid decomposition (the material obtained may also have contained some di-*n*-butyl ether), it did undergo reactions similar to the lighter alkylstibines and produced a product with $(\text{CH}_3)_2\text{SiCl}_2$ analyzing successfully as $(\text{C}_4\text{H}_9\text{Sb})_x$.

Discussion

We have previously reported that methylarsine, CH_3AsH_2 , with a large variety of halogen sources (both organic and inorganic), produces a purple-black crystalline "polymer", empirical formula $(\text{CH}_3\text{As})_x$, possessing a novel ladder structure constructed entirely of arsenic atoms.^{2,3} We have concluded from a variety of viewpoints that this macromolecular crystalline form is more thermodynamically stable than the much better known cyclooligomer pentamethylcyclopentaarsine, $(\text{CH}_3\text{As})_5$.⁹ Well-purified samples of the cyclooligomer convert slowly to the polymer over a period of months at 60 °C. At 200 °C, however, catena forms rapidly revert to cyclooligomer; this suggests that the free energy difference between catena and cyclo forms is small, and that, as could be reasonably assumed, the catena-cyclo transformation occurs with a positive change in entropy.

In contrast, all attempts to prepare analogue arsenic ladder structures with organic groups other than methyl fail to produce stable high-molecular-weight crystalline products; transient polymeric products inevitably give way to cyclooligomeric products. The only consistent explanation for the unique properties of the methyl derivative is based upon steric considerations, not along a ladder strand but rather between parallel ladder strands where the interladder approach distance would be forced by large substituents to an unstable length. The larger antimony-atom van der Waals radius, however, can accommodate larger substituents.

Few cyclopolystibines are known. Red amorphous *tert*-butylcyclohexastibine is a minor product in the reduction of $(t\text{-Bu})_2\text{SbCl}$,⁷ and very recently an orange-red solid analyzing as $(\text{C}_6\text{H}_5\text{Sb})_6\cdot\text{C}_6\text{H}_6$ has been reported as a high-yield product of the reaction of $\text{C}_6\text{H}_5\text{SbH}_2$ and styrene in benzene.⁶ (In remarkable contrast, no reaction occurs when diphenylstibine and styrene are similarly combined.¹⁵) While cyclopolystibines and arsines generally behave as feeble Lewis bases, this cyclostibine would appear to behave as a Lewis acid. Other than these two cyclooligomers, no other polystibine compounds with satisfactory analyses as RSb have previously been reported.

We have not found any evidence for the formation of cyclooligomers of antimony in the present study. We, therefore, conclude that, in continuation of the evident trend toward increasing degrees of association on descending the group 5 elements and homoatomic catenates, only in special cases where substituent bulk prevents macromolecular formation would cyclooligomers of antimony prevail.

The electrical properties of $(\text{RSb})_x$ and $(\text{RSbI}_{0.4})_x$ will be described in future reports. Preliminary results (for compressed powders) suggest that $(\text{RSb})_x$ is a better conductor than $(\text{RAs})_x$ by several orders of magnitude, in keeping with the trend toward more metallic properties on descending a main-group family. We hope to expand our short list of R groups to include substituents possessing both +I and -I inductive effects, to ascertain the effect of inductive phenomena on charge carrier density and mobility.

Experimental Section

Published procedures were used for the synthesis of dichloro(methyl)arsine,¹⁶ dimethylidoarsine,¹⁷ and carbon tetraiodide.¹⁸ The preparations of dichloro(methyl)stibine, dichloro(ethyl)stibine, *n*-

butyldichlorostibine, methylstibine, ethylstibine, and *n*-butylstibine are described in an earlier publication.¹²

SbCl₃ (Alfa) was used as obtained. The organosilicon halides (Alfa) were fractionally distilled before use. Alkylstibines were stored at -196 °C and transferred into reaction tubes on an all-glass vacuum line of standard design as quickly as possible to reduce loss by decomposition. The benzene and carbon tetrachloride employed in all studies were spectrograde and were freshly distilled from molecular sieve. Before each experiment, benzene was degassed thoroughly by repeated freeze-pump-thaw cycles.

IR spectra were recorded on a Perkin-Elmer 221G spectrophotometer using a 10-cm path length gas cell fitted with NaCl windows. NMR spectra were recorded on a Perkin-Elmer R20B spectrometer in sealed 5-mm tubes. All NMR chemical shifts are referred to benzene (Me₄Si = δ 0.00) which was the solvent in all NMR studies. Mass spectra were recorded on a Du Pont 21-492 spectrometer at 70 eV at 2 × 10⁻⁶ mmHg. Elemental analyses were performed by either Integral Analytical Laboratory, Raligh, N.C., or Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Reactions of Alkylstibines with Iodine Sources. In all cases, a 0.5 M solution of the halogen-containing reactant in benzene was introduced into a medium-wall 5-mm o.d. NMR tube and thoroughly degassed by repetitive freeze-pump-thaw cycles. The alkylstibine was condensed into the NMR tube so that the RSbH₂:reactant ratio was 2:1. The NMR tube was then sealed on the vacuum line. Solid products were isolated by opening the tubes on the vacuum line and removing volatile materials by distillation. With I₂, ICl, Cl₄, and dimethyldiiodoarsine, the major antimony-containing reaction products are RSbI₂ (identified by ¹H NMR) and RSbI_{0.4}, the former being a yellow solid readily soluble in common organic solvents and the latter being an involatile purple-black solid insoluble in the same solvents.

For RSbI_{0.4} the analytically determined R:Sb:I ratio of 1:1:0.4 was nearly constant despite variations in R group and molar ratio of reactants. (Anal. Calcd for CH₃I_{0.4}Sb: C, 6.40; H, 1.61; I, 27.07; Sb, 64.92. Found: C, 6.29; H, 1.57; I, 27.37; Sb, 65.09. These data are typical of all results.) The mass spectrum of EtSbI_{0.4} curiously shows no fragments containing both iodine and more than one antimony atom. At 70 eV and 350 °C, the major peaks correspond to (EtSb)_n⁺, *n* = 2-4.

Reaction of Alkylstibines with Organosilicon Chlorides. Equimolar ratios of alkylstibine and (CH₃)₂SiCl₂, (CH₃)₃SiCl, or (C₆H₅)₃SiCl were combined as 10% solutions in benzene and monitored by ¹H NMR spectroscopy. In all cases a pale greenish purple, metallic-looking solid, (RSb)_n, was found. (Anal. Calcd for CH₃Sb: C, 8.77; H, 2.19. Found: C, 8.51; H, 2.16. Calcd for C₂H₅Sb: C, 15.93; H, 3.34. Found: C, 15.76; H, 3.29. Calcd for C₄H₉Sb: C, 26.85;

H, 5.07. Found: C, 26.31; H, 4.94.)

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Registry No. (CH₃Sb)_x, 62173-60-8; (C₂H₅Sb)_x, 68781-08-8; (C₄H₉Sb)_x, 68781-10-2; CH₃SbH₂, 23362-09-6; C₂H₅SbH₂, 68781-03-3; *n*-C₄H₉SbH₂, 68781-04-4; (CH₃)₂SiCl₂, 75-78-5; (CH₃)₃SiCl, 75-77-4; (C₆H₅)₃SiCl, 76-86-8; MeSbI₂, 30982-87-7; EtSbI₂, 68781-05-5; I₂, 7553-56-2; ICl, 7790-99-0; Cl₄, 507-25-5; (CH₃)₂AsI, 676-75-5; CH₃AsCl₂, 593-89-5; (CH₃As)_x, 26403-94-1; CH₃SbCl₂, 42496-23-1; C₂H₅SbCl₂, 68781-06-6; C₄H₉SbCl₂, 5613-73-0.

References and Notes

- (a) J. S. Miller and A. J. Epstein, *Prog. Inorg. Chem.*, **20**, 1 (1976). (b) E. P. Goodings, *Chem. Soc. Rev.*, **5**, 95 (1976). (c) A. D. Yoffe, *Chem. Soc. Rev.*, **5**, 51 (1976).
- A. L. Rheingold and J. M. Bellama, *Chem. Commun.*, 1058 (1969).
- A. L. Rheingold, J. E. Lewis, and J. M. Bellama, *Inorg. Chem.*, **12**, 2845 (1973). The X-ray crystal structure has been determined: J. J. Daly and F. Sanz, *Helv. Chim. Acta.*, **53**, 1879 (1970).
- J. E. Lewis and M. Edris, *Phys. Rev. B*, **11**, 4033 (1975); **12**, 4231 (1975).
- J. E. Lewis, *Phys. Status Solidi A*, **8**, 483 (1971).
- K. Issleib and A. Balszuweit, *Z. Anorg. Allg. Chem.*, **418**, 158 (1975); **419**, 89 (1976).
- K. Issleib, B. Hamann, and L. Schmidt, *Z. Anorg. Allg. Chem.*, **339**, 298 (1965).
- F. Klages and W. Rapp, *Chem. Ber.*, **88**, 384 (1955).
- A. L. Rheingold in "Homoatomic Rings, Chains and Macromolecules of Main-Group Elements", A. L. Rheingold, Ed., Elsevier, Amsterdam, 1977, p 385.
- A. L. Rheingold and P. Choudhury, *J. Organomet. Chem.*, **128**, 155 (1977).
- P. Choudhury and A. L. Rheingold, *Inorg. Chim. Acta*, **28**, L127 (1978).
- A. L. Rheingold, P. Choudhury, and M. F. El-Shazly, *Synth. React. Inorg. Met.-Org. Chem.*, in press.
- This result may be contrasted to the behavior of (CH)_x and (SN)_x which form stable halogen adducts in substoichiometric quantities when placed in halogen atmospheres: M. Akhtav, C. K. Chiang, M. J. Cohen, J. Kleppinger, A. J. Heeger, E. J. Louis, A. G. MacDiarmid, J. Milliken, N. J. Moran, D. L. Peebles, and H. Shirakawa, *Ann. N.Y. Acad. Sci.*, in press.
- E. Wiberg and K. Mödritzer, *Z. Naturforsch.*, **B**, **12**, 128 (1957).
- A. N. Nesmeyanov, A. E. Borisov, and N. V. Novikova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 815 (1967).
- G. P. Van der Kelen, *Bull. Soc. Chim. Belg.*, **65**, 343 (1956).
- W. R. Cullen, *Can. J. Chem.*, **38**, 439 (1960).
- R. E. McArthur and J. A. Simons, *Inorg. Synth.*, **3**, 37 (1955).

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Electrochemistry of Iminodiacetate Complexes of Cobalt at Stationary Electrodes

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The redox behavior of *cis*- and *trans*-bis(iminodiacetato)cobaltate(III) has been studied in aqueous solution at stationary electrodes. The *cis* complex exhibits quasi-reversible behavior and a reduction potential estimated to be +0.36 V vs. the SHE. The *trans* isomer, however, exhibits more complex behavior, and upon reoxidation the *cis* isomer of the Co(III) system forms quantitatively. The results can be interpreted in terms of a model in which the *cis* isomer of the Co(II) system is the more stable and forms to the virtual exclusion of the corresponding *trans* species, whereas the *trans* species is preferred in the case of Co(III). The model also neatly rationalizes the synthetic methods which have been used to prepare the *cis* and *trans* isomers of the Co(III) complex. In addition, according to this model, an upper limit of 0.17 V vs. the SHE can be assigned to the reduction potential of the *trans* system. Finally, complications which occur in studying the complex at a mercury electrode are discussed, and conditions are described under which these effects are minimized.

Introduction

Two isomeric forms of a 2:1 complex of the iminodiacetate ligand with Co(III) have been characterized.¹ Both complexes are pseudooctahedral with the ligands coordinated on opposite triangular faces. The structures are distinguished by the

relative disposition of the nitrogen donors. In one structure the nitrogens coordinate in a *cis* fashion and in the other *trans*. We became interested in the redox properties of *cis*- and *trans*-bis(iminodiacetato)cobaltate(III), denoted *cis*-Co(IIA)₂⁻ and *trans*-Co(IIA)₂⁻, respectively, when we found that these