Equilibrium Studies of the Axial Addition of Chiral Bases to Chiral Metal Schiff Base Complexes

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The syntheses of new chiral 1,2-diphenylethylene-bridged nickel(II) and methylcobalt(III) Schiff base complexes are described. The equilibrium constants for the axial addition of the chiral bases (*R*)- and (*S*)-1-phenylethylamine to the enantiomerically pure metal complexes have been determined by means of spectrophotometric titrations. Comparison of the constants for the cyclohexanediyl-bridged complexes (type **1**) with those for the more bulky 1,2-diphenylethylene-bridged complexes (type **2**) reveals that chiral recognition is only observed in the case of type-2 complexes.

Introduction

In recent years, catalytic asymmetric synthesis has become increasingly important[1]. In this context, the enantioselective epoxidation of unfunctionalized alkenes reported by Jacobsen and Katsuki et al. has been one of the highlights of the current decade[2]. Recently, Mukaiyama et al. reported on the enantioselective hydrogenation of ketones with sodium tetrahydroborate in the presence of optically active cobalt(II) complexes[3]. These reactions are mediated by chiral metal complex catalysts and are based on the capacity of such species for chiral recognition of the substrates. Thus, some metal Schiff base complexes have emerged as particularly effective catalysts by virtue of their chiral carbon centers being situated in the vicinity of the central atom.

Our work is concerned with studies of the structure-reactivity relationships of Schiff base complexes with regard to the basic features of reactivity that are of importance for the catalytic performance, i.e. investigations of the redox behavior and Lewis acidity of coordinatively unsaturated planar complexes.

In previous publications we reported on new chiral nickel and copper [N_2O_2]-coordinated Schiff base complexes derived from 1,2-diaminocyclohexane and β-oxo aldehydes. These were characterized with regard to their ability to bind Lewis bases at their free axial coordination sites (Lewis acidity) and to accept electrons (redox potentials). However, upon applying the chiral bases (*R*)- and (*S*)-1-phenylethylamine, no chiral recognition could be observed[4]. The same result was found by Elias et al. for the addition of (*S*)-(−)-nicotine to chiral salene complexes[5].

Differences in the adduct stabilities were observed for the diastereomeric complexes *meso*-Ni**1a** and (*R*,*R*)-Ni**1a**, which can be attributed to the orientation of the cyclohexanediyl group in relation to the [N_2O_2] plane[6].

In the present work, new chiral nickel and cobalt Schiff base complexes derived from 1,2-diphenylethylenediamine are described (type 2). Spectrophotometric titrations with chiral bases have been carried out so as to allow the determination of the stability constants of the adducts. Planar nickel complexes are known to give consecutive equilibria associated with 1:1 and 1:2 base adduct formation. Because of the change of spin state from S = 0 to S = 1, the octahedral 1:2 adduct is normally strongly favored ($K_2 >> K_1$). For investigations of pure 1:1 adduct formation we used a pentacoordinated methylcobalt(III) derivative. Such complexes usually have a sufficiently high Lewis acidity at the sole vacant coordination site and allow the determination of the equilibrium constants for the 1:1 base addition with high precision[7]. This is seemingly the first time that chiral recognition has been observed in measurements of this kind.

Results and Discussion

The ability of complexes to show chiral recognition depends mainly on the steric environment of the active site, i.e. the central metal atom. In view of the aforementioned negative results concerning the addition of chiral bases to complexes with the 1,2-cyclohexanediyl group as the chiral bridge, this group was replaced by the sterically more demanding 1,2-diphenylethylene bridge (Figure 1).

The substituents R^1 and R^2 also have a considerable influence on the electronic properties of the metal, as well as being responsible for steric effects. Substitution pattern **b** is sterically more demanding than arrangement **a**. However, the Lewis acidity of Ni**2b** is too low to permit quantitative studies of axial ligation. Spectral changes upon base addition could only be observed for nickel complexes with the electron-withdrawing substituents CN and OEt (type **a**). In

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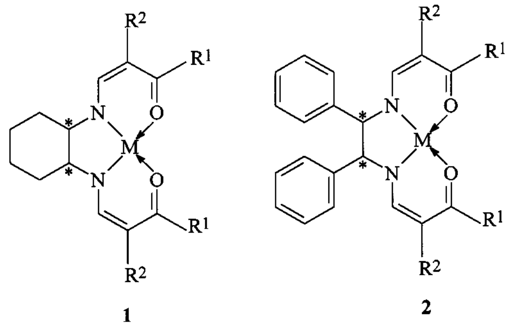
Figure 1. Nomenclature of the Schiff base complexes



M = 2H, Ni, Co

a: R^1 = OEt; R^2 = CN

b: R^1 = Ph; R^2 = COOEt

contrast to the nickel complexes, where both types (Ni**2a** and Ni**2b**) could be prepared, we were not successful in isolating the corresponding cobalt complex Co**2a**. Thus, only the complex (*R*,*R*)-Co**2b** could be synthesized, which was subsequently methylated at the axial position so as to obtain the diamagnetic methylcobalt(III) complex (*R*,*R*)-MeCo**2b**. Such organocobalt complexes are very suitable as base acceptors in spectrophotometric titrations, since the spectral changes that accompany the transition from the pentacoordinated to the octahedral state are highly sensitive, and usually the calculated constants are of such an order of magnitude and of such a high precision that gradations of the constants for titrations with relatively weak bases can be determined unambiguously[7].

The compounds were characterized by means of NMR spectroscopy. As expected, in the ^{1}H-NMR spectrum of (*R*,*R*)-MeCo**2b** the protons attached to the chiral carbon atoms, as well as the olefinic protons (N−CH=), exhibit a double set of signals, i.e. they are no longer equivalent. This non-equivalence is due to the C_2 symmetry and the axial methyl group. This effect could not be observed in the spectrum of the corresponding square-planar nickel complex (*R*,*R*)-Ni**2a** or in that of (*R*,*R*)-Ni**2b**. Upon addition of [D_5]pyridine to the solution of (*R*,*R*)-MeCo**2b** used to record the NMR spectrum, the signal of the axial methyl group is shifted to lower field ($\delta = 2.70 \rightarrow 2.98$).

Spectrophotometric titrations were carried out using the (*S*,*S*) enantiomers of the optically active complexes Ni**1a** and Ni**2a** with both enantiomers of the chiral base 1-phenylethylamine in chloroform and in benzene (Ni**2a** only). Nickel complexes preferentially form octahedral base diadducts, i.e. $K_1 < K_2$ for equations 1 and 2.

$$\mathrm{NiL + B} \overset{K_1}{\rightleftharpoons} \mathrm{NiLB} \qquad (1)$$

$$\mathrm{NiLB + B} \overset{K_2}{\rightleftharpoons} \mathrm{NiLB_2} \qquad (2)$$

The constants K_1 (= β_1) and β_2 (K_1K_2) thus determined are listed in Table 1. It was confirmed that the cyclohexanediyl-bridged complex (*S*,*S*)-Ni**1a** cannot distinguish between (*R*)- and (*S*)-1-phenylethylamine. For these substrates, the measured constants are the same within the margin of error. However, following introduction of the sterically more demanding chiral 1,2-diphenylethylene bridge into the complex [(*S*,*S*)-Ni**2a**], the β_2 values differ significantly. In both the solvents used, i.e. $CHCl_3$ and benzene, the constants determined by titration with the (*R*)-amine are significantly higher than those determined by titration with the (*S*)-amine. This means that the base adduct of (*S*,*S*)-Ni**2a** with (*S*)-1-phenylethylamine is thermodynamically less stable than the adduct with the (*R*)-amine. The reason for this should be that the addition of the (*S*) enantiomer of the base is sterically more hindered by the chiral diamine bridge than that of the (*R*) enantiomer. Unfortunately, the margin of error in K_1 (and K_2) is much higher than that in β_2 and thus it is not possible to establish whether the chiral recognition occurs to a greater extent in the first or the second step of the axial base addition.

Furthermore, we carried out titrations of the organocobalt(III) complex (*R*,*R*)-MeCo**2b** with (*R*)- and (*S*)-1-phenylethylamine in benzene. (This complex is very light-sensitive in solution, and hence preparations and the measurement itself had to be carried out in the dark.) In the course of the base addition, a transition from the pentacoordinated to the octahedral state occurs, as depicted in Scheme 1.

An example of a titration of (*R*,*R*)-MeCo**2b** with a chiral base is illustrated in Figure 2. The intense charge transfer band at 645 nm is seen to decrease with increasing concentration of (*S*)-1-phenylethylamine.

The calculated values of *K* are listed in Table 2. It can be seen that the difference between the constants derived from the two titrations is even larger than in the case of the nickel complex (*S*,*S*)-Ni**2a**. The constant for the adduct of (*R*,*R*)-MeCo**2b** with (*S*)-1-phenylethylamine is approximately three times larger than that of the adduct with the (*R*)-amine. It seems that the bulky substituents R^1 = phenyl and R^2 = COOEt enhance the differentiation of the stabilities of the corresponding base adducts, i.e. with (*R*)- or (*S*)-1-phenylethylamine, respectively.

From the equation $K = [\mathrm{CoLB}]/([\mathrm{CoL}][\mathrm{B}])$ for the equilibrium according to Scheme 1, it follows that for the titration of complex (*R*,*R*)-MeCo**2b** with the racemic base 1-phenylethylamine, one would obtain an adduct mixture of a composition such that $[\mathrm{CoLB}_{(R)}]/[\mathrm{CoLB}_{(S)}] = K_{(R)}/K_{(S)}$, where (*R*) and (*S*) refer to (*R*)- and (*S*)-1-phenylethylamine, respectively. Thus, in the present case, a mixture of 36.4% of the (*R*)-amine adduct and 63.6% of the (*S*)-amine adduct would result.

Conclusions

The results show the significant influence of the complex periphery on chiral recognition properties. Such an effect has been observed simply by replacing the cyclohexadienyl group in previously studied compounds by the sterically

Table 1. Equilibrium constants for the titration of (*S*,*S*)-Ni**1a** and (*S*,*S*)-Ni**2a** with the chiral bases (*R*)- and (*S*)-1-phenylethylamine at 20 (± 1)°C (in $CHCl_3$) and at 25 (± 0.1)°C (in benzene)

	Base	Solvent	K_1 [l mol^{-1}]	β_2 [l^2 mol^{-2}] (s[a])	e[b] (10^{-3})
(*S*,*S*)-Ni**1a**	(*R*)-1-phenylethylamine	$CHCl_3$	0.05	24[4]	5.4
(*S*,*S*)-Ni**1a**	(*S*)-1-phenylethylamine	$CHCl_3$	0.05	24	4.5
(*S*,*S*)-Ni**2a**	(*R*)-1-phenylethylamine	$CHCl_3$	< 0.01	12 (0.8)	0.6
(*S*,*S*)-Ni**2a**	(*S*)-1-phenylethylamine	$CHCl_3$	< 0.01	4.5 (0.5)	0.8
(*S*,*S*)-Ni**2a**	(*R*)-1-phenylethylamine	benzene	0.01	8.4 (0.1)	1.1
(*S*,*S*)-Ni**2a**	(*S*)-1-phenylethylamine	benzene	0.04	5.1 (0.1)	1.8

[a] Standard deviation of the equilibrium constant. – [b] Average of the square errors for the fit of the values of the extinctions.

Scheme 1. Equilibrium between the pentacoordinated methylcobalt complex and the octahedrally coordinated complex upon base addition

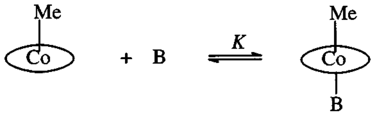


Figure 2. Spectrophotometric titration of (*R*,*R*)-MeCo**2b** with (*S*)-1-phenylethylamine in benzene

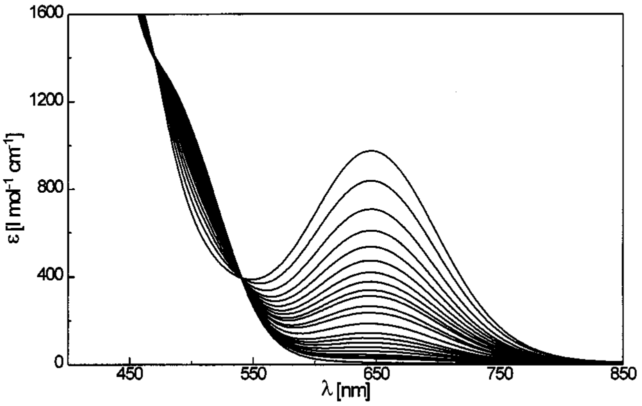


Table 2. Equilibrium constants for the titration of (*R*,*R*)-MeCo**2b** with (*R*)- and (*S*)-1-phenylethylamine in benzene at 20 (± 0.1)°C

Base	*K* [l mol^{-1}] (s[a])	e[b] (10^{-3})
(*S*)-1-phenylethylamine	770 (25)	4.5
(*R*)-1-phenylethylamine	316 (12)	1.5

[a] Standard deviation of the equilibrium constants. – [b] Average of the square errors for the fit of the values of the extinctions.

more demanding 1,2-diphenylethylene bridge. To the best of our knowledge, this is the first time that chiral recognition has been observed in the addition of a base to coordinatively unsaturated complexes. The results are of importance with regard to enantioselective catalytic investigations. Appropriate experiments are in progress, the results of which will be reported in due course.

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Experimental Section

The following chemicals were used without further purification: Ethyl 2-cyano-3-ethoxyacrylate (Merck), (1*S*,2*S*)-(+)- and (1*R*,2*R*)-(–)-1,2-diphenylethylenediamine (97%, Fluka), (*R*)-(+)- and (*S*)-(–)-1-phenylethylamine (98%, Fluka). Ethyl (ethoxymethylene)-benzoylacetate was prepared according to a literature method[8]. – NMR spectra were recorded with a Bruker AC-200 spectrometer (^{1}H, ^{13}C, ^{1}H-^{13}C-COSY, ^{13}C APT NMR) and are reported as δ in ppm from HMDS. – FT IR spectroscopy was performed with a Perkin-Elmer 2000 FT-IR instrument. – Mass spectra were obtained with a Finnigan MAT SSQ 710 spectrometer. – Elemental analyses were carried out with a Leco CHNS-932 analyzer (CHN) and by complexometric titration (Ni, Co), respectively. – Specific rotation values were determined with a Polartronic E polarimeter (Schmidt-Haensch). – Spectrophotometric titrations were carried out at constant temperature with a Varian Cary 5E spectrophotometer equipped with a temperature controller. The calculation of the equilibrium constants was carried out at six wavelengths $\lambda(i)$ and with at least twenty base (axial ligand) concentrations $c_B(j)$, under optimized conditions as described in the literature[9a]. The constants β_1 (= K_1) and β_2 (K_1K_2) as well as the extinction coefficients $\varepsilon_1(\lambda)$ and $\varepsilon_2(\lambda)$ for the 1:1 and the 1:2 adduct, respectively, were calculated iteratively by a non-linear fit of the absorbance data $A = E/(c_K d)$ (*E:* extinction; c_K: total complex concentration) according to

$$A_{i,j} = \Sigma\varepsilon_{\nu,i}\beta_\nu[B]_j^{\nu}/(\Sigma\beta_\nu[B]_j) \qquad (3)$$

$(\nu = 0, 1, 2;\ \beta_0 \equiv 1)$

A home-made computer programme SPEGA was used for the iteration, based on the algorithm of Marquardt[9b]. A special procedure was included to calculate the equilibrium base concentrations $[B]_j$ from the known total concentrations c_{Bj} by iteration according to

$$c_{Bj} = [B]_j + c_{Kj}\Sigma\nu\beta_\nu[B]_j^{\nu}/(\Sigma\beta_\nu[B]_j^{\nu}) \qquad (4)$$

$(\nu = 0, 1, 2;\ \beta_0 \equiv 1)$

Ligands: Diethyl (Z,Z)-(trans)-3,3′-(1,2-Diphenyl-1,2-ethanediyldiimino)bis(2-cyano-2-propenoate) [(*R*,*R*)- and (*S*,*S*)-2H**2a**]: 105 mg (0.5 mmol) of (*R*,*R*)- or (*S*,*S*)-diphenylethylenediamine was dissolved in 10 ml of methanol. To this solution, 170 mg (1 mmol) of ethyl 2-cyano-3-ethoxyacrylate, dissolved in 5 ml of methanol, was added dropwise. The mixture was refluxed for 30 min. The solvent was then partially evaporated in vacuo until a white powder precipitated. The solid was filtered off and washed with diethyl ether, yield 211 mg (92%), m.p. 214°C. – CI MS (H_2O); *m/z* (%): 459 $[M + H]^+$ (35), 413 $[M - CO]^+$ (2), 229 $[L/2]^+$ (95). – IR (Nujol): $\tilde{\nu}_{max}$ = 3199 cm^{-1} (NH_{str}), 2215 (CN_{str}), 1698 ($C{=}O_{str}$). –

(*R*,*R*)-2H**2a**: $C_{26}H_{26}N_4O_4$: calcd. C 68.12, H 5.72, N 12.22; found C 68.0, H 5.7, N 12.1. − $[\alpha]^{20}_D = -157 \pm 10$ ($c = 0.18$ in ethanol). − (*S*,*S*)-2H**2a**: found C 68.1, H 5.7, N 12.1. − $[\alpha]^{20}_D = +157 \pm 10$ ($c = 0.18$ in ethanol).

Diethyl (E,E)-(trans)-3,3′-(1,2-Diphenyl-1,2-ethanediyldiimino)bis(2-benzoyl-2-propenoate) [(*R*,*R*)- and (*S*,*S*)-2H**2b**]: 1.0 g (4.75 mmol) of (*R*,*R*)- or (*S*,*S*)-diphenylethylenediamine was dissolved in 20 ml of methanol. A solution of 2.36 g (9.5 mmol) of ethyl (ethoxymethylene)benzoylacetate in 10 ml of methanol was added dropwise. The mixture was refluxed for 30 min and then the solvent was evaporated in vacuo. The crude product was obtained in the form of a yellow oil. It was used for complexation without purification.− CI MS (H_2O); *m/z* (%): 617 $[M + H]^+$ (37), 571 $[M - C_2H_5O]^+$ (8), 308 $[L/2]^+$ (30).

Nickel Complexes

{[Diethyl (Z,Z)-(trans)-3,3′-(1,2-Diphenyl-1,2-ethanediyldiimino)]bis(2-cyano-2-propenoato)(2−)-N^3,$N^{3'}$,O^1,$O^{1'}$}nickel [(*R*,*R*)- and (*S*,*S*)-Ni**2a**]: 120 mg (0.26 mmol) of the ligand was suspended in 40 ml of ethanol. Then, 0.7 ml (0.52 mmol) of $N(Et)_3$ was added. To this mixture, a suspension of 64.7 mg (0.26 mmol) of $Ni(AcO)_2 \cdot 4H_2O$ in 20 ml of ethanol was added. The mixture was refluxed for 1 h, whereupon the substances dissolved and the solution became red in colour. The solvent was then evaporated in vacuo to leave a brown residue. The crude product was washed with water and finally with ethanol, yield 120 mg (89%), m.p. 257°C. − EI MS; *m/z* (%): 514 $[M^+]$ (30), 286 $[M - L/2]^+$ (40), 229 $[L/2]^+$ (100), 183 $[L/2 - C_2H_5OH]^+$ (30). − IR (Nujol): $\tilde{\nu}_{max} = 2208\ cm^{-1}$ (CN_{str}). − (*R*,*R*)-Ni**2a**: $C_{26}H_{24}N_4NiO_4$: calcd. C 60.61, H 4.70, N 10.87, Ni 11.39; found C 60.6, H 4.8, N 10.5, Ni 11.32. − (*S*,*S*)-Ni**2a**: found C 60.49, H 4.78, N 10.57, Ni 11.29.

{Diethyl (E,E)-(trans)-3,3′-[(1,2-Diphenyl-1,2-ethanediyldiimi)-no]bis(2-benzoyl-2-propenoato)(2−)-N,N′,O^2,$O^{2'}$}nickel [(*R*,*R*)-Ni**2b**]: 250 mg (0.4 mmol) of *trans*-2H**2b** was dissolved in 40 ml of methanol. To this solution, 100 mg (0.4 mmol) of $Ni(AcO)_2 \cdot 4\ H_2O$, dissolved in 10 ml of methanol, was added. The mixture was refluxed for 30 min. After cooling, an orange precipitate was collected by filtration and dried in air, yield 245 mg (91%), m.p. 270°C. − EI MS; *m/z* (%): 672 $[M^+]$ (12), 365 $[M - L/2]^+$ (100), 105 $[C_6H_5CO^+]$ (45). − IR (Nujol): $\tilde{\nu}_{max} = 1706\ cm^{-1}$ ($C{=}O_{str}$), 701, 770 ($C{-}H_{def}$). − $C_{38}H_{34}N_2NiO_6$: calcd. C 67.78, H 5.09, N 4.16, Ni 8.71; found C 67.7, H 5.2, N 4.1, Ni 8.70.

Cobalt Complexes

{Diethyl (E,E)-(trans)-3,3′-[(1,2-Diphenyl-1,2-ethanediyl)diimino]bis(2-benzoyl-2-propenoato)(2−)-N,N′,O^2,$O^{2'}$}cobalt [(*R*,*R*)- and (*S*,*S*)-Co**2b**]: The following procedures were carried out under inert conditions using argon. 3.08 g (5 mmol) of the ligand was dissolved in 80 ml of dry DMF and the solution was heated to boiling. To the hot solution of the ligand, 5 mmol of $Co(AcO)_2 \cdot 4\ H_2O$ in 100 ml of DMF was added dropwise. A dark-red solution was obtained, which was refluxed for 1 h. The solvent was then evaporated until the complex precipitated. The solid was filtered off and washed with dry methanol. The dry orange complex was found to be stable in air, yield 2.56 g (76%), m.p. 253°C. − EI MS; *m/z* (%): 673 $[M^+]$ (30), 628 $[M - C_2H_5O]^+$ (2), 366 $[M - L/2]^+$ (100). − IR (Nujol): $\tilde{\nu}_{max} = 1710\ cm^{-1}$ ($C{=}O_{str}$), 701 ($C{-}H_{def}$). − Magn. mom.: $\mu_{eff} = 2.18$ B.M. − (*R*,*R*)-Co**2b**: $C_{38}H_{34}CoN_2O_6$: calcd. C 67.76, H 5.09, Co 8.75, N 4.16; found C 67.2, H 5.1, Co 8.81, N 4.1. − (*S*,*S*)-Co**2b**: found C 67.5, H 5.3, Co 8.84, N 4.2.

{Diethyl (E,E)-(trans)-3,3′-[(1,2-Diphenyl-1,2-ethanediyl)diimino)]bis(2-benzoyl-2-propenoato)(2−)-N,N′,O^2,$O^{2'}$}methylcobalt [(*R*,*R*)-MeCo**2b**]: 0.05 g (2.14 mmol) of sodium was pressed into 0.5 ml mercury under inert conditions. To the obtained amalgam, 1.44 g (2.14 mmol) of (*R*,*R*)-Co**2b**, dissolved in 25 ml of dry THF, was added. The mixture was stirred for 12 h, whereupon a violet colour appeared. The solution was then decanted from the mercury and cooled at −78°C. At this temperature, a solution of 0.456 g (3.2 mmol) of iodomethane in 10 ml of dry THF was added dropwise, resulting in the precipitation of a red solid. The suspension was poured into water, and the red solid was filtered off and dried in air. The obtained product still contained traces of water and THF, which could not be removed in vacuo. However, in noncoordinating solvents these molecules dissociate. These green solutions are very light-sensitive, yield 1.53 g (94%). − EI MS; *m/z* (%): 688 $[M^+]$ (2), 673 $[M - CH_3]^+$ (16), 366 $[M - L/2 - CH_3]^+$ (17). − IR (Nujol): $\tilde{\nu}_{max} = 1667\ cm^{-1}$ ($C{=}O_{str}$), 704 ($C{-}H_{def}$). − ^1H NMR (200 MHz; $CDCl_3$): $\delta = 0.74$ (t, 6 H, CH_2CH_3), 2.70 (s, 3 H, CH_3), 3.78 (q, 4 H, CH_2CH_3), 4.69 (ds, 1 H, N−CHPh), 4.96 (ds, 1 H, N−CHPh), 7.05−7.35 (m, 20 H, Ph), 7.65 (s, 1 H, N−CH=), 7.79 (s, 1 H, N−CH=). − ^{13}C NMR (200 MHz, $CDCl_3$): $\delta = 13.5$ (CH_2CH_3), 29.7 (CH_3), 59.6 (CH_2), 78.8, 81.1 (N−*C*HPh), 102.8, 103.6 (CH=*C*), 125.9−130.6 (Ph), 136.1, 136.9, 141.2 (C_q, Ph), 162.7, 163.9 (*C*H=C), 184.6 (C=O). − $C_{39}H_{37}CoN_2O_6$: calcd. C 68.02, H 5.42, Co 8.55, N 4.07; found C 68.70, H 6.28, Co 7.74, N 3.62. − TG: calcd. (from found value of Co) −9.5 (%) (THF, H_2O); found −9.1% (150°C).

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