Mechanistic Control by the Size of the Outgoing Group in a Palladium(II) Substitution Reaction

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Summary Kinetic studies of the substitution reactions of [Pd(1,1,7,7-tetraethyldiethylenetriamine)XCN]$^+$ with bromide ion in dimethylformamide indicate that, for X = S, an S_N1 or solvent-assisted ligand interchange process is operative whereas, for X = Se, a concurrent S_N2 path involving chelate ring-opening is also involved—a unique example of mechanistic control by an outgoing group.

PALLADIUM(II) complexes containing the bulky ligand 1,1,7,7-tetraethyldiethylenetriamine (Et_4dien) have generally been found[1,2] to undergo substitution reactions in aqueous solution at rates which are unaffected by the nature and concentration of the incoming ligand, except for the ligands OH^- and $S_2O_3^{2-}$, *i.e.*,

$$[Pd(Et_4dien)Br]^+ + Y^{n-} \rightarrow [Pd(Et_4dien)Y]^{(2-n)+} + Br^- \quad (1)$$

$$\text{rate} = k_1[\text{substrate}] \text{ (generally)} \quad (2)$$

$$\text{rate} = k_1[\text{substrate}] + k_2[\text{substrate}][Y^{n-}] \ (Y^{n-} = OH^-, S_2O_3^{2-}) \quad (3)$$

The reagent-dependent path (k_2) also is not followed in relatively polar nonaqueous solvents such as methanol,[3] but is followed in acetonitrile.[3] The steric hindrance created by the Et_4dien ligand, which generally obstructs the reagent path, has also been found to cause

$$[Pd(XCN)_4]^{2-} \xrightarrow{Et_4dien} [Pd(Et_4dien)XCN]^+ \longrightarrow [Pd(Et_4dien)NCX]^+$$

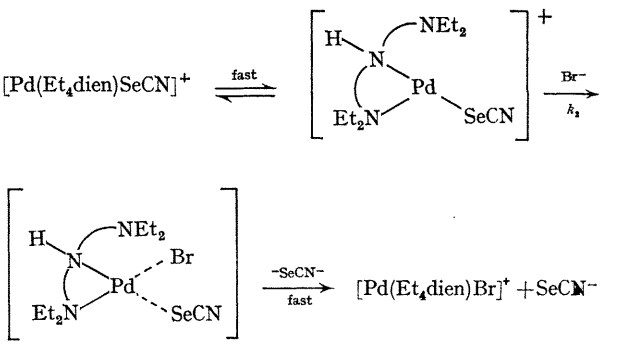
the ambidentate thiocyanate (SCN^-)[4] and selenocyanate ($SeCN^-$)[5] ions to co-ordinate at the reverse end of the ion. The results of our study of the isomerization and substitution reactions of these bonding isomers in dimethyl formamide (DMF) solution has provided a unique example of mechanistic control by the size of the co-ordinated atom of the *outgoing* group in an inorganic substitution reaction.

The thiocyanato-complex reacts (see Table) with bromide ion at a rate which is comparable to its rate of isomerization, the rate being unaffected by increasing bromide ion concentration. This behaviour was previously observed[4] for substitution reactions of the complex in aqueous solution, and is in accord with a dissociative S_N1 type of mechanism or a solvent-assisted ligand interchange process.[6]

$$[Pd(Et_4dien)SCN]^+ + DMF \xrightarrow{k_1} [Pd(Et_4dien)DMF]^{2+} + SCN^-$$

$$\xrightarrow[\text{fast}]{Br^-} [Pd(Et_4dien)Br]^+ + DMF \quad (4)$$

However, the rate of the substitution reaction between the selenocyanato-complex and bromide ion was found to follow the two-term rate law shown in equation (3), the value of k_1 being virtually identical to that observed for its first-order isomerization rate constant. The k_1 path therefore most probably involves a reaction sequence analogous to that shown in equation (4). The main variable between the two substrates appears to be the size of the co-ordinated atom (sulphur compared with selenium) of the ambidentate group. It therefore seems reasonable that the rate dependence of the Pd–SeCN → Pd–Br reaction on the concentration of the bromide ion could result from the nucleophilic attack of the bromide ion on an intermediate created by the opening of one or more of the chelate rings due to the steric strain created by the large selenium atom. The mechanism suggested for the k_2 path is therefore as follows:



The ring-opening would not lead to isomerization, since it eliminates the driving force behind the isomerization. The existence of the ring-opening step is supported by the following observations:

(a) Despite their greater basicity, *N*-alkyl multidentate amines form less stable complexes, due to steric hindrance, than the corresponding *N*-hydrogen amines.[7] The inherent instability of tertiary amine complexes has also been pointed out by Chatt and Wilkins.[8]

(b) The concentration of all other nucleophiles investigated (I^-, $SeCN^-$, N_3^-, CN^-, NO_2^-) was found to affect the rate of their reaction with the selenocyanato-complex, as is required by the postulated mechanism. However, the nucleophilic reactivity constant[9] of the reagent ion is not the determining factor in the rate of the k_2 path, since the azide ion (nPt = 3·58) reacted at a rate too fast to measure (as did the cyanide ion) by the method used in this study, and the bromide ion (nPt = 4·18) was found to be more reactive than the iodide ion (nPt = 5·42). Instead, the observed order of increasing reactivity follows the order of decreasing size of the nucleophile. The addition of free selenocyanate was found to affect the rate of isomerization only to a slight extent, a limiting rate being reached at the higher selenocyanate concentrations. This can be explained on the basis of the observation that an S_N2 reaction by the free selenocyanate in the k_2 path *via* its selenium atom would result in effectively no reaction at all and would have no effect on the measured rate, which was determined on the basis of substrate disappearance. Only the small fraction proceeding *via*

attack by the less nucleophilic nitrogen atom would tend to enhance the rate of substrate disappearance, leading to the small rate increase observed. The plots for the nitrite substitution reaction exhibited pronounced curvature, possibly due to a concurrent Pd–ONO → Pd–NO_2 isomerization.

Kinetic data for the isomerization and substitution reactions of $[Pd(Et_4dien)XCN]^+$ *and* $[Pd(Et_4dien)NCX]^+$ *in dimethylformamide at 30°*

Reaction[a,b]	10^4k_1, sec.$^{-1}$	10^4k_2, M^{-1} sec.$^{-1}$
Pd–SCN → Pd–NCS	4·4	—
Pd–SeCN → Pd–NCSe	3·2	—
Pd–SCN → Pd–Br	7·1	0
Pd–SeCN → Pd–Br	3·4	740
Pd–NCS → Pd–Br	1·0	0
Pd–NCSe → Pd–Br	4·7	0

[a] Concentration of substrate $2{\cdot}00 \times 10^{-3}$ M; concentration of bromide varied from $5{\cdot}00 \times 10^{-3}$—$1{\cdot}00 \times 10^{-1}$ M. [b] Ionic strength maintained at $\mu = 0{\cdot}100$ with sodium perchlorate.

(c) When the selenocyanate group is *N*-bonded in the substrate, thereby relieving the steric strain, the k_2 path becomes insignificant, and a rate law corresponding to equation (2) is followed.

We thank the National Science Foundation for financial support of this work and Professor C. Trumbore and Dr. L. Rennick for stimulating discussions.

(*Received, August 5th*, 1969; *Com.* 1205.)

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