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Kinetics and Mechanism of Ligand Substitution in Four-Coordinate Nickel(II) Chelate Complexes: Study on the Reactivities of Planar and Tetrahedral Configurational Isomers and Octahedral Adducts

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Stopped-flow spectrophotometry has been used to study the kinetics of ligand substitution in neutral four-coordinate bis chelate nickel(II) complexes NiA_2 (=bis(*N*-alkylsalicylaldiminato)nickel(II) ($Ni(R\text{-}sal)_2$), bis(*N,N'*-dialkyl-2-aminotropone iminato)-nickel(II) ($Ni(R_2\text{-}ati)_2$), bis(*N*-alkylbenzoylacetone iminato)nickel(II) ($Ni(R\text{-}bza)_2$)) by acetylacetone (=HB) and by *N,N'*-disalicylideneethylenediamine ($=H_2B$) at different temperatures. Substitution by HB in methanol takes place in two observable steps, both following a two-term rate law; rate = $(k_S + k_{HB}[HB])[NiA_2]$. For substitution by H_2B in acetone only one step is observed, which follows a simple rate law; rate = $k_{H_2B}[H_2B][NiA_2]$. Complexes $Ni(R\text{-}sal)_2$, $Ni(R_2\text{-}ati)_2$, and $Ni(R\text{-}bza)_2$ are subject to a fast configurational equilibrium: planar ⇌ tetrahedral. The equilibrium constant $K_{p,t}$ for this isomerization was determined by ^1H NMR spectroscopy in acetone for several complexes $Ni(R_2\text{-}ati)_2$ differing in the alkyl group R. It is shown by correlation of the data obtained for $K_{p,t}$, k_{H_2B}, and the activation parameters ΔH^* and ΔS^* that the entering ligand H_2B attacks only the planar configurational isomer and that the tetrahedral isomer is inert toward ligand substitution by H_2B. For several complexes $Ni(R\text{-}sal)_2$ the equilibrium constants K_1 and K_2 for adduct formation with pyridine in acetone were determined by spectrophotometric titration. It is found that $K_1(Ni(R\text{-}sal)_2py) \ll K_2(Ni(R\text{-}sal)_2(py)_2)$ and that substituents in the 5-position of the salicylaldehyde ring have a marked effect on the size of K_1 and K_2. Correlation of K_1 and K_2 with rate constant k_{H_2B} as determined in the presence of pyridine proves quantitatively that in the presence of pyridine the substitution reaction $Ni(R\text{-}sal)_2 + H_2B \rightarrow NiB + 2R\text{-}salH$ takes place exclusively via the pyridine-free planar complex, which is in a fast equilibrium with $Ni(R\text{-}sal)_2py$ and $Ni(R\text{-}sal)_2(py)_2$. The octahedral complex $Ni(R\text{-}sal)_2(py)_2$ is completely inert toward ligand substitution by H_2B. The mechanistic implications of these results are discussed.

Introduction

The coordination chemistry of nickel(II) is characterized by a remarkable flexibility in coordination number and coordination geometry. The formation of four-coordinate square-planar complexes (as to be expected by extrapolation for the d^8 series Pt(II)–Pd(II)–Ni(II)) is observed for a very limited number of ligands only.[1] The tendency of the $3d^8$ metal center of nickel(II) to become six-coordinate is strong. Another interesting aspect is that with several ligands[2] (such as the *N*-alkylsalicylaldimines) nickel(II) forms four-coordinate complexes, which are subject to a fast configurational equilibrium: planar ⇌ tetrahedral.[2]

Recently we reported[1] on the kinetics of ligand substitution in several bis(*N*-alkylsalicylaldiminato)nickel(II) complexes, $Ni(R\text{-}sal)_2$ = I = NiA_2, by bidentate ligands HB (such as *N*-alkylsalicylaldimines, β-diketones, 8-hydroxyquinoline) in alcohol solvents according to (1). The kinetics observed follow the

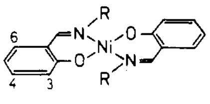
$$NiA_2 + 2HB \rightarrow NiB_2 + 2HA \qquad (1)$$

two-term rate law (2), typically found for ligand substitution in

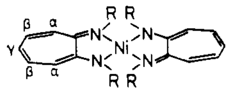
$$\text{rate} = k_{obsd}[NiA_2] = (k_S + k_{HB}[HB])[NiA_2] \qquad (2)$$

d^8 metal complexes. The relative contributions of the "solvent path" k_S and of the "ligand path" $k_{HB}[HB]$ depend on the coordination geometry of $Ni(R\text{-}sal)_2$.[1] Interestingly enough the solvent path k_S has to be mechanistically interpreted as being initiated by solvent attack at the *donor oxygen*, not at the metal.[1,3]

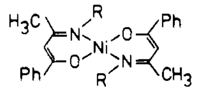
Complexes I–III basically prefer a planar coordination geometry. In solution they are subject to the fast configurational equilibrium (3), which can be detected and characterized by ^1H NMR spectroscopy due to the change in spin state involved. Sterically demanding groups R shift equilibrium 3 to the right side; i.e., they favor the formation of the tetrahedral isomer.



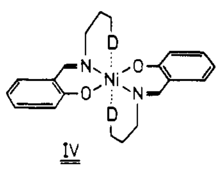
I ≡ $Ni(R\text{-}sal)_2$



II ≡ $Ni(R_2\text{-}ati)_2$



III ≡ $Ni(R\text{-}bza)_2$



IV

$$\begin{array}{ccc} \text{planar} & \rightleftharpoons & \text{tetrahedral} \\ S = 0 & & S = 1 \end{array} \qquad (3)$$

When it is taken into account that the planar form of complexes I and III tends to become octahedral by addition of Lewis bases[1,4] (e.g., solvent molecules, pyridine) or by self-association at higher concentrations, the complete description of the system is given by (4). Octahedral coordination is also observed for complexes IV, in which the alkyl group R attached to the donor nitrogen offers an additional donor group D.

$$\text{octahedral} \xrightleftharpoons{K_{o,p}} \text{planar} \xrightleftharpoons{K_{p,t}} \text{tetrahedral} \qquad (4)$$

The present contribution focuses on the question of which of the three species involved in equilibrium 4 is the most reactive one when ligand substitution in complexes I–IV = NiA_2 according to (5a) and (5b) takes place ((5a), solvent methanol, HB = acetylacetone = Hacac; (5b), solvent acetone, H_2B = *N,N'*-disalicylideneethylenediamine = H_2salen).

$$NiA_2 + 2HB \rightarrow NiB_2 + 2HA \qquad (5a)$$

$$NiA_2 + H_2B \rightarrow NiB + 2HA \qquad (5b)$$

In addition to these kinetic studies spectroscopic investigations were carried out. The ligand field spectra of complexes I–IV in

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(1) Schumann, M.; von Holtum, A.; Wannowius, K. J.; Elias, H. *Inorg. Chem.* **1982**, *21*, 606.

(2) (a) Holm, R. H.; Everett, G. W.; Jr.; Chakravorty, A. *Prog. Inorg. Chem.* **1966**, *7*, 83. (b) Holm, R. H.; O'Connor, M. J. *Ibid.* **1971**, *14*, 241.

(3) Ligand substitution in the corresponding copper(II) complexes $Cu(R\text{-}sal)_2$ as studied in methanol also follows rate law 2, and the ligand-independent contribution k_S is also initiated by methanol attack at the donor oxygen through hydrogen bonding. See: Elias, H.; Hasserodt-Taliaferro, Chr.; Hellriegel, L.; Schönherr, W.; Wannowius, K. J. *Inorg. Chem.*, following paper in this issue.

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acetone were used for a qualitative description of the state of coordination of these complexes in solution. For complexes II the equilibrium constant $K_{p,t}$ was determined by ^{1}H NMR spectroscopy. Finally, for some of the type I complexes studied the equilibrium constants K_1 and K_2 for pyridine addition according to (6) were obtained by spectroscopic titration in acetone (py =

$$\underset{\text{planar}}{NiA_2} + 2py \underset{}{\overset{K_1}{\rightleftharpoons}} \underset{\text{pyramidal}}{NiA_2py} + py \overset{K_2}{\rightleftharpoons} \underset{\text{octahedral}}{NiA_2(py)_2} \qquad (6)$$

pyridine). Equilibrium constants $K_{p,t}$, K_1, and K_2 and their correlation with the rate data obtained are taken as the basis for an analysis of the relative reactivities of the planar, tetrahedral, and octahedral forms of complexes I–IV.

Experimental Section

Abbreviations. For the organic group R in complexes I–III the following symbols are used: Me = methyl; Et = ethyl; *n*-Pr = *n*-propyl; *i*-Pr = isopropyl; *n*-Pe = *n*-pentyl; *t*-Bu = *tert*-butyl; All = allyl; Bz = benzyl; Ph = phenyl.

Complexes and Ligands. Complexes I and IV were prepared as described earlier;[1] the preparation of complexes III followed standard procedures.[5] The following method was applied to obtain complexes II: 2-chlorotropone was prepared[6] by chlorination of tropolone (as obtained from cyclopentadiene and dichloroketene in a two-step procedure[7]) and purified by recrystallization from water (<70 °C). The reaction of 2-chlorotropone with triethyloxonium tetrafluoroborate ("Meerwein's salt") and absolute ethanol led to 1,2-diethoxytropylium tetrafluoroborate.[8] To 1.0 g (3.8 mmol) of this salt was added an excess (0.5–1.0 mL) of the corresponding primary amine, which led to a mixture of intense yellow color. A soluton of 0.47 g (1.9 mmol) of $Ni(OAc)_2 \cdot 4H_2O$ in 15 mL of MeOH was added to this mixture, which was then heated for 30 min. The solution became reddish brown to black-brown upon formation of the corresponding complex $Ni(R_2\text{-ati})_2$, which precipitated directly or precipitated upon concentrating and cooling the solution. Recrystallization from methanol or acetic acid ethyl ester yielded shiny red-brown to black crystals. The results of elemental analysis agreed well with the data calculated, and the melting points were in satisfying agreement with those reported.[9] The complex Ni(*i*-Pr_2-ati)$_2$ (mp 136–137 °C) has not yet been described. Anal. Calcd for $C_{26}H_{38}N_4Ni$: C, 67.11; H, 8.23; N, 12.04. Found: C, 66.90; H, 8.33; N, 11.91.

Acetylacetone (reagent grade, Merck, Darmstadt, West Germany) was distilled before use (bp 136 °C). *N,N'*-Disalicylideneethylenediamine was prepared from salicylaldehyde and ethylenediamine in ethanol and recrystallized from acetone (mp 125–126 °C).

Solvents. Methanol and acetone (reagent grade, Merck, Darmstadt, West Germany) were dried dynamically and statically over 3-Å molecular sieves. For part of the experiments the solvent acetone was used without previous drying.

Kinetic Measurements. Most of the kinetic measurements were done with a modified[10] Durrum stopped-flow spectrophotometer connected to a transient recorder (type 513A, IEEE 488 interface; Physical Data Inc.). The slow reactions were followed with a Zeiss DMR22 spectrophotometer. The experiments were carried out under pseudo-first-order conditions ([ligand] ≥ 10[complex]) and monitored at 550–620 nm. Rate constants were obtained by fitting an exponential function to a total of 100 data points with a computer program based on the least-squares method (deviation from ideal first-order kinetics ≤1%).

^{1}H NMR Measurements. A Fourier-transform spectrometer, Bruker WH-90 (90 MHz), was used to study the configurational equilibria (3) of complexes II. The spectra were recorded in acetone-d_6 in the temperature range 193–323 K (standard $(CH_3)_4Si$). The paramagnetic band shift observed is a direct measure for the fraction of the tetrahedral (paramagnetic) isomer present in solution.[2b,11] Assuming that the paramagnetic shift follows Curie's law ($\Delta\nu_{para} \sim T^{-1}$), the chemical shift $\Delta\nu$ of a proton is given by (7) ($\Delta G_{p,t}°$, $\Delta H_{p,t}°$, and $\Delta S_{p,t}°$ are the thermodynamic parameters describing equilibrium 3; $\Delta\nu_{dia}$ = diamagnetic shift). The second term in (7) presents the paramagnetic shift $A \cdot T^{-1}$ multiplied by the mole fraction of the paramagnetic isomer (A depends on the hyperfine coupling constant and on the radiation frequency of the spectrometer).

$$\begin{aligned}\Delta\nu(T) &= \Delta\nu_{dia} + AT^{-1}[\exp(\Delta G_{p,t}°/RT) + 1]^{-1} \\ &= \Delta\nu_{dia} + AT^{-1}[\exp(\Delta H_{p,t}°/RT)\exp(-\Delta S_{p,t}°/R) + 1]^{-1} \qquad (7)\end{aligned}$$

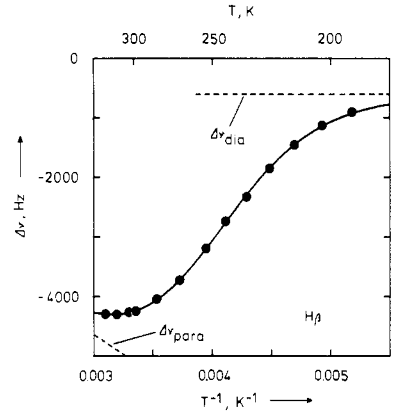

Figure 1. Temperature dependence of the chemical shift of the H_β resonance for the complex $Ni(Bz_2\text{-ati})_2$ in acetone-d_6.

Table I. Thermodynamic Parameters Describing the Configurational Equilibrium Planar ⇌ Tetrahedral of Several Complexes $Ni(R_2\text{-ati})_2$ in Acetone

R	$\Delta H_{p,t}°$, kJ/mol	$\Delta S_{p,t}°$, kJ/(mol K)	$\Delta G_{p,t}°(298)$, kJ/mol	$K_{p,t}^{298}$ [a]
Me	30.9 ± 0.8	70.2 ± 2.0	+10.0 ± 1.0	0.018 (0.016)
Et[b]	8.4 ± 2.4	69 ± 13	−12.2 ± 4.5	140 (36)
n-Pr[b]	8.2 ± 2.8	67 ± 15	−11.7 ± 5.2	110 (57)
i-Pr	*c*	*c*	<−12[d]	>100[d]
All	16.2 ± 0.6	81.3 ± 2.6	−8.1 ± 1.0	26 (13)
Ph	6.9 ± 0.6	36.7 ± 3.2	−4.1 ± 1.1	5.2 (3.0)
Bz	20.4 ± 0.5	79.9 ± 2.4	−3.4 ± 0.9	4.0 (5.2)

[a] The numbers in brackets refer to the solvent chloroform and were taken from the literature.[2b,12] [b] The relatively large error for ΔH, ΔS, and ΔG is due to the fact that even at the lowest temperature the fraction of the planar species is very small. [c] Not determinable; Ni(*i*-Pr_2-ati)$_2$ is almost completely tetrahedral over the whole temperature range. [d] Estimated.

Least-squares fitting of (7) to the experimentally obtained data for $\Delta\nu(T)$ led to the unknown parameters A, $\Delta H_{p,t}°$, and $\Delta S_{p,t}°$ (the value for $\Delta\nu_{dia}$ was taken from the diamagnetic complex $Zn(Et_2\text{-ati})_2$ or from the complex $Ni(Me_2\text{-ati})_2$ at low temperatures). The results of this fitting procedure were in all cases best for the β protons in complexes II. For the complex Ni(*i*-Pr_2-ati)$_2$, which is tetrahedral (=paramagnetic) over the whole temperature range, only the chemical shift of the β protons led to the expected straight line for $\Delta\nu = f(T^{-1})$ with an intercept corresponding to $\Delta\nu_{dia}$ of the reference complex.

Figure 1 demonstrates the temperature dependence of the H_β resonance for the complex $Ni(Bz_2\text{-ati})_2$.

Equilibrium Constants. Equilibrium constants K_1 and K_2 for pyridine addition according to (6) were determined as described earlier.[1]

Results and Discussion

Configurational Equilibria and State of Coordination. The temperature dependence of the chemical shift of the β protons of complexes II dissolved in acetone-d_6 was used to calculate the thermodynamic parameters describing equilibrium 3. Fitting of eq 7 to the data obtained for $\Delta\nu(T)$ led to $\Delta H_{p,t}°$, $\Delta S_{p,t}°$, $\Delta G_{p,t}°(298)$ and $K_{p,t}(298)$ as compiled in Table I. It follows from the positive $\Delta H_{p,t}°$ values that the isomerization planar → tetrahedral is endothermic in all cases; i.e., the planar configurational isomer is the energetically more stable one. The effect of the organic group R, however, is very significant in the sense that R = Me yields an almost completely planar complex ($K_{p,t}$ = 0.018),

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Table II. Qualitative Description of the Configurational State of Complexes $Ni(R\text{-}sal)_2$ and $Ni(R\text{-}bza)_2$ in Acetone As Based on Visible and Near-IR Spectra

$Ni(R\text{-}sal)_2$		$Ni(R\text{-}bza)_2$	
R	main confignl isomer[a]	R	main confignl isomer[a]
Et, *n*-Pr, All, *n*-Pe, Bz	p	Me	p
i-Pr	$p \rightleftharpoons t$	Et, *n*-Pr	$p \rightleftharpoons t$
t-Bu	t	*i*-Pr	t

[a] Meaning of the symbols: p = planar; t = tetrahedral.

Table III. Equilibrium Constants K_1 and K_2 for the Addition of Pyridine to Complexes $Ni(R\text{-}sal)_2$ in Acetone at 298 K according to Reaction 6

R	X^5 [a]	K_1, M^{-1}	K_2, M^{-1}	$\beta = K_1K_2$, M^{-2}	K_2/K_1
n-Pr	OCH_3	0.49 ± 0.12	14.6 ± 3.2	7.2	29.6
n-Pr	H	0.96 ± 0.21	28.4 ± 5.6	27.2	29.7
n-Pr	Br	4.61 ± 0.84	138 ± 24	636	30.0
i-Pr	H	4.35 ± 0.36[b]	10.5 ± 1.4	45.7	2.4[c]
i-Pr	Br	24.0 ± 2.0[b]	49.9 ± 5.6	1200	2.1[c]

[a] X^5 = substituent in 5-position of the salicylaldehyde ring. [b] The planar complex $Ni(i\text{-}Pr\text{-}sal)_2$ is in equilibrium with its (pseudo) tetrahedral configurational isomer. The number obtained for K_1 is therefore $K_1' = K_1/(1 + K_{p,t})$. Assuming $K_{p,t} \approx 1$, one obtains $K_1 = 2K_1'$. [c] K_2/K_1' (see footnote *b*).

whereas R = Et, *n*-Pr, *i*-Pr ($K_{p,t}$ = 140, 110, >100) shifts the equilibrium strongly to the side of the tetrahedral isomer. With R = All, Ph, Bz an intermediate situation is produced, favoring the tetrahedral species. It is worthwhile to note that the equilibrium constants $K_{p,t}$ as determined for chloroform[2b,12] instead of acetone (see Table I) are somewhat smaller but appear to follow roughly the same pattern as far as the effect of the organic group R is concerned.

The visible and near-IR absorption spectra of complexes II are in full agreement with the equilibrium constants $K_{p,t}$ (Table I) in the sense that the typical "square-planar bands"[13] ($K_{p,t}$ small) and "tetrahedral bands"[13] ($K_{p,t}$ large) are consistently observed. In the case of the complexes $Ni(R\text{-}sal)_2$ (type I) and $Ni(R\text{-}bza)_2$ (type III) the absorption spectra were therefore used as the basis for a qualitative description of the configurational state of these complexes in acetone solution (see Table II). It is not surprising to see that only for R = *i*-Pr and *t*-Bu are complexes I and III forced to become (pseudo) tetrahedral, whereas complexes II are strongly distorted even by R = Et. The explanation lies in the fact that in complexes $Ni(R_2\text{-}ati)_2$ each ligand carries two R groups, which creates enormous steric hindrance in a planar arrangement.

The equilibrium constants K_1 and K_2 describing the addition of pyridine to the complexes $Ni(n\text{-}Pr\text{-}sal)_2$ and $Ni(i\text{-}Pr\text{-}sal)_2$ in acetone according to eq 6 are compiled in Table III. These data reflect the Lewis acidity of the complexes and allow the calculation of the fractions of the planar, five-coordinate, and six-coordinate species present at a given pyridine concentration. The finding that $K_2 \gg K_1$ for $Ni(n\text{-}Pr\text{-}sal_2$ and its substituted analogues is in agreement with earlier studies in toluene and benzene.[1,4] Substituents X^5 in the complex $Ni(n\text{-}Pr\text{-}sal)_2$ have a distinct effect on the size of K_1 and K_2 but no effect on the ratio K_2/K_1 (~30). As to be expected, an electron-withdrawing substituent such as X^5 = Br increases the Lewis acidity of the metal center (and, hence, the size of K_1 and K_2) and vice versa (see Table III).

The ratio K_2/K_1 obtained for adduct formation of the complex $Ni(i\text{-}Pr\text{-}sal)_2$ is much smaller ($K_2/K_1 \approx 1$) than that obtained for the complex $Ni(n\text{-}Pr\text{-}sal)_2$ ($K_2/K_1 \approx 30$). This behavior is possibly due to the sterically more demanding isopropyl groups, which hinder the formation of the bis adduct. The fact that with 2-methylpyridine adduct formation is clearly restricted to the monoadduct[14] is in line with this steric argument.

Table IV. Rate Constants[a] for the First and Second Step of Reaction 8 at 298 K in Methanol

	first step		second step	
R	$k_S(1)$, s^{-1}	$k_{HB}(1)$, M^{-1} s^{-1}	$k_S(2)$, s^{-1}	$k_{HB}(2)$, M^{-1} s^{-1}
Me	*b*	7.87 ± 0.94	0.066 ± 0.023	0.269 ± 0.045
Et	*b*	0.383 ± 0.017	(9.4 ± 2.6) × 10^{-3}	0.094 ± 0.012
n-Pr	*b*	0.575 ± 0.029	(3.6 ± 0.6) × 10^{-3}	0.153 ± 0.009
i-Pr	*b*	(1.07 ± 0.06) × 10^{-5}	*d*	*d*
All	*b*	1.04 ± 0.06	(1.5 ± 0.3) × 10^{-3}	0.064 ± 0.004
Ph	(2.6 ± 0.2) × 10^{-3}	0.160 ± 0.004	*d*	*d*
Bz	*b*	*c*	<4 × 10^{-4}	0.033 ± 0.003

[a] From measurements at five to eight different concentrations in the range [Hacac] = [HB] = 0.01–1.0 M; $k_{obsd} = (k_S + k_{HB}[HB])$; $[Ni(R_2\text{-}ati)_2] = (1\text{–}2.5) \times 10^{-4}$ M. [b] Negligibly small. [c] Not clearly determinable. [d] Not observed.

Kinetic Results. Table IV summarizes the rate constants obtained for ligand substitution in several complexes $Ni(R_2\text{-}ati)_2$ ($=NiA_2$) by acetylacetone (=HB) in methanol according to (8).

$$NiA_2 \xrightarrow[\text{+HB, -HA}]{\text{step 1}} NiAB \xrightarrow[\text{+HB, -HA}]{\text{step 2}} NiB_2 \tag{8}$$

In contrast to the corresponding complexes $Ni(R\text{-}sal)_2$[1] the two steps involved in (8) are both observed and both follow rate law 2, although the ligand-independent term k_S is negligibly small for the first step. Exceptions are the complexes $Ni(Ph_2\text{-}ati)_2$ and $Ni(i\text{-}Pr_2\text{-}ati)_2$, for which only one step is observed.

For comparative studies it is most desirable to have a reaction and reaction conditions as simple as possible. We therefore decided to replace the system NiA_2/Hacac/MeOH (reaction 8) by the system NiA_2/H_2salen/acetone (reaction 5b) for the following reasons: (i) the conversion of $NiA_2 \rightarrow Ni(salen)$ is a one-step process for all types of complexes studied, accompanied by sufficiently large changes in absorbance, and (ii) the rate of reaction 5b follows rate law 9, which is practically a simple one-term rate equation, since in acetone k_S is negligibly small.[15]

$$\text{rate} = k_{obsd}[NiA_2] = (k_S + k_{H_2B}[H_2B])[NiA_2] \approx k_{H_2B}[H_2B][NiA_2] \tag{9}$$

The rate constants k_{H_2B} obtained for a variety of complexes I–IV reacting according to (5b) are compiled in Table V. Table VII presents the rate constants for some substituted complexes $Ni(R\text{-}sal)_2$. There is good reason to assume that k_{H_2B} describes the substitution of the first of the two leaving ligands HA in NiA_2, the substitution of the second being a fast consecutive step. One argument is that the observed change in absorbance corresponds exactly to pure complex NiA_2 at $t = 0$ and to pure product Ni(salen) at $t = \infty$. In addition, the absorbance/time data follow a single-exponential function with an accuracy >99%.

Kinetic Comparison of Planar and Tetrahedral Configurational Isomers. Tables I and II summarize the information on the configurational state of complexes I–III in acetone solution. Taking this information and comparing it with the rate constants presented in Table IV and Table V, one immediately recognizes qualitatively that (i) for a given type of complex the nature and steric demands of the organic group R determine the fraction of the tetrahedral isomer present according to (3) and (ii) the higher the fraction of the tetrahedral isomer, the slower the complex reacts. An extreme example of this difference in reactivity is the

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(15) The aprotic solvent acetone is obviously not able to open a solvent-initiated, ligand-independent reaction channel for reaction 5b. The very small and not really reproducible k_S values obtained are probably due to protic trace impurities such as residual water or alcohol.

Table V. Rate Constants[a] for Reaction 5b of Complexes I–IV at 298 K in Acetone

complexes I		complexes II		complexes III		complexes IV	
R	k_{H_2B}, M^{-1} s^{-1}	R	k_{H_2B}, M^{-1} s^{-1}	R	k_{H_2B}, M^{-1} s^{-1}	D	k_{H_2B}, M^{-1} s^{-1}
Et	86.1 ± 2.7	Me	4.35 ± 0.14	Me	39.3 ± 1.7	Et	69.2 ± 2.2
n-Pr	57.6 ± 2.0	Et	0.0282 ± 0.0011	Et	19.8 ± 1.2	$N(CH_3)_2$	1.81 ± 0.08
i-Pr	154 ± 5	*n*-Pr	0.0303 ± 0.0026	*n*-Pr	13.6 ± 0.9	OCH_3	42.4 ± 1.4
All	94.9 ± 2.9	*i*-Pr	$<10^{-3}$	*i*-Pr	0.0240 ± 0.0008		
t-Bu	0.0280 ± 0.0011	All	0.393 ± 0.013				
n-Pe	69.2 ± 2.2	Ph	2.18 ± 0.07				
Bz	48.8 ± 1.5	Bz	0.0607 ± 0.0022				

[a] From measurements at six different concentrations in the range $[H_2B] = [H_2salen] = 0.01–0.1$ M; $k_{obsd} = (k_S + k_{H_2B}[H_2B])$, but k_S is negligibly small; [complex] = 2.5×10^{-4} M (complexes II) and 1×10^{-3} M (complexes I, III, IV).

Table VI. Activation Parameters[a] for Reaction 5b of Complexes $Ni(Me_2\text{-ati})_2$, $Ni(Et_2\text{-ati})_2$, and $Ni(All_2\text{-ati})_2$ in Acetone

R	ΔH^*, kJ/mol	ΔS^*, J/(mol K)	ΔH^*_{cor},[b] kJ/mol	ΔS^*_{cor},[b] J/(mol K)
Me	49.8 ± 1.8	−66 ± 6	49.8 ± 1.8[c]	−66 ± 6[c]
Et	38.9 ± 1.9	−144 ± 7	47.3 ± 4.3	−75 ± 20
All	29.7 ± 1.8	−153 ± 6	45.9 ± 2.4	−72 ± 9

[a] From measurements at six different temperatures in the range 289–314 K at [complex] = 2.5×10^{-4} and $[H_2B] = [H_2salen] = 0.1$ M; $k_{H_2B} = k_{obsd}/[H_2B]$. [b] $\Delta H^*_{cor} = \Delta H^* + \Delta H_{p,t}°$ and $\Delta S^*_{cor} = \Delta S^* + \Delta S_{p,t}°$ (for $\Delta H_{p,t}°$ and $\Delta S_{p,t}°$ see Table I). [c] The correction according to footnote *b* is not applied to the complex $Ni(Me_2\text{-ati})_2$, which is almost completely planar.

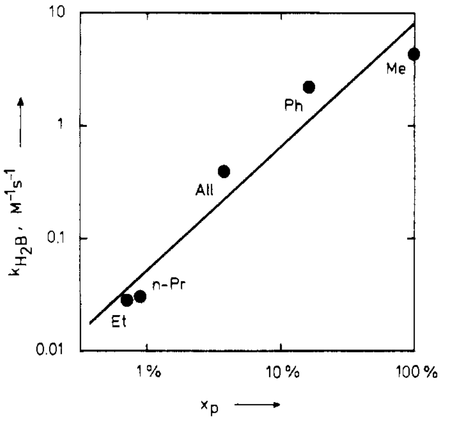
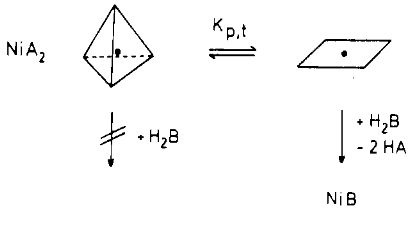


Figure 2. Plot of rate constant k_{H_2B} (see Table V) vs. the mole fraction of the planar isomer of complexes $Ni(R_2\text{-ati})_2$.

finding (see $k_{HB}(1)$ values in Table IV) that the planar complex $Ni(Me_2\text{-ati})_2$ reacts almost 10^6 times faster than the tetrahedral complex $Ni(i\text{-}Pr_2\text{-ati})_2$. For the complexes $Ni(R_2\text{-ati})_2$, for which the equilibrium constant $K_{p,t}$ was determined (see Table I), the mole fraction x_p of the planar isomer can be calculated for any complex concentration. It is interesting to note that the plot of log k_{H_2B} (data taken from Table V) vs. log x_p gives a somewhat linear relationship with a slope of 1.10 (see Figure 2).[16] This means that independent of the nature of the organic group R the fraction of the planar isomer roughly controls the rate of ligand substitution of complexes $Ni(R_2\text{-ati})_2$ according to (5b).

A more direct proof for the assumption that only the planar configurational isomer is the reactive one follows from the activation parameters compiled in Table VI. The data obtained for ΔH^* and ΔS^* differ considerably for the planar complex $Ni(Me_2\text{-ati})_2$ and for the mainly tetrahedral complexes $Ni(Et\text{-ati})_2$ and $Ni(All_2\text{-ati})_2$. Interestingly enough, however, the values of the activation enthalpy and of the activation entropy become identical for all three complexes (within the limits of error), when the values originally obtained are "corrected" for $\Delta H_{p,t}°$ and $\Delta S_{p,t}°$, the enthalpy and entropy changes associated with the conversion tetrahedral → planar (see Table I).

Scheme I. Kinetic Behavior of Planar and Tetrahedral Configurational Isomers in Ligand Substitution



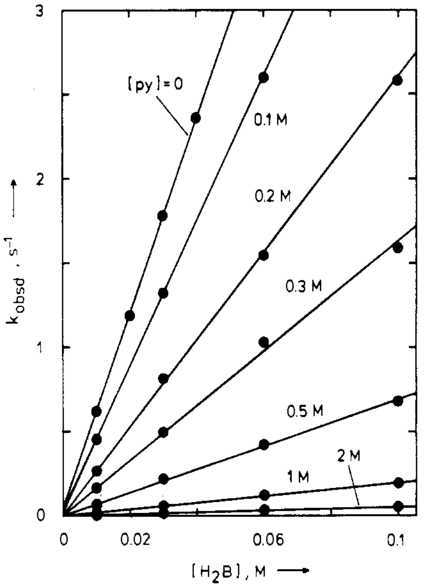


Figure 3. Plot of the experimental rate constant k_{obsd} vs. the concentration of the entering ligand for the complex $Ni(n\text{-}Pr\text{-}sal)_2$ reacting according to eq 5b in the presence of pyridine.

In summary, the behavior of complexes I–III toward ligand substitution according to (5b) can be described as shown in Scheme I.

Kinetic Comparison of Square-Planar and Octahedral Complexes. It can be concluded from similar systems[17] that the type IV complex with D = $N(CH_3)_2$ is subject to a fast ($k \approx 10^6–10^7$ s^{-1}) intramolecular planar ⇌ octahedral isomerization. The fact that rate constant k_{H_2B} for this complex reacting according to (5b) is 38-fold smaller than for the four-coordinate planar complex $Ni(n\text{-}Pe\text{-}sal)_2$ (see Table V) is an indication for a reduced (or even nonexisting) reactivity of the octahedral complex as compared to that for the planar complex. The slight decrease in k_{H_2B} for the type IV complex with D = OCH_3 instead of D = Et could point to a weak interaction of the methoxy group with the nickel.

For further proof of the inertness of the octahedral species the reaction of the complex $Ni(n\text{-}Pr\text{-}sal)_2$ according to (5b) was studied in the presence of increasing amounts of pyridine. Since the

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(16) The data for R = Bz (k_{H_2B} = 0.061 M^{-1} s^{-1}; x_p = 20%) were omitted in Figure 2 because k_{H_2B} lies far below the straight line (i.e., appears to be too small), which is probably due to the four large phenyl rings of the benzyl groups shielding the nickel.

(17) Godfrey, A. F.; Beattie, J. K. *Inorg. Chem.* **1983**, *22*, 3794.

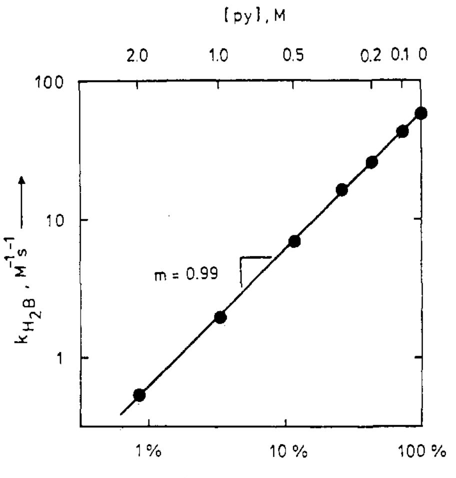
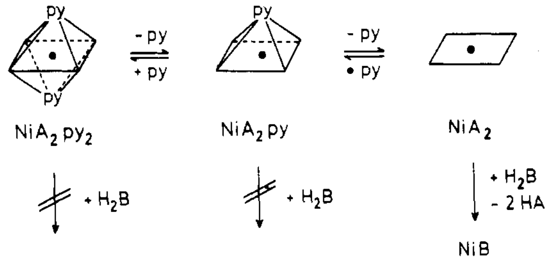


Figure 4. Dependence of rate constant k_{H_2B} on the fraction of the pyridine-free planar complex Ni(n-Pr-sal)$_2$ reacting according to eq 5b in the presence of pyridine.

Scheme II. Kinetic Behavior of Five- and Six-Coordinate Adducts in Ligand Substitution



equilibrium constants K_1 and K_2 for pyridine addition are known (see Table III), the concentration of the planar complex Ni(n-Pr-sal)$_2$ and of its mono- and bisadducts can be calculated for any pyridine concentration. Figure 3 proves that the rate of the second-order reaction between Ni(n-Pr-sal)$_2$ and H$_2$salen is considerably reduced with increasing pyridine concentration. In Figure 4 the data for k_{H_2B} (obtained from the slope of the straight lines in Figure 3) are plotted vs. the mole fraction x_{NiA_2} of the pyridine-free planar complex Ni(n-Pr-sal)$_2$, as calculated from $K_1 = 0.96$ M^{-1} and $K_2 = 28.4$ M^{-1} (see Table III). The linear correlation between log k_{H_2B} and log x_{NiA_2} is excellent for a range of more than 2 orders of magnitude and yields a slope of 0.99, which means that rate constant k_{H_2B} obtained in the presence of pyridine can be described by $k_{H_2B} = 57.6x_{NiA_2}$ M^{-1} s^{-1} (57.6 M^{-1} s^{-1} = k_{H_2B} for Ni(n-Pr-sal)$_2$ in the absence of pyridine). This means that the reaction observed takes place exclusively via the planar complex Ni(n-Pr-sal)$_2$. Scheme II summarizes the findings.

Two further findings are of interest. The addition of 1.0 M of the sterically hindered base 2,6-dimethylpyridine instead of pyridine has no effect on k_{H_2B} at all, which supports the interpretation that adduct formation is the rate-reducing factor. The second point of interest is the fact that even at a pyridine concentration of 2 M plot of $k_{H_2B} = f(H_2B)$ is still linear (see Figure 3). This means that the equilibration octahedral ⇌ planar is so fast[18] that even at [H$_2$B] = 0.1 M the reaction octahedral → planar, which precedes the attack of H$_2$salen, does not become rate controlling. Even with the stronger nucleophile 4-methylpyridine (which increases K_1K_2 by a factor of 2) and at [4-Mepy] = 4 M (where the rate of ligand substitution in Ni(n-Pr-sal)$_2$ with X^5 = Br is reduced by a factor of 10^4!) the experimental rate constant k_{obsd} increases linearly with increasing concentration of the attacking ligand H$_2$salen and does not fall off.

Table VII. Rate Constants[a] for Reaction 5b of X^5-Substituted[b] Complexes Ni(R-sal)$_2$ at 298 K in Acetone and Equilibrium Constants K_1 for Pyridine Addition

R	X^5	k_{H_2B}, M^{-1} s^{-1}	K_1,[c] M^{-1}
n-Pr	OCH$_3$	64.4 ± 2.2	0.49
n-Pr	H	57.6 ± 2.0	0.96
n-Pr	Br	105 ± 4	4.6
i-Pr	H	154 ± 5	4.4
i-Pr	Br	266 ± 9	24

[a] From measurements at six different concentrations in the range [H$_2$B] = [H$_2$salen] = 0.01–0.1 M; $k_{obsd} = k_{H_2B}$[H$_2$B]; [complex] = 1 × 10^{-3} M. [b] X^5 = substituent in 5-position of the salicylaldehyde ring. [c] Data taken from Table III.

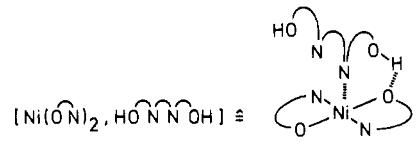
Mechanism of Ligand Substitution. Rate constant k_{H_2B} is a second-order rate constant obviously describing the bimolecular process ("ligand pathway") typically observed for ligand substitution in planar d^8 metal complexes. The associative character of the rate term k_{H_2B}[H$_2$B][NiA$_2$] in (9) is confirmed by the finding[19] that any variation in the nature of the attacking ligand H$_2$salen (introduction of substituents in the salicylaldehyde ring or in the ethylene bridge) has a distinct effect on the size of k_{H_2B}. Within the sequence of steps 10–12 with Ni(O⌒N)$_2$ = NiA$_2$

$$\mathrm{Ni(O{\frown}N)_2 + HO{\frown}N{\frown}N{\frown}OH \rightleftharpoons [Ni(O{\frown}N)_2,HO{\frown}N{\frown}N{\frown}OH]} \quad (10)$$

$$\mathrm{[Ni(O{\frown}N)_2,HO{\frown}N{\frown}N{\frown}OH] \xrightarrow{slow} (O{\frown}N)Ni(O{\frown}N{\frown}N{\frown}OH) + HO{\frown}N} \quad (11)$$

$$\mathrm{(O{\frown}N)Ni(O{\frown}N{\frown}N{\frown}OH) \xrightarrow{fast} Ni(O{\frown}N{\frown}N{\frown}O) + HO{\frown}N} \quad (12)$$

(planar form) and HO⌒N⌒N⌒OH = H$_2$salen, equilibrium 10 is very fast. The rate-controlling step is (11), whereas step 12 is a fast consecutive reaction. As pointed out earlier,[1] the formation of the "adduct" [Ni(O⌒N)$_2$,HO⌒N⌒N⌒OH] can best be described as a "double acid/base reaction" in the sense that both the complex and the entering ligand act as "biphilics" according to (13). The



(13)

rate-controlling step would then involve rupture of the Ni–O(leaving ligand) bond and proton transfer from the entering to the leaving ligand.

It follows from Table VII that the effect of substituents X^5 on K_1 (equilibrium constant for the formation of the monoadduct with pyridine) is much more pronounced than on rate constant k_{H_2B}. On the basis of sequence (10)–(12) and (13) this is not surprising, because any substituent effect on the electron density at the nickel will be accompanied by a corresponding effect on the electron density at the donor oxygen of the coordinated ligand. This means that an electron-withdrawing substituent X^5 will make the nickel a better Lewis acid and the coordinated oxygen a poorer Brønsted base or proton acceptor. Both effects are counteracting and partly compensating each other as far as the formation of the intermediate shown in (13) is concerned. The overall substituent effect on k_{H_2B} is therefore small.

The mechanistic interpretation given here for reactions 5b and 8 is rather close to suggestions made by other authors[20,21] to explain the kinetics of ligand substitution in similar nickel(II) complexes, mainly those with a S$_4$ set of donor atoms.

Conclusions

Ligand substitution in neutral four-coordinate nickel(II) complexes of type I–III occurs in acetone exclusively through a lig-

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(18) Relaxation techniques were applied to measure the rate of the forward and backward reactions of the equilibrium planar ⇌ octahedral for several nickel(II) complexes; see for example: (a) Kluiber, R. W.; Kukla, R.; Thaller, F. *J. Coord. Chem.* **1973**, *3*, 39. (b) Sachinidis, J.; Grant, M. W. *Aust. J. Chem.* **1983**, *36*, 2019. (c) Reference 17.

(19) Hess, D.; Elias, H., to be submitted for publication.

(20) Fayyaz, M. U.; Grant, M. W. *Aust. J. Chem.* **1979**, *32*, 2159.

(21) Pearson, R. G.; Sweigart, D. A. *Inorg. Chem.* **1970**, *9*, 1167.

and-dependent pathway with an associative mode of activation (A mechanism). Complexes I–III are subject to a fast configurational equilibrium; planar ⇌ tetrahedral. It follows from the sum of data collected that only the planar isomer is attacked by the entering ligand (attack at the tetrahedral isomer is undetectably small). The planar form of complexes I tends strongly to become octahedral in the presence of nucleophiles such as pyridine. It is clearly shown that the octahedral pyridine adducts of the complexes are inert toward ligand substitution and that substitution occurs exclusively through the four-coordinate planar complex, which in the presence of pyridine is in a fast equilibrium with the octahedral adduct.

Acknowledgment. The authors thank the "Deutsche Forschungsgemeinschaft" and the "Verband der Chemischen Industrie e.V." for support. Salicylaldehyde was kindly provided by Bayer AG, Leverkusen, West Germany.

Registry No. I (R = *n*-Pr, X^5 = OCH_3), 97403-47-9; I·2py (R = *n*-Pr, X^5 = OCH_3), 97403-43-5; I (R = *n*-Pr), 35795-69-8; I·2py (R = *n*-Pr), 35829-38-0; I (R = *n*-Pr, X^5 = Br), 97403-48-0; I·2py (R = *n*-Pr, X^5 = Br), 97403-44-6; I (R = *i*-Pr), 35968-67-3; I·2py (R = *i*-Pr), 35829-39-1; I (R = *i*-Pr, X^5 = Br), 97403-49-1; I·2py (R = *i*-Pr, X^5 = Br), 97403-45-7; I (R = Et), 35968-61-7; I (R = All), 55292-18-7; I (R = *t*-Bu), 40706-02-3; I (R = *n*-Pe), 35968-70-8; I (R = Bz), 68510-29-2; II (R = Me), 15379-97-2; II (R = Et), 14880-23-0; II (R = *n*-Pr), 15391-41-0; II (R = *i*-Pr), 77095-86-4; II (R = All), 97403-41-3; II (R = Ph), 97403-42-4; II (R = Bz), 16828-51-6; III (R = Me), 97465-97-9; III (R = Et), 97465-98-0; III (R = *n*-Pr), 14568-02-6; III (R = *i*-Pr), 41553-43-9; IV (D = Et), 97415-90-2; IV [D = $N(CH_3)_2$], 97415-91-3; IV (D = OMe), 97403-46-8; acetylacetone, 123-54-6; *N*,*N'*-disalicylideneethylenediamine, 94-93-9.

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Effect of the Coordination Geometry and of Substituent Shielding on the Kinetics of Ligand Substitution in Copper(II) Chelates

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Stopped-flow spectrophotometry has been used to study the kinetics of ligand substitution in bis(*N*-R-salicylaldiminato)copper(II) complexes CuA_2 (R = H, OH, Me, Et, *i*-Pr, *t*-Bu, *neo*-Pe, phenyl) by bidentate ligands HB (*N*-ethylsalicylaldimine, acetylacetone) in methanol and ethylene glycol monomethyl ether at 298 K. A two-term rate law, rate = $(k_S + k_{HB}[HB])[\text{complex}]$, has been found. The substitution of the first ligand in CuA_2 is rate determining. The relative contributions of the terms k_S and $k_{HB}[HB]$ to the overall rate are controlled by the *N*-alkyl group R in the following sense: (i) small groups R (such as R = Me) favor a planar *trans*-N_2O_2 coordination geometry of the complex, whereas bulky groups (such as R = *t*-Bu) force the complex to become strongly tetrahedrally distorted, and (ii) with increasing extent of tetrahedral distortion (due to the effect of R) the size of k_S increases, whereby the contribution of the term $k_{HB}[HB]$ can become negligibly small. A systematic study of the kinetic effect of substituents X^3 and X^5 (introduced in the 3- and 5-positions of the salicylaldehyde ring) and substituents Y^2, Y^4, and Y^6 (introduced in the 2-, 4-, and 6-positions of the *N*-phenyl ring) reveals that substituents X^3 = CH_3, Cl, Br, I, NO_2, which are neighboring to the oxygen donor atom, reduce the size of k_S according to their steric substituent constant E_s. Substituents Y^2 = CH_3, F, Cl, Br, I and $Y^2 = Y^6$ = CH_3, Cl (neighboring the nitrogen donor atom in the *N*-phenyl complexes) reduce both k_S and k_{HB}, which can be correlated with the electronic and steric properties of these substituents. The sum of the experimental results supports consistently the following mechanistic interpretation of the observed rate law, namely: (i) the second-order rate constant k_{HB} describes the nucleophilic attack of the entering ligand HB at the copper; (ii) the first-order rate constant k_S describes the attack of a protic solvent molecule, surprisingly not at the copper but at the oxygen donor atom instead.

Introduction

The rate of ligand substitution in square-planar complexes with d^8 metal centers such as platinum(II) and palladium(II) follows a two-term rate law:[1,2]

$$\text{rate} = (k_S + k_L[\text{ligand}])[\text{complex}] \qquad (1)$$

The ligand-independent contribution (k_S) and the ligand-dependent contribution (k_L[ligand]) can be mechanistically attributed to the nucleophilic attack of a solvent molecule and ligand molecule, respectively. It is commonly accepted for both the "solvent path" and "ligand path" that nucleophilic attack occurs at the metal center.

It was important to prove but not surprising to find[3] that ligand substitution in planar $3d^8$ nickel(II) complexes is associative in character as well, although so far only for one nickel(II) system was a solvent path shown to exist in addition to the ligand path. This system,[4] in which we studied ligand substitution in bis(*N*-alkylsalicylaldiminato)nickel(II) with bidentate entering ligands, led in addition to an interesting aspect concerning the mechanism of the solvent path. Experimental evidence could be provided supporting the unusual interpretation that solvent attack does not occur at the metal but at the donor oxygen of the coordinated salicylaldimine ligand instead. Moreover, similar studies[5] with the corresponding bis(*N*-alkylsalicylaldiminato)copper(II) complexes ($3d^9$ metal center) revealed that ligand substitution in these complexes again follows rate law 1 and that the data obtained are indeed compatible with solvent attack taking place at the donor oxygen and not at the metal.

The present study was undertaken to further collect experimental data that should allow a more detailed mechanistic interpretation of the two pathways through which ligand substitution in bis(*N*-alkylsalicylaldiminato)copper(II) complexes occurs. This type of complex appears to be especially well suited for such a mechanistic study because of the various possibilities one has to modify the coordination geometry and electron density distribution by the introduction of substituents.

Type I and type II complexes, which basically prefer a square-planar *trans*-N_2O_2 coordination geometry,[6] are subject to the following substituent and R-group effects: (i) substituents

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(1) Hartley, F. R. "The Chemistry of Platinum and Palladium"; Applied Science Publishers: London, 1973.

(2) Wilkins, R. G. "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes"; Allyn and Bacon: Boston, 1974.

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(4) Schumann, M.; von Holtum, A.; Wannowius, K. J.; Elias, H. *Inorg. Chem.* **1982**, *21*, 606.

(5) Elias, H.; Fröhn, U.; von Irmer, A.; Wannowius, K. J. *Inorg. Chem.* **1980**, *19*, 869.

(6) (a) Holm, R. H.; Everett, G. W., Jr.; Chakravorty, A. *Prog. Inorg. Chem.* **1966**, *7*, 83. (b) Holm, R. H.; O'Connor, M. J. *Prog. Inorg. Chem.* **1971**, *14*, 241.