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"Mechanisms of Substitution Reactions of Metal Complexes"

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PUBLICATIONS

The following publications have appeared since the Technical Progress Report for 1968-1969, Document No. C00-1087-124.

1. M. Meier, F. Basolo, and R. G. Pearson, "Rates of Substitution Reactions of Tetrakis(triethylphosphite)metal(0) Compounds of the Nickel Triad". *Inorg. Chem.*, 8, 785 (1969).
2. R. A. Bauer and F. Basolo, "Syntheses and Reactions of Some Diacidobis(ethylenediamine)iridium(III) Complexes". *Coord. Chem.*, Plenum Press, New York, 1969.
3. V. G. Myers, F. Basolo and K. Nakamoto, "Far-Infrared Spectra of Tetrakis(triethylphosphite) Complexes of Nickel(0), Palladium(0) and Platinum(0)". *Inorg. Chem.*, 8, 1204 (1969).
4. F. Basolo, "Substitution Reactions of Zerovalent Metal Compounds of the Nickel Triad". *Trans. N. Y. Acad. Sci.*, 31, 676 (1969).
5. R. A. Bauer and F. Basolo, "The Preparation and Characterization of Some Diacidobis(ethylenediamine)iridium(III) Complexes". *Inorg. Chem.*, 8, 2231 (1969).
6. R. A. Bauer and F. Basolo, "The Rates of Substitution Reactions of Some Diacidobis(ethylenediamine)iridium(III) Complexes". *Inorg. Chem.*, 8, 2237 (1969).
- 7,8. R. G. Pearson, "A Symmetry Rule for Predicting Molecular Structure, I, II". *J. Am. Chem. Soc.*, 91, 1252, 4947 (1969).
9. R. G. Pearson and W. Waltz, "A Pulse Radiolysis Study of Some Cobalt(III) Complexes". *J. Phys. Chem.*, 73, 1941 (1969).
10. R. G. Pearson, "Hard and Soft Acids and Bases". *Survey of Progress in Chemistry*, Vol. 5, 1969, Academic Press, New York.
11. R. G. Pearson, "Symmetry Rules for Predicting the Course of Chemical Reactions". *Theor. Chim. Acta*, 16, 107 (1970).
12. R. G. Pearson, "Symmetry Rules for Predicting the Structures of Molecules". III, *J. Chem. Phys.*, 52, 2167 (1970).

RESEARCH

1. Symmetry Rules for Molecular Structures and Chemical Reactions.

R. G. Pearson

Recently there has been great interest in the devising of symmetry rules for predicting whether a concerted chemical reaction can occur with relatively low activation energy (symmetry allowed) or would require excessive activation energy (symmetry forbidden). The most general method of using symmetry properties to predict the course of a chemical reaction is to apply group theory to the variation of potential energy with changing nuclear coordinates.

Figure 1 shows the usual adiabatic plot of potential energy vs. reaction coordinate, showing possible features. The reactant molecules at each point generate a certain point group and the possible nuclear motions can be classified as the normal modes of vibration of a pseudo-molecule of that symmetry. For the ground electronic state the energy may be written as

$$\begin{aligned}
 E = E_0 + Q \left\langle \psi_0 \left| \frac{\partial U}{\partial Q} \right| \psi_0 \right\rangle + \frac{Q^2}{2} \left\langle \psi_0 \left| \frac{\partial^2 U}{\partial Q^2} \right| \psi_0 \right\rangle \\
 + Q^2 \frac{\sum_k \left[\left\langle \psi_0 \left| \frac{\partial U}{\partial Q} \right| \psi_k \right\rangle \right]^2}{E_0 - E_k}
 \end{aligned}
 \tag{1}$$

Here Q represents the normal mode representing the reaction coordinate and also the magnitude of the displacement from any

arbitrary point on the diagram, Q_0 , for which $E = E_0$. While (1) is valid only for Q small, the point $Q = 0$ can be selected anywhere and hence (1) is general for the purpose of displaying symmetry properties. The wave functions, ψ_0 and ψ_k , must belong to one of the symmetry species of the group. Q and $(\partial U/\partial Q)$ have the same symmetry, where U is potential energy.

If ψ_0 is non-degenerate, the usual case, we can immediately conclude that the reaction coordinate must belong to the totally symmetric representation for all points which are not on a maximum or minimum. Furthermore, since the wave function corresponding to (1) is

$$\psi = \psi_0 + Q \sum_k \frac{\langle \psi_0 | \frac{\partial U}{\partial Q} | \psi_k \rangle}{E_0 - E_k} \psi_k \quad (2)$$

only excited state wave functions of the same symmetry as ψ_0 can mix in under the influence of changing Q . It is essential to have efficient mixing in order to have a reaction of low activation energy. It has been shown in a number of examples that the infinite sums of (1) and (2) may be replaced by one or two terms corresponding to the lowest excited states.

In molecular orbital theory $\psi_0\psi_k$ has the same symmetry as $\phi_i\phi_j$, where ϕ_i is the MO occupied in ψ_0 and ϕ_j is the MO occupied in its stead in ψ_k . Thus ϕ_i and ϕ_j will usually, but not always, be the highest occupied MO and the lowest empty MO of the system.

The requirements are (a) that they belong to the same symmetry species in the point group of the reacting system; (b) that they be close in energy; (c) ϕ_i must represent bonds that are broken during the reaction and ϕ_j bonds to be made, assuming both are bonding MO's, the reverse if anti-bonding.

It may happen that the highest occupied MO and the lowest empty MO of the system do not correspond to bonds that must be broken or made during the reaction. In this case it is necessary to examine the next lower and higher MO's. However, the symmetry rule must still be obeyed. Also as the energy gap increases, the activation energy will obviously increase.

These conclusions are identical with those which could have been drawn from other perturbation theories of chemical reactivity. Previously the perturbation operator used was the interaction Hamiltonian. Since this is also totally symmetric, as is $(\partial U / \partial Q)$, the same conclusions would follow about the rising and falling parts of Fig. 1. The approximation of using only the lowest excited state is the same as that of Fukui's frontier orbital theory. The overall physical picture is that electrons will flow between orbitals when there is a positive overlap between them in the region where new bonds are to form.

Once a system starts on a given reaction path, it must maintain the same point group until a maximum or minimum in the potential energy is reached. This follows because a symmetric mode cannot change the point group. A non-adiabatic process involving a forbidden transition could change the point group, however. For a

transition state (maximum in Fig. 1) the reaction coordinate will correspond to one of the normal modes of the activated complex, or combination of modes of the same symmetry. As shown by Bader, the symmetries of ψ_0 and the lowest excited ψ_k of the activated complex will determine which normal mode is selected. It should be noted that a number of point groups depend upon a unique value of Q_0 . For example, a tetrahedral structure depends upon fixed bond angles. All such cases will correspond to either maxima or minima in plots such as Fig. 1. A non-symmetric mode will be needed for the reaction to proceed.

Unimolecular reactions start at a minimum in Fig. 1. For shallow wells, the lowest ψ_k dominates, but this need not be true for deep wells (substantial activation energy). Instead the bonds to be made or broken select ϕ_i and ϕ_j , and these in turn select Q . The direct product of ϕ_i and ϕ_j must contain the symmetry species of Q .

Fig. 1

2. Cleavage Reactions of Acylmetal and Alkylmetal Derivatives.

R. W. Johnson

We have previously found that the only nucleophiles that attack the acyl carbonyl of $\text{CH}_3\text{COMn}(\text{CO})_5$ are the very hard bases such as methoxide ion and dialkylamines. A study has now been made on the reaction of $\text{CH}_3\text{COMn}(\text{CO})_5$ with hydroxide ion in water. It offers an informative comparison with the attack by methoxide ion in methanol (see Figure 2).

In water, the initial four-coordinate intermediate has an acidic proton which is not present following attack by OMe^- . Removal of this proton provides the extra driving force. This behavior is closely analogous to unreactive organic acyl compounds such as amides where the resonance form $\text{R}-\overset{\oplus}{\text{C}}=\overset{\ominus}{\text{O}}\text{NH}_2$ is important. Our results are consistent with the low ν_{CO} of these acylmetal compounds (1650 cm^{-1} instead of $1700\text{--}1750\text{ cm}^{-1}$). The kinetic data provide further evidence for the appreciable double-bond character of the acyl-metal bond due to $d_{\pi}\text{--}p_{\pi}$ bonding.

The acid-catalyzed cleavage of $\text{CH}_3\text{COMn}(\text{CO})_5$ in water is extremely slow, being about two orders of magnitude slower than the same reaction in methanol. This is attributed to the stability of H_3O^+ compared to CH_3OH_2^+ .

Cleavage of $\text{CH}_3\text{COMn}(\text{CO})_5$ Methanol:

$$\text{Rate law: } r = (0.11 \text{ M}^{-1}\text{sec.}^{-1})[\text{OMe}^-][\text{AcMn}(\text{CO})_5]$$

Mechanism:

Water:

Rate law:

$$r = (0.03 \text{ M}^{-1}\text{sec.}^{-1})[\text{OH}^-][\text{AcMn}(\text{CO})_5] + (25 \text{ M}^{-2}\text{sec.}^{-1})[\text{OH}^-]^2[\text{AcMn}(\text{CO})_5]$$

Mechanism:

(3)

We have investigated the cleavage of alkyl-metal bonds by electrophilic reagents.

EX = HCl, CH₃CO₂H, HClO₄, HgCl₂, etc. The kinetic results closely parallel the behavior found for the cleavage of alkyl-mercury bonds. In both cases the data indicate a concerted mechanism involving electrophilic attack on carbon and nucleophilic attack on the metal.

$$\text{For HCl: } r = (9.0 \times 10^{-4}) [\text{HCl}][\text{CH}_3\text{Mn}(\text{CO})_5] \text{ at } 25^\circ\text{C.}$$

The rate is dramatically reduced by adding small amounts of water to the methanol.

The reaction with other protonic acids was extremely slow. In fact, the rate could not be separated from the rate of decomposition. This result shows the importance of both electrophilic and nucleophilic participation. Perchloric acid is completely dissociated; nucleophilic interaction is negligible. The reaction with CH₃CO₂H is slow due to the weak electrophilic interaction.

The Lewis acid, HgCl₂, shows identical behavior to HCl, but the reaction is much faster since HgCl₂ is a soft acid.

$$r = (1.1 \times 10^{-2} \text{M}^{-1} \text{sec}^{-1}) [\text{HgCl}_2][\text{CH}_3\text{Mn}(\text{CO})_5] \text{ at } 25^\circ \text{ in MeOH}$$

Stereochemistry of Formation and Cleavage of Carbon-Metal Bonds.

We have investigated the stereochemistry of nucleophilic attack on alkyl halides by transition metal nucleophiles. In these cases the nucleophilic reagent has a high occupied d orbital which will seek out the best possible interaction with the σ^* anti-bonding orbital of the C-X bond. This can happen in two ways (see Figure 2).

We determined that for the anion $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)^-$, the attack occurs in the normal manner -- inversion. This was done by the series of reactions shown below. Other examples have just recently been published which agree with this result.

Stereochemistry of Alkylation of $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)^-$

$\geq 74\%$ inversion in attack at carbon by $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)^-$

(5)

The problem with the mechanism involving a front-side attack is that it requires a reaction intermediate with a coordination number increased by two. This intermediate must then lose halide ion to form the final product. Such a mechanism is not expected to be favored when the nucleophile has only one available coordination site. This problem is not relevant in the case of oxidative addition reactions of alkyl halides to four-coordinate d^8 or d^{10} systems. The stereochemistry of these reactions are now under

investigation.

We have attempted to determine the stereochemistry of cleavage of alkyl-metal bonds, but so far have been unsuccessful. Bromine cleavage reactions must be carried out in polar solvents such as pyridine, but under such conditions sec-BuFe(CO)₂(Cp) undergoes an elimination reaction to give olefin. Mercuric chloride reacts with sec-BuFe(CO)₂(Cp) to form Hg₂Cl₂ and/or Hg in a complex disproportionation. Protic acid cleavage would have to be done with a deuterium label to maintain an asymmetric carbon atom. This presents added experimental problems and has not yet been attempted.

Presently we are using ethyl 2-bromopropionate as the optically active alkyl halide:

Orbital Symmetry in Nucleophilic Substitution Reactions

For a nucleophile of σ -symmetry (e.g., "p" lone pair):

For a nucleophile of π -symmetry (e.g., d_{xy}):

Fig. 2

3. Rates of Substitution of Molecular Nitrogen Complexes.

Peter Maples

The purpose of this investigation is to define a mechanism of molecular nitrogen displacement and to study the effect of structural variation on the ease of nitrogen substitution.

Complexes of the type $\text{Os}(\text{N}_2)\text{X}_2[\text{PR}_2\text{Ph}]_3$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{R} = \text{methyl, ethyl, n-propyl}$) were chosen since they represent the only extensive series of characterized isolatable compounds in which significant variation of appended ligands has been achieved.

Rates of reaction were determined under pseudo-first order conditions by following the disappearance of the bound nitrogen stretching vibration.

The stereochemistry of the compounds $\text{Os}(\text{N}_2)\text{X}_2[\text{P}(\text{CH}_3)_2\text{Ph}]_3$ was unequivocally determined by ^1H nmr. An analysis of the methyl resonance pattern of the bound phosphine ligands indicated a configuration I in which the nitrogen molecule occupies a site trans to a halogen. By analogy, all compounds studied are assumed

to have identical configurations. The stereochemistry of the final reaction products as determined by ^1H nmr can be represented by structure II.

Os(N₂)X₂[P(CH₃)₂Ph]₃ Compounds:

The stoichiometry of the reaction of Os(N₂)X₂[P(CH₃)₂Ph]₃ with various phosphine ligands is given in (1). The overall stoichiometry was established by monitoring the reaction by ¹H nmr and observing the spectral changes.

where L = P(CH₃)₂Ph, P(C₂H₅)₂Ph, P(C₃H₇)₃, etc.

Kinetic data are presented in Table I and II.

The rate of reaction was first order in Os(N₂)X₂[P(CH₃)₂Ph]₃ and independent of free ligand concentration. Changes in the steric and nucleophilic properties of the reacting phosphine had little effect on the observed rate constant. The replacement of bromine for chlorine in the nitrogen complex produced three-fold increase in rate.

The stoichiometry of the reaction of Os(N₂)X₂[P(CH₃)₂Ph]₃ with certain phosphites is given in (7).

Where L' = P(OCH₃)₃, P(OCH₃)₂Ph, P(OCH₂)₃CCH₃

The observed rate of nitrogen displacement was again independent of ligand concentration and first order in starting complex. Both

the reactions with phosphites and phosphines studied proceeded at virtually identical rates. However, ^1H nmr studies indicate that the unique $\text{P}(\text{CH}_3)_2\text{Ph}$ ligand trans to a halogen is displaced by an added phosphite molecule either prior to or subsequent to displacement of coordinated nitrogen.

$\text{Os}(\text{N}_2)\text{Cl}_2[\text{P}(\text{C}_2\text{H}_5)_2\text{Ph}]_3$

The kinetic data for the reaction of $\text{Os}(\text{N}_2)\text{Cl}_2[\text{P}(\text{C}_2\text{H}_5)_2\text{Ph}]_3$ with phosphines and phosphites is given in table III. Rates were independent of free ligand concentration but were markedly dependent on ligand type.

In the cases where a phosphite was employed a second I.R. active nitrogen stretching vibration appeared, reached a maximum and subsequently decreased to zero intensity during the course of the reaction. The detection of a second molecular N_2 containing species along with the evidence for phosphine ligand replacement in $\text{Os}(\text{N}_2)\text{X}_2[\text{P}(\text{CH}_3)_2\text{Ph}]_3$ systems strongly suggests that the reaction sequence can be represented as in (8).

Values of both k_1 and k_2 calculated from a standard series first order reaction treatment of the data is given in table IV.

GENERAL CONCLUSIONS:

The results indicate that the reactions of $\text{Os}(\text{N}_2)\text{X}_2[\text{PR}_2\text{Ph}]_3$ compounds with phosphines proceed by a simple $\text{S}_{\text{N}}1$ mechanism involving dissociation of coordinated nitrogen and subsequent attack of the free phosphine. In contrast, reactions with the phosphites studied appear to involve stereospecific replacement of a coordinated phosphine by phosphite and subsequent dissociation of nitrogen.

The effect of structural variation of the molecular nitrogen compound on reaction rate indicates that a change in the halogen group trans to nitrogen has a smaller effect than does variation of the phosphine ligands. This is illustrated by the relative rates of reaction of the three nitrogen compounds with $\text{P}(\text{C}_2\text{H}_5)_2\text{Ph}$ under identical conditions, $\text{Os}(\text{N}_2)\text{Cl}_2[\text{P}(\text{C}_2\text{H}_5)_2\text{Ph}]_3 : \text{Os}(\text{N}_2)\text{Cl}_2[\text{P}(\text{CH}_3)_2\text{Ph}]_3 : \text{Os}(\text{N}_2)\text{Br}_2[\text{P}(\text{CH}_3)_2\text{Ph}]_3$, 1:9:30.

Table I

Rates of Reaction of $\text{Os}(\text{N}_2)\text{Cl}_2[\text{P}(\text{CH}_3)_2\text{Ph}]_3^{\text{a}}$ with
Various Phosphines^b and Phosphites^b in Toluene

Ligand	Temp. °C	$10^5 k, \text{sec}^{-1}$
$\text{P}(\text{OCH}_3)_3$	69.5	7.08
$\text{P}(\text{OCH}_3)_3$	75.0	14.1
$\text{P}(\text{OCH}_3)_3$	79.2	27.6
$\text{P}(\text{OCH}_3)_3$	83.0	40.0
$\Delta H^\ddagger = 30.5 \pm 0.3 \text{ kcal/mole}$		$\Delta S^\ddagger = 11.1 \pm 0.9 \text{ e.u.}$
$\text{P}(\text{OCH}_3)_2\text{Ph}$	69.5	6.38
$\text{P}(\text{CH}_3)_2\text{Ph}$	69.5	7.10
$\text{P}(\text{C}_2\text{H}_5)_2\text{Ph}$	69.5	6.72
$\text{P}(\text{C}_3\text{H}_7)_3$	69.5	6.42

^a $[\text{Os}(\text{N}_2)\text{Cl}_2[\text{P}(\text{CH}_3)_2\text{Ph}]_3] \cong 5.0 \times 10^{-3} \text{ M.}$

^b Concentration of ligand 0.05 - 0.12 M. Rates
independent of concentration

Table II

Rates of Reaction of $\text{Os}(\text{N}_2)\text{Br}_2[\text{P}(\text{CH}_3)_2\text{Ph}]_3^{\text{a}}$ with
Various Phosphines^b and Phosphites^b in Toluene

Ligand	Temp. °C	$10^5 k, \text{sec}^{-1}$
$\text{P}(\text{OCH}_3)_3$	69.5	23.0
$\text{P}(\text{OCH}_3)_3$	60.6	7.09
$\text{P}(\text{OCH}_3)_3$	64.8	12.3
$\text{P}(\text{OCH}_3)_3$	75.0	49.6

$$\Delta H^\ddagger = 30.5 \pm 0.4 \text{ kcal/mole} \quad \Delta S^\ddagger = 13.7 \pm 1.2 \text{ e.u.}$$

$\text{P}(\text{OCH}_3)_2\text{Ph}$	69.5	22.7
$\text{P}(\text{CH}_3)_2\text{Ph}$	69.5	23.4
$\text{P}(\text{C}_2\text{H}_5)_2\text{Ph}$	69.5	22.8
$\text{P}(\text{C}_3\text{H}_7)_3$	69.5	21.7
PPh_3	69.5	17.6

^a $[\text{Os}(\text{N}_2)\text{Br}_2[\text{P}(\text{CH}_3)_2\text{Ph}]_3] \cong 5.0 \times 10^{-3} \text{M}$.

^b 0.05 - 0.20 M. Rates independent of concentration.

Table III

Rates of Reaction of $\text{Os}(\text{N}_2)\text{Cl}_2[\text{P}(\text{C}_2\text{H}_5)_2\text{Ph}]_3^a$ with
Various Phosphines and Phosphites in Toluene

Ligand	Temp. °C	$10^5 k, \text{ sec}^{-1}$
$\text{P}(\text{OCH}_3)_3$	65.5	6.93
$\text{P}(\text{OCH}_3)_3$	69.5	13.1
$\text{P}(\text{OCH}_3)_3$	74.5	27.2
$\text{P}(\text{OCH}_3)_3$	85.0	1.09

$$\Delta H^\ddagger = 33.2 \pm 0.4 \text{ kcal/mole} \quad \Delta S^\ddagger = 20.3 \pm 1.2 \text{ e.v.}$$

$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	69.5	13.6
$\text{P}(\text{OCH}_3)_2\text{Ph}$	69.5	14.0
$\text{P}(\text{CH}_3)_2\text{Ph}$	69.5	2.63
$\text{P}(\text{C}_2\text{H}_5)_2\phi$	69.5	0.75

^a $[\text{Os}(\text{N}_2)\text{Cl}_2[\text{P}(\text{C}_2\text{H}_5)_2\text{Ph}]_3] \cong 5.0 \times 10^{-3} \text{ M.}$

Table IV
 Rate Constants for the Reaction of
 $\text{Os}(\text{N}_2)\text{Cl}_2[\text{P}(\text{C}_2\text{H}_5)_2\text{Ph}]_3$ with Phosphites

Ligand	Temp. °C	$k_1[\text{obs}]10^4, \text{sec}^{-1}$	$k_2[\text{calc}]10^4, \text{sec}^{-1}$
$\text{P}(\text{OCH}_3)_3$	69.5	1.31	≈ 8
$\text{P}(\text{OCH}_3)_2\text{Ph}$	69.5	1.40	8.35
$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	69.5	1.36	9.50

4. Electrophilic Reactions of Tetrakis(trialkyl(or aryl)phosphite) metal(0) of the Nickel Triad.

Steven Clarkson

A great deal of research has been done in different laboratories on the reactions of $M(PPh_3)_4$, where $M = Ni, Pd$ or Pt and $PPh_3 = P(C_6H_5)_3$. The results of these studies show that these systems are extensively dissociated in solution, which then means the metals contain active coordination sites that can be used to effect the homogeneous catalysis of certain types of reactions. For example Halpern (J. Am. Chem. Soc. 90, 4491 (1968); Inorg. Chem. 7, 2672 (1968)) has shown that the addition of reagents such as CH_3I to $Pt(PPh_3)_4$ involves the following reaction sequence.

The reaction requires the intermediate formation of the bis complex which is readily generated by this system in solution. Reactions of this type occur with alkyl halides, halide acids, carboxylic acids, acyl halides, sulfonyl halides, metal halides, olefins, alkynes, carbon oxygen and carbon sulfur double bonds, carbon monoxide and oxygen (R. Ugo, Coord. Chem. Rev. 3, 319 (1968)).

No work of this type has been reported for the corresponding

phosphite compounds, $M[P(OR)_3]_4$. Our research on the kinetics of ligand substitution and exchange reactions in solution of these systems suggest they are not extensively dissociated and the reactions of the $Ni(0)$ and $Pt(0)$ compounds are fairly slow. This might mean that new compounds formed by the addition of reagents such as CH_3I , SO_2 , HCl , etc. (see above) to the zero valent metal phosphites would be more stable than those formed by the corresponding metal(0) phosphine compounds. Should this be true it may be possible to isolate certain reaction intermediates, and kinetic studies could be used to determine if the reaction mechanism of the phosphite compounds is the same as that for the phosphine systems. Considerable time and effort has been spent this year conducting exploratory experiments on reactions (of $M[P(OEt)_3]_4$ and $M[P(OPh)_3]_4$, where $M = Ni$ or Pt).

The $Ni(0)$ compounds were prepared by the methods described in the literature and solutions of the compounds were permitted to react with several reagents to give the results briefly summarized here. The reaction with Cl_2 resulted in the formation of a greenish-blue oil from which only $NiCl_2$ could be isolated. When gaseous HCl was bubbled through these solutions there was an immediate precipitation of $NiCl_2$. Ethylene, tetrafluoroethylene and methyl iodide did not appear to react with the $Ni(0)$ phosphites even after standing for five hours at room temperature. Phenylacetylene did react over a period of six hours to give a dark brown precipitate which could not be characterized. Carbon

disulfide addition caused the solutions to become yellowish-red, then dark red, and finally after thirty-six hours a black precipitate of NiS was formed. Sulfur dioxide caused the solutions of $\text{Ni}[\text{P}(\text{OR})_3]_4$ to become yellow-red in a few minutes, however all attempts to isolate this material failed. In every case the starting material was all that could be obtained, suggesting that the SO_2 adduct is not very stable. Bubbling O_2 through these solutions results in the formation of green precipitates which have not been adequately characterized.

Reactions do occur with the $\text{Ni}(\text{O})$ compounds but thus far our efforts to find a well-defined reaction that can be studied in detail have failed. For this reason we have temporarily shelved the frustrating $\text{Ni}(\text{O})$ system and are examining reactions of the corresponding $\text{Pt}(\text{O})$ compounds. Our experience with $\text{Ni}(\text{O})$ compounds suggests that $\text{Pt}[\text{P}(\text{OPh})_3]_4$ may be more apt to yield crystalline products, whereas the corresponding $\text{P}(\text{OEt})_3$ systems often give oils which are difficult to purify. Thus we have prepared $\text{Pt}[\text{P}(\text{OPh})_3]_4$ and are beginning to study some of its reactions.

The addition of CH_3I to a solution of $\text{Pt}[\text{P}(\text{OPh})_3]_4$ resulted in no detectable reaction at room temperature after 48 hours. The reaction mixture was then kept at 60°C for 48 hours, after which time a pale yellow product was isolated. The elemental analysis and the ir and nmr spectra of the product clearly identify it to be the expected $\text{Pt}[\text{P}(\text{OPh})_3]_2(\text{CH}_3)(\text{I})$. The product is similar to that obtained by the reaction of CH_3I with $\text{Pt}(\text{PPh}_3)_4$, but the

reaction is much slower. This implies that the rate determining step for the reaction of the phosphite system may be its rate of dissociation, whereas we indicated initially that this is fast for the phosphine system. Investigations are being initiated on the kinetics and mechanism of this reaction of $\text{Pt}[\text{P}(\text{OPh})_3]_4$ with CH_3I .

Preliminary observations indicate that $\text{Pt}[\text{P}(\text{OPh})_3]_4$ reacts with SO_2 to give a yellow product which may be sufficiently stable to permit its isolation and characterization.

5. Stereochemistry of Induced Aquation Reactions of Some Chromium (III) Complexes.

Marino Nicolini

On the basis of a symmetry rule (Pearson, J. Am. Chem. Soc. 91, 1252 (1969)) for predicting molecular structure, it was suggested in our Proposed Technical Program for 1969-1970 that the induced aquation reactions of chromium(III) complexes may take place with stereochemical rearrangement. This was a bold prediction because spontaneous aquation reactions of chromium(III) complexes occur with largely complete retention of configuration. However the spontaneous reactions may not involve a five-coordinated intermediate. Such an intermediate is more apt to be formed in induced reactions and for a d^3 system the five-coordinated species is expected to favor a trigonal bipyramidal structure which permits rearrangement to occur.

The cis and trans isomers of $[\text{Cr}(\text{en})_2\text{Cl}_2]^+$ and $[\text{Cr}(\text{en})_2\text{H}_2\text{OCl}]^{2+}$ were prepared and carefully purified by methods described in the literature. The stereochemistry of the induced aquation reactions of these complexes was examined, as represented by the following equations.

The ultraviolet-visible absorption spectra of the isomers of all of the complexes involved had previously been reported and were used to analyze the spectra of the products obtained from these reactions. Our reaction conditions were such that the reactions were very rapid at room temperature, and the resulting spectra were examined immediately. This procedure assured us that we were monitoring the stereochemistry of the kinetic products without any complication due to slow subsequent rearrangement.

The quantitative results obtained show, within the limits of experimental error, that all of these induced aquation reactions take place with retention of configuration. Thus the results are not in accord with our initial postulate that a five-coordinated species in such systems would have a trigonal bipyramidal structure which could permit stereochemical change to occur. Different explanations can be given to rationalize the observation that rearrangement does not take place, but one of the simplest is that the presumed five-coordinated intermediate has a tetragonal pyramidal which leads to retention of structure.

The same reaction sequence for the corresponding Co(III) complex does result in rearrangement. This may be due to the greater π

bonding tendency promoting a trigonal bipyramidal structure of the five-coordinated intermediate of Co(III) compared with Cr(III) which appears to have a smaller tendency to π bond.

One other set of experiments were done in an attempt to determine if such induced reactions of Cr(III) do involve the intermediate formation of five-coordinated species. These were competition experiments of the type represented by the following reaction schemes.

Extensive studies of this type have been done for reactions of Co(III) complexes, but when we initiated our investigations there had been no report of this for Cr(III) systems. Experiments were conducted for $\text{X} = \text{NO}_3^-$ and SO_4^{2-} with the result that the same product distributions were obtained for the HgCl^+ and the HNO_2 reactions. This suggests that intermediates (I) and (I') are the same and are presumably the five-coordinated species $[\text{Cr}(\text{H}_2\text{O})_5]^{3+}$. It is of interest to note that in the latest issue of the J. Am. Chem. Soc. (92, 1215 (1970)), King reaches the same conclusion on the basis of competition experiments between water and methanol. He also concluded that the same active intermediate is involved in the spontaneous reaction of $[\text{Cr}(\text{H}_2\text{O})_5\text{I}]^{2+}$. We think this should be tested using other nucleophiles of the type X^- , because there is some reason to feel that spontaneous reactions of Cr(III) complexes involve displacement processes.

6. Linkage Isomerism of Rh(III) and Ir(III) Complexes of the Type Trans-[M(en)₂ONOX]⁺.

Victor Myers

This project could have been completed during the past year, but it was temporarily shelved in favor of the more urgent research described in the next section. However some kinetic data were collected on the linkage isomerization reaction

where M = Rh(III) and Ir(III) and X = Cl⁻ and I⁻. The rates of isomerization in aqueous solution are given in the following table.

<u>Complex</u>	<u>Temp. °C</u>	<u>k, sec⁻¹</u>
<u>trans-[Rh(en)₂ONOC1]⁺</u>	13.8	3.6 x 10 ⁻⁴
	25.1	1.4 x 10 ⁻³
	30.1	2.3 x 10 ⁻³
<u>trans-[Ir(en)₂ONOC1]⁺</u>	25.0	5.0 x 10 ⁻⁵
	35.0	1.6 x 10 ⁻⁴
	45.0	5.1 x 10 ⁻⁴
<u>trans-[Ir(en)₂ONOI]⁺</u>	15.7	3.8 x 10 ⁻⁴
	25.0	1.2 x 10 ⁻³
	34.8	3.9 x 10 ⁻³

It is of interest to note that the rate of isomerization of the iodo complex of Ir(III) is about 25 times faster than that of

its chloro complex. This is roughly the same magnitude of trans effect as we found earlier for substitution reactions in these systems. One might have expected a smaller effect for this linkage isomerization, which is believed to take place by a synchronous bond making, bond breaking process. The trans-effect of I^- compared with Cl^- for substitution reaction of $Rh(III)$ complexes enhances the rate by a factor of about 800. It will be of interest to see if this same large effect is found for isomerization of the $Rh(III)$ systems.

7. Metal Nitrene Chemistry.Mark Carter and Victor Myers

Extensive studies have been made of the reaction of trans- $[\text{Ir}(\text{en})_2(\text{N}_3)_2]^+$ with acid. Our efforts to characterize the Ir(III) product have been time consuming and frustrating, but we are now certain that the azo formulation given in our last report is not correct.

We decided to prepare $[\text{Ir}(\text{NH}_3)_5\text{N}_3]^{2+}$ and examine its reaction with acid. From the elemental analysis and infrared spectrum of the Ir(III) product and from gas evolution studies we are fairly certain that the reaction involved is that represented by the equation

We are now in the process of trying to identify the hydroxylamine, which is presumably formed by an attack of water on the metallated nitrene, $[(\text{NH}_3)_5\text{Ir}-\text{NH}]^{3+}$.

8. Mechanism of Oxidative-Addition Reactions.

Warren R. Muir

Our continued study of the oxidative-addition reactions of square planar d^8 metal complexes with alkyl halides has yielded much useful new information.

Although heterolytic cleavage of the R-X bond was established for the reaction

by our kinetic studies varying the nature of the R group, the reaction was found to proceed without the formation of ionic intermediates. No other ion incorporation was found when the reaction occurred in the presence of large excess of Y^- ions (e.g. SCN^- , CN^- , NO_2^-). Also, the reaction proceeded smoothly between alkyl halide (gas) and metal complex (solid).

An analysis of the stereochemistry of the products by infrared and far-infrared spectra indicate the entering R and X groups end up trans- to one another. The far-infrared data of Bennett and co-workers who reported cis- addition were found to be in error. Trans- addition is reported by several groups studying similar systems.

A trans- one-step addition is allowed by orbital symmetry rules (see Figure 3). This study predicts that if the reaction occurs at an optically active carbon center, the reaction should proceed with retention of configuration about that center. The

reaction between

supports this interpretation. Both the reactant and the product have the same sign of rotation at the Na^{D} line. The use of Brewster's rules allows us to correlate these rotations to similar structures about the active center. This conclusion is further confirmed by the ready reaction of the metal complexes above with neopentylbenzenesulfonate. Reactions of neopentylhalides must substitute with retention of configuration due to steric hindrance of backside attack. These are the first known examples of reactions of alkyl halides with nucleophiles which go with retention of configuration.

In addition to the above conclusions, some reactions have been found which will generate different stereoisomers of the metal complex products. The interconversion of these isomers has been studied and appear to be examples of intramolecular isomerism. The details are still obscure, but some kind of trigonal twist seems likely.

Fig. 3

9. Ligand Exchange Reactions of Five-Coordinated Complexes.Carol J. Grimes

In an attempt to correlate structure with reactivity, we are looking at a series of complexes, $\text{Ni}(\text{CN})_2(\text{PR}_3)_3$, where PR_3 is a monodentate phosphine or phosphite. It has been found for a number of these complexes that the five-coordinate moiety is labile with respect to exchange of coordinated phosphite with free phosphite ligand:

This exchange proceeds at a rate amenable to study by NMR line-broadening techniques.

The complex that has been most extensively studied to date is $\text{Ni}(\text{CN})_2[\text{P}(\text{OEt})_3]_3$. Spectral measurements show that the formation constant for the reaction

is 900 in CH_2Cl_2 . This is sufficiently large enough to insure that at higher concentrations of complex and ligand, essentially all of the complex present will be in the five-coordinate form.

It has been impossible to isolate the four-coordinate product $\text{Ni}(\text{CN})_2[\text{P}(\text{OEt})_3]_2$, so no kinetics could be studied for the above reaction.

The NMR spectra of the five-coordinated complex and the ligand show a triplet for the methyl group of the phosphite as expected.

The triplet for the complex in CH_2Cl_2 is centered at 1.23 ppm, while that for the ligand is centered at 1.16 ppm. When the spectrum of a mixture of the two is taken, one triplet is observed at an intermediate position, showing that rapid exchange is taking place between the phosphite groups complexed to the nickel and the free ligand.

When the exchanging system is cooled, the triplet broadens, coalesces, and resolves into a new spectrum showing the "frozen-out" species; i.e., the two non-exchanging forms of phosphite.

Coalescence temperature is about -43°C .

The final spectrum is not two triplets, but rather a quadruplet which may exhibit asymmetries in the larger peaks. This happens because the two triplets that are expected occur so close to one another. The final spectrum is essentially two triplets superimposed:

The analysis problem appears to be soluble by use of a complete line shape fitting technique. Initial experiments do not allow any statement of the order of the reaction with respect to complex or ligand just yet.

Personnel

Professors Basolo and Pearson worked on the project part-time during the year and full-time for one month during the summer.

Dr. Marino Nicolini spent nine months on the project. He was chiefly supported by a NATO grant. In January he returned to the University of Padova, in Italy.

Dr. Wilfried Hölzle, after 18 months on the project, left in September, 1969, to take a job with DuPont. He was largely supported by the German Federal Government.

Dr. Peter Maples joined the project in September, 1969, from the W. M. Kellogg Company. He will remain for some months at least.

The graduate students now working on the project are Victor Myers, John McDonald, Robert Johnson, Warren Muir, Steve Clarkson and Carol Grimes. Myers and Johnson will obtain their Ph.D.'s this summer. McDonald and Muir have NIH fellowships and Mrs. Grimes has a Danforth fellowship. Rajaram Jayaraman will start working on the project this spring. Bruce Lane, from Oxford University, will join us as a post-doctor this fall.