THE RATES AND MECHANISMS OF SUBSTITUTION REACTIONS OF PALLADIUM(II) DITHIOLATE COMPLEXES

Ralph G. Pearson[a]; Michael J. Hynes[a]

[a] Contribution from the Chemical Laboratory, Northwestern University, Evanston, Illinois

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RALPH G. PEARSON and MICHAEL J. HYNES

Contribution from the Chemical Laboratory, Northwestern University, Evanston, Illinois 60201

The kinetics of the substitution reactions of planar palladium(II) dithiolate complexes with both monodentate and bidentate nucleophiles have been studied in aqueous solution at 25°C using the stopped-flow technique. For both monodentate and bidentate nucleophiles, most of the reactions are second-order overall, first-order in the metal complex and first-order in the nucleophile. Mechanisms are proposed for the substitution reactions. The results demonstrate that palladium(II) dithiolates have a smaller tendency to form five-coordinate adducts than do nickel(II) dithiolates. The rates of the substitution reactions are slower than might have been expected from a consideration of the corresponding reaction with nickel(II). This correlates with the instability of five-coordinated intermediates.

INTRODUCTION

Although there is a large amount of data on the rates and mechanisms of substitution reactions of square-planar platinum(II) complexes,[1,2] until recently the work reported on similar nickel(II) and palladium(II) systems was very sparse. A recent publication[3] reports the rates and mechanisms of the substitution reactions of square-planar nickel (II) dithiolate complexes. The kinetics of substitution of a number of square-planar palladium(II) complexes have also been reported,[4-11] while more recently the rates and mechanisms of anation of tetraaquopalladium(II) by halide ions have been discussed.[12] While it has been possible in many instances to make direct comparisons of the rates and mechanisms of palladium(II) and platinum(II) reactions, very few such comparisons have been made for nickel(II) and palladium(II) systems. No doubt this has largely been due to the difficulty of obtaining suitable systems for comparison, as very few square-planar complexes of nickel(II) with simple ligands are known.

The dithiolate complexes of these metals which have been shown to be planar[13,14] should provide a suitable basis for a comparison which may also be extended to the platinum(II) systems. It was also hoped to ascertain the relative tendencies of the dithiolate complexes of nickel(II) and palladium(II) to form transient five-coordinate adducts, the existence of such adducts having already been proved for the nickel(II) complexes.[3]

The structures of the ligands used in this work are shown in Table I.

EXPERIMENTAL

Preparation of the Ligands.

Pottasium N-cyanodithiocarbimate, K_2cdc[15] and sodium 1, 1-dicyanoethylene-2, 2-dithiolate, Na_2i-mnt[16] were prepared by literature methods. Potassium 1-nitroethylene-2, 2-dithiolate, K_2ned was prepared by the method of Freund.[17] Potassium dithiooxalate (Eastman Kodak) was purified as previously described.[18] Sodium maleonitriledithiolate, Na_2mnt was prepared by a published method.[19]

Preparation of the Metal Complexes.

A stock solution of K_2PdCl_4 was prepared as described in the literature.[20] Aliquots of this solution were used in the preparation of the palladium dithiolate complexes.

$K_2Pd(dto)_2$ was prepared as described in the literature.[21] $[(CH_3)_4N]_2Pd(mnt)_2$ was prepared by a modification of a published method,[22] using an aliquot of the stock solution of K_2PdCl_4 instead of $PdCl_2$. $[(CH_3)_4N]_2Pd(i-mnt)_2$ was prepared by adding, with stirring, 0.614 g (0.0033 mole) of Na_2i-mnt in 5 ml of 50:50 ethanol-water to 0.49 g (0.0015 mole) of K_2PdCl_4 in 4 ml of water. On addition of 0.51 g (0.0033 mole) of $(CH_3)_4NBr$ in 5 ml of 50:50 ethanol-water, yellow crystals of

TABLE I

The ligands used in this investigation.

$$\begin{array}{ccc}
\overset{-S}{\diagdown}C=C\overset{\diagup CN}{\diagdown CN} & \overset{-S}{\diagdown}C=C\overset{\diagup NO_2}{\diagdown H} & \overset{-S}{\diagdown}C=N-CN \\
\text{i--mnt} & \text{ned} & \text{cdc}
\end{array}$$

$$\begin{array}{cc}
\overset{-S}{\diagdown}\underset{\diagup CN}{C}=\overset{-S}{\underset{\diagdown CN}{C}} & \overset{-S}{\diagdown}\underset{\diagdown O}{\overset{\diagup}{C}}-\overset{-S}{\underset{\diagup O}{\diagdown}}C \\
\text{mnt} & \text{dto}
\end{array}$$
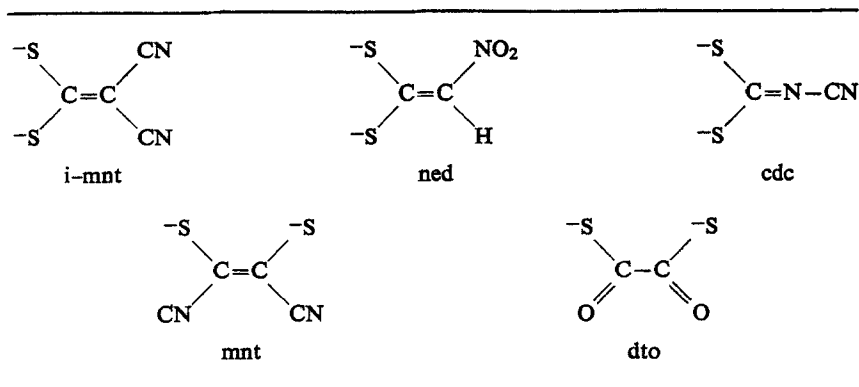
[(CH$_3$)$_4$N]$_2$Pd(i–mnt)$_2$ formed. The product was recrystallized from 50:50 ethanol-water. *Anal.* Calcd for C$_{16}$H$_{24}$N$_6$S$_4$Pd: C, 35.9; H, 4.5; N, 15.7. Found: C, 35.8; H, 4.4; N, 15.5. [(CH$_3$)$_4$N]Pd(cdc)$_2$ was prepared from K$_2$PdCl$_4$ by a published method.[15] K$_2$Pd(ned)$_2$ was prepared by the method used for [(CH$_3$)$_4$N]$_2$Pd(i–mnt)$_2$. On addition of a solution of K$_2$ned in 50:50 ethanol-water to an aliquot of the K$_2$PdCl$_4$ stock solution, K$_2$Pd(ned)$_2$ precipitated. *Anal.* Calcd for K$_2$C$_4$H$_2$N$_2$O$_4$S$_4$Pd: C, 10.6; N, 6.2. Found: C, 10.4; N, 6.2.

Mixed complexes, e.g. Pd(mnt)(ned)$^{2-}$, were prepared *in situ* by adding a solution of the ligand forming the stronger complex to an aqueous solution of the palladium complex of the weaker ligand. The electronic spectra of these solutions showed that the major species in solution was the mixed complex. The mixed complex Pd(ned)(CN)$_2^{2-}$ was prepared similarly.

Ultraviolet and visible spectra were recorded on a Cary 14 spectrophotometer. Either a commercially available stopped-flow device[23] or a Beckman DU-2 spectrophotometer equipped with a Gilford Model 220 optical density converter was used to follow the kinetics. All kinetics runs were made under pseudo first-order conditions at 25°C. The temperature was maintained constant to within ±0.1°C. The ionic strength was maintained constant at 0.1 M using sodium perchlorate as the inert electrolyte. In order to obtain the concentration dependence of the rate constants the reactions were studied at a number (five to ten) of different concentrations of excess nucleophile. The reported rate constants represent the average of two or more kinetic runs at each concentration. For a typical reaction the concentration of complex was 2.5 × 10^{-5} M, while the concentration of nucleophile was varied between 10^{-3} M and 10^{-2} M.

Analyses. Microanalyses for C, H, and N were performed in this department by Miss H. Beck.

RESULTS

The nucleophile dependences of the observed rate constants for the substitution of square-planar palladium(II) dithiolates with cyanide ion as nucleophile are shown in Table II. For the reaction of Pd(dto)$_2^{2-}$ with cyanide ion to give Pd(CN)$_4^{2-}$, one reaction step was observed. At lower cyanide concentrations the rate constant exhibited a second-order dependence on cyanide concentration, while at higher nucleophile concentrations the dependence tended to be first-order. This was ascertained by plotting log k_{obsd} vs. log [CN]. Two steps were observed for the reactions between both Pd(cdc)$_2^{2-}$, Pd(i–mnt)$_2^{2-}$ and cyanide ion. The reaction product is Pd(CN)$_4^{2-}$ in both cases. These rates showed a first-order dependence on cyanide concentration. Two steps were observed for the Pd(ned)$_2^{2-}$-cyanide ion reaction, the nucleophilic dependence of which is shown in Table II. One step, having a first-order dependence on cyanide concentration, was observed for the reactions of the mixed-ligand complexes Pd(mnt)(i–mnt)$^{2-}$ and Pd(mnt)(ned)$^{2-}$ with cyanide ion to give Pd(mnt)(CN)$_2^{2-}$. The reaction between Pd(mnt)$_2^{2-}$ and cyanide ion is extremely slow and its rate could not be accurately measured owing to the slow decomposition of the reactants in solution.
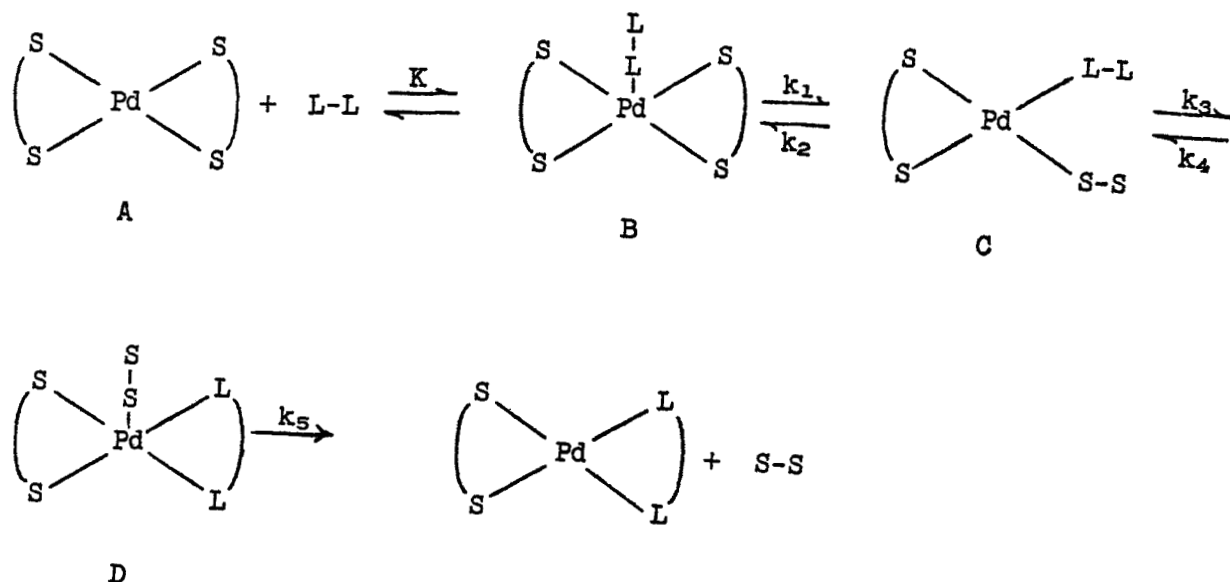
FIGURE 1   Proposed mechanism for the substitution of palladium(II) dithiolates with bidentate nucleophiles.
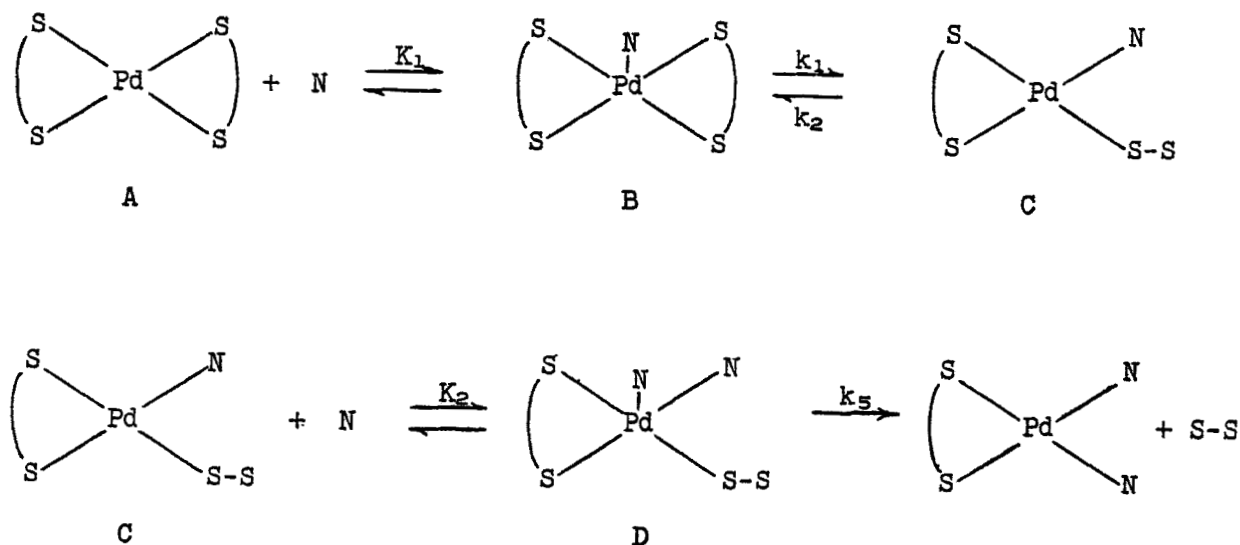

FIGURE 2   Proposed mechanism for the substitution of palladium(II) dithiolates with unidentate nucleophiles.

The rate constants for the substitution of square-planar palladium(II) dithiolates by bidentate ligands are shown in Table III. For all of the reactions shown in the Table, one reaction step was observed, and in all cases the rate constants show a first-order dependence on nucleophile concentration.

The typical two-term rate law for reactions of square planar complexes[1,2] has been observed for the reactions of some palladium(II) complexes.[6,9] In the present investigation a solvent path was not detected for any of the reactions studied. Such behaviour is not unusual, however, and whether or not the solvent path actually appears in the rate

law for a particular reaction depends on the relative magnitudes of the rates for the two paths.

The general mechanism we propose for the substitution of square-planar palladium(II) dithiolate complexes with bidentate nucleophiles is the same as that postulated for the substitution of nickel(II) dithiolates.[3] The general features of the mechanism are shown in Figure 1. Assuming steady states for C and D, for excess ligand one calculates

$$k_{obsd} = \frac{kK[L]}{1 + K[L]} \qquad (1)$$

where

$$k = \frac{k_1 k_3 k_5}{k_2(k_4 + k_5) + k_3 k_5} \qquad (2)$$

Similarly the mechanism proposed for the substitution reactions with cyanide ion as nucleophile is shown in Figure 2. Taking (C + D) to be in a steady state, the following relationship is obtained

$$k_{obsd} = \frac{k_1 k_5 K_1 K_2 [X]^2}{(1 + K_1[X])(k_2 + K_2 k_5[X])} \qquad (3)$$

This equation may be written in the following form:

$$k_{obsd} = \frac{k_1 k_5 K_1 K_2 [X]^2}{k_2 + [X](K_2 k_5 + K_1 k_2) + [X]^2(K_1 K_2 k_5)} \qquad (4)$$

It is apparent from equation (4) that, dependent on the relative magnitudes of the various rate and equilibrium constants, k_{obsd} may show zero, first or second-order dependence on cyanide concentration.
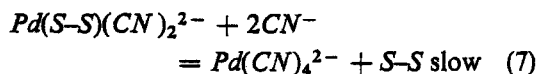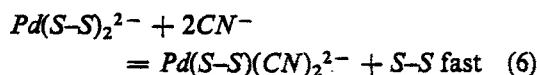
For the substitution reactions of square-planar nickel(II) dithiolates, the differences in the dependence of k_{obsd} on nucleophile concentration for mono and bidentate ligands provided a simple means of testing the proposed mechanism.[3] Furthermore the formation of the five-coordinate intermediates could be observed in a number of instances. Unfortunately no such test is possible in the present investigation, as k_{obsd} shows a first-order dependence on nucleophile concentration for both unidentate and bidentate entering groups in many of the reactions. The mechanism proposed allows for this possibility and there is other strong supporting evidence for the mechanism.

Attempts to prepare $Pd(dto)(CN)_2^{2-}$ in situ were unsuccessful. When solutions containing cyanide ion were added to solutions of $Pd(dto)_2^{2-}$ an equilibrium mixture of $Pd(dto)_2^{2-}$ and $(Pd(CN)_4^{2-}$ was obtained. This was confirmed by both spectro-
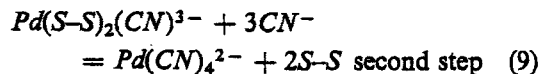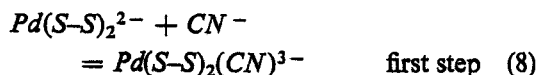
scopic and kinetic measurements. Previous attempts to prepare solutions containing $Pd(dto)(CN)_2^{2-}$ have also been unsuccessful, as were attempts to prepare $Pt(dto)(CN)_2^{2-}$.[24] A solution containing cyanide ion was added to an aqueous solution of $Pd(ned)_2^{2-}$. The spectrum of the resultant solution was markedly different from that of $Pd(ned)_2^{2-}$, and did not correspond to that computed for an equimolar mixture of $Pd(CN)_4^{2-}$ and $Pd(ned)_2^{2-}$. Traces of $Pd(ned)_2^{2-}$ were present, however, as evidenced by the spectrum. When these solutions were reacted with excess cyanide ion, a reaction having the same rate and absorbance change as that of the slower of the two reactions observed when solutions of $Pd(ned)_2^{2-}$ were reacted with cyanide ion was observed. No reaction corresponding to the faster of the two reactions observed when solutions of $Pd(ned)_2^{2-}$ were reacted with cyanide was seen. Therefore, the reaction seen on reacting solutions of $Pd(ned)_2^{2-}$ to which two equivalents of cyanide ion were first added, with further cyanide ion must be:

$$Pd(ned)(CN)_2^{2-} + 2CN^-$$
$$= Pd(CN)_4^{2-} + ned^{2-} \qquad (5)$$
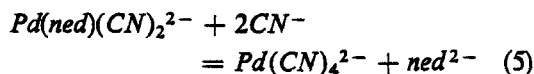
It is therefore reasonable to assign the steps observed on reacting palladium dithiolates with excess cyanide ion to the following reactions:

$$Pd(S-S)_2^{2-} + 2CN^-$$
$$= Pd(S-S)(CN)_2^{2-} + S-S \text{ fast} \qquad (6)$$

$$Pd(S-S)(CN)_2^{2-} + 2CN^-$$
$$= Pd(CN)_4^{2-} + S-S \text{ slow} \qquad (7)$$

A possible alternative assignment is that the faster of the two observed reactions is due to the formation of a metastable five-coordinate intermediate. This then reacts with cyanide in a slower reaction to give the product $Pd(CN)_4^{2-}$. viz

$$Pd(S-S)_2^{2-} + CN^-$$
$$= Pd(S-S)_2(CN)^{3-} \qquad \text{first step} \qquad (8)$$

$$Pd(S-S)_2(CN)^{3-} + 3CN^-$$
$$= Pd(CN)_4^{2-} + 2S-S \text{ second step} \qquad (9)$$

However in view of the results with $Pd(ned)_2^{2-}$ this does not seem likely. The experiments described below also rule out the alternative assignment.

Attempts were made to detect the formation of the five-coordinate adducts postulated in the

TABLE II

Rate constants for substitution reactions of palladium(II) dithiolates
with cyanide ion as nucleophile. Water solution at 25°C.

Reactant	Product	k_{obsd}, sec^{-1}
Pd(dto)$_2$$^{2-}$	Pd(CN)$_4$$^{2-}$	2.7×10^4 [CN$^-$]^2
Pd(cdc)$_2$$^{2-}$	Pd(cdc)(CN)$_2$$^{2-}$	920 [CN$^-$]
Pd(cdc)(CN)$_2$$^{2-}$	Pd(CN)$_4$$^{2-}$	66 [CN$^-$]
Pd(i–mnt)$_2$$^{2-}$	Pd(i–mnt)(CN)$_2$$^{2-}$	800 [CN$^-$]
Pd(i–mnt)(CN)$_2$$^{2-}$	Pd(CN)$_4$$^{2-}$	77 [CN$^-$]
Pd(ned)$_2$$^{2-}$	Pd(ned)(CN)$_2$$^{2-}$	$\dfrac{9.36 \times 10^6 \,[\text{CN}^-]^2}{1 + 1.33 \times 10^3 \,[\text{CN}^-]}$
Pd(ned)(CN)$_2$$^{2-}$	Pd(CN)$_4$$^{2-}$	$\dfrac{9.4 \times 10^5 \,[\text{CN}^-]^2}{1 + 1.64 \times 10^2 \,[\text{CN}^-]}$
Pd(i–mnt)(mnt)$^{2-}$	Pd(mnt)(CN)$_2$$^{2-}$	0.575 [CN$^-$]
Pd(ned)(mnt)^2	Pd(mnt)(CN)$_2$$^{2-}$	2.6 [CN$^-$]

TABLE III

Rate constants for substitution reactions of palladium(II)
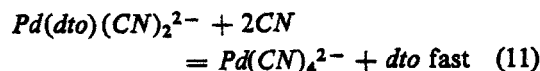dithiolates with bidentate nucleophiles. Water solution at
25°C

Reactant	Nucleophile	Product	k_{obsd}, sec^{-1}, M^{-1}
Pd(i–mnt)$_2$$^{2-}$	dto^{2-}	Pd(dto)(i–mnt)$^{2-}$	12.5
Pd(ned)$_2$$^{2-}$	dto^{2-}	Pd(ned)(dto)$^{2-}$	197
Pd(ned)(dto)$^{2-}$	dto^{2-}	Pd(dto)$_2$$^{2-}$	3.8
Pd(ned)$_2$$^{2-}$	mnt^{2-}	Pd(ned)(mnt)$^{2-}$	4560
Pd(ned)$_2$$^{2-}$	i–mnt^{2-}	Pd(ned)(i–mnt)$^{2-}$	152
Pd(ned)(i–mnt)$^{2-}$	i–mnt^{2-}	Pd(i–mnt)$_2$$^{2-}$	7.0

reaction mechanism. Arguments regarding the metal-ligand bonding similar to that previously proposed,[3] suggest that Pd(mnt)(ned)$^{2-}$ and Pd(mnt)(i–mnt)$^{2-}$ would be most likely to form stable five-coodinate adducts. Furthermore, the reactions of these mixed-ligand complexes with cyanide ion are relatively slow and the absorbance changes may be monitored without recourse to stopped-flow devices at low cyanide concentrations. For the reactions between both Pd(mnt)(i–mnt)$^{2-}$ and Pd(mnt)(ned)$^{2-}$ with cyanide ion to give Pd(mnt)(CN)$_2$$^{2-}$, only one reaction was observed in both cases. The rate data are given in Table II. There was no evidence of a rapid initial reaction corresponding to the formation of a five-coordinate adduct. The rate of adduct formation would be expected to be more rapid than the observed

reactions. This can only mean that the equilibrium constant for formation of the five-coordinate adduct is small and that its concentration never becomes appreciable in solution, or, alternatively, that the absorbance changes associated with its formation are small. In view of the results for nickel, the latter possibility is unlikely.

In order to see if the trend regarding the decrease in stability of five-coodinate adducts on going from nickel to palladium is carried on to platinum, a number of reactions of platinum dithiolates were examined. The tetramethylammonium salts of Pt(cdc)$_2$$^{2-}$, Pt(i–mnt)$_2$$^{2-}$ and Pt(ned)$_2$$^{2-}$ were prepared and reacted with excess cyanide. Although the substitution reactions are quite slow, adduct formation, if it occurs, should be quite rapid. Preliminary experiments show no evidence of a rapid initial reaction corresponding to adduct formation.

The fact that only one reaction is observed when Pd(dto)$_2$$^{2-}$ is reacted with cyanide, is probably due to the apparent instability of Pd(dto)(CN)$_2$$^{2-}$. The reaction sequence in this case appears to be:

$$Pd(dto)_2^{2-} + 2CN = Pd(dto)(CN)_2^{2-} + dto \quad \text{slow} \quad (10)$$

$$Pd(dto)(CN)_2^{2-} + 2CN = Pd(CN)_4^{2-} + dto \quad \text{fast} \quad (11)$$

The reactions between Pd(ned)$_2$$^{2-}$, Pd(ned)(CN)$_2$$^{2-}$ and cyanide are both less than

second order, but greater than first order in cyanide. The form of the rate equations is identical to that obtained for similar reactions with nickel.[3] For the reaction between $Pd(ned)_2{}^{2-}$ and cyanide ion to give $Pd(ned)(CN)_2{}^{2-}$, extrapolation of the stopped-flow data to the time of mixing showed a small rapid initial absorbance change. This is the only reaction where such a change was observed and it may be evidence for the formation of a small concentration of five-coordinated adduct. However, the results with nickel suggest that ned should be the least likely ligand for stabilizing such an adduct.[3]

DISCUSSION

The overall results obtained in the present investigation appear to similar to those obtained for the substitution reactions of square-planar nickel(II) dithiolate complexes.[3] There are some significant differences however. Differences in the intimate details of the reaction mechanism appear to be best interpreted in terms of the relative tendencies of nickel and palladium to form stable five-coordinate intermediates. A number of articles have appeared in the literature dealing with five-coordinate complexes of transition metal ions.[25-32] A large number of the complexes so far reported are formed by metals of the first-row transition series. There is certainly a pronounced decrease in the tendency toward five-coordination on going down a given group. In the case of nickel, palladium and platinum, the first element has by far the least tendency to form planar complexes, and the greatest to add a fifth or sixth group. However some examples of ligands adding to planar dithiolate complexes of palladium and platinum are known.[33]

The rates of reaction of the planar palladium(II) dithiolates are much slower than those of the corresponding nickel(II) complexes. Unfortunately not too many direct comparisons can be made. The most useful nucleophile for the nickel complexes was mnt. In the case of palladium, mnt was not a useful nucleophile because the absorption spectrum of the free dianion overlaps appreciably with the spectrum of $Pd(mnt)_2{}^{2-}$. The only reaction reported here with mnt as a nucleophile is the substitution of $Pd(ned)_2{}^{2-}$ to give $Pd(mnt)(ned)^{2-}$. It was possible to measure the rate of this reaction with good accuracy owing to the fact that $Pd(ned)_2{}^{2-}$ has very intense absorption bands at the longer wavelengths of the visible spectrum. The

corresponding reaction was very fast for nickel[3]. For the reaction

$$M(mnt)(L-L)^{2-} + 2CN^-$$
$$= M(mnt)(CN)_2{}^{2-} + L-L \quad (12)$$
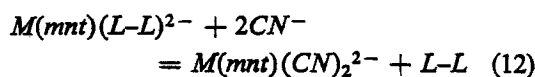
$k_{Ni}/k_{Pd} = 830$ for $L-L =$ ned (with $[CN^-] = 0.01\ M$), while for $L-L =$ i-mnt, $k_{Ni}/k_{Pd} = 400$. For nickel, i-mnt is more rapidly replaced than ned while the reverse is true for palladium. Similarly, for the reaction

$$M(dto)_2{}^{2-} + 2CN^- = M(dto)(CN)_2{}^{2-}$$
$$+ dto^{2-} k_{Ni}/k_{Pd} = 1470 \quad (13)$$
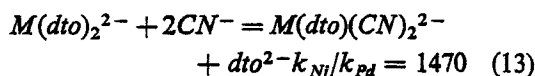
The rate increases on going from palladium to nickel are unusually large. Earlier work on the relative reactivities of these two metal ions has given ratios of the order of $10,^{2,12}$ with nickel(II) being more labile than palladium(II), which in turn is much more labile than platinum(II)[34]. While the reason for the high ratios is not clear, it seems logical to attribute the low reactivity of palladium (II) dithiolates to the instability of the required five-coordinated intermediate species.

The nucleophilic reactivity of the various ligands appears to follow a similar order to that observed for the nickel system, e.g., mnt $>$CN $>$ dto $>$ i-mnt. The order is reversed for mnt and cyanide ion compared to the nickel reactions, but the difference in reactivity is not great, as was the case for nickel also.[3] As far as they can be compared, the ratio of the nucleophilic reactivities of the different nucleophiles is very similar for both metals. Similarly the *trans* effects follow a similar order. It has been proposed that the *trans* effect in nickel dithiolates operates by affecting the stability of the five-coordinate adduct.[3] A similar situation may exist for palladium.

ACKNOWLEDGEMENT

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34. These remarks hold only for the divalent ions. Zerovalent metal complexes show the reactivity sequence $Ni \ll Pd > Pt$.[20]