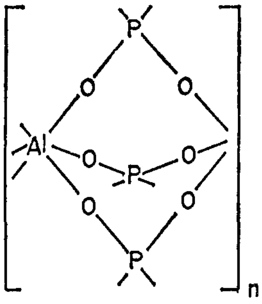

Figure 1. Postulated structure of the poly[tris(phosphinato)-alanes] (in solution with alkyl groups deleted).

Structural data for other metal phosphinates support this conclusion.[13,14]

From available data, we conclude that the predominant structural feature is repeating units of tris(phosphinato) triple bridges. The aluminum(III) ion is therefore in a six-coordinate octahedral configuration (Figure 1). This postulated structure is consistent with rigid, rodlike polymer chains in solution. A study has been initiated to determine the solid-state structures by X-ray fiber photography, but the results are too preliminary to report at this time.

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The Relationship between Isotope Effects and Reactivity[1]

Sir:

Isotope effect theory predicts that the magnitude of primary hydrogen isotope effects on reaction rates will vary smoothly and pass through a maximum value as transition-state symmetry is changed in a regular way.[2] Such behavior has been observed for a series of isotope effects on base-catalyzed proton removal from carbon when the comparison is made in terms of differences in basicity between the proton donor and the proton acceptor (ΔpK_a);[3] this suggests that the latter quantity is a good measure of transition-state symmetry. These isotope effects, however, do not correlate at all well with the rates of these reactions,[3a] despite the fact that relative reactivities are a popularly employed measure of transition-state structure.[4] We wish here to present some new data which, when coupled with other measurements, indicate the circumstances under which relative reactivity can correlate the magnitude of isotope effects and, by implication, serve to measure transition-state symmetry.

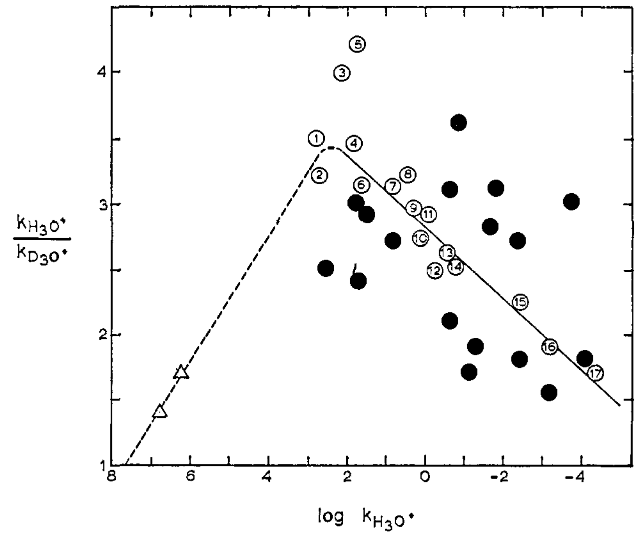

Figure 1. Relationship between $k_{H_3O^+}/k_{D_3O^+}$ and log $k_{H_3O^+}$ for rate-determining proton-transfer reactions. Open circles represent hydrolysis of the following vinyl ethers: (1) ethyl isopropenyl ether, (2) ethyl cyclopentenyl ether, (3) ethyl α-phenylvinyl ether, (4) ethyl cyclohexenyl ether, (5) methyl α-phenylvinyl ether, (6) methyl cyclohexenyl ether, (7) phenyl isopropenyl ether, (8) α-naphthyl isopropenyl ether, (9) ethyl vinyl ether,[7c] (10) isopropyl *cis*-propenyl ether, (11) methyl vinyl ether, (12) ethyl *cis*-propenyl ether, (13) methyl *cis*-propenyl ether, (14) β-chloroethyl vinyl ether,[7b] (15) phenyl vinyl ether, (16) *m*-bromophenyl vinyl ether, (17) 2,5-dimethylfuran.[7a]

We have determined the isotope effect, $k_{H_3O^+}/k_{D_3O^+}$, on the hydrolysis of 14 vinyl ethers in wholly aqueous solution at 25°.[5] These, together with three other examples for the same reaction reported in the literature,[7] increase regularly with log $k_{H_3O^+}$ up to a value of $\sim$3.5 (Figure 1, open circles). Inclusion of two isotope effects on a closely similar reaction, proton transfer to the α carbon of enolate anions (Figure 1, triangles),[8] suggests, in accordance with theory,[9,11] that this is the maximum normal value of this isotope effect and that the two reactions showing high values of $k_{H_3O^+}/k_{D_3O^+}$ may be experiencing tunnel effects.[3a] When similar isotope effects on other rate-determining proton-transfer reactions are added, however, this correlation is destroyed (Figure 1, filled circles.)[12]

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[1] This research was supported by a grant (GP 6580) from the National Science Foundation.

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[5] Standard criteria[6] were used to show that proton transfer from H_3O^+ is rate determining in each of these reactions.

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[7] (a) E. J. Stamhuis, W. Drenth, and H. van den Berg, *Rec. Trav. Chim.*, **83**, 167 (1964); (b) P. Saloma, A. Kankaanpera, and M. Lajunen, *Acta Chem. Scand.*, **20**, 1790 (1966); (c) A. J. Kresge and Y. Chiang, *J. Chem. Soc., B*, 58 (1967).

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[9] The rate ratio $k_{H_3O^+}/k_{D_3O^+}$ contains an inverse secondary isotope effect[10] in addition to the normal primary effect; it has been estimated[11] that the former will serve to reduce the over-all isotope effect to approximately half the expected value for simple oxygen-hydrogen bond breaking.

[10] A. J. Kresge and D. P. Onwood, *J. Am. Chem. Soc.*, **86**, 5014 (1964); M. M. Kreevoy, P. W. Steinwand, and W. Y. Kayser, *ibid.*, **86**, 5013 (1964).

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[12] These additional values are restricted to isotope effects which can be identified as $k_{H_3O^+}/k_{D_3O^+}$ measured in dilute, wholly aqueous solution at 25°. They include the acid cleavage of mercurials (vinylmercuric iodide,[13] allylmercuric iodide,[14] and 2,4-dimethoxyphenylmercuric chloride[15]), 2,4-dimethoxybenzeneboronic acid,[16] and tetraphenylborate ion;[17] the hydration of carbon-carbon double bonds (isobutylene,[18] 1-

These data would seem to indicate that kinetic isotope effects can show the theoretically expected dependence on transition-state structure when the latter is measured by relative reactivity provided that comparison is restricted to a single reaction type. In the present case, this is proton addition to a carbon–carbon double bond activated by a single oxygen atom; protonation of an aromatic ring, a triple bond, or even a double bond bearing other heteroatoms is a sufficiently different process to upset the expected correlation. Each of these other reactions would presumably show a correlation of its own between isotope effect and relative reactivity, but at the present time there are insufficient data to determine whether or not this is so.

N-morpholino-1-isobutylene,[19] cyanoketene dimethyl acetal,[20] dimethylketene dimethyl acetal,[21] and methylbromoketene diethyl acetal[21]) and carbon–carbon triple bonds (ethylthioethyne,[22] 1-ethylthio-3-hydroxy-3-methyl-1-butyne,[23] and 1-(*cis*-propenyloxy)-1-propyne[24]); the hydrolysis of 2-ethoxy-1-cyclopentene-1-carboxylic acid[25] and its anion;[25] the deiodination of 2,4,6-trimethoxyiodobenzene;[26] and the protonation of 1,3,5-trimethoxybenzene.[27]

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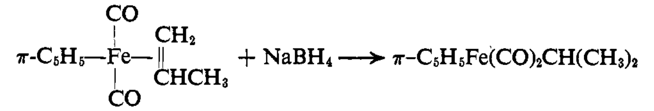
Nuclear Magnetic Resonance Evidence for $\pi \rightarrow \sigma$ Ligand Conversion in Platinum(II) Complexes

Sir:

The catalytic conversion of olefins to functionalized derivatives, *e.g.*, ethylene to acetaldehyde,[1] as well as other olefin reactions carried out in the presence of transition metal complexes, are assumed to all involve olefin coordination *via* a π complex followed by rearrangement to a σ-alkyl complex. The reaction of this type which has received most investigation as to mechanism is the insertion of olefins into metal–hydrogen bonds.[2]

$$RCH{=}CH_2 + M{-}H \rightleftharpoons R{-}CH_2{-}CH_2{-}CH_2M$$

Although the indicated direction of addition is probably the preferred one, and when R and other ligands are large may be the exclusive one,[2] Markovnikov addition followed by elimination of MH is a commonly accepted explanation for transition metal catalysis of olefin isomerization. In the many examples of such isomerization where the hydride cannot be shown to be present as such, it is postulated to be the intermediate. In one important example,[3] a hydride is added externally to the olefin complex to secure the $\pi \rightarrow \sigma$ conversion.



$$\pi\text{-}C_5H_5{-}\underset{\displaystyle CO}{\overset{\displaystyle CO}{Fe}}{-}\left\Vert\begin{matrix}CH_2\\CHCH_3\end{matrix}\right. + NaBH_4 \longrightarrow \pi\text{-}C_5H_5Fe(CO)_2CH(CH_3)_2$$

Although the sequence of steps in the $\pi \rightarrow \sigma$ conversion remains unsettled because intermediates have not been isolated, it is likely that nucleophilic (or hydride) attack occurs on the π complex just prior to the $\pi \rightarrow \sigma$ rearrangement.

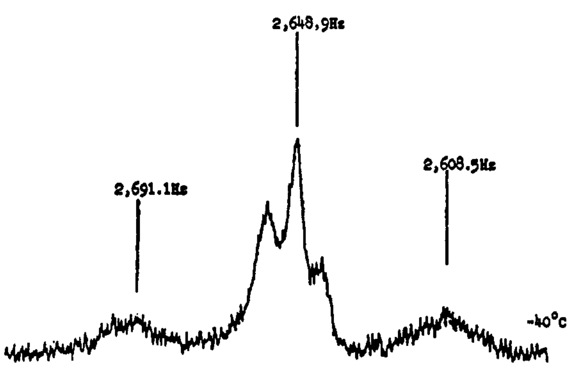
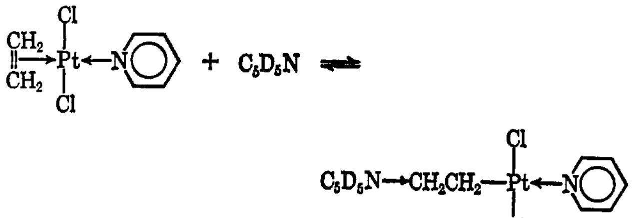


Figure 1. Nmr spectrum of σ complex.

We now wish to report that we have secured nmr evidence for the formation of an unstable σ complex at −50° resulting from $\pi \rightarrow \sigma$ rearrangement. The unstable compound is formed when deuterated pyridine is added to a chloroform solution of 1,3-dichloro-2-ethylene-4-pyridineplatinum(II).



The evidence for the rearrangement is based exclusively on the nmr spectrum. The chemical shifts as well as the coupling constants for both species are listed in Table I. The alkyl CH_2 attached to platinum is characterized by occurring much further upfield than the CH_2 group of the olefin and by having a larger Pt-H coupling constant.[4-6] In addition, the presence of an additional CH_2 group would be expected to split the original resonance peak into a triplet and this is observed (Figure 1). The second triplet (not shown) of the CH_2 group attached to pyridine is partially buried in the resonance peak due to platinum-hydrogen coupling in ethylene and can be observed by care-

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