Reactivity of some Coordinated Ligands Containing Sulphur Towards Nucleophilic Substitution Reactions.
Part II. Kinetics and Mechanism of the Reaction of [1,2-Diphenylethanediylidene Bis(S-methylhydrazinecarbodithioate)*NN'SS'*(−2)] Nickel(II) and Palladium(II) Complexes with Alicyclic Secondary Amines

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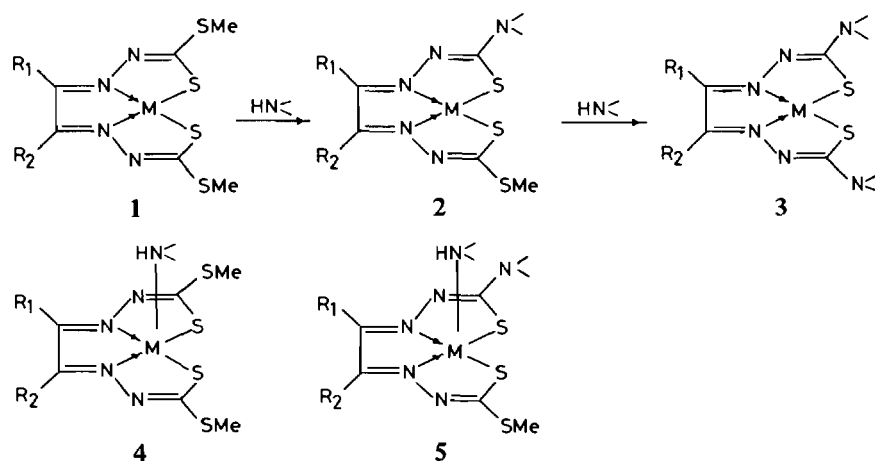
Abstract

The substitution reactions of 1,2-diphenylethanediylidene bis(S-methylhydrazinecarbodithioate)*NN'SS'*(−2) nickel(II) and palladium(II) complexes with piperidine and morpholine were followed spectrophotometrically in benzene. Two successive steps were observed, the substitution of the first SMe group deactivating the second SMe group. The first substitution step shows third order kinetics, first order in the substrate and second order in the nucleophile. The third order rate constants increase with the greater basicity of piperidine relative to morpholine, and it was noted that the nickel(II) complex is more susceptible to nucleophile catalysis than the palladium(II) complex. The values of activation parameters show that the higher rate of substitution of the palladium(II) complex is due to entropy effects. It was deduced that the initial attachment of the nucleophile on the SMe carbon to give a dipolar intermediate is followed by the rate determining nucleophile catalyzed formation of the monosubstituted product.

Introduction

The nucleophilic substitution of the SMe groups in metal(II) complexes of the type 1 by different secondary amines (e.g. piperidine (pip) or morpholine (morph)) have been studied [1]. Both mono- (2) and disubstituted (3) complexes have been isolated and characterized. In some cases, monoadducts (4, R_1 = Ph, R_2 = H, M = Ni and $>$NH = pip or morph) as well as monosubstituted monoadducts (5, R_1 = Ph, R_2 = H, M = Ni and $>$N = pip or morph) have been identified [1].

In the present work, the reactions of 1 (R_1 = R_2 = Ph, M = Ni and Pd), with piperidine or morpholine have been followed spectrophotometrically in

benzene solutions and the kinetics of these reactions are discussed. The relevance of the kinetic measurements to the mechanism of nucleophile catalysis in these substitution reactions is pointed out.

Experimental

Materials

[1,2-Diphenylethanediylidene bis(S-methylhydrazinecarbodithioate)$NN'SS'(-2)$] nickel(II) and palladium(II) complexes (1, $R_1 = R_2 = Ph$, $M = Ni$ and Pd) were prepared as previously described [2] and were crystallized several times from chloroform–petroleum ether (40–60 °C). The mono- and disubstituted complexes 2 and 3 ($R_1 = R_2 = Ph$, $M = Ni$ or Pd and $>N$ = pip or morph) were prepared from the reaction of 1 with piperidine or morpholine as previously described [1]. The purity of the mono- and disubstituted complexes was checked by elemental analyses, TLC and ^1H NMR spectra.

Piperidine and morpholine were stored over KOH for a week and distilled just before use. Benzene was dried and distilled over sodium metal.

Kinetic Measurements

A small measured volume (1 cm^3) of a known concentration of each of the reactants (metal(II) complex and the nucleophile) was placed in a two compartment cell (light path length = 0.433 cm). The cell was placed to reach thermal equilibrium in the thermostatted (±0.1 °C) cell holder of an SP 1801 Pye Unicam spectrophotometer. The contents of the cell were then thoroughly mixed by rapid shaking and the variation of absorbance measured at 400 nm as a function of time was recorded on a chart recorder.

The rate constants of these substitution reactions were measured under pseudo first order conditions. The different base concentrations were all greatly in excess of the substrate concentration. Since plots of $\log(A_t\text{obs} - A_\infty)$ against t (s) gave straight lines up to about 85% of the reaction, the experimental data were fitted to the equation

$$\ln(A_t\text{obs} - A_\infty) = -k_{\text{obs}} \times t + \ln(A_0 - A_\infty) \qquad (1)$$

where k_{obs} is the observed rate constant, A_0 is the absorbance at zero time, $A_t\text{obs}$ is the measured absorbance at time t and A_∞ is the limiting absorbance.

The value of A_∞ for each kinetic run was first taken as the experimentally determined value; k_{obs} and $\ln(A_0 - A_\infty)$ were obtained from the slope and intercept of the least-squares fit. However, the value of A_∞ is subject to some uncertainty owing to the possible presence of another slower process (presumably a second substitution step). A_∞ was therefore varied, and for each new value, updated k_{obs} and $\ln(A_0 - A_\infty)$ were computed, and then used to obtain calculated absorbance values, $A_t\text{calc}$, according to the equation

$$A_t\text{calc} = A_\infty + \exp(a + bt)$$

where $a = \ln(A_0 - A_\infty)$ and $b = -k_{\text{obs}}$.

This procedure was employed so as to minimize, to within a preset relative tolerance (usually 5×10^{-4}), the quantity $\Sigma(A_t\text{obs} - A_t\text{calc})^2$, the summation being taken over all the data points. When the iterations converged, the final values of k_{obs}, A_∞ and $\ln(A_0 - A_\infty)$ were taken as the best values, and their estimated standard deviations were calculated.

The observed first order rate constants were determined at different nucleophile concentrations C_{Nu}, and then fitted to one of the following functions

$$k_{\text{obs}} = k' C_{\text{Nu}} \qquad (2)$$

$$k_{\text{obs}} = k'k'' C_{\text{Nu}}^2 \qquad (3)$$

$$k_{\text{obs}} = k' C_{\text{Nu}} + k'' C_{\text{Nu}}^2 \qquad (4)$$

using the least-squares treatment given by Wolberg [3]. The choice between the functions was based on (i) the sum of the squared residuals, (ii) the pattern of the residuals and (iii) the magnitude of k' or k'' compared to its standard deviation. Negative rate constants were rejected.

The enthalpies and entropies of activation were calculated using the Eyring equation written in a logarithmic form

$$\ln k = (\Delta S^{\neq}/R) + 23.76 + \ln T - (\Delta H^{\neq}/RT) \qquad (5)$$

where k is the rate constant (k' or k''), T is the absolute temperature and R is the gas constant in J mol^{-1} K^{-1}. Again the data were treated using the non-linear least-squares method given by Wolberg [3].

Three computer programs were written to perform the above calculations. Both Texas Instruments CC-40 BASIC (for the TI compact computer 40) and Applesoft BASIC (for the Apple IIe desk top computer) versions were used.

Results and Discussion

Spectrophotometric Studies and Identification of the Reaction Products

The spectral variations observed on adding piperidine (0.200–0.300 mol dm^{-3}) as a function of time are shown in Figs. 1 and 2. The successive absorption curves pass through fixed isosbestic points at 448, 600 and 700 nm. After complete reaction the observed spectrum shows maximum absorption bands at 385, 445(sh), 470, 560(sh) nm which are identical to those recorded for the monosubstituted complex 2 ($R_1 = R_2 = Ph$, $M = Ni$ and $>N$ = pip) in benzene [1]. The reaction of 1 ($R_1 = R_2 = Ph$ and $M = Pd$) with piperidine was also followed, Fig. 3, and the spectrum of the reaction product (λ_{max} = 315, 385, 445(sh), 470 and 560 nm [1]) indicates the formation of the monosubstituted complex 2 ($R_1 = R_2 = Ph$, $>N$ = pip and $M = Pd$).
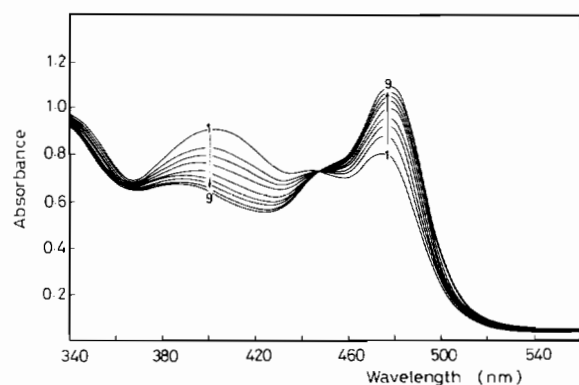
Fig. 1. Variation of the electronic spectra of 1 ($R_1 = R_2 = Ph$, M = Ni) (5.0×10^{-5} mol dm^{-3}) in presence of piperidine (0.20 mol dm^{-3}) as a function of time (min) in benzene at 25 °C: (1) 4.0, (2) 12.0, (3) 17.0, (4) 22.0, (5) 33.0, (6) 45.0, (7) 57.0, (8) 68.0, (9) 86.0.
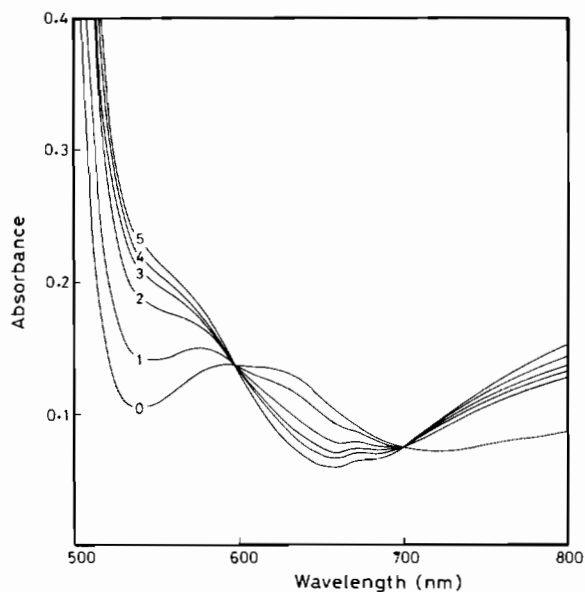

Fig. 2. Variation of the electronic spectra of 1 ($R_1 = R_2 = Ph$, M = Ni) (1.89×10^{-4} mol dm^{-3}) in presence of piperidine (0.35 mol dm^{-3}) as a function of time (min) in benzene at 25.0 °C: (0) 0.0, (1) 0.5, (2) 7.5, (3) 11.5, (4) 15.5, (5) 20.5.

The reaction of **1** ($R_1 = R_2 = Ph$, M = Ni or Pd) (2.00×10^{-4} mol dm^{-3}) with a large excess of piperidine (5.00 mol dm^{-3}) results in the rapid formation of the corresponding monosubstituted complex, and the observed spectral changes as a function of time are due to the gradual formation of the disubstituted complex **3** ($R_1 = R_2 = Ph$, M = Ni or Pd and $>$N = pip) from the initially formed monosubstituted complex. Moreover, the addition of piperidine (5.00 mol dm^{-3}) to a benzene solution of an authentic sample of **2** ($R_1 = R_2 = Ph$, M = Ni or Pd and $>$N = pip) ($1.00–2.00 \times 10^{-4}$ mol dm^{-3}) causes a time depen-
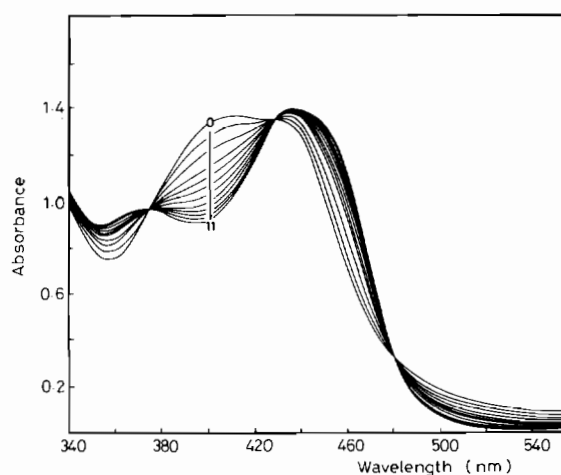

Fig. 3. Variation of the electronic spectra of 1 ($R_1 = R_2 = Ph$, M = Pd) (4.6×10^{-5} mol dm^{-3}) in presence of piperidine (0.126 mol dm^{-3}) as a function of time (min) in benzene at 25.0 °C: (0) 0.0, (1) 10.0, (2) 20.0, (3) 30.0 (4) 40.0, (5) 50.0, (6) 60.0, (7) 75.0, (8) 90.0, (9) 110.0, (10) 130.0, (11) 150.0.

dent change in the spectrum which is also in agreement with the formation of the disubstituted product.

Similar spectral changes were also observed during the reaction of **1** and **2** ($R_1 = R_2 = Ph$, M = Ni or Pd and $>$N = morph) with morpholine.

The present spectrophotometric studies indicate that substitution of the two SMe groups in **1** proceeds by a stepwise mechanism as shown in Scheme 1. The substitution of the first SMe group is much faster than that of the second group and at relatively low concentration (0.05–1.0 mol dm^{-3}) the monosubstituted product (**2**, $R_1 = R_2 = Ph$, M = Ni or Pd and $>$N = pip or morph) is practically the sole reaction product. It is thus apparent that substitution of the first SMe group results in the deactivation of the SMe group in the formed monosubstituted complex. The formation of the disubstituted complex is observed only in the presence of a very large excess of the nucleophile ($\geqslant 5.00$ mol dm^{-3}).

Kinetic Measurements and Reaction Mechanism

The order of the substitution reaction of the first SMe group in **1** ($R_1 = R_2 = Ph$, M = Ni or Pd) by piperidine or morpholine was determined using the initial rate method [4]. In all cases the reactions show overall third order kinetics and the rate equation can be represented by

$$\text{Rate} = k'' [1] [>NH]^2 \qquad (6)$$

where k'' (mol^{-2} dm^6 s^{-1}) is the third order rate constant.

For all systems, plots of k_{obs} *versus* C_{Nu}^2 give straight lines passing through the origin.

$1 + HN{<}$

$k_{-1} \parallel k_1$

6a   Path 1 k_2

6    $k_{-3} \parallel k_3[NH]$

6b   Path 2

7   Fast $(-H^+)$

8    $k_4 \downarrow -(\overset{\oplus}{S}Me\ H_2\overset{\oplus}{N}{<})$

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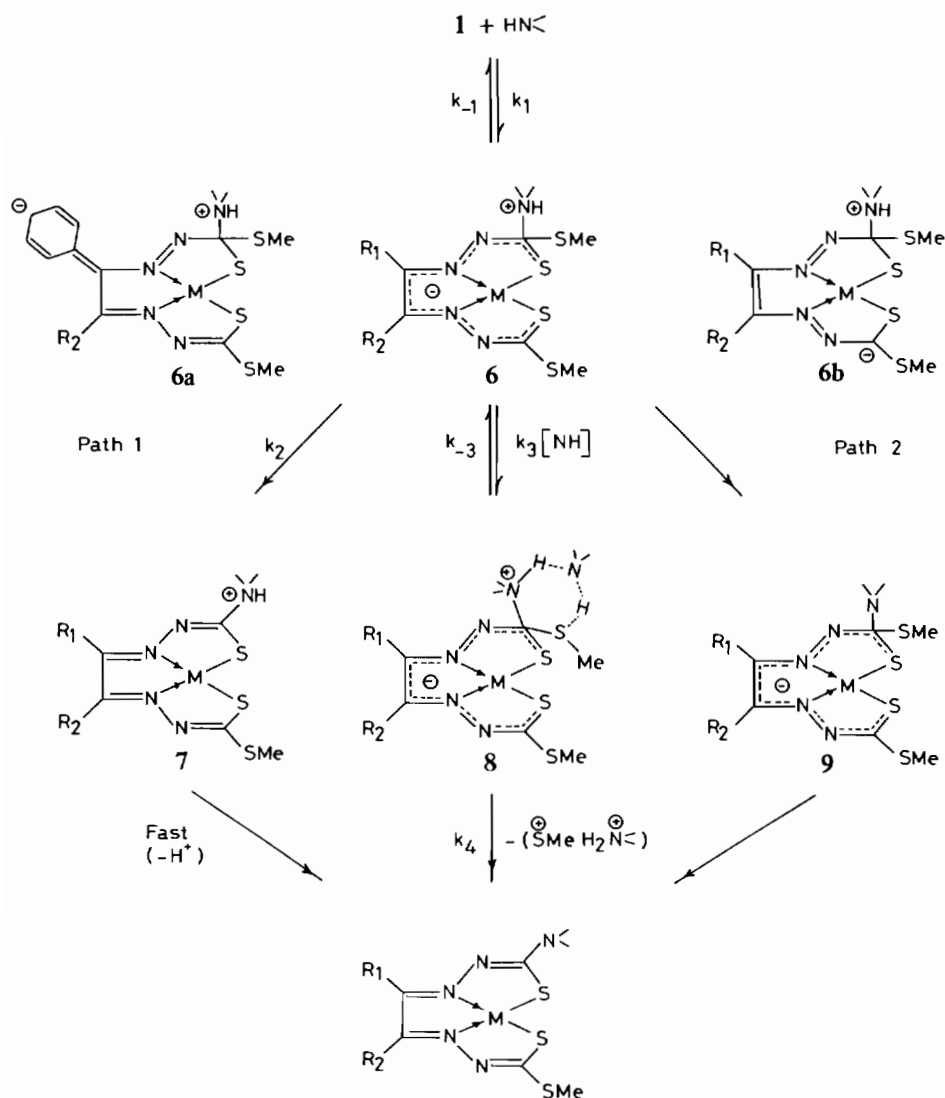
Scheme 1.

As expected, attempts to fit the k_{obs} and C_{Nu} values using eqn. (2) were unsuccessful according to the criteria mentioned in 'Experimental'. Equation (4), on the other hand, gave values of k' which were either within their estimated standard deviations or less than zero. The most reliable values of the third order rate constants k'' were obtained using eqn. (3). The values of k'' together with the estimated standard deviations are listed in Table 1.

Similar to nucleophilic substitution reactions on aromatic [5–9], heterocyclic [10–12] and vinylic carbon [13], the reaction of 1 ($R_1 = R_2 = Ph$, M = Ni or Pd) with piperidine or morpholine to give the corresponding monosubstituted complex 2 is assumed to proceed by the initial attack of the nucleophile on the C–SMe carbon to form the dipolar intermediate 6. The decomposition of 6 to give the final product may proceed either via the uncatalyzed (path 1) and

or the catalyzed path (path 2) as shown in Scheme 1. In the catalyzed path both the specific base–general acid (SB–GA) [6–8] and the cyclic intermediate mechanism [9, 12, 14, 15] have been widely accepted.

In hydroxylic solvents, the (SB–GA) mechanism is much more favoured as the highly ionic transition state(s) are stabilized by extensive solvation. Aprotic solvents on the other hand, are unable to stabilize such ionic intermediates or transition states but are quite suitable to promote a cyclic intermediate mechanism which allows non ion generating decomposition of 6 to give 8. The observed overall third order (second order in nucleophile) kinetics in benzene as solvent indicate that the reaction of 1 ($R_1 = R_2 = Ph$, M = Ni or Pd) with piperidine or morpholine is wholly nucleophile catalyzed and no spontaneous decomposition of 7 into the final monosubstituted product is detectable ($k_2 = 0$). It seems

TABLE 1. Third Order Rate Constants for the Reactions of Nickel(II) and Palladium(II) Complexes of the Type 1 with Piperidine and Morpholine in Benzene at Different Temperatures

Nucleophile	Temperature ($^\circ$C)	C_{Nu} (mol dm^{-1})	No. of solutions	$k'' \times 10^4$ (mol^{-2} dm^6 s^{-1})
1, R$_1$ = R$_2$ = Ph, M = Ni				
Piperidine	25.0	0.0505–0.4040	8	155.5 ± 2.9
	30.0	0.1010–0.4040	8	178.7 ± 1.0
	35.0	0.1510–0.4016	6	201.5 ± 1.9
	40.0	0.1010–0.4016	7	224.8 ± 1.9
Morpholine	25.0	0.6920–1.2975	6	11.7 ± 0.6
	30.0	0.6920–1.9050	6	14.3 ± 0.4
	35.0	0.6920–1.2990	6	17.8 ± 0.4
	40.0	0.6920–1.3850	6	21.3 ± 0.6
1, R$_1$ = R$_2$ = Ph, M = Pd				
Piperidine	25.0	0.1253–0.3500	8	220.1 ± 5.2
	30.0	0.1250–0.3500	8	257.6 ± 6.6
	35.0	0.1100–0.4500	8	305.9 ± 5.3
	40.0	0.1250–0.3500	7	347.8 ± 7.7
Morpholine	30.0	0.6180–1.2360	6	28.3 ± 0.7
	35.0	0.4120–1.1320	7	33.3 ± 3.0
	40.0	0.4000–1.1500	7	45.5 ± 1.8
	45.0	0.4000–1.1500	7	48.9 ± 2.1

very likely that the second nucleophile molecule in 8 acts as a bifunctional catalyst, assisting both the removal of the ammonium proton and the SMe ion [9].

Treating both 6 and 8 as steady state intermediates affords

$$k_{obs} = \frac{k_1 k_3 k_4 [\text{>NH}]^2}{k_{-1}(k_{-3} + k_4) + k_3 k_4 [\text{>NH}]} \qquad (7)$$

and two kinetic behaviours may be observed. In the case where the formation of the cyclic intermediate 8 is much more favoured relative to the reverse decomposition of 6 and the rate of catalytic departure of the SMe group from 8 is much faster than its reverse reaction, *i.e.* $k_3[\text{>NH}] > k_{-1}$ and $k_4 > k_{-3}$, eqn. (7) is reduced to

$$k_{obs} = k_1 [\text{>NH}] \qquad (8)$$

and the substitution reaction shows first order dependence on the nucleophile concentration. This behaviour, however, cannot account for the observed rate equation, eqn. (6). In the second case, the reverse situation may hold and $k_{-1} > k_3[\text{>NH}]$, $k_{-3} > k_4$ then eqn. (7) is simplified to

$$k_{obs} = K_1 K_3 k_4 [\text{>NH}]^2 \qquad (9)$$

where $K_1 = k_1/k_{-1}$ and $K_3 = k_3/k_{-3}$, which is in agreement with the observed rate equation, eqn. (6), and the calculated third order rate constant k'' is equal to $K_1 K_3 k_4$. This kinetic behaviour indicates

that the decomposition of the cyclic intermediate 8 is the rate determining step while the reversible formation of both 6 and 8 are fast preequilibria.

The observed deactivation of the second SMe group towards further nucleophilic substitution is in agreement with the formation of 6 where the positive charge is located on the nucleophile nitrogen while the negative charge is located either on the aromatic phenyl ring (6a) or on the carbon atom of the other C—SMe group (6b) through extended conjugation.

The kinetic data cited in Table 1 show that the third order rate constant k'' depends on the nature of the central metal(II) of the substrate as well as the basicity of the nucleophile used. The more basic piperidine (pK_a in water = 11.12) shows higher rates relative to the less basic morpholine (pK_a in water = 8.33). It is also observed that the nickel(II) complex shows a higher reactivity ratio k''_{pip}/k''_{morph} (13.3 at 25 $^\circ$C) as compared to that of the corresponding palladium(II) complex (8.0 at 25 $^\circ$C) implying that the nickel(II) complex is more susceptible to nucleophile catalysis. In both cases, the reactivity ratios are much greater than unity which is in agreement with the cyclic transition state 10. Electrophilic catalysis either via transition state 11 or 12 seems unlikely, where the reactivity ratio is expected to be around unity or less than unity.

The rate eqn. (9) indicates that the measured activation parameters $\Delta H^{\neq}$, $\Delta S^{\neq}$ are composite terms and can be represented by

TABLE 2. Third Order Rate Constants and Activation Parameters at 25.0 °C

Nucleophile	$k'' \times 10^4$ [a] (mol^{-2} dm^6 s^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})
1, R$_1$ = R$_2$ = Ph, M = Ni			
Piperidine	155.90	16.1 ± 0.4	226 ± 2
Morpholine	11.70	28.1 ± 0.5	206 ± 2
1, R$_1$ = R$_2$ = Ph, M = Pd			
Piperidine	221.70	21.5 ± 0.7	204 ± 3
Morpholine	28.54	28.9 ± 2.9	196 ± 10

[a]Calculated from eqn. (5).

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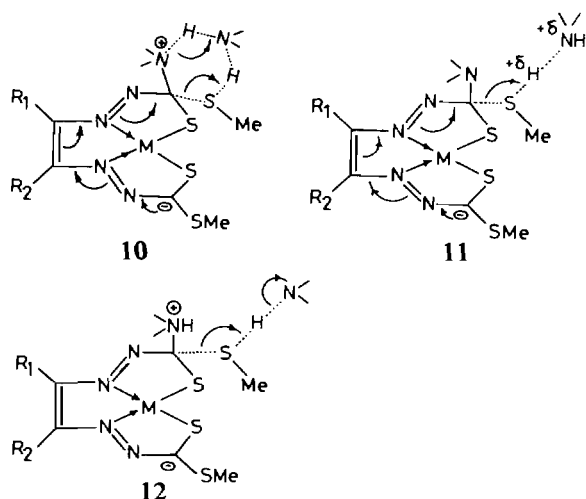
$$\Delta H^{\neq} = (\Delta H_1{}^{\circ} + \Delta H_3{}^{\circ}) + \Delta H_4{}^{\neq}$$

$$\Delta S^{\neq} = (\Delta S_1{}^{\circ} + \Delta S_3{}^{\circ}) + \Delta S_4{}^{\neq}$$

The relatively low $\Delta H^{\neq}$ values measured for these substitution reactions, Table 2, are most probably due to the negative contribution of $(\Delta H_1{}^{\circ} + \Delta H_3{}^{\circ})$. It is also observed for the substitution reactions of both nickel(II) and palladium(II) complexes that the measured $\Delta H^{\neq}$ values decrease with increasing nucleophile basicity. However, for the same nucleophile, the $\Delta H^{\neq}$ values measured for the Ni(II) complex are more or less similar (in case of piperidine) or slightly lower than that of the corresponding palladium(II) complex. This indicates that the observed higher rates measured for the palladium(II) complex relative to that of nickel(II) are due to entropy effects.

The entropy of activation of substitution reactions of the nickel(II) complex are usually more negative as compared to the reactions of the corresponding palladium(II) complex. This implies that the negative charge in the transition state(s) of the nickel(II) complex is more delocalized relative to that of the palladium(II) complex which resists charge redistribution.

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