The Dehydrogenation of Nickel(II) Chelates of *rac*- and *meso*-2,2′-[(1,2-Diphenylethylene)bis(iminomethylene)]diphenol and Related Compounds

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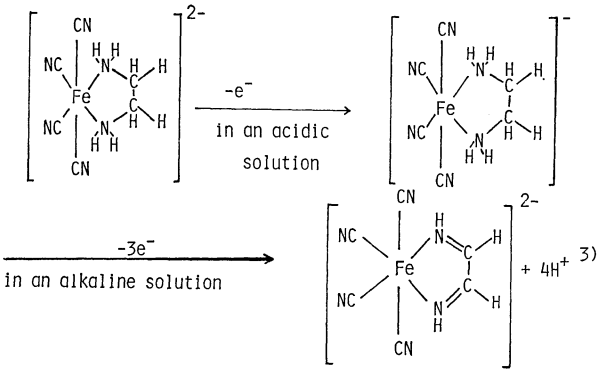
Nickel(II) acetate tetrahydrate and *rac*- and *meso*-2,2′-[(1,2-diphenylethylene)bis(iminomethylene)]diphenol (*rac*- and *meso*-BzPhen-H_2) formed pale green complexes in methanol. A pyridine solution of these complexes deposited deep red diimine complexes after prolonged heating under aerobic conditions. The saturated ligand system of the initial complexes was dehydrogenated to an unsaturated one by molecular oxygen. From the pyridine solution of the *meso*-isomer, [2,2′-{(*cis*-1,2-diphenylethenylene)bis(nitrilomethylidyne)}diphenolato]nickel(II) ([Ni(SalStil)]) was isolated in addition to the diimine complex ([Ni(*meso*-SalPhen)]). In this case, the –HN–CH–CH–NH– bridge was dehydrogenated to =N–C=C–N= conjugated double bonds; that is, a fully conjugated metal chelate was formed by the dehydrogenation of the coordinated ligand.

The dehydrogenation of coordinated ligands has become of interest in recent years, and several reports have been published concerning the dehydrogenation of macrocyclic polyamines to polyimines,[1,2] of aliphatic 1,2-diamines to 1,2-diimines,[3,4] of primary amines to nitriles,[5,6] and of 3,3′,4,4′-tetrahydro-2,2′-bi-2*H*-benzoxazines to fully conjugated metal chelates.[7]

In these oxidations the net reaction is considered to necessarily involve the prior oxidation of a metal ion to unstable, higher oxidation states, followed by the oxidation of the ligands and the reduction of the metal ion. In practice, iron(III) and ruthenium(III) complexes were isolated as intermediates of the dehydrogenation described below:



$$[(bipy)_2Ru(en)]^{2+} \xrightarrow{-e^-} [(bipy)_2Ru(en)]^{3+}$$

$$\xrightarrow{-3e^-} [(bipy)_2Ru(diimine)]^{2+} + 4H^{+}\ ^{4)}$$

Macrocyclic tetramine complexes were oxidized to imine complexes of varying degrees of unsaturation, depending upon the reaction conditions. Iron(II) complexes were readily dehydrogenated by molecular oxygen,[1,3] while nickel(II) complexes generally required stronger oxidizing reagents such as Br_2 or HNO_3.[3] In the present case, nickel(II) complexes undergo dehydrogenation under mild conditions.

The structures and abbreviations of nickel(II) chelates are given in Fig. 1.

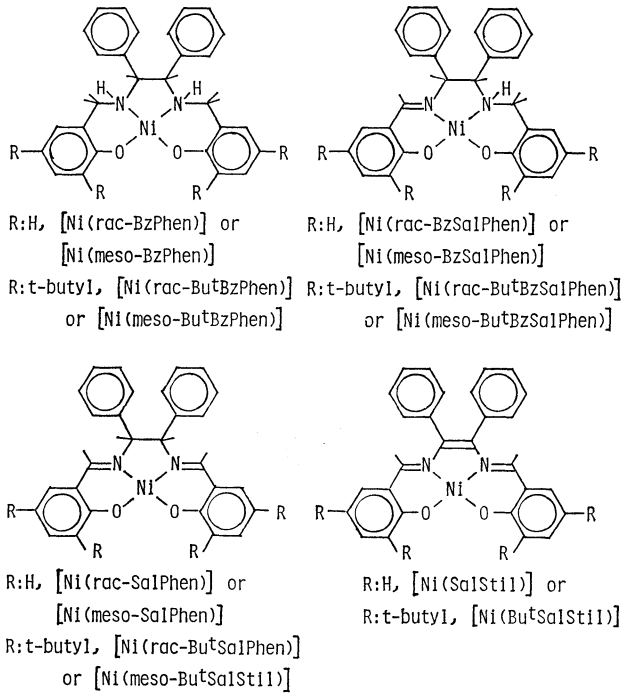


Fig. 1. Structural formulas and abbreviations for starting materials and oxidized products.

Experimental

The analytical data for the free ligands and the nickel(II) chelates are listed in Tables 1 and 2. All the nickel(II) chelates were dried under a vacuum over P_2O_5 at 50 °C.

General Procedure for the Preparation of rac- *and* meso-*BzPhen-H_2, and* rac- *and* meso-*But BzPhen-H_2.* A Schiff base (5 g) was dissolved in pyridine (200 cm³) and to the resulting yellow solution crystals of sodium borohydride were added in small portions on a water bath until the yellow color of the solution disappeared. The reaction mixture was then evaporated to about 50 cm³ under reduced pressure. To the resulting syrup was added dilute acetic acid (300 cm³). The white crystals which separated out were collected by suction and washed with water. The solvents used for recrystallization and the yield of each ligand are listed in Table 1.

*N-(2-Hydroxybenzyl)-N′-salicylidene-*meso*-1,2-diphenylethylenedi-*

TABLE 1. ANALYTICAL DATA FOR THE LIGANDS

Compound	Formula	Calcd(%)			Found(%)			Yield %	Recryst solvents
		C	H	N	C	H	N		
rac-BzPhen-H_2	$C_{28}H_{28}N_2O_2$	79.21	6.65	6.60	79.28	6.77	6.60	80	Pyridine-Water
meso-BzPhen-H_2	$C_{28}H_{28}N_2O_2$	79.21	6.65	6.60	79.12	6.55	6.87	75	Pyridine-Water
meso-BzSalPhen-H_2	$C_{28}H_{26}N_2O_2$	79.60	6.20	6.63	79.31	6.15	6.66		Methanol
rac-Bu^{t}BzPhen-H_2	$C_{44}H_{60}N_2O_2$	81.43	9.37	4.32	81.16	9.24	4.46	60	Chloroform-Methanol
meso-Bu^{t}BzPhen-H_2	$C_{44}H_{60}N_2O_2$	81.43	9.37	4.32	81.37	9.28	4.56	65	Chloroform-Methanol

TABLE 2. ANALYTICAL DATA FOR NICKEL(II) CHELATES

Compound	Formula	Calcd(%)			Found(%)		
		C	H	N	C	H	N
[Ni(*rac*-BzPhen)]	$C_{28}H_{26}N_2O_2Ni \cdot 2H_2O$	65.68	5.91	5.47	65.47	5.66	5.05
[Ni(*meso*-BzPhen)]	$C_{28}H_{26}N_2O_2Ni \cdot 3/2\ H_2O$	66.17	5.57	5.51	66.34	5.64	5.25
[Ni(*rac*-BzSalPhen)]	$C_{28}H_{24}N_2Ni$	70.18	5.05	5.85	69.91	4.99	5.84
[Ni(*meso*-BzSalPhen)(py)]	$C_{28}H_{24}N_2O_2Ni \cdot C_5H_5N$	70.99	5.24	7.53	71.20	5.21	7.51
[Ni(*meso*-Bu^{t}BzSalPhen)]	$C_{44}H_{56}N_2O_2Ni \cdot 3/2\ H_2O$	72.23	8.13	3.83	72.65	8.14	3.98
[Ni(*rac*-Bu^{t}SalPhen)]	$C_{44}H_{54}N_2O_2Ni$	75.32	7.76	3.99	75.10	7.80	3.94
[Ni(*meso*-Bu^{t}SalPhen)]	$C_{44}H_{54}N_2O_2Ni$	75.32	7.76	3.99	75.16	7.82	3.98
[Ni(SalStil)]	$C_{28}H_{20}N_2O_2Ni$	70.77	4.24	5.90	70.90	4.17	6.01
[Ni(Bu^{t}SalStil)]	$C_{44}H_{52}N_2O_2Ni$	75.54	7.49	4.00	75.38	7.49	4.07

*amine (*meso-*BzSalPhen-*H_2*)*. *N*-Benzylidene-*N'*-benzoyl-*meso*-1,2-diphenylethylenediamine[8] (8 g, 0.02 mol) was suspended in concentrated hydrochloric acid (130 cm^3), and the mixture was heated on a water bath for 2 h. After cooling, a colorless precipitate was collected by filtration; from this precipitate *N*-benzoyl-*meso*-1,2-diphenylethylenediamine hydrochloride (1) was extracted by the use of hot methanol (200 cm^3). *N*-Benzoyl-*N'*-salicylidene-*meso*-1,2-diphenylethylenediamine (2) was prepared as colorless crystals from (1) and salicylaldehyde using the ordinary method. (2) was reduced to *N*-benzoyl-*N'*-(2-hydroxybenzyl)-*meso*-1,2-diphenylethylenediamine (3) with sodium borohydride as has been described above. (3) was hydrolyzed by concentrated hydrochloric acid on prolonged heating (24 h) to afford *N*-(2-hydroxybenzyl)-*meso*-1,2-diphenylethylenediamine (4). (4) was then treated with salicylaldehyde to give *N*-(2-hydroxybenzyl)-*N'*-salicylidene-1,2-diphenylethylenediamine (*meso*-BzSalPhen-H_2) as pale yellow crystals, which were subsequently recrystallized from methanol. Yield, 2.5 g.

Preparation of Nickel(II) Complexes. [*Ni(*rac-*BzPhen)*]: *rac*-BzPhen-H_2 (420 mg, 1 mmol) and nickel(II) acetate tetrahydrate (240 mg, 1 mmol) were dissolved in hot methanol (40 cm^3), and the resulting light green solution was allowed to stand overnight at room temperature. The light blue crystals which separated out were collected by filtration and washed with methanol. Yield, 450 mg.

[*Ni(*meso-*BzPhen)*]: *meso*-BzPhen-H_2 (210 mg, 0.5 mmol) and nickel(II) acetate tetrahydrate (120 mg, 0.5 mmol) were dissolved in gently boiling methanol (15 cm^3), after which 4 drops of a 20% sodium hydroxide solution were added to the solution. The pale green crystals which immediately separated out from the pink solution were collected by filtration and washed with methanol. Yield, 200 mg.

[*Ni(*meso-*BzSalPhen)(py)*]: *meso*-BzSalPhen-H_2 (210 mg, 0.5 mmol) and nickel(II) acetate tetrahydrate (120 mg, 0.5 mmol) were dissolved in pyridine (10 cm^3) and water was added to the resulting red solution until it began to become turbid. After the solution had stood several hours, the orange-red crystals which separated out were collected by filtration and washed with pyridine–water. Yield, 180 mg.

[*Ni(*meso-*BzSalPhen)(py)*] *from* [*Ni(*meso-*BzPhen)*]: To a solution of *meso*-BzPhen-H_2 (420 mg, 1 mmol) in acetone (30 cm^3) was added nickel(II) acetate tetrahydrate (240 mg, 1 mmol) in methanol (20 cm^3). To the resulting pale green solution, a 20% sodium hydroxide solution was then added dropwise until the solution turned deep red. After standing overnight at room temperature, the solution was placed in 100-cm^3 flask equipped with a gas inlet tube and a condenser. Air was continuously bubbled through the solution for 5 h at room temperature. After then removing the condenser, the volume of the solution was reduced to 10 cm^3 by air bubbling. The resulting orange-red precipitate was collected by filtration, washed with water, and dissolved in methanol (20 cm^3). The insoluble products were removed by filtration, and the filtrate was evaporated to dryness. The orange-red residue was recrystallized from pyridine–water. Yield, 200 mg (42%).

[*Ni(*meso-*Bu^{t}BzSalPhen)*] *from* [*Ni(*meso-*Bu^{t}BzPhen)*]: *meso*-Bu^{t}BzPhen-H_2 (650 mg, 1 mmol) and nickel(II) acetate tetrahydrate (720 mg, 3 mmol) were dissolved in acetone–methanol (60 cm^3) on a water bath, and 20 drops of a 20% sodium hydroxide solution were added to the solution. The resulting deep red solution was allowed to stand 2 d at room temperature, and the volume of the solution was reduced to about 10 cm^3 by air bubbling. The deep red precipitate was filtered, washed with water, and recrystallized from methanol to give red plates. Yield, 550 mg (75%).

[*Ni(*rac-*BzSalPhen)*] *from* [*Ni(*rac-*BzPhen)*]: *rac*-BzPhen-H_2 (210 mg, 0.5 mmol) and nickel(II) acetate tetrahydrate (120 mg, 0.5 mmol) were dissolved in hot methanol (50 cm^3), after which 12 drops of a 20% sodium hydroxide solution were added to the pale blue solution. The resulting deep red solution was allowed to stand overnight at room temperature, and the orange-red crystals which separated out were collected by filtration and washed with methanol. Yield, 200 mg (84%).

Dehydrogenation in Pyridine Solution. *A)* [*Ni(SalStil)*]

and [*Ni*(meso-*SalPhen*)] *from* [*Ni*(meso-*BzPhen*)]: *meso*-BzPhen-H_2 (420 mg, 1 mmol) and nickel(II) acetate tetrahydrate (240 mg, 1 mmol) were dissolved in pyridine (15 cm^3). The resulting light green solution was heated on a water bath for 30 h. A deep red color formed after heating for 1 h. After cooling, methanol (70 cm^3) was added to the reaction mixture to induce crystallization. The orange-red needles ([Ni(SalStil)]) thus precipitated were filtered and washed with methanol. Yield, 60 mg (13%). After the filtrate had stood overnight at room temperature, [Ni(*meso*-SalPhen)] precipitated from the filtrate as deep red plates. Yield, 200 mg (42%).

B) [*Ni*(*Bu*^{t}*SalStil*)] *from* [*Ni*(meso-*Bu*^{t}*BzPhen*)]: The procedure was the same as that described for the preparation of [Ni(SalStil)] and [Ni(*meso*-SalPhen)]. *meso*-Bu^{t}BzPhen-H_2 (650 mg, 1 mmol) and nickel(II) acetate tetrahydrate (480 mg, 2 mmol) afforded 430 mg (61%) of [Ni(Bu^{t}SalStil)]. From the filtrate, a trace amount (15 mg) of [Ni(*meso*-Bu^t-SalPhen)] was obtained.

C) [*Ni*(rac-*SalPhen*)] *from* [*Ni*(rac-*BzPhen*)]: *rac*-BzPhen-H_2 (420 mg, 1 mmol) and nickel(II) acetate tetrahydrate (240 mg, 1 mmol) afforded 200 mg (42%) of [Ni(*rac*-SalPhen)].

D) [*Ni*(rac-*Bu*^{t}*SalPhen*)] *from* [*Ni*(rac-*Bu*^{t}*BzPhen*)]: *rac*-Bu^{t}BzPhen-H_2 (650 mg, 1 mmol) and nickel(II) acetate tetrahydrate (240 mg, 1 mmol) afforded 320 mg (46%) of [Ni(*rac*-Bu^{t}SalPhen)].

E) [*Ni*(meso-*SalPhen*)] *from* [*Ni*(meso-*BzSalPhen*)]: *meso*-BzSalPhen-H_2 (210 mg, 0.5 mmol) and nickel(II) acetate tetrahydrate (300 mg, 1.25 mmol) were dissolved in pyridine (10 cm^3), and the resulting red solution was heated on a water bath for 30 h. After cooling, water was added to the reaction mixture until it began to become turbid. The resulting crystals were collected by filtration and washed with methanol. Yield, 150 mg (63%).

F) Formation of [*Ni*(meso-*SalPhen*)] *by* H_2O_2 *oxidation of* [*Ni*(meso-*BzSalPhen*)]: Five drops of a 30% hydrogen peroxide solution were added to a solution of [Ni(*meso*-BzSalPhen)(py)] (110 mg, 0.2 mmol) in pyridine (15 cm^3), after which the mixture was heated on a water bath for 5 h. After cooling, water was added until the mixture began to become turbid. The resulting red crystals were filtered and washed with methanol. Yield, 70 mg (73%).

Measurements. IR spectra and electronic spectra were recorded on a Hitachi EPI S2 spectrometer and a Hitachi EPS 3T spectrometer respectively. NMR spectra were obtained on a Hitachi Model R-24 spectrometer, with Me_4Si as an internal standard.

Results and Discussion

The reaction of *rac*-BzPhen-H_2 or *meso*-BzPhen-H_2 with nickel(II) acetate afforded a pale green nickel(II) chelate, [Ni(*rac*-BzPhen)] or [Ni(*meso*-BzPhen)]. Pyridine solutions of these complexes or a pyridine solution containing an equimolar ligand (*rac*-BzPhen-H_2 or *meso*-BzPhen-H_2) and nickel(II) acetate changed color from light green to deep red on prolonged heating in air. The change was irreversible, and red crystals were deposited from the resulting red-colored solution in each case.

It was found that [Ni(*rac*-BzPhen)] afforded only one deep red product, while [Ni(*meso*-BzPhen)] gave two products, orange-red needles and deep red plates. The deep red products from the *rac*- and *meso*-chelates were identified as [Ni(*rac*-SalPhen)] and [Ni(*meso*-SalPhen)] respectively by a comparison of their IR spectra with those of authentic samples[9] and by elemental analyses.

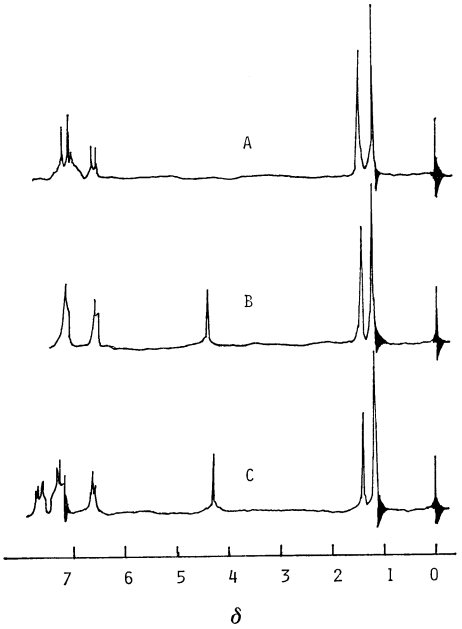


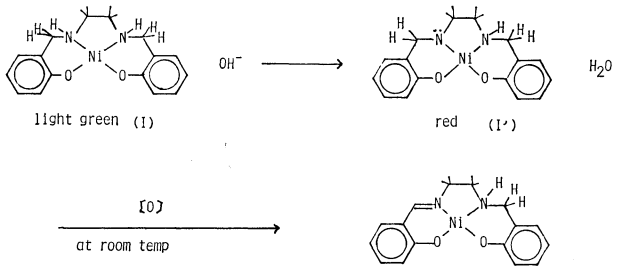
Fig. 2. NMR spectra of [Ni(Bu^{t}SalStil)] (A), [Ni(*meso*-Bu^{t}SalPhen)] (B), and [Ni(*rac*-Bu^{t}SalPhen)] (C).

The IR spectrum of the orange-red product from [Ni(*meso*-BzPhen)] was apparently different from that of [Ni(*meso*-SalPhen)]. It exhibits no absorptions in the region of 2900 cm^{-1}, where the C–H stretching vibrations due to the benzylmethylene and methine on the diamine moiety are expected to appear. The latter was observed at 2900 cm^{-1} in the spectrum of [Ni(*meso*-SalPhen)]. This, together with the analytical data, suggested that this chelate contained a fully conjugated ligand system, namely, [Ni(SalStil)], as is illustrated in Fig. 1.

It was difficult to obtain the precise NMR spectrum of this chelate because of its low solubility in organic solvents. For the purpose of increasing the solubility, *meso*-Bu^{t}BzPhen-H_2 was prepared and allowed to react with nickel(II) acetate. Although the corresponding nickel(II) chelate, [Ni(*meso*-Bu^{t}BzPhen)], could not be isolated as crystals from the methanol solution, a red nickel(II) chelate was obtained successfully from the pyridine solution on prolonged heating. The NMR spectrum of this chelate is compared with those of [Ni(*meso*-Bu^{t}SalPhen)] and [Ni(*rac*-Bu^{t}SalPhen)] in Fig. 2. The spectrum apparently lacks a signal attributable to methine protons on the diamine moiety, which is observed in the spectra of [Ni(*rac*-Bu^{t}SalPhen)] and [Ni(*meso*-Bu^{t}SalPhen)] at δ 4.36 and 4.69 respectively. This indicates that the dehydrogenation took place at the bridged carbon atoms to form the *cis*-stilbene moiety. It can deffinitly be concluded that the reaction of *meso*-Bu^{t}BzPhen-H_2 with the nickel(II) ion in the presence of molecular oxygen proceeds with the dehydrogenation of the ligand and affords predominantly the nickel(II) chelate containing a fully conjugated ligand system, namely, [Ni(Bu^{t}SalStil)], while scarcely [Ni(*meso*-Bu^{t}SalPhen)] was formed in

this reaction.

As has been mentioned above, *meso*-BzPhen-H_2 and nickel(II) acetate in methanol formed a pale pink solution upon the addition of a few drops of an aqueous sodium hydroxide solution, and [Ni(*meso*-BzPhen)] separated out as light green crystals from the solution. Dehydrogenation did not proceed under the present reaction conditions. On the other hand, the addition of more aqueous sodium hydroxide to the pink solution before the precipitation of the chelate produced a deep red color and an orange-red precipitate separated out when the mixture stood overnight at room temperature. Recrystallization from pyridine–water gave brilliant red crystals. It was found that a two-electron oxidation took place in this case; the crystals were identified as [Ni(*meso*-BzSalPhen)(py)], the structure of which is shown in Fig. 1. For the purpose of identification, the ligand, *meso*-BzSalPhen-H_2 was prepared by a different route, and the IR spectrum of its nickel(II) chelate was compared with that of the above sample. Under the same reaction conditions, *rac*-BzPhen-H_2 and *meso*-Bu^{t}BzPhen-H_2 also gave the same types of chelates, [Ni(*rac*-BzSalPhen)], and [Ni(*meso*-Bu^{t}BzSalPhen)], in good yields. Thus, it is clear that this type of dehydrogenation reaction readily occurs for these chelates in a basic solution, even at room temperature. The reaction mechanism can be formulated as in Scheme 1. The addition of alkali causes deprotonation, and the deprotonated species I′ is apparently sensitive to molecular oxygen and is readily oxidized to the mono imine nickel(II) chelates.



Scheme 1.

The electronic spectra of [Ni(*meso*-Bu^{t}BzSalPhen)], [Ni(*meso*-Bu^{t}SalPhen)], and [Ni(Bu^{t}SalStil)] in pyridine are compared in Fig. 3. The spectra of [Ni(*meso*-Bu^{t}BzSalPhen)] and [Ni(*meso*-Bu^{t}SalPhen)] show d-d transition bands at 580 and 570 nm respectively. The band for [Ni(Bu^{t}SalStil)] is not observed because of the tailing of an intense charge-transfer band. The spectral changes with the time are shown in Fig. 4 for [Ni(*meso*-Bu^{t}BzSalPhen)] in pyridine and for a pyridine solution containing *meso*-Bu^{t}BzPhen-H_2 and nickel(II) acetate in Fig. 5. As may be seen in Fig. 4, the band at 430 nm increases, and the absorption around 500 nm decreases, in intensity with the time. This indicates that [Ni(*meso*-Bu^{t}BzSalPhen)] is formed exclusively from [Ni(*meso*-Bu^{t}BzSalPhen)] and that the formation of [Ni(Bu^{t}SalStil)] does not occur at all under these conditions. On the other hand, as is shown in Fig. 5, the band around 500 nm which is due to the [Ni(Bu^{t}SalStil)] species increases in intensity with the time from the initial stage. This

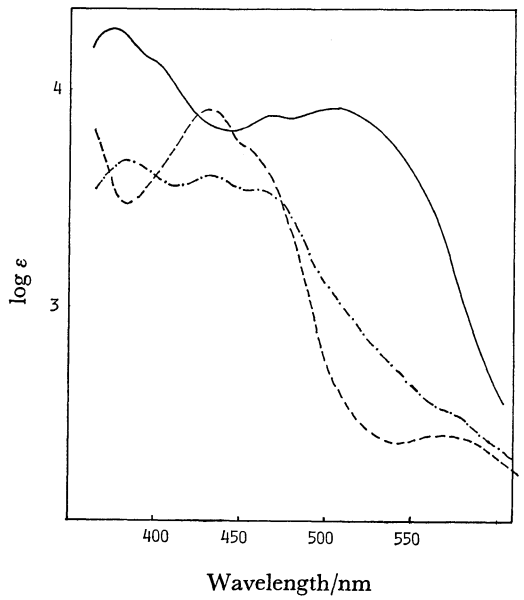


Fig. 3. The electronic spectra of [Ni(Bu^{t}SalStil)] (——), [Ni(*meso*-Bu^{t}SalPhen)] (----), and [Ni(*meso*-Bu^{t}BzSalPhen)] (—·—) in pyridine.

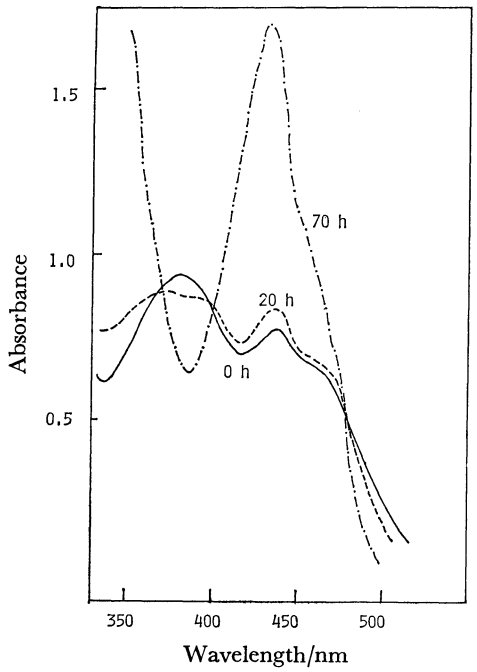


Fig. 4. Spectral changes with the time for the dehydrogenation of [Ni(*meso*-Bu^{t}BzSalPhen)] (1.97×10^{-5} mol) in pyridine (10 cm^3) at 90 °C.

result is consistent with the fact that [Ni(Bu^{t}SalStil)] is exclusively formed in the solution. In other words, the formation of [Ni(Bu^{t}SalStil)] occur even at the initial stage of dehydrogenation. These results give some insight into the formation mechanism of [Ni(Bu^{t}SalStil)] and [Ni(*meso*-Bu^{t}SalPhen)]. The formation of [Ni(*meso*-Bu^{t}SalPhen)] by the dehydrogenation of [Ni(*meso*-Bu^{t}BzPhen)] proceeds in two step by-step processes via the formation of [Ni(*meso*-Bu^{t}BzSalPhen)]. While the formation mechanism of [Ni(Bu^{t}SalStil)] is still unclear, the process via the formation of [Ni(*meso*-

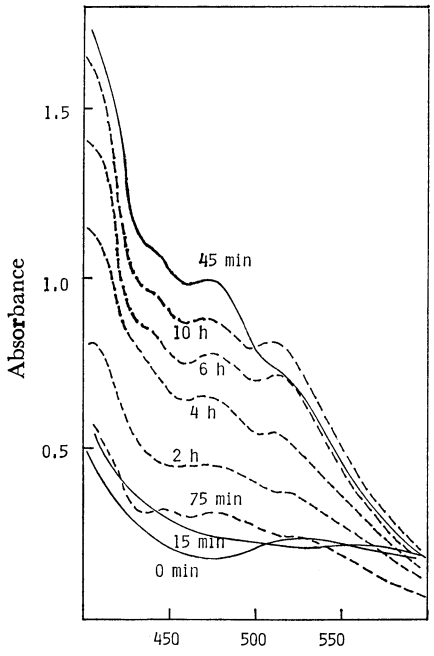
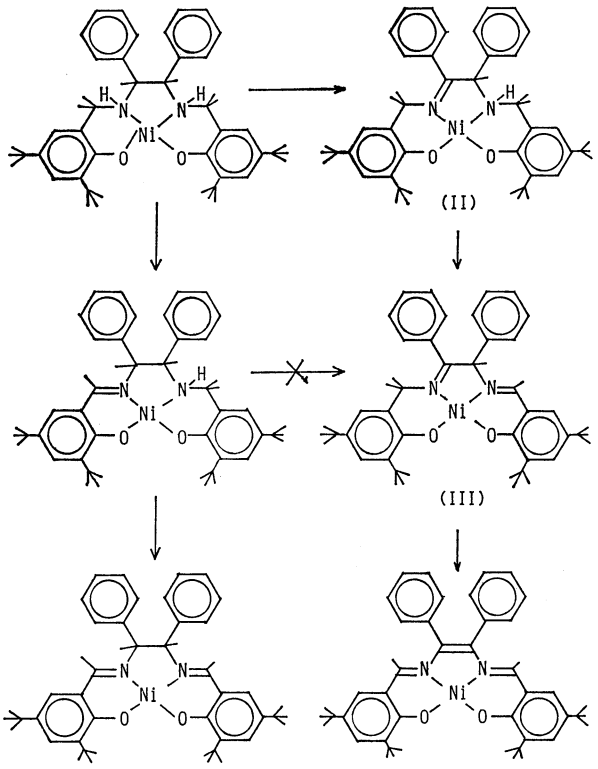


Fig. 5. Spectral changes with the time for the dehydrogenation [Ni(*meso*-Bu^{t}BzPhen)] [*meso*-Bu^{t}BzPhen-H_2 (2.4×10^{-5} mol) and nickel(II) acetate tetrahydrate (3.5×10^{-5} mol) in pyridine (10 cm^3) at 90 °C]; [—— obtained by using 1 cm quartz cell and ---- obtained by using (1 cm quartz cell+9 mm quartz spacer)].



Scheme 2.

Bu^{t}BzSalPhen)] can be disregarded, as has been described above. Therefore, it is most probable for the formation of [Ni(Bu^{t}SalStil)] to postulate the existence of an intermediate containing an enamine-type ligand system (III). Such intermediates have been isolated in the metal-ion-induced rearrangement of 3,3′,4,4′-tetrahydro-2,2′-bi-2*H*-1,3-benzoxazines and subsequent dehydrogenation reactions,[7] though the isolation of such species was unsuccessful in these cases. The proposed reaction mechanism of the dehydrogenation is summarized in Scheme 2. As has been mentioned before, [Ni(*meso*-BzPhen)] was dehydrogenated to give [Ni(*meso*-SalPhen)], and to give [Ni(SalStil)] as a by-product. This dehydrogenation also proceeds in a manner quite similar to that described in Scheme 2. In practice, the reaction of *meso*-BzSalPhen-H_2 with nickel(II) acetate in pyridine or the dehydrogenation of [Ni(*meso*-BzSalPhen)] with H_2O_2 in pyridine afforded [Ni(*meso*-SalPhen)] as the sole product.

The electron-transfer mechanism in the oxidative dehydrogenation of the nickel(II) chelates is not clear, but probably molecular oxygen combines with the nickel(II) ion at the axial positions and transfers electrons through the nickel(II) ion. If an initial electron loss from the nickel(II) ion is assumed, the transition state of the dehydrogenation may involve the trivalent oxidation state of nickel. The formation of such species has previously been reported in the dehydrogenation of macrocyclic nickel(II) chelates.[10,11] The nickel(III) complexes which were formed by electrochemical or chemical oxidation gave nickel(II) ligand radical species upon treatment with basic solvents such as pyridine according to this scheme;

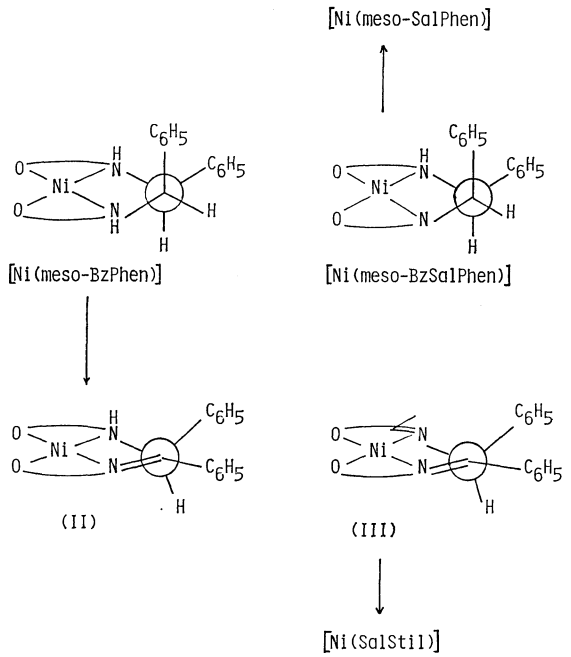
$$\text{Ni(III)N-H} + :\text{B} \longrightarrow \text{Ni(II)N}\cdot + \text{HB}^+$$

Further, the free radical species afforded, via several different processes, monoimine nickel(II) chelates.[11] In the present case, similar nickel(III) chelates and free radical species must be involved prior to the ligand oxidation.

It should be noted that the nickel(II) chelates containing a fully conjugated ligand system were formed only when *meso*-chelates were dehydrogenated. In addition, the *t*-butyl groups on the benzene nucleus promoted the formation of fully conjugated chelates. In the dehydrogenation of [Ni(*meso*-BzPhen)], [Ni(SalStil)] was obtained in a low yield as a by-product, while [Ni(Bu^{t}SalStil)] was exclusively obtained from [Ni(*meso*-Bu^{t}BzPhen)]. It is clear that the *t*-butyl groups situated in the *ortho* position of the phenol oxygen atoms exerted such an effect on the dehydrogenation because in the dehydrogenation of a *meso*-chelate having a *t*-butyl group in the position *para* to the OH group of the hydroxybenzyl moiety the situation was quite similar to that of [Ni(*meso*-BzPhen)].

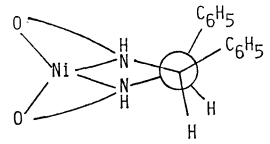
The stereospecific dehydrogenation of *meso*-chelates may be attributable to the conformation of phenyl groups on the diamine moiety; that is, the only possible conformation for the two phenyl groups is axial-equatorial, and they are crowded on one side relative to the metal chelate plane. On the other hand, on the formation of intermediates (II) and (III) from *meso*-chelates, the conformational changes in the two phenyl groups can be assumed to be as is shown in Scheme 3. These conformational changes accompany the partial removal of the unfavourable strain, which

is due to the crowding state of the two phenyl groups in the starting chelate. Thus, this will be the reason why the formation of [Ni(SalStil)] was possible only in the dehydrogenation reaction of the *meso*-chelates.



Scheme 3.

In the [Ni(*meso*-Bu^{t}BzPhen)], the steric repulsion due to the two bulky *t*-butyl groups situated in the *ortho* position of the phenol oxygen atoms may produce a considerable distortion, as is depicted below:



Scheme 4.

In fact, the splitting of the d-d band (540 nm and 630 nm) was observed in the reflectance spectrum of [Cu(*meso*-Bu^{t}SalPhen)], which was considered to be due to a tetrahedral distortion of the chelate ring.[12] Such distortion is common among *meso*-Bu^t-chelates; it may be the reason why the isolation of [Ni(*meso*-Bu^{t}BzPhen)] was difficult. It is apparent that the serious strain in [Ni(*meso*-Bu^{t}BzPhen)] is removed by the formation of the intermediates (II) and (III); this makes it likely to afford [Ni(Bu^{t}SalStil)].

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