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TRANSITION METAL COMPLEXES OF DERIVATIZED CHIRAL DIHYDRO-1,2,4-TRIAZIN-6-ONES. PART I. NICKEL (II) COMPLEX OF *(D)-3*-ACETYL-5-BENZYL-1-PHENYL-4,5-DIHYDRO-1,2,4-TRIAZIN-6-ONE OXIME. AN INSTANCE OF A CARBON-CARBON COUPLING REACTION

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Abstract- The reaction of (*D*)-3-acetyl-5-benzyl-1-phenyl-4,5-dihydro-1,2,4-triazin-6-one oxime **(2)** with nickel acetate in refluxing ethanol afforded the respective square planar Ni(II) complex. This is evidenced from an X-Ray study which reveals that the Ni(II) ion is coordinated to the ring N(4) and oxime nitrogen atoms. The crystallographic data of the complex **(3)** also unravelled that the nickel-complexation has led to the formation of one π-bond across the N(14)-C(15) bond and one σ-bond between a benzylic carbon atom of one ligand and the chiral (C5) carbon atom of the other ligand in the bis-ligand complex **(3)**. Evidently, the complexed Ni(II) ion plays a template effect role in initiating such a cascade of π- and σ-bond forming reactions. ^{1}H-, ^{13}C-NMR and FD-MS spectral data of **3** are in full agreement with its molecular structure.

INTRODUCTION

Recently, we have described a versatile and efficient one-pot synthesis of chiral 4,5-dihydro-1,2,4-triazin-6-ones (e.g. compound (*D*)-**1**, Scheme 1) utilizing available α-amino esters and hydrazonoyl chlorides (precursors of nitrile imines, the reactive 1,3-dipolar species).[1] The respective 4,5-dihydrotriazinone oximes

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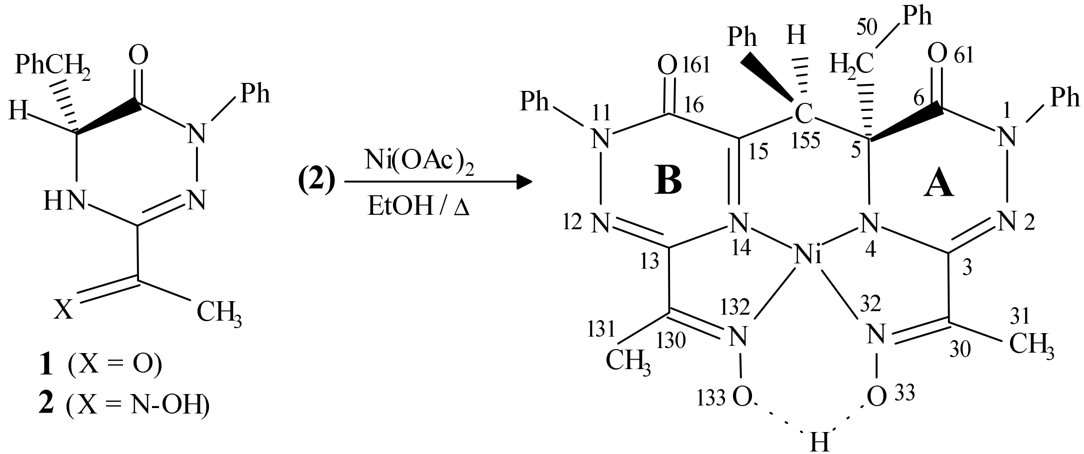
(exemplified by (*D*)-**2***,* Scheme 1) are readily accessible *via* oximation of the C3-acetyl group using hydroxylamine. These oximated triazinones would be convenient ligands for metal complexation. In this paper, the reaction of the model oxime **(2)** with nickel(II) acetate tetrahydrate is investigated. Initially, it is thought that the reaction will produce a simple bis-oximatonickel(II) complex, but preliminary spectral data of the resulting complex indicated some unexpected structural features. This has prompted us to determine the crystal structure for the complex. The crystallographic data, which are presented in this paper, revealed that the amidrazone nitrogen HN(4) and the oxime nitrogen are coordinated to the nickel ion to give the bis-ligand nickel(II) complex **(3)**. Concurrently with that, an interesting carbon-carbon coupling has taken place between the benzylic carbon of one oxime ligand and the chiral carbon center of the other oxime ligand (Scheme 1).

Scheme 1



1 (X = O)
2 (X = N-OH)

(3)

RESULTS AND DISCUSSION

Structure of the Ni(II) complex (3)

On the onset, an X-Ray crystal structure for **3** has been determined. The results of crystallographic data (Tables 1-3) have shown that the complexation to the nickel ion involves the ring-nitrogen atom HN(4) and the oxime nitrogen atom as the coordinating sites with the ultimate formation of a square planar Ni(II) complex **(3)**. This is in accordance with the experimental results which show that the complex is diamagnetic and neutral. The molecular structure of **3**, based on crystallographic data, is displayed in Figure 1.

Interestingly, the data unravelled an instance of formation of a π-bond across N(14)-C(15) as well as a σ-bond linking the benzylic carbon of one ligand to the chiral C(5) carbon of the other partner ligand in the Ni(II) complex **(3)** (Figure 1). Clearly, these events of azomethine π-making and carbon-carbon σ-coupling reactions operate under the Ni^{2+} template effect.[2] The salient features of the role of Ni^{2+} is not clear yet.

The X-Ray data show that the N(4)-C(5) bond length (ring A) is 1.427 Å, whereas that of N(14)-C(15) bond

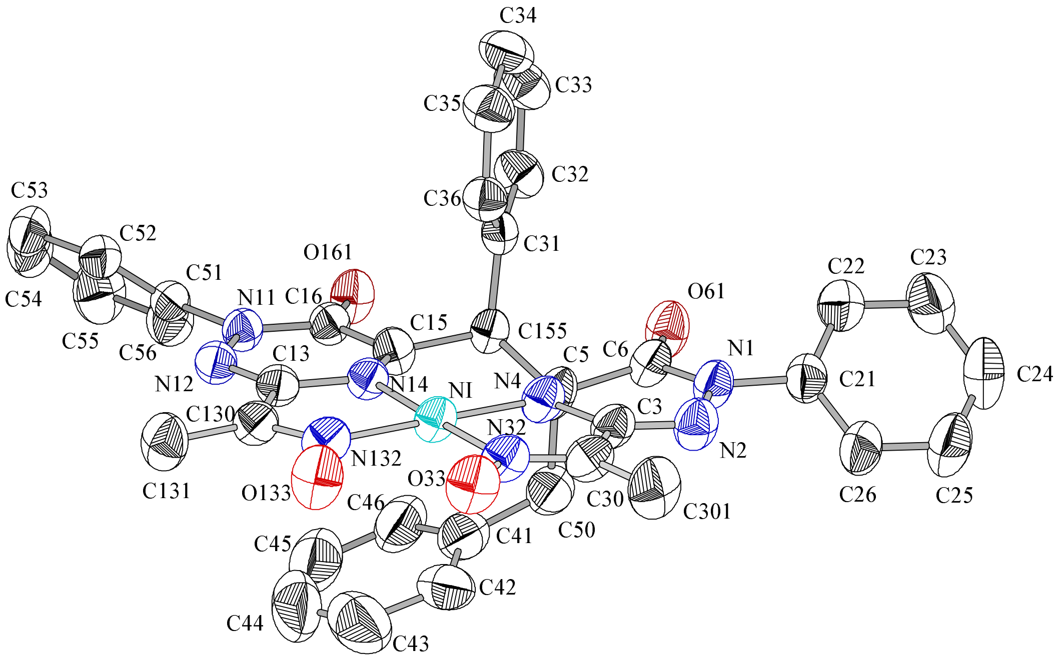


Figure 1. ORTEP plot of the molecular structure of **3**. All hydrogen atoms are omitted for clarity

(ring B) is truely shorter, being 1.310 Å, which is in conformity with a π-azomethine bond-making process (Table 1). Moreover, the N(4)-C(5)-C(6) angle in ring A is 111.3° (acceptable value for an unstrained sp^3 carbon), whereas that of N(14)-C(15)-C(16) in ring B is 12l.0° which is a normal value for unstrained sp^2 carbon. Values of the bond angles around the nickel ion (Table 1) provide further evidence for an approximately square planar geometry of the Ni(II) complex **(3)**.

The NMR spectral data for **3** (in CDC1$_3$) are in full agreement with the X-Ray molecular structure. Thus, in DEPT experiments, and due to the dissymmetry of **3**, signal doubling is observed for the sp^2 carbons (and the methyl groups) that are duplicated in rings A and B, and in those substituents anchored to N1/N11 and C3/C13. The aliphatic sp^3-carbons resonate at δ 10.6 and 11.7 (two CH$_3$), 46.6 (one CH$_2$Ph), 53.4 (one CHPh) and 65.3 ppm (one quaternary C(5)). The occurrance of the latter three signals constitutes a diagnostic criterion for structure **(3)**. The twelve different CH sp^2-carbons (belonging to the four different phenyl groups) display 12 signals in the range δ 124.0-131.6 ppm, whereas the eleven different sp^2-carbons (devoid of hydrogen atoms, and including C(15)) resonate in the range δ 132-169 ppm thereby displaying 11 signals. The ^{1}H NMR spectrum of **3** displays a characteristic signal at δ 5.65 (s, 1H, CHPh). The prochiral benzylic

Table 1. Selected bond lengths and angles for **3**.

Bond lengths (Å)			
Ni-N(4)	1.854(2)	C(30)-C(301)	1.490(4)
Ni-N(32)	1.868(2)	C(130)-C(131)	1.480(4)
Ni-N(132)	1.863(2)		
Ni-N(14)	1.866(2)	Bond angles (°)	
O(33)-N(32)	1.357(3)	N(4)-Ni-N(32)	83.82(10)
O(33)-O(133)	2.444(3)	N(4)-Ni-N(132)	178.55(11)
O(133)-N(132)	1.334(3)	N(32)-Ni-N(132)	97.26(11)
N(l)-C(6)	1.373(4)	N(4)-Ni-N(14)	95.00(9)
N(1)-N(2)	1.400(3)	N(32)-Ni-N(14)	178.64(10)
N(2)-C(3)	1.300(4)	N(132)-Ni-N(14)	83.92(10)
N(4)-C(3)	1.354(3)	C(15)-N(14)-C(13)	118.2(2)
N(4)-C(5)	1.427(4)	O(33)-N(32)-Ni	124.1(2)
N(1l)-N(12)	1.371(3)	O(133)-N(132)-Ni	123.2(2)
N(ll)-C(16)	1.381(3)	N(4)-C(5)-C(155)	112.6(2)
N(12)-C(13)	1.294(4)	N(4)-C(5)-C(6)	111.3(2)
N(14)-C(15)	1.310(3)	C(155)-C(5)-C(6)	109.1(2)
N(14)-C(13)	1.389(3)	N(4)-C(5)-C(50)	111.3(3)
N(32)-C(30)	1.289(4)	C(155)-C(5)-C(50)	109.3(3)
N(132)-C(130)	1.302(4)	C(6)-C(5)-C(50)	102.9(2)
C(3)-C(30)	1.466(4)	N(14)-C(15)-C(16)	121.0(2)
C(5)-C(155)	1.538(4)	N(14)-C(15)-C(155)	122.5(2)
C(5)-C(6)	1.542(4)	C(16)-C(15)-C(155)	115.8(2)
C(5)-C(50)	1.627(5)	C(15)-C(155)-C(31)	104.7(2)
C(13)-C(130)	1.455(4)	C(15)-C(155)-C(5)	114.4(2)
C(15)-C(16)	1.477(4)	C(31)-C(155)-C(5)	116.8(2)
C(15)-C(155)	1.515(4)		

C$\underline{H}_2$Ph protons are mutually coupled and resonate at δ 3.18 (d, *J* = 12.9 Hz, 1H) and 3.25 (d, *J* = 12.9 Hz, 1H). The aromatic-C$\underline{H}$ protons' signals (belonging to the four phenyl rings) are overlapped and cummulated in the range δ 7.18-8.14 ppm (20 H), while the exchangeable proton bridging both oxime oxygens resonates at δ 17.84 (s, 1H, O....$\underline{H}$....O).

The m/z value for the molecular ion of **3**, as determined by FD-MS, was found to be around 696 which is in agreement with the calculated value of about 696, based on the empirical formula $C_{36}H_{30}N_8O_4Ni$.

The Ni(II) complex (**3)** exhibits optical activity indicating that the coupling reaction proceeds with a degree of stereoselectivity.[3] However, the assignment of the absolute configuration at both stereogenic centers (C5 and C155) requires extensive investigation.

Table 2. Crystal data and structure refinement parameters for **3**.

Empirical formula	$C_{36}H_{30}N_8O_4Ni$
Formula weight	697.39
Temperature (K)	213(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	9.7590(9)
b (Å)	12.2470(11)
c (Å)	14.617(2)
α (°)	68.194(9)
β (°)	79.335(8)
γ (°)	87.485(8)
Volume (Å^3)	1593 .4(3)
Z	2
Density (calculated) (mg/m^{-3})	1.458
Absorption coefficient (mm^{-1})	1.333
F(000)	724
Crystal description	brown block
Crystal size (mm)	0.30 x 0.25 x 0.20
θ range for data collection (0)	5.17 - 64.97
Index ranges	$-11 \leq h \leq 11, -14 \leq k \leq 14, -17 \leq l \leq 17$
Reflections collected	12666
Independent reflections	5389 [$R_{int} = 0.0476$]
Criterion for observation	$> 2\,\sigma\,(I)$
No. of standard reflections	3
Interval count/time	400/3600
Decay	none %
Molecular graphics	Diamond
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	Calc $w=1/[\sigma^2 (F_o)^2 + (0.0766P)^2 + 1.0260P]$
	where $P=(F_o)^2 + 2(F_c)^2/3$
Data *I* restraints / parameters	5389 / 0/ 562
Final R indices [I> 2 σ (I)]	$R_1 = 0.0499$, $wR_2 = 0.1400$
Goodness-of-fit on F^2	1.033
Final R indices (all) R_1 / wR_2	0.0600 /0.1492
Largest difference peak (e. Å^3)	0.669
Largest difference hole (e. Å^3)	-0.303

Table 3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **3**.

	x	y	z	U(eq)*
Ni	360(1)	3051(1)	5946(1)	44(1)
0(33)	782(3)	3727(2)	3818(2)	66(1)
0(61)	-2949(2)	-366(2)	8615(2)	59(1)
0(133)	2197(3)	4791(2)	4448(2)	70(1)
0(161)	-319(2)	2001(2)	9820(1)	53(1)
N(1)	-2732(3)	-33(2)	695 1(2)	50(1)
N(2)	-2081(3)	536(2)	5952(2)	56(1)
N(4)	-916(3)	1796(2)	6493(2)	46(1)
N(1 1)	1136(2)	3549(2)	8756(2)	42(1)
N(12)	1786(2)	4226(2)	7808(2)	45(1)
N(14)	521(2)	3124(2)	7175(2)	41(1)
N(32)	156(3)	2965(2)	4729(2)	50(1)
N(132)	1668(3)	4292(2)	5423(2)	50(1)
C(3)	-1259(3)	1417(3)	5802(2)	48(1)
C(S)	-1095(4)	968(3)	7500(2)	52(1)
C(6)	-2380(3)	150(3)	7751(2)	49(1)
C(13)	1469(3)	3991(3)	7078(2)	43(1)
C(15)	-63(3)	2438(3)	8080(2)	47(1)
C(16)	228(3)	2616(3)	8972(2)	43(1)
C(21)	-3700(3)	-963(3)	7086(2)	52(1)
C(22)	-4935(4)	-1155(3)	7755(3)	63(1)
C(23)	-5822(4)	-2074(4)	7878(3)	76(1)
C(24)	-5460(5)	-2790(4)	7340(3)	85(1)
C(25)	-4244(5)	-2592(4)	6674(3)	80(1)
C(26)	-3352(4)	-1678(3)	6536(3)	65(1)
C(30)	-648(3)	2137(3)	4765(2)	53(1)

Table 3 (contd.)

C(301)	-920(6)	1942(5)	3867(3)	77(1)
C(31)	-2568(3)	2228(2)	8405(2)	40(1)
C(32)	-3477(3)	1872(3)	9321(2)	54(1)
C(33)	-4631(4)	2516(4)	9468(3)	67(1)
C(34)	-4901(4)	3519(4)	8708(3)	65(1)
C(35)	-4036(3)	3879(3)	7792(3)	59(1)
C(36)	-2865(3)	3236(3)	7639(2)	47(1)
C(41)	1586(4)	599(3)	7499(3)	64(1)
C(42)	2384(4)	1021(3)	6554(3)	69(1)
C(43)	3658(5)	1661(5)	6385(5)	112(2)
C(44)	4073(7)	1803(5)	7179(8)	121(2)
C(45)	3333(7)	1290(6)	8144(7)	118(2)
C(46)	2058(5)	692(4)	8309(4)	82(1)
C(50)	182(4)	55(3)	7658(3)	61(1)
C(51)	1481(3)	3906(3)	9525(2)	44(1)
C(52)	1600(3)	5104(3)	9327(3)	53(1)
C(53)	1962(4)	5455(4)	10050(3)	68(1)
C(54)	2171(4)	4644(5)	10941(4)	81(1)
C(55)	2072(5)	3457(4)	11128(3)	78(1)
C(56)	1733(4)	3081(3)	10409(3)	60(1)
C(130)	2137(3)	4643(3)	6049(2)	48(1)
C(131)	3239(5)	5565(4)	5755(3)	67(1)
C(155)	-1232(3)	1563(2)	8271(2)	39(1)

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*(U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor).

Over the years, metal-catalyzed carbon-carbon cross-coupling reactions are receiving continued interest and are extensively employed in many areas of preparative organic chemistry.[4] To the best of our knowledge, nickel- complexation with ligands of type (**2**) and the subsequent reactions involving azomethine π-making and carbon-carbon σ-coupling, as noted above, are hitherto unprecedented in the literature.

EXPERIMENTAL

Melting points (uncorrected) were determined using a Gallenkamp melting point apparatus in one-end open glass capillaries. The magnetic moment was measured for a finely ground solid sample of **3** at ambient temperature using a Johnson Matthey Magnetic susceptibility balance. Optical rotations were measured on a Perkin-Elmer 141 photoelectric spectropolarimeter. NMR spectra were recorded on a Bruker WM - 400 MHz spectrometer for solutions in $CDC1_3$ with TMS as internal reference. MS spectra (El) were obtained using a Finnigan MAT TSQ-70 spectrometer at 70 eV. Ion source temperature = 200 °C (for El), and 35 °C (for FD). Elemental analysis were performed at the laboratories of Quantitative Technologies Inc., New Jersey, USA. 1-Chloro-1-phenylhydrazono-2-propanone (required for the synthesis of **1**) was prepared *via* direct coupling of 3-chloropentane-2,4-dione (Acros) with benzenediazonium chloride (Japp-Klingemann reaction[5]); mp : 141-142 °C, in agreement with the reported values.[6] Other related synthetic routes were described.[7] *D*-Phenylalanine methyl ester hydrochloride was prepared by treating a suspension of *D*-phenylalanine (Biochemical grade, Aldrich) in methanol, with thionyl chloride following a literature procedure.[8]

D-3-Acetyl-5-benzyl-1 -phenyl-4,5-dihydro-1, 2, 4-triazin-6-one (1)

This compound was prepared *via* direct interaction between 1-chloro-1-phenylhydrazono-2-propane and *D*-phenylalanine methyl ester hydrochloride in methanol/dichloromethane (v/v = 1/1) in the presence of triethylamine, following a general procedure.[1] The product was obtained in the form of prismatic crystals and characterized as **1** (78%). mp 114-115 °C (recrystallized from aqueous ethanol). $[\alpha]_D^{20} = +244.7^\circ$ (c ~ 1, $CHCl_3$).

Anal. Calcd for $C_{18}H_{17}N_3O_2$: C, 70.34; H, 5.58; N,13.67. Found: C, 70.41; H, 5.52; N, 13.58. MS m/z (% rel. int.): 307.13028 ($M^{+\cdot}$, 20, Calcd 307.13208), 216 ($M–CH_2Ph$, 100), 188 (12), 146 (10), 119 (8), 104 (8), 92 (22), 77 (17). ^1H-NMR ($CDC1_3$) δ (ppm): 2.33 (s, 3H, CH_3), 3.09 (m, 2H, $C\underline{H_2}Ph$), 4.43 (m,1H, CH-5), 5.79 (br s, 1H, NH-4), 7.13 - 7.49 (m, 10H, CH-aromatic). ^{13}C-NMR ($CDC1_3$) δ (ppm): 23.6 (CH_3), 40.1 (CH_2), 55.0 (CH-5), 124-130 (6CH-aromatic : 124.7, 127.0, 127.4, 128.5, 128.8, 129.6), 135-141 (2C-aromatic, C-3: 135.2, 140.5, 141.0), 161.4 (C-6), 192.7 ($O=\underline{C}-CH_3$).

D-3-Acetyl-5-benzyl-1-phenyl-4, 5-dihydro-1, 2,4-triazin-6-one Oxime **(2)**

To a solution of compound **(1)** (2.7 g, 8.7 mmol) in warm methanol (80 mL) was added hydroxylamine hydrochloride (1.81 g, 26.1 mmol) and sodium acetate (2.15 g, 26.1 mmol). The resulting mixture was refluxed for 1 h. The solvent was then removed in *vacuo*, the residue was digested with water (150 mL), and the insoluble solid product was collected under suction, washed with water (2 x 30 mL), dried, recrystallized from ethanol in the form of scales and characterised as **2** (2.4 g, 87%). mp 185-187 °C. $[\alpha]_{D}^{20}$ = + 101.4° (c ~ 0.3, C_2H_5OH). Anal. Calcd for $C_{18}H_{18}N_4O_2$: C 67.07; H, 5.63; N, 17.38. Found : C, 66.98; H, 5.61; N, 17.35. MS m/z (% rel. int.) : 322.14434 ($M^{+\cdot}$, 14, Calcd 322.14298), 231 (M−CH_2Ph, 100), 215 (5), 203 (7), 186 (5), 104 (10), 91 (29), 77 (23). ^{1}H-NMR (DMSO-d_6) δ (ppm) : 1.81 (s, 3H, CH_3), 3.01 (d, *J* = 4.9 Hz, 2H, CH_2), 4.36 (dt, *J* = 4.9 Hz, 1.6 Hz, 1H, CH-5), 6.92 (d, *J* = 1.6 Hz, 1H, NH-4), 7.15-7.36 (m, 10H, CH-aromatic), 11.68 (s, 1H, OH). ^{13}C-NMR (DMSO-d_6) δ (ppm) : 8.1 (CH_3), 38.0 (CH_2), 53.3 (CH-5), 123-129 (6CH-aromatic : 123.5, 125.1, 125.7, 127.0, 127.2, 128.8), 135-147 (2C-aromatic, 2 C=N- : 135.1, 140.1, 142.1, 147.0), 160.5 (C-6).

D-3-Acetyl-5-benzyl-1-phenyl-4,5-dihydro-1,2,4-triazin-6-one Oxime-Nickel (II) Complex **(3)**

To a solution of the oxime derivative **(2)** (2.1 g, 6.4 mmol) in absolute ethanol (50 mL) was added a solution of nickel acetate tetrahydrate (0.8 g, 3.2 mmol) in absolute ethanol (100 mL). The resulting reaction mixture was refluxed with continuous stirring for 1-1.5 h, set aside to cool to rt, and refrigerated overnight. The precipitated deep-brown solid product was collected by suction filtration, washed with cold ethanol (2 x 10 mL), dried in vacuo and identified as complex **(3)** (2.1 g, 94%). mp >330 °C. $[\alpha]_{D}^{20}$ = -264.8° (c ~ 0.02, CH_2C1_2). Anal. Calcd for $C_{36}H_{30}N_8O_2Ni$: C, 62.00; H, 4.31; N, 16.07. Found:C, 61.70; H, 4.49; N, 16.05. FD-MS m/z ~ 696 ($M^{+\cdot}$, Calcd ~ 696). ^{1}H-NMR ($CDC1_3$) δ (ppm): 2.06 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 3.18 (d, 1H, *J* =12.8 Hz, CH$\underline{\text{H}}$Ph), 3.25 (d, 1H, *J* = 12.8 Hz C$\underline{\text{H}}$HPh), 5.65 (s, 1H, C$\underline{\text{H}}$-155), 7.18- 8.14 (overlapped, 20H, CH-aromatic), 17.84 (s, 1H, O... $\underline{\text{H}}$ ...O). ^{13}C- NMR ($CDC1_3$) δ (ppm): 10.6 (CH_3), 11.7 (CH_3), 46.6 ($\underline{\text{C}}H_2$Ph), 53.4 ($\underline{\text{C}}$H-155), 65.3 (C5), 124.0-131.6 (12 CH-aromatic: 124.0, 124.5, 126.5, 128.0, 128.3, 128.5, 128.9, 129.1, 129.2, 129.5, 131.0, 131.6), 132-169 [11 $\underline{\text{C}}$ (4$\underline{\text{C}}$-aromatic, 5 C=N, 2 $\underline{\text{C}}$=O): 132.1, 136.0, 139.3, 140.9, 145.7, 146.2, 149.5, 151.2, 157.3, 159.1,169.0)].

A solution of the title complex **(3)** in chloroform (10^{-3} M) is non-conducting indicating that **3** is neutral. The magnetic moment measurement shows that the complex is also diamagnetic (μ ~ 0) which is consistent with d^8 metal ion in a square planar geometry.[9]

Collection of X-Ray diffraction data

Brown bloc crystals were grown by evaporating slowly the solvent from the solution of **3** in $CHCl_3$ /MeCN (1: 1 v/v) at rt. Data collection was made at -60 °C, using an ENRAF-NONIUS CAD4 diffractometer operating in the omega scan mode. 4559 Independent data were collected within the range θ = 5.53-64.90° using CuK_α radiation (λ = 1.54184 Å) . The cell parameters and the orientation matrix for the data collection were obtianed using the setting angles of 25 reflections (θ = 15.02-25.0°) . The structure was solved by direct method using the program SHELXS 86.[10] All non-hydrogen atoms were refined anisotropically by full-matrix least-squares procedure based on F^2 using all unique data with SHELXL 93.[11] The hydrogen atoms have been found in the difference Fourier map and were refined isotropically. This results in an R values R_1 = 0.0485 and wR_2 = 0.1400 for the observed data and 562 parameters.

Supplimentary Material

Further information for the crystal structure determination of 3 can be ordered from Cambridge Crystallographic Data Center under the depository number CCDC 135042. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union road, Cambridge CB21EZ,UK (fax : int. code +(1223) 336-033; e-mail: deposit@ccdc.cam.ac.uk).

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3. The space group $P\bar{1}$ implies that the crystal of compound **3** is a racemate. The observed optical activity of **3** may be explained as a result of the presence of enantiomeric excess (ee) since the starting ligand **2** is chiral.
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