to −25° in a Dry Ice–2-propanol bath. The KOH–dioxane solution was heated to the reflux temperature and 41.0 g (0.334 mol) of 1,4-dichloro-2-butyne was added to the solution at a rate of 2–3 drops/sec. The diacetylene gas produced (a yield of 55% based on 1,4-dichloro-2-butyne was assumed) was carried by a slow stream of nitrogen through the scrubbing towers and condensed into the cold solution of $B_{10}H_{12}\cdot 2S(CH_2CH_3)_2$. After diacetylene production was complete, the short section of Tygon tubing connecting the inlet tube to the drying tower was clamped shut and the Dry Ice condenser was allowed to warm to room temperature. In this manner, any diacetylene that was condensed on the cold finger was allowed to return to the reaction flask. The reaction solution was slowly warmed to 80° and stirred for 12 hr. The solution was cooled and stripped on a rotary evaporator by a water aspirator to an oily solid. This solid and 500 ml of methanol, which destroyed any unreacted boranes,[8] were added to a 1-l. round-bottom flask equipped with a Friedrichs condenser. The solution was slowly heated over a steam bath to the reflux temperature and maintained at this temperature until hydrogen evolution terminated. A 3–5-ml amount of 50% aqueous HCl was cautiously added and the solution again was slowly warmed to the reflux temperature. When hydrogen evolution had terminated, the condenser was replaced by a distillation head and Liebig condenser. Ethanol was added to increase the boiling point of the solution and the alcohol–diethyl sulfide solution codistilled until all diethyl sulfide was removed (more ethanol was periodically added). The solvent was removed by a rotary evaporator and a water aspirator and the resulting solid dissolved in 1 l. of benzene. The solution was cooled to 5°, 1 l. of cold 10% aqueous NaOH was added, and the mixture was vigorously stirred for 15 min. The aqueous and organic phases were separated; the aqueous phase was washed once with 250 ml of benzene and the aqueous phase discarded. The combined organic phases were washed two times with 500-ml portions of H_2O and dried over anhydrous $MgSO_4$. The dry benzene solution was filtered through a bed of basic alumina (500 ml dry volume) and the solvent was removed with a rotary evaporator and water aspirator to afford 16.7 g of crystalline I (58.3% based on $B_{10}H_{14}$).

Preparation of Ethynylcarborane, II. Bis(acetonitrile)decaborane, $B_{10}H_{12}\cdot 2CH_3CN$, was prepared by the method of Schaeffer[9] from 45.2 g (0.37 mol) of decaborane. As described above, 67.0 g (0.54 mol) of 1,4-dichloro-2-butyne was added dropwise to a solution of 500 ml of H_2O, 55 ml of *p*-dioxane, and 73.2 g of KOH at the reflux temperature. Again the diacetylene was scrubbed with a 10% aqueous KOH solution and dried. The dry gas was condensed into a preweighed 100-ml, three-necked flask equipped with a Dry Ice condenser maintained at −80°, an inlet tube which connected to the diacetylene generation train, and a glass stopper. The flask contained 40 ml of acetonitrile cooled to −35° in a Dry Ice–2-propanol bath. After diacetylene generation was complete, the flask was warmed to room temperature, the inlet tube was replaced by a glass stopper, and the flask was reweighed to determine the yield of diacetylene (15 g, 0.37 mol).

The acetonitrile solution of diacetylene was added to the addition funnel under a stream of nitrogen and the diacetylene solution was added to the stirring suspension of $B_{10}H_{12}\cdot 2CH_3CN$ over a 45-min period. The reactants were stirred for 4 hr, then slowly warmed to 40° and stirred for 12 hr, and finally heated to the reflux temperature for 2 hr. The solution was cooled to room temperature and using the purification methods previously described,[4,5] 3 g (3.3%) of I and 35.3 g of II (70% based on $B_{10}H_{14}$) were obtained.

Registry No. $B_{10}H_{12}\cdot 2Et_2S$, 32124-79-1; HCCCCH, 460-12-8; [1-(1′-1′,2′-$B_{10}C_2H_{11}$)-1,2-$B_{10}C_2H_{11}$], 12075-02-4; $B_{10}H_{12}\cdot 2CH_3CN$, 28377-97-1; $HCCC_2B_{10}H_{11}$, 23883-21-8.

Acknowledgment. The authors wish to thank the Office of Naval Research for its generous support of this research.

[8] There is an induction period for the decomposition reaction which is an exothermic process, and therefore while heating or adding reagents to this solution, caution should be employed.

[9] R. O. Schaeffer, *J. Amer. Chem. Soc.*, 79, 1006 (1957).

Correspondence

A Topological Approach to Boron Hydride Reactivities. Electrophilic and Nucleophilic Substitution.

Sir:

The topological approach is perhaps the simplest, yet potentially one of the most powerful methods which can be applied to the study of electron-deficient molecules. No parameters, experimental or theoretical, need be introduced. No equations are solved. The entire conceptual apparatus of the method consists of a few simple counting rules, which may be summarized as (1) conservation of topology, (2) conservation of electrons, and (3) conservation of orbitals.

In a recent paper,[1] we showed how the Dickerson-Lipscomb approach[2] could be simplified and extended by incorporating certain results from self-consistent field (SCF) and localized molecular orbital (LMO) calculations. Elimination of open three-center boron framework bonds[3] from our topological picture made possible the rapid evaluation of possible boron hydride frameworks. Our results were in agreement with the hypothesis that topologies which give rise to at least one, but preferably many, allowable valence structures are found in stable boron hydrides, while topologies with few or no such structures do not give rise to stable molecular frameworks. With this hypothesis as a starting point, one can use the topological method to predict the stability of proposed boron hydrides or to suggest likely structures for new species.

The synthetic chemistry of electron-deficient molecules is experiencing a remarkable growth. The plethora of new compounds has made clear the need for a generally applicable scheme for systematizing boron chemistry to a degree approaching that of carbon chemistry.[4] Some progress in this direction has been made by employing purely geometric considerations.[5] Although the geometrical approach is a profitable one when applied to structural questions, we believe that the complementary topological method can be equally useful in predicting structures and more fruitful in the study of reactions. In this correspondence we show how topological notions may be employed to predict the course of ionic substitution reactions in the boron hydrides.

The Topological Approach to Reactivity. Given that one

[1] I. R. Epstein and W. N. Lipscomb, *Inorg. Chem.*, 10, 1921 (1971). Several errors appear in the counting rules given in this reference. In rule (4) the number of B–B bonds should be $s - q/2$, not $(s - q)/2$. In footnote 14 there should be $s - q/2 - 3l/2$ two-center and $p - s + l$ three-center bonds. The undefined parameter y should not appear in footnote 14.

[2] R. E. Dickerson and W. N. Lipscomb, *J. Chem. Phys.*, 27, 212 (1957).

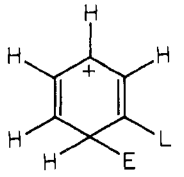
[3] Further localized orbital calculations (D. S. Marynick, I. R. Epstein, and W. N. Lipscomb, submitted for publication) have given evidence for the existence of an open three-center *boron-carbon-boron* bond in at least one carborane. However, these calculations also confirm the absence of open B–B–B bonds in either the carboranes or the boron hydrides.

[4] One possible scheme has been suggested by R. W. Parry and L. J. Edwards, *J. Amer. Chem. Soc.*, 81, 3554 (1959).

[5] R. E. Williams, *Inorg. Chem.*, 10, 210 (1971).

can predict (from the existence or nonexistence of topologically allowed valence structures) whether a given boron hydride topology will be a stable one, one has only to conduct a topological study of the possible transition states for a reaction. If there exists a stable transition state (in the above topological sense), then the reaction will be said to be topologically allowed. If no transition state for the reaction has a topologically allowable valence structure, then we shall say that the reaction is topologically forbidden.

In general, cataloging all the possible transition states for a reaction is an exceedingly difficult task. However, for the case of simple electrophilic and nucleophilic substitutions *which take place without any intramolecular rearrangement*, the job is considerably simpler. We shall take an approach similar to that employed by Wheland[6] in his study of the substitution reactions of aromatic compounds. To investigate, for example, the attack of an electrophile E^+ at the ortho position of the substituted benzene C_6H_5L (I), Wheland considered a transition state of the form II. The difference in energies between species I and II was estimated using the Huckel molecular orbital approximation. This energy difference was then employed as an indicator of the activation energy required for the reaction.



II

In the present method, we consider transition states similar to those postulated by Wheland, but instead of calculating energies, we investigate the topological acceptability of these species. Figure 1 illustrates, for terminal hydrogen substitutions at B2 in the B_4H_{10} molecule, the type of reaction pathway which this approach considers. For dissociative reaction mechanisms (SN1 or SE1), the hydride ion or proton is presumed to leave before the attacking group becomes attached. Associative mechanisms (SN2 or SE2) are assumed to proceed with the attachment of the attacking group preceding the detachment of the hydrogen. This ability to distinguish between first- and second-order kinetics is an important feature of the topological method, since many other approaches to reactivity are unable to come to grips with kinetic questions.

The topological investigation of a molecule's reactivity consists of generating transition states like those in the middle column of Figure 1 for all the symmetry-unique positions in the molecule.[7] One then tests each of these transition-state topologies (four per unique hydrogen) to see if it has any allowable valence structures, *i.e.*, to see if the reaction is topologically allowed. It is a straightforward matter to build the generation and testing of the transition states into a topological computer program such as the one described in ref 1.

Results. The procedure described in the previous section was applied to five of the most common neutral boron hydrides, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, and $B_{10}H_{14}$. In addition to providing some experimental results for comparison, these molecules have also been studied by the self-consistent field molecular orbital method.[8]

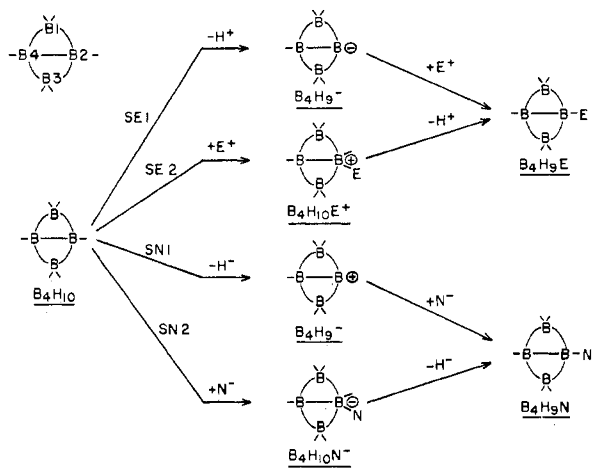
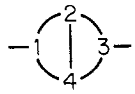
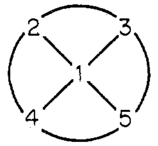
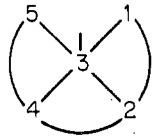
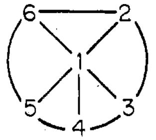
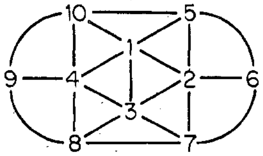


Figure 1. Reaction pathways and transition states for ionic substitution at the B2 terminal hydrogen of B_4H_{10}. (The line connecting B2 and B4 represents a topological connection in the sense of ref 1; that is, B2 and B4 must be bonded, but not necessarily by a *two*-center bond.)

Table I. Topologically Allowed Boron Hydride Substitution Reactions

Molecule[a]	Structure[b]	Allowed reactions[a,c]
B_4H_{10} (1)		SN1 at B1[d] (4) SE1 at B1-B2[e] (4)
B_5H_9 (4)		SN1 at B1 (1) SE2 at B1 (2) SN1 at B2 (4) SE1 at B2-B3 (12) SN1 at B2-B3 (4)
B_5H_{11} (1)		SE1 at B3 (6) SE1 at B1-B2 (2) SE1 at B2-B4 (1)
B_6H_{10} (3)		SE1 at B1 (4) SN1 at B1 (1) SE2 at B2 (2) SN1 at B3 (2) SE1 at B2-B3 (2) SE1 at B3-B4 (4)
$B_{10}H_{14}$ (24)		SE1 at B1 (8) SN1 at B1 (22) SE1 at B2 (40) SE1 at B5 (24) SN1 at B5 (16) SN1 at B6 (10) SE1 at B5-B6 (4)

[a] Numbers in parentheses are the number of topologically allowable valence structures for the neutral molecule or for the transition state of the given reaction. [b] *n* = BH group at position *n*; *n*- = BH_2 group at position *n*. Curved lines represent BHB bridges. Straight lines between borons represent topological connections. [c] Allowed reactions are those for which the transition state possesses at least one topologically allowable valence structure. [d] Substitution at either of the B1 terminal hydrogens. [e] Substitution at the bridge hydrogen connecting B1 and B2.

Our results are shown in Table I. Several general features are apparent. First, there appears to be a strong preference for first-order over second-order kinetics, and, in fact, no SN2 reactions are predicted. In view of the high coordination numbers and large degree of steric hindrance of many of the

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(6) G. W. Wheland, *J. Amer. Chem. Soc.*, 64, 900 (1942).

(7) For simplicity, one uses protons as the electrophiles and hydride ions as the nucleophiles. Even the scheme shown in Figure 1 is an oversimplification, since many possible transition states, particularly those involving four-center interactions, are ignored.

(8) (a) E. Switkes, I. R. Epstein, J. A. Tossell, R. M. Stevens, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 92, 3837 (1970); (b) I. R. Epstein, J. A. Tossell, E. Switkes, R. M. Stevens, and W. N. Lipscomb, *Inorg. Chem.*, 10, 171 (1971); (c) E. A. Laws, R. M. Stevens, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 94, 4467 (1972).

boron atoms in these molecules, such a result is not surprising. Although SN2 reactions have been observed at boron atoms,[9] they have involved tetracoordinate borons attached to an amine group and to only a single bulky aryl or alkyl group. Bulky disubstituted boranes were found[10] to react by a first-order mechanism.

A second universally observed feature is that all bridge hydrogens are substitutable by an SE1 mechanism. Topologically this result is trivial, since the transition state may be formed simply by removing a proton from the bridge and using the electrons that are left behind to form a B–B bond, thus maintaining the topological connection between the borons. There is strong evidence for the acidity of bridge hydrogens. For example, $\mu\text{-}B_5H_8^-$ and $\mu\text{-}B_6H_9^-$ have been prepared by reactions of B_5H_9 and B_6H_{10} respectively with metal hydrides and with methyllithium.[11] Bridge deprotonations of B_4H_{10} and B_5H_{11} by ammonia in ether and in CH_2Cl_2, respectively, have been reported.[12] The Bronsted acidity of the bridge protons in decaborane(14) is well established.[13] Finally, SCF-MO calculations[8] on these molecules give Mulliken charges which suggest that bridge protons will be considerably more acidic than terminal hydrogens. The potential synthetic utility[14] of these boron hydride anions for generating larger boron frameworks is enormous.

Relatively little work has been done on other ionic substitution reactions of B_4H_{10}, B_5H_{11}, and B_6H_{10}, probably because of the tendency of these molecules to decompose into smaller fragments. Friedel-Crafts ethylation,[15] deuteration,[16] and halogenation[17] of B_5H_9 have been observed to occur at the apical boron B1, in agreement with both the topological theory and the SCF calculation of the boron charges.[8a]

Terminal hydrogen substitutions in the more stable decaborane molecule have been studied somewhat more thoroughly. Friedel-Crafts ethylation[15] and methylation[18] of $B_{10}H_{14}$ appear to occur at the 1 and 2 positions, though the interpretation of the nmr spectra is by no means unambiguous. Some evidence for Friedel-Crafts methylation at the 5 position was also observed.[18] Deuterium exchange of $B_{10}H_{14}$ under electrophilic conditions was found to take place at the 1 and 2 positions,[19] while electrophilic iodination gave 2,4-[20] and 2,5- or $1,2\text{-}B_{10}H_{12}I_2$.[21] Nucleophilic substitution of $B_{10}H_{14}$ by methyl- and ethyllithium gave mainly 6-substituted and smaller amounts of 5-substituted product.[22] Boron charges from the SCF calculation[8c] agree with our results in predicting that electrophilic substitution is least likely at B6 and that nucleophilic substitution is least likely at B2.

The interpretation of B_2D_6 deuterium exchanges[23] and alkyne addition reactions[24] with the boron hydrides is unclear. It is likely that these reactions proceed by mechanisms involving BH_3 fragmentation and/or free radicals, rather than by direct ionic substitutions.

Discussion. The generally good agreement of our predictions with the experimental data is encouraging. Although the range of experiments is rather limited at the present time, improved techniques should make possible a more systematic investigation of boron hydride reactivities.

It seems appropriate to point out a few of the more significant limitations and drawbacks of this topological approach. The method is a completely qualitative one. Since we put in no parameters and solve no equations, we cannot expect to generate any numbers which might correspond to activation energies, rate constants, etc. One could, of course, introduce empirical energy parameters[6] or attempt to use the charge distributions of the various valence structures to estimate their stability.[1] However, such heuristic approaches are unlikely to produce very reliable numbers, and it is highly improbable that purely topological considerations will ever produce more than purely qualitative predictions of reactivity.

Since the theory gives no information about the magnitude of the activation energy, one should probably give more credence to its negative predictions than to its positive ones. That is, it is probably safe to conclude that a topologically forbidden reaction has no low-lying transition state. However, the existence of a topologically allowed transition state does not necessarily imply that the state has a low enough energy to make it accessible.

Even topologically forbidden reactions may take place, if a pathway involving intramolecular rearrangement is available. The present theory is applicable only to direct reactions, which is a serious limitation in view of the considerable importance of framework rearrangements[25] in the boron hydrides and carboranes.

One would also like to be able to take steric effects and a larger range of possible transition states into consideration. The discussions of valence strain and nonbonded interactions in $B_{18}H_{22}$ by Plesek, *et al.*,[26] illustrate how one might attempt to build such features into a theory like the one described here.

In conclusion, the topological approach to reactivity should prove to be a useful one for synthetic and structural boron chemists. All the calculations presented in this paper can be done by hand in a few hours, and only the decaborane calculations require a piece of paper larger than the back of a legal-size envelope. Alternatively one can employ a simple computer program.[1] The savings over even the simplest of semiempirical methods are considerable. Further extensions of this method to reactions involving nonionic substitutions, molecular rearrangement, and fragmentation are now in progress.

Registry No. B_4H_{10}, 18283-93-7; B_5H_9, 19624-22-7;

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(9) W. L. Budde and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 93, 3147 (1971); D. E. Walmsley, W. L. Budde, and M. F. Hawthorne, *ibid.*, 93, 3150 (1971).

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(12) H. D. Johnson and S. G. Shore, *J. Amer. Chem. Soc.*, 92, 7586 (1970).

(13) J. J. Miller and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 81, 4501 (1959); W. V. Hough and L. J. Edwards, *Advan. Chem. Ser.*, No. 32, 191 (1961).

(14) H. D. Johnson and S. G. Shore, *J. Amer. Chem. Soc.*, 93, 3798 (1971).

(15) N. J. Blay, I. Dunstan, and R. L. Williams, *J. Chem. Soc.*, 430 (1960).

(16) T. P. Onak and R. E. Williams, *Inorg. Chem.*, 1, 107 (1962).

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(19) M. F. Hawthorne, *J. Amer. Chem. Soc.*, 81, 4998 (1959).

(20) R. Schaeffer, *J. Amer. Chem. Soc.*, 79, 2726 (1957).

(21) M. Hillman, *J. Amer. Chem. Soc.*, 82, 1096 (1960); R. E. Williams and T. P. Onak, *ibid.*, 86, 3159 (1964).

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(24) R. N. Grimes and C. L. Bramlett, *J. Amer. Chem. Soc.*, 89, 2557 (1967); R. N. Grimes, C. L. Bramlett, and R. L. Vance, *Inorg. Chem.*, 7, 1066 (1968); 8, 55 (1969); D. A. Franz and R. N. Grimes, *J. Amer. Chem. Soc.*, 93, 387 (1971).

(25) W. N. Lipscomb, *Science*, 153, 373 (1966).

(26) J. Plesek, S. Hermanek, B. Stibr and F. Hanousek, *Collect. Czech. Chem. Commun.*, 32, 1095 (1967).

B_5H_{11}, 18433-84-6; B_6H_{10}, 23777-80-2; $B_{10}H_{14}$, 17702-41-9.

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Department of Chemistry,
Brandeis University
Waltham, Massachusetts 02154
Irving R. Epstein

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Antisymbiosis and the Trans Effect

Sir:

The concept of chemical symbiosis was introduced by Jorgensen in 1964[1] and has proved useful in understanding a number of chemical facts. The interpretation of symbiosis is very simple: hard bases (electronegative donor atoms) retain their valence electrons when attached to a given central atom, hence keeping the positive charge of that atom high and making it a hard Lewis acid. Soft bases (donor atoms of low electronegativity) substantially give up their valence electrons to the same central atom, reducing its positive charge and making it a softer Lewis acid.

Despite this elementary interpretation and its obvious predictions, it has been known for some time that class b metal ions, more often than not, behave in an antisymbiotic manner.[2] That is, soft bases attached to an already soft Lewis acid can lower the affinity for another soft base. An example would be the synthesis of *trans*-Ir$[P(C_6H_5)_3]_2(CO)$-NCS, which is the N-bonded, rather than the S-bonded, linkage isomer expected for the soft iridium(I) acceptor atom.[2]

The purpose of this note is to point out a number of examples of antisymbiosis for class b metal ions and to show that a simple explanation exists based on the trans effect or trans influence.[3] The examples show that far reaching consequences exist for the structure, stability, and reactivity of complexes of the class b metal ions.

In 1968, Chatt and Heaton pointed out "that groups of high trans effect, as ethylene in $Pt(C_2H_4)Cl_3^-$, render the position in mutual trans position more susceptible to bonding by what are now known as hard bases."[4] They also pointed out that this result was a natural consequence of the theory of the trans effect. Whether a trans activating group is a σ donor or a π acceptor is of little consequence.[5] In either case it is advantageous to have an ionic ligand trans to a strongly covalent ligand.

The evidence of Chatt and Heaton dealt with the kinds of coligands that would stabilize hydroxo complexes of platinum(II). Tobias discussed the stabilities and structures of alkyl derivatives of the transition metals.[6] He pointed out that all dialkyl derivatives of gold(III) had cis structures, virtually all dialkyl derivatives of platinum(II) and platinum(IV) also had cis structures, and all trialkyl complexes of Pt(IV) had fac structures. An explanation was given in terms of the trans influence of one alkyl ligand on another, leading to mutual repulsion. Alkyl groups are known to have a high trans influence.

Since ligands of large trans influence are invariably soft bases, we can put the rules of Chatt and Heaton, and of Tobias, into a more compact form: *two soft ligands in mutual trans position will have a destabilizing effect on each other when attached to class b metal atoms.* That is, they will show antisymbiotic behavior. This rule explains many otherwise puzzling phenomena.

For example, it has been found that *cis*-$Rh(CO)_2Cl_2^-$ is formed in preference to $Rh(CO)_2I_2^-$ and that the thermodynamically stable form of *cis*-$Ir(CO)_2X_4^-$ is $Ir(CO)_2Cl_2I_2^-$ with Cl trans to CO.[7] Since Rh(I) is normally a soft metal ion, the preference for Cl^- over I^- must be due to the CO ligand trans to halogen.

Dimethylmercury is readily cleaved by dilute acid to form $CH_3HgH_2O^+$. However, this cation resists cleavage even by a strong mineral acid.[8] While the methylmercury cation is often regarded as the prototype soft acid, it must now be borne in mind that its affinity for soft bases is markedly reduced by virtue of the CH_3^- ligand in the trans position.

The Pd(II) and Pt(II) ions in dimethyl sulfoxide solution form a solvate with two S-bonded and two O-bonded solvent molecules, in mutual cis positions.[9] There are a number of chelate complexes containing ligands with both S and O donors, or S and N donors. The structures of these always show that each S-donor atom has an O- or N-donor atom trans to it for planar Pd(II) and Pt(II) and for octahedral Co(III) and V(III) complexes.[10] This is not true for planar Ni(II), nor is it necessarily expected, since Ni(II) is not a class b metal ion.

As already mentioned, soft ligands can make a soft metal ion invert its normal preference for S over N in thiocyanate complexes.[2,11] The explanation offered here is that the inversion results when the thiocyanate ligand binds trans to a soft ligand. This may not cover every case since steric factors can also enter in. Very few structures are known. A fascinating example is PdL(NCS)(SCN), where L is 1-diphenylphosphino-3-dimethylaminopropane. The structure is as predicted: the N-bonded thiocyanate is trans to P and the S-bonded thiocyanate is trans to N.[12]

The classic example of $Pt[P(C_2H_5)_3]_2(NCS)_2$ reported by Turco and Pecile[13] is thus predicted to be the cis isomer. From kinetic behavior, it is clear that *trans*-$Pt[P(C_2H_5)_3]_2Cl_2$ reacts with thiocyanate ion to form the S-bonded isomer, at least initially.[14]

Table I shows some data for the first and second formation constants of complexes of Cu(I), Ag(I), Hg(II), and Cd(II)

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[2] N. J. DeStefano and J. Burmeister, *Inorg. Chem.*, 10, 998 (1971).

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[5] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965, Chapter 2.

[6] R. S. Tobias, *Inorg. Chem.*, 9, 1296 (1970).

[7] D. Forster, *Inorg. Chem.*, 11, 1686 (1972).

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