mineral and biologic types can be explained in terms of the theory proposed by McConnell—Santos and González-Díaz[1] surely have not proposed the correct formula for it. Their sixth (final) formula, $Ca_{10-x}(PO_4)_{6-5x/4}(CO_3)_{3x/2}(HPO_4)_{x/4}(OH)_{2-x/4}(H_2O)_{x/4}$, is out of balance by 1.5 electrons when $x = 1$. Thus, we conclude that they have befuddled a somewhat complex topic.

Registry No. Carbonate apatite, 12286-89-4.

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Concerning the Mechanism of Uncatalyzed Cis to Trans Isomerization of [Pt(PEt$_3$)$_2$RX] Complexes

Sir:

In a series of papers[1] we have suggested a dissociative asynchronous mechanism (see Scheme I) for the spontaneous cis to trans isomerization of *cis*-[Pt(PEt$_3$)$_2$RX] (X = halide ions; R = alkyl or substituted aryl groups) in protic solvents. Such a mechanism involves as a rate-determining step the breaking of the Pt–X bond to yield a 14-electron 3-coordinate T-shaped species. This is converted to its "trans-like" counterpart, which subsequently links with the halide ion to give the trans product. In all the cases the isomeric equilibrium was found to lie well to the trans form. The derived rate law:

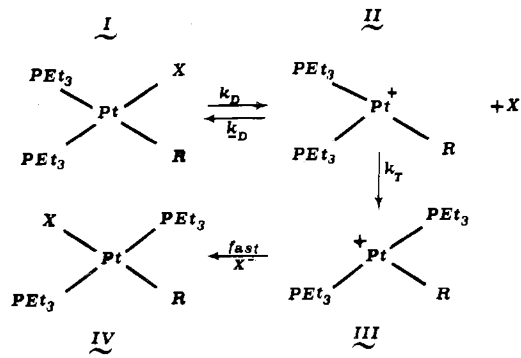
$$k_i = \frac{k_D k_T}{k_{-D}[X^-] + k_T} \tag{1}$$

accounts for the mass law retardation produced by small amounts of added halide ions and for the linearity of the plots of k_i^{-1} vs. $[X^-]$. While we are well aware of the great propensity for the metal to undergo bimolecular substitutions and are familiar with the fact that, in most of the known cases (except for photochemical reactions), a catalyst was required to produce isomerization,[2] we still favor the dissociative mechanism for the above reactions for the following reasons.

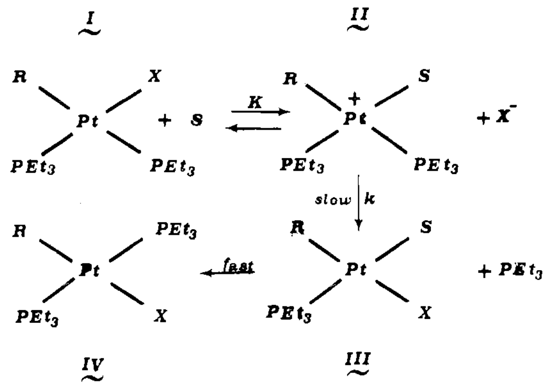
(a) The addition of small amounts of X^- inhibits the rate of isomerization (k_i, s^{-1}) but does not affect the rate of halide substitution by the solvent (k_S, s^{-1}).

(b) The rates of solvolysis of Br in *cis*-[Pt(PEt$_3$)$_2$RBr] are dramatically reduced by the increasing steric crowding produced by ortho alkyl substituents on the coordinated aromatic ring (e.g., 10^3k_S (s^{-1}, 30 °C): 6.000, R = Ph; 54.4, R = *o*-MeC$_6$H$_4$; 16.2, R = *o*-EtC$_6$H$_4$; 0.19, R = 2,4,6-Me$_3$C$_6$H$_2$) and approach the rates of isomerization (k_i values) which in contrast are not affected significantly.[1c] In the complex *cis*-[Pt(PEt$_3$)$_2$(2,4,6-Me$_3$C$_6$H$_2$)Br] in which steric congestion is at its peak, isomerization and bromide substitution proceed at the same rate.

Scheme I



Scheme II



(c) Large values of enthalpy and entropy of activation are associated with isomerization in agreement with a dissociative mode of activation, while the low $\Delta H^{\ddagger}$ and the largely negative $\Delta S^{\ddagger}$ found for solvolysis fit well in the simplified picture of an associative mechanism.

(d) Cis–trans isomerization is particularly sensitive to factors controlling bond dissociation, viz., the nature of the halide ion and changes in the electron density at the reaction center, brought about by para substituents on the aromatic ring.[1b] The same factors hardly affect the rates of solvolysis.

Such findings (a–d) give unmistakable evidence that the solvolysis step is not rate determining for the isomerization and suggest the dissociative mechanism as the most reasonable interpretation, unless one objects to three-coordinate (i.e., 14 electron) Pt^{II} intermediates, which we do not.

Very recently Louw[3] has proposed an alternative mechanism (see Scheme II) for isomerization, which assumes a fast preequillibrium between *cis*-[Pt(PEt$_3$)$_2$RX] and a solvento intermediate II followed by a rate-determining step in which the halide added or released from the starting material removes the phosphine ligand on II. A fast reentry of PEt$_3$ on III produces isomerization. Unfortunately, the rate law derived from this mechanism by Louw

$$k_i = \frac{kK}{K + [X^-]} \tag{2}$$

is incorrect and should be

$$k_i = \frac{kK[X^-]}{K + [X^-]} \tag{3}$$

which does not fit the experimental observations.

Although this alone must rule out Louw's mechanism, it is useful to add some other comments, since the assessment of the new mechanism appears to have been made while ignoring all the experimental evidence available. Halide retardation can be very important if the halide ion competes effectively with another reaction pathway in capturing a reaction in-

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termediate (in Scheme I the efficiency of X^- in the competition is measured by the ratio k_{-D}/k_T). Mass law retardation of substitution in a solvento intermediate by the leaving group chloride is well-known in the substitution reactions of *trans*-[$Pt(PEt_3)_2RCl$] complexes and requires that the product of the rate constant for chloride anation of the solvento complex and the concentration of chloride is comparable in magnitude to the analogous product for the entering nucleophile.[4] It can also be important when there is a fast and reversible solvolysis (as in Scheme II), but the solvento intermediate can offer a favorable pathway for reaction *with a reagent other than the halide ion produced in the solvolysis.* Furthermore addition of Ag^+ to methanolic solutions of the starting complexes produces cis–trans isomerization,[5] instead of inhibiting it through elimination of the halide ion. It is also difficult to understand why Scheme II assumes a facile removal of the phosphine ligand by small amounts of X^- in species II which incorporates a molecule of solvent when the corresponding chloride I is stable as long as one likes in concentrated solutions of X^-.

A reaction scheme based on an associative consecutive displacement mechanism (such as that in Scheme II) fails to explain either the large $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ associated with isomerization or the fact that the rate of isomerization is almost insensitive to steric crowding produced by the ligand R.

In conclusion we wish to point out that there can be a variety of mechanisms for isomerization of square-planar complexes, and it is dangerous to extrapolate from one system to another when conditions or species are changed and, at this stage at least, each system needs to be investigated by itself before its mechanism can be assumed with confidence.

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Origin of the Word "Pnictide"

Sir:

Because there is far from universal agreement regarding whether the transition elements and the posttransition "representative" elements are to be designated subgroups "A" and "B" or the reverse in the periodic table, it is useful to have other names for them in order to prevent misunderstanding. For example, for the representative elements and ions of group 7 (F, Cl, Br, I, At), the terms halogens, halogenides, and halides are or have been used, while the corresponding terms chalcogens, chalcogenides, and chalconides are employed for the representative elements and ions of group 6 (S, Se, Te, Po, and sometimes O).

For the posttransition elements and ions of group 5 (N, P, As, Sb, Bi), the relatively new terms pnigogens (or pnicogens) and pnictides are being employed. The origin of these is, to say the least, obscure except perhaps to their coiner, but there appears to be a widespread belief that they derive from an acronym comprising the first letters of *p*hosphorus and *n*itrogen and possibly the last two letters of arsen*ic*.

It is much more probable, however, that they are derived from "pnigo", the Greek word for suffocate. Since nitrogen, which heads the subgroup, is called "stickstoff" (literally "suffocating stuff") in German, it seems extremely likely that someone chose the corresponding Greek root to coin a new name for the subgroup.

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Large Closo Boron Hydrides

Sir:

Closo boron hydrides and metallocarboranes are among the simplest metal cluster systems.[1] Polyhedra with up to 14 vertices have been observed for metallocarboranes.[2] Recently,[3] a broad outline has been presented for future theoretical studies on closo boron hydrides with 13 to 24 boron atoms. In this note, we report some results of an extensive theoretical study of these molecules; some surprising findings are the following: (i) the discovery that some structures can have the full polyhedral symmetry only if they are neutral, i.e., contain only $2n$ framework electrons, where n is the number of vertices; (ii) the finding that there is no significant difference between the average stabilities of even and odd numbered polyhedra; (iii) the likelihood that 22 vertices represents an upper limit for truly stable structures.

All of the computations were carried out using the PRDDO (partial retention of diatomic differential overlap) approximation.[4] The standard bond lengths given previously[3] were employed. In addition, a new systematic approach to orient the hydrogens was developed, invariably providing lower calculated energies. The absolute value of the energy per BH unit, denoted $\bar{E}$, was used to compare relative stabilities. A plot of $\bar{E}$ vs. n for the most stable doubly negative structure(s) for each n ($24 \geq n \geq 9$) is given in Figure 1.

Three cases were discovered where, if the structure was treated as a doubly negative ion with ($2n + 2$) framework electrons, it underwent Jahn–Teller distortions; in these cases the full molecular symmetry could be restored by considering the structure to be a neutral one, with only $2n$ framework electrons. In Table I we list the pertinent information on these neutral structures. A series of large, neutral closo metallocarboranes can be constructed conceptually from the neutral boron hydrides by the replacement of BH units at vertices of high connectivity by other structural moieties each of which contributes two electrons to the framework bonding. Among these, $(Co(\pi\text{-}C_5H_5))_4B_{12}H_{12}$ and $(Fe(CO)_3)_4B_{12}H_{12}$ may be considered as strong candidates for synthesis. These two examples have T_d symmetry (Figure 2), like the hypothetical parent neutral closo boron hydride structure.

Table I. Large Neutral Closo Boron Hydrides (B_nH_n, $n \geqslant 13$)

n	symmetry	label[a]	E, au
16	T_d	IV	25.244
19	C_{3v}	VIIa	25.243
22	T_d	Xa	25.249

[a] The labels are those given in ref 3.

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